SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ
NEAR LEIPZIG

LONDON · NEW YORK.

APRIL 1907.

Contents.

List of abbreviations.

d = specific gravity.

d_{20° = specific gravity at 20°, compared with water at 15°.

$d\,\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.

$\alpha_{D\,20^\circ}$ = optical rotation at 20°, in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

$n_{D\,20^\circ}$ = index of refraction at 20°.

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Miltitz near Leipzig, April 1, 1907.

With feelings of satisfaction we are able to place on record that the year 1906, from a commercial point of view, has run an eminently favourable course, and that the hopes to which we gave expression in our last Report, have been realised in every respect. It was granted to the German industry to enjoy a continuation of the blessings of peace among civilised peoples, and in the peaceful contest of the nations on the World's market not only to maintain its position, but also to advance a mighty step on the road of economic progress. The fears entertained in many quarters with regard to the new German Commercial Treaties and Tariffs which came into force on March 1, 1906, have fortunately not come true, and our branch of industry in particular has every reason to rejoice in the renewed strength which has thereby been given to commercial intercourse. The sales have reached figures which have put the results of the most favourable years of commerce in the shade, and although the profits have been impaired to a not inconsiderable extent by the constantly growing expenses, the results can nevertheless be characterised as magnificent. The strained financial situation has no doubt on occasion acted as an impediment, but on the other hand it has also imposed a check on the speculative elements from which the healthy development of commerce has benefitted. Thanks to the quiet political situation which has been greatly consolidated by the new German Reichstag, and to the splendid employment of all branches of industry, the future prospect appears to be no less promising, in spite of the still strained condition of the money market, and the growing output of the first quarter points to the fact that the favourable state of affairs has by no means reached its zenith. The imports of chemical raw material and manufactured products from abroad amounted in 1906 to 430,8 million marks, against 377,6 million in the previous year; it therefore shows an increase of 14,1 %, against 7 % in 1905. The exports rose from 473,5 to 542,3 million marks, and consequently advanced by 14,5 %, whilst in 1905 the exports had only advanced 5 % over those of 1904, although at that time the situation was also by no means unfavourable. These figures speak for themselves so plainly that they require no further comment.

Our Bodenbach branch has been exceptionally well employed, and for the present not a trace of any unfavourable influence of the tension between Austria and Hungary on the commercial situation in our industrial branch can be discovered. Our trade with both countries has increased considerably. There are bitter complaints from the Austrian manufacturers of essential oils and essences about the price-cutting, a consequence of the habit of underquoting each other, and attempts are made to bring about a combination of the interested parties for the purpose of agreeing upon price-limits for our articles. We, naturally, stand entirely outside this movement, as we have always, in spite of the ridicule which has from time to time been heaped upon us, kept ourselves away from such unhealthy competition. We have preferred, by unceasing efforts, and by shirking no sacrifice whatever, to strive after this, that our customers of their own free will pay us correspondingly higher prices for our superior goods. We are pleased to say that the results confirm the correctness of the attitude we have taken up.

The gratifying strengthening of the commercial relations with France has made further progress, and the growing intercourse with this valuable market is a satisfactory guarantee that the ill-humour to which we had still to refer last year, has, on the part of our neighbours, now finally disappeared.

The general state of the trade in the United Kingdom can be called very favourable, for the figures of imports and exports show considerable increases for every month. Our products also have during the last few months constantly found a good sale, but the advancing prices, combined with the unfavourable and in part even unhealthy conditions from which the soap industry has suffered now for some considerable time, do not show the future in a particularly rosy light. Trade with the British Colonies has been regular, and gives no occasion for any special remarks.

The improvement in the economic condition of Russia which became clearly manifest already in the latter half of 1906, was naturally bound to exert a favourable influence on the commercial situation, and our increasing trade proves that there is a legitimate expectation of an early return to normal conditions. Thanks to the energetic attitude of the Government, and partly no doubt also owing to the establishment of a representative institution in the form of the Duma, it was possible in the course of last autumn to master the forces of the revolution, and since that time the improvement in the economic life of Russia has made distinct progress.

Following the example of Switzerland, the Dutch Government published some 18 months ago a draft Patent law, which, however, has dropped into oblivion owing to a change of Ministry at the time.

Recently, the Association for the Protection of Industrial Property, supported by the Association for the Protection of the Interests of the German chemical industry, has taken steps to bring the proposal again before the Dutch Parliament, either in the original or in an amended form. We need not assure our readers, that especially our industry, at least in so far as it occupies itself with the manufacture of artificial perfumes, has the greatest interest in bringing to an end the condition existing up to the present in Holland, by which all intellectual property which has been acquired outside that country's frontiers occasionally at the heaviest sacrifice, is placed at the mercy of the general public.

The Dutch Indies are beginning to occupy a more and more important place among the markets of the Far East.

The longed-for reform of the notorious Alcohol Act in Spain is still in abeyance, for the liberal party has last year made an absolute fiasco, in accomplishing the feat of letting five individual Cabinets follow one another in one and the same year. Since two months the Conservatives are now again at the helm, and it would appear that the country is putting up with this clerical cabinet. It is a matter of regret that this ministry also includes the author of this eventful Alcohol Act, as the hope of obtaining the reform of this Act for which every effort has been made during the last two years by continued agitation, has now been frustated for an indefinite time. For this reason the trade in the branches affected by this Act, that is to say in the circles of our clients, continues to be in a state of depression, and for the immediate future an improvement can hardly be hoped for. It was likewise impossible, in spite of all efforts made by the respective Powers, to come to a definite conclusion with regard to the Commercial Treaties with Germany, France and other nations, as the continuous political quarrels and the frequent changes of Government, occupied the whole of the valuable time. The drought which has now prevailed for months without a prospect of rain, adds to the commercial despondency from which the country suffers, and gives rise to fears of a very severe economic crisis. There is even some talk of an imminent famine in case an abundant rainfall does not change the extremely critical situation.

Business in the United States has been extremely satisfactory. The largely increased sales of our New York branch prove sufficiently that its efforts, continued now for 35 years, to advance our principles in this greatly sought-after and much consuming market, may be characterised as very successful. If the results of the past year may be called brilliant, the same applies to the prospects for the near future, the more so, as there is every hope that, when the provisional arrangement lapses on June 30 of this year, a new treaty between

Germany and the United States will come into being, built up on the basis of mutual good-will.

We welcome with satisfaction the enactment of the Food and Drugs Act which came into force in the United States on January 1, 1907. This Act applies in the first place to the inter-state and foreign trade in food-stuffs and drugs containing injurious or deteriorated substances, or which have been inadmissibly weighted, or contain an excess of taste-, flavour- or preserving admixtures; but it is chiefly directed against incorrect or incomplete labelling of the goods. Very strict directions have been issued; for example, for mixtures, a word indicating this circumstance must be added on the label, and certain constituents such as preserving agents, substances affecting the odour or taste, alkaloids, alcohol and its preparations, as well as the quantities, in which they are employed, must be specified. Drugs without any further description must agree with the United States Pharmacopœia or the "National Formulary". Products imported from abroad must not be subject to commercial restrictions in the country of production, and according to Consular certificate must satisfy all requirements of the Act. The manufacturer or importer can protect himself against seizure or possible legal proceedings, if he submits samples, and gives a written guarantee to the Board of Agriculture which is the Authority entrusted with the carrying out of the Act.

Although the exact observance of the new regulations may cause a good deal of apparently paltry extra work to the German exporter, we welcome in this Act a measure which is directed against the dishonest elements of our branch. The latter have always devoted special attention to the United States, and their retirement from the competition can only be an advantage both to the consumers and to our branch of industry.

Of the remaining countries of the New World, the Argentine Republic stands unquestionably in the front rank; that country, owing to its natural economic relations with the German Empire, justifies the highest hopes as to an important future for the sale of manufactures of Germany, which country occupies the first place among all the customers of the Argentine. But it should not be overlooked that the state of the trade in that country depends in every respect upon the result of the harvest, and that the increase in the exports to the Argentine Republic can only be regarded as a consequence of the favourable results of the harvests of the last four years. A failure of the harvest may therefore only too readily bring about a crisis.

The export to Brazil also moves slowly but surely in an upward direction. Unfortunately it is still very often necessary to complain that certain officials, in carrying out the inspection of foods, are apt to proceed in a totally unbusiness-like manner, and thereby cause many needless formalities, wasting much time and expense, even to firms who make a point of only supplying unobjectionable goods. It is to be hoped that in this respect a definite improvement may soon be effected.

Chile is gradually recovering from the heavy blows from which it suffered last year. In many cases Europe showed an accommodating spirit by allowing prolongations, thus offering to most firms a possibility of overcoming the disaster.

The relations with Central America call for no comment.

In our last Report we gave expression to certain fears that the increase in the duties would tend to restrict trade with Japan, but we are now able to state with satisfaction that also during the past months an exceptionally brisk export of our manufactures to this important market has taken place. Moreover, the Japanese importers have, in the interest of the growing soap industry, energetically opposed the increase in the duties on our articles which amounted to 10—20 $^0/_0$, and they have obtained the concession from the Government, that the duties on all oils and perfumes employed in the above-mentioned branch of industry are now considerably reduced. The stimulating effect of this measure on the trade already makes itself distinctly felt. The turn of the Japanese for strong perfumes is, for the rest, of great advantage to the sale of essential oils and artifical perfumes.

A disagreeable surprise has been sprung upon the exporters of pharmaceutical products, by the fact that the Japanese Home Office has issued an order anticipating the date up to which pharmaceutical preparations which answer the requirements of the old (II) Japanese Pharmacopœia are admitted for testing by the Government Laboratory, and has fixed it, contrary to what had previously been determined, at June 30, 1907. This curtailment of the period (originally extended to December 31, 1907) touches the European manufacturers all the more heavily, as the publication of the translation of the new (III) Pharmacopœia is unfortunately delayed, and may now probably not be expected before May. Although an appeal against this ministerial decision has been lodged by the German Consulate-General at Yokohama on behalf of a number of German firms interested in the chemical trade, it can now hardly be expected that the decision will be altered in good time.

With regard to the soap industry of Japan, the Minister of the Swiss Republic has recently reported¹) that about 50 factories, mostly in Osaka, have gradually been established, which produce monthly about 15 million tablets, and which not only cover the largest home demand, but also export already considerable quantities. The

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¹) Chem. Ztg. **31** (1907), 14.

exports to China, Korea, British India, the Philippines and Asiatic Russia were:

in	1905	1459678	doz.,	value	596059 yen
„	1904	808477	„	„	316889 „
„	1903	554265	„	„	194184 „

Although these figures make it already sufficiently clear that the Japanese soap export acquires a growing importance, the quantity reached in the months from January to June of last year is quite striking: the exports from January 1 to June 30, 1906, were already 1013310 doz., value 459096 yen.

Before entering into the usual discussion of the individual articles of our branch, we wish to mention still that the past commercial year has with few exceptions brought upward movements in the prices, which have stimulated to a not inconsiderable extent the interest of purchasers.

Commercial notes and scientific information on essential oils.

Almond oil, bitter. The demand for both sorts of essential oil of bitter almonds continued to be very brisk, so that our own production was insufficient to meet the requirements. As a makeshift we distilled several truck-loads of Italian press-cakes, which, however, also could be obtained only with difficulty.

Almond oil, pressed, from apricot-kernels. The tone of the Syrian market of apricot-kernels, has, unfortunately, bitterly disappointed all hopes, as the speculators succeeded, in spite of the favourable results of the harvest, in keeping the prices above 70 marks per 100 kilos, so that pressed oil could not be supplied below 190 marks per 100 kilos. As already reported by us, the result of this year's harvest could be characterised as a very rich one, for whereas with a good average yield about 6000 to 7000 bales are usually put on the market in Damascus, there were this time optimists who talked of a crop of 20000 bales, which, however, in the opinion of our informants, must be considered as a somewhat exaggerated estimate. As, moreover, the reports from the country behind Mersina and from Aleppo announced an exceptionally rich crop, it was all the more necessary to reckon on a fall in the prices, as according to previous experience the consumers were not capable of absorbing such quantities. On the other hand, the failure of the harvest in California had not been allowed for sufficiently, and as, in consequence of the high prices of almonds, many manufacturers (such as Lübeck and Königsberg manufacturers of "marzipan" who otherwise use bitter almonds), now turned their attention to apricot-kernels, only a slight impetus on the part of the Hamburg speculators was needed to drive the prices up. Large parcels were secured in this place for forward delivery, something like 8000 bales, for shipment from July onwards, whilst as a rule in that month nothing is yet placed on the market. The price paid at first was 54 marks, but subsequently it advanced to 63, 64, and 67 marks for forward delivery, and it was finally driven up to 74 marks, owing to the fact that the various parcels changed hands three to four times, even before they were shipped. The exceptionally early and briskly starting demand led in Damascus, as early as July, to a real hunt for kernels, and the purchase-price advanced by short leaps up to 75.50 marks, so that the exporters who had foolishly entered into heavy engagements for early delivery, lost a good deal of money. It is impossible to say exactly how much has been exported during last season, as no official record of it is kept, and one has consequently to rely upon personal observations. Our friends estimate the shipments from Syria up to the end of 1906 at about 10500 to 11000 bales, of which about 8000 bales belong to Beyrout, 100 to 150 bales to Tripoli, 500 to 600 to Aleppo, and about 2000 bales to Mersina. With regard to the stocks still in hand, the opinions differ considerably, and at the moment nothing definite can be said about them. But in any case it is certain that the extraordinary position of this article, which has brought losses to every one participating in it except to the Syrian peasants and the Hamburg people, is exclusively due to the Hamburg speculators.

An oil recently pressed by us from sweet apricot-kernels free from prussic acid, may possibly have a certain amount of interest, and for this reason may be mentioned here. The kernels which are about half the size of almonds, originated from the island Mallorca, and yielded on pressing 36 to 37 % oil, which, as might be expected, was absolutely identical with ordinary oil from apricot-kernels. It had a yellow colour, and at 15° the specific gravity 0,9198; sapon. no. 188,4; iodine no. 100,0. The fatty acids separated off melted at about $+5^\circ$ (determined in a tube open at both ends). This oil also differs from genuine almond oil above all by the elaidine test, in which the (solid) layer of oil is not colourless, but, as in the case of peach-kernel oil, reddish.

Almond Oil, pressed, from almonds. Since our last Report the prices of the material have maintained themselves at the same level, and the numerous consumers of our Pharmacopœia oil have had to accustom themselves gradually to accepting proportionately higher quotations. If, in spite of this, we were compelled to increase our production considerably, this may be taken as a striking proof that our product can hold its own against the competition of the numerous "cheap" qualities with which the market is flooded.

Angelica Oil. Owing to the exceptionally low prices obtained in the 1905 season, a large number of the Thuringian angelica growers gave up the cultivation last year, as other plantings were more remunerative. The crop was in consequence proportionately smaller, and the quotations for fresh root free from earth advanced from 4.50 marks per 100 kilos in 1905, to about 6.50 marks. But many complaints were made about a bad yield of oil, and for this reason we were glad to have at our disposal our own Miltitz crop of which the yield was completely satisfactory. The slight increase in the price which we were compelled to make for our own distillate, is really not at all proportionate to the position of the crude material.

Anise Oil. Only after the second anise market at Alexejewka it was possible to take an approximately correct view of the result of the Russian anise harvest, and the information received from our correspondents practically confirms the estimate given in our last Report. The total harvest is said to be about 135000 poods, i. e. about 15000 poods more than in 1905. Although the quality of the seed brought to the market at Alexejewka turned out somewhat better than at the first market at Krasnoje, it could by no means be called good, as the yield of oil again proved to be insufficient. Really green anise could but rarely be found, and if found, could only be bought at an increased price. The unfavourable weather immediately before and during the harvest, as already mentioned, has had a most injurious effect on the quality. The high average price of the goods (about 2.50 roubles per pood) was not sufficiently inviting, in view of the deficient yield of oil, to induce large purchases of anise on the part of our industrial branch. In consequence of an insufficient demand the prices of anise oil distilled in Russia declined in the course of the last few months to the parity of about 14 marks cost-price per kilo, without, however, exciting any particular interest in the article.

From the other anise-producing districts no recent information is available. As already stated by us on a previous occasion, the use of anise oil is distinctly falling off, since in anethol there is placed a product at the disposal of the consumers, the use of which, in view of its purer taste and greater richness, offers advantages which no one can gainsay.

Artemisia Oils. Fr. Rabak, to whose contributions to the knowledge of these oils we referred already in our October Report of 1905[1]), has continued the chemical examinations of the oils then described.[2])

1. Oil of *Artemisia frigida* Willd.: —

distilled	Spec. grav.	α_D	Acid no.	Ester no.	Sap. no.	Sap. no. after acetylation
1904	0,927	—24° 48′	1,2	31,8	33,0	—
1904	0,931	—25° 10′	3,0	45,0	48,0	143
1905	0,933	—23° 40′	2,0	35,0	37,0	139

The oils formed clear solutions with 0,5 vol. and more 90 per cent. alcohol, and had a distinct odour of cineol, which could be determined qualitatively by the phosphoric acid reaction.

2. Oil of *Artemisia leudoviciana* Nutt.: —

distilled	Spec. grav.	α_D	Acid no.	Ester no.	Sap. no.	Sap. no. after acetylation
1904	0,929	—16° 14′	4,0	10,0	14,0	—
1904	0,930	—13° 32′	4,3	14,0	18,3	—
1905	0,931	—17° 20′	0,0	26,0	26,0	116

The oil dissolved in 0,5 vol. and more 90 per cent. alcohol, and with phosphoric acid gave the cineol-reaction.

3. Oil of *Artemisia caudata* Michx.: —

distilled	Spec. grav.	α_D	Acid no.	Ester no.	Sap. no.	Sap. no. after acetylation
1904	0,920	—12° 30′	0,0	17,0	17,0	not determined owing to insufficient material
1904	0,887	inactive	20,0	73,0	93,0	
1905	0,8418	—24° 20′	0,0	29,0	29,0	

The odour of the oil (which with 2 vol. and more 90 per cent. alcohol formed a cloudy solution) was at first sweetish, and gradually became lemon-like.

For the purpose of comparison we quote here the constants of two oils which we examined ourselves some time ago.[3])

1. Oil of *Artemisia variabilis* Ten.: d_{15° 0,9115; α_D — 9° 20′; acid no. 1,7; sap. no. 15,5°; sap. no. after acetylation 49,1; incompletely soluble in alcohol (even in absolute alcohol); the solution which is at first clear, becomes cloudy when 10 to 12 vol. are added.

2. Oil of *Artemisia annua* L.: yield of oil from the green herb cultivated by ourselves, 0,29 $^0/_0$; d_{15° 0,8912; α_D — 1° 18′; acid no. 3,8; ester no. 19,2; ester no. after acetylation 44,5; soluble in 1 to 1,5 vol. 80 per cent. alcohol; when more solvent is added cloudiness occurs owing to separation of paraffin.

Basil Oil. The regrettable state of affairs of this oil unfortunately continues, as the present producing districts, and particularly Réunion,

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[1]) Pharm. Review **23** (1905), 128; Report October **1905**, 12; comp. also Reports April **1902**, 77; October **1904**, 13; April **1905**, 85.

[2]) Pharm. Review **24** (1906), 324.

[3]) Reports April **1902**, 77 and April **1905**, 85.

are completely exhausted. We hope in the course of this summer, with the help of our own cultivations, to make once for all an end of the scarcity.

Cade Oil. The information by C. Pépin, on the origin, production, and properties of cade oil given in our last Report[1]), may here be supplemented by some further details from the hand of the same author[2]). According to these, an oil derived from *Juniperus oxycedrus* is mobile, has a smoky odour, an acidity of less than 1,5 % (calculated for acetic acid), and gives a brown coloration with petroleum ether and copper acetate. Between 150 and 300° (ordinary pressure), at least 65 % must pass over; between 100 and 215° (65 mm. pressure), at least 70 to 75 % of the oil.

Cajeput Oil. In the shipments from Macassar during last year a further falling off is to be recorded, for, according to the export lists received, only 3713 baskets have been exported between January 1 and December 31, 1906, against 3935 baskets in the previous year. The prices remained unchanged, as the demand from the consumers leaves much to be desired.

In the above figures for 1906 are naturally not included the considerable quantities received by us, as previously mentioned, from a German producer in Buru direct.

As the first part of a work on the Australian melaleucas, R. T. Baker and H. G. Smith[3]) give a description of the two species *Melaleuca thymifolia* Sm. ("thyme-leaved tea tree") and *M. linariifolia* Sm. ("tea tree"). As in the case of the eucalypts described by the same authors, they give here also detailed information on the oils contained in the above species, of which we quote the important points in the following.

Melaleuca thymifolia Sm. Leaves distilled in April yielded 2,28 % essential oil of a faint yellow colour, which behaved exactly like a good eucalyptus oil rich in cineol, except in so far as it was much more difficultly soluble. $d_{15°}$ 0,9134; $\alpha_{D23°} + 2° 1'$; $n_{D23°}$ 1,4665; sap. no. 3,1; ester no. after acetylation 33,6; the oil is insoluble in 10 vol. 70 per cent. alcohol, but dissolves already in 0,5 vol. 80 per cent. alcohol; when more alcohol is added, cloudiness occurs soon; with 90 per cent. alcohol it behaves in a similar manner.

The bulk of the oil (86 %) boils between 172 to 183°. The cineol-content determined by the phosphoric acid method amounted to 53 %; in addition to this, very small quantities of aldehydes were present, whilst pinene and phellandrene could not be detected. The

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[1]) Report October **1906**, 13.

[2]) Journ. de Pharm. et Chim. VI. **24** (1906), 248.

[3]) The Australian Melaleucas and their essential oils. Proceed. of the Linnean Soc. of N. S. W. **40** (1906), 60.

alcoholic constituent of the oil, judged by the odour, appears to be closely allied to borneol.

Melaleuca linariifolia Sm.[1]). Yield of oil from leaves distilled in September, 1,214 %. The crude oil was pale yellow, and had a turpentine-like odour. d_{15° 0,9129; $\alpha_D + 2{,}5^\circ$; n_{D22° 1,4741; sap. no. 6,4; ester no. after acetylation 40,3; insoluble in 10 vol. 70 per cent. alcohol, soluble in 1 vol. 80 per cent. alcohol, with 10 vol. slight cloudiness.

On distillation 52 % passed over between 175 and 183°, and a further 23 % up to 250°. The oil does not contain pinene and phellandrene; the content of cineol is small. In the portions passing over first, small quantities of aldehydes could be detected; the alcohol present in the oil appears to be identical with the one contained in the oil of *M. thymifolia.*

Calamus Oil, Japanese. According to researches by Y. Asahina[2]), the mother-plant of this oil appears to be morphologically identical with the European *Acorus Calamus* L. The coarsely cut-up roots yielded on steam-distillation about 3 % oil of a yellowish colour, an unpleasant odour and bitter taste; d_{15° 0,976; $\alpha_{D21^\circ} + 23$ to $+ 25^\circ$; n_{D13° 1,513; sap. no. 0; sap. no. after acetylation 17; methoxyl-content 9,299 %. On fractional distillation the bulk of the oil passed over between 250 and 280°. A more detailed examination showed that the oil contained no terpene of the formula $C_{10}H_{16}$. Methyl eugenol was detected with certainty, as the principal distillate of the oil on oxidation yielded veratric acid. As the distillate was moreover optically strongly active, contained considerably more carbon than is found in methyl eugenol, and acquired a green colour when acetic acid and sulphuric acid were added, Asahina concludes that a sesquiterpene is present.

We would here refer to our previous communications[3]) on Japanese calamus oil.

Camphor Oil. The critical position of this important material has during the last few months grown decidedly worse, and since all the old stocks have now gone into consumption, the calamity begins to make itself felt to its full extent. Offers of crude camphor oil could during the last six months only be obtained in isolated cases, and white Japanese oil also was only sparingly offered. Owing to our exceptionally favourable position in this article, for which we are chiefly indebted to the reliability of our suppliers and their supporters, we were able to lay in for the present sufficient quantities of crude oil to cover the current demand for safrol and also for light and heavy camphor oil, and to concentrate the trade in these important articles

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[1]) Comp. also Gildemeister and Hoffmann, The Volatile Oils, p. 523.

[2]) Apotheker Ztg. **21** (1906), 987.

[3]) Bericht April **1889**, 7; Comp. also Gildemeister and Hoffmann, The Volatile Oils, p. 304.

in our hands. Supported by the high prices of turpentine oil, we obtained without difficulty for light oil 160 marks per 100 kilos, and occasionally interested parties, for example in England, were prepared to pay even considerably more. Heavy camphor oil advanced to 100 marks per 100 kilos, and in spite of these high quotations we are hardly able to accumulate a stock.

A review of the movement of the prices of these two articles during the last ten years may not be devoid of interest.

The prices on March 1st were: —

	Light camphor oil		Heavy camphor oil
1907	160 marks per 100 kilos	1907	100 marks per 100 kilos
1906	190 „ „ 100 „	1906	45 „ „ 100 „
1905	170 „ „ 100 „	1905	40 „ „ 100 „
1904	170 „ „ 100 „	1904	40 „ „ 100 „
1903	170 „ „ 100 „	1903	40 „ „ 100 „
1902	170 „ „ 100 „	1902	40 „ „ 100 „
1901	155 „ „ 100 „	1901	40 „ „ 100 „
1900	155 „ „ 100 „	1900	40 „ „ 100 „
1899	140 „ „ 100 „	1899	38 „ „ 100 „
1898	145 „ „ 100 „	1898	40 „ „ 100 „

With regard to the production of camphor and camphor oil down to the year 1904, vol. VI. of the Financial and Economic Year Book for 1906, issued by the Imperial Japanese Treasury, gives fresh information which may be a welcome addition to the statistics already available from former years.

Production of camphor and camphor oil (Japan).

Year	Number of works	Workpeople			Camphor		Camphor oil		Total value
		male	female	Total	Measurement and Weight	Value	Measurement and Weight	Value	
					Kwan	Yen	To	Yen	Yen
1895	—	—	—	—	358 142	1 526 831	82 687	40 923	1 567 754
1896	—	—	—	—	258 826	1 119 197	89 417	93 483	1 212 680
1897	—	—	—	—	417 319	1 318 292	175 176	181 535	1 499 827
1898	—	—	—	—	389 444	1 174 577	103 686	82 450	1 257 027
1899	282	735	60	795	171 657	535 130	20 492	51 363	586 493
1900	1193	2181	53	2234	252 021	1 178 924	9 797	79 612	1 258 536
1901	932	1824	69	1893	320 195	1 309 375	42 695	195 853	1 505 228
1902	1299	2335	96	2431	407 629	1 841 910	26 875	158 052	1 999 962
1903	1219	1955	111	2066	353 830	1 828 953	14 496	129 826	1 958 779
1904	1717	3458	296	3754	633 796	330 043	714 370	202 191	532 234

Note. As it is not possible to give the exact production for the years previous to 1898, the figures for those years are given for the quantities exported.

The figures of the production of Formosa agree on the whole with those given in our Report of April 1906: —

Year	Camphor kin	Camphor oil kin
1896	—	—
1897	1534596	638603
1898	2064406	1120979
1899	1819227	1369887
1900	3479179	2362108
1901	3667887	2587186
1902	3148742	2388135
1903	3595813	2678794
1904	3540953	2805809

The export of camphor in the year 1905 to the individual consuming countries was as follows: —

Australia	23917	yen
British America	20487	„
British India	525266	„
Straits Settlements	15894	„
China	28985	„
France	573175	„
Germany	115012	„
United Kingdom	258973	„
Hong Kong	11677	„
United States	985484	„
Other countries	7363	„
Total	2566233	yen
Against in 1904	3168197	„
and in 1903	3537844	„

The large falling off in the exports during the last two years becomes all the more apparent, as the market value of the article, on which the above figures are based, has in this period undergone an uninterrupted and considerable advance. According to a notice of the British Foreign Office (Ann. Series No. 3713), the total production of the Japanese Empire in 1905 was quantitatively as follows: —

Formosa	4800000	lbs.
Japan	1226607	„
Total	6026607	lbs.

Of this, 837333 lbs. were refined at Kobe and Osaka, 400000 lbs. were used up for home consumption, whilst the balance, and also the bulk of the camphor refined in Japan, were exported.

The exports of camphor and camphor oil from Formosa were:

	in 1889	1902	1904	1905
	Value: Yen			
Camphor	1935001	3718549	3057923	2683523
Camphor oil	1075858	921536	1235684	1156454

According to a report from the German Consul in Twatutia[1], the camphor production in Formosa has now for some years been growing smaller. In the districts in which it was possible to work with comparative safety under the protection of the frontier guards, all the trees have fairly well been felled. For this reason the chain of posts has to be pushed forward, in order not to let the production fall too low, as the trees stand already in the Savage district, or at least on its frontiers. This also explains the serious mistake made by the Japanese Government in calculating the purchases, as it obtained instead of the calculated quantity of about 5,7 million kin (1 kin = 601 g), over 1 million kin less. According to the Custom's statistics, there were exported in the year 1905 from Formosa, 2923117 kin camphor and 2579782 kin camphor oil, the oil exclusively to Japan, and of the camphor over 75 % abroad.

According to the same report, the high expectations based on the production of camphor from the leaves, have up to the present not yet been realised; the experiments cannot, however, as yet be considered as concluded, as it is generally accepted that the trees must be 4 to 5 years old[2] before the leaves can be utilised for the production of camphor oil.

In the course of the last few years the Japanese Government has planted out more than a million young camphor trees, and it now supplies the young trees free, and the land free of rent if it is Government land, and even makes a present of it to the planter if the plantations thrive. Unfortunately, about 70 % of all the trees planted out are generally lost, as the Chinese are in the habit of burning off the dry grass, which easily gives rise to tremendous conflagrations.

From a newspaper article which deals once more with the doings of the notorious head-hunters, we see what difficulties beset the Japanese civilisation in wild Formosa, and how the labourers in the camphor-districts carry on their difficult trade at the risk of their own lives. In the autumn of last year a sanguinary battle was fought between savages and a body of 200 camphor labourers working in 3 batches in the district of Foroku; of the 200 men only one returned to tell the tale of disaster. Recently the Japanese have sent a punitive expedition, which between December 30 and January 3 rased the

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[1] Deutsches Handelsarchiv **1907**, January number, part II., p. 35.

[2] Comp. Report October **1906**, 20.

villages Randai, Gundai, and Tandai to the ground. The savages had fled into the forests, where, as usual, they could not be caught. It is said that the Japanese would best like to smoke out the savages, but this cannot be done, as in such case the valuable camphor forests would also be destroyed.

A new camphor-producing district in the Japanese sphere of influence has lately been mentioned in a Report of the Imperial German Consul at Seoul, i. e., the island Quelpart, situated in the South of the Korean peninsula, where in 1905 experiments with camphor plantations have been made, which are said to have up to the present given very satisfactory results.

From a communication in *The Chemist and Druggist*¹) we learn that in the Far East, also outside the Japanese sphere of influence, attempts are made to cultivate camphor trees. A report of the first results worth mentioning originates from the experimental garden at Batu Tiga in Indo-China. The shoots, which were only planted in the year 1904, yielded already after one year 3000 lbs. leaves and branches, from which in the first crop 30 lbs. camphor, of a value of 40/-, were obtained. But as experience shows that two or even three crops can be gathered in every year, the favourable result has led to this, that larger areas for new plantations of camphor trees have been taken in contemplation.

The British Consul at Foochow (China) reports as follows²) on the camphor market of his district. The camphor trade does not on the whole warrant any high expectations, although, as compared with previous years, it shows a steady increase. At the beginning of the year the situation was not unfavourable; on the European markets a strong demand prevailed, and as it was possible to obtain sufficient quantities at advantageous prices, a good profit was realised, the more so, as the prices kept at a high level. The monopoly which had existed for a number of years was abrogated, and the native traders who now took up the camphor production with energy, could be induced to supply goods at sensible prices. In this manner a large number of contracts had already been concluded, when the situation underwent a complete change. Certain districts were by proclamation excluded from the manufacture, and the production of camphor by private individuals was prohibited. All representations in this direction were without avail, and business could only be transacted under the greatest possible difficulties. The price of camphor which in Foochow had

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1) Chemist and Druggist **69** (1906), 379; from the report of Resident-General Taylor for 1905.

2) Oil, Paint and Drug Reporter **70** (October 1, 1906), 10.

already risen in January 1905 to $ 118 per picul, and towards the end of the year to as much as $ 130 (in 1904 $ 70 to 80), jumped up to $ 190 in the first three months of 1906. In spite of this, the trade in camphor has steadily advanced, as is shown by the following export statistics: —

1902	264 cwts.	£ 1460
1903	1362 „	„ 8287
1904	1421 „	„ 10084
1905	4482 „	„ 43039

At the end of May 1906 the transactions already amounted to 5200 cwts., value £ 52000.

One of the principal factors in the enormous increase in the price of camphor is the celluloid industry, which has made considerable progress during the last decade. In Japan, great interest is now also taken in the celluloid manufacture, and the Board of the Camphor Monopoly has already made contracts for deliveries with two Syndicates. The one is British, with a capital of 5 million yen, and proposes establishing its works either in Kobe or in Osaka; the Franco-Austrian Syndicate intends putting down celluloid works at Misshima near Shidyuoka.

In a paragraph in a Hamburg newspaper it was said that within a not very distant time the market would have to reckon with large offers of American camphor, namely, with the product of the State of Texas. It was stated that under the auspices of the Bureau for Botanical Industry of the Board of Agriculture, large experiments in the cultivation of camphor trees were in progress, which gave hopes of apparently good results. It is said that the experimental farms in question are situated in Wharton and Floresville, Tex., and the method followed there, is to sow camphor seed in the manner of wheat or oats, and when the shrubs had reached a height of about 3 ft. to cut them down with a mowing machine to a height of about 1 foot from the ground. From the portions cut off the camphor would then be extracted by means of a distillation process. This operation could be repeated once a year for several years, as new shoots soon sprout from the stumps. In this manner a larger percentage and a better quality of camphor should be obtained than in Japan or Formosa. At the present prices the Texas camphor cultivation is said to yield a profit of about $ 450 per acre (!). This sensational report appeared to us sufficiently interesting to make enquiries in authoritative quarters, and our New York branch received from the Department of Agriculture the information that the above statements do not agree with the facts. Some experiments had no doubt been made last year, also in Texas, with the cultivation of camphor trees, but the experiments had chiefly been confined to Florida. With regard to the latter, an official report will probably be published shortly. In any case, it appears that for the present no practical result can be expected.

The statements made in our last Report[1]) have induced T. Kumagai[2]) to enter into the question of the danger which might threaten Japan, if it were possible to make serious competition to the Monopoly, on the one hand by the production of natural camphor in other countries, and on the other hand by the manufacture of artificial and synthetic camphor. That such a danger is actually possible, Kumagai believes to be beyond a shadow of doubt. For this reason he considers it advisable that Japan should in good time take preventive measures; apart from suitable steps to be taken by the Treasury and the Management, he looks for such measures chiefly in the forestry policy and the chemical technology.

With regard to the measures of forestry policy, the Japanese Government should, in Kumagai's opinion, take care that new cultivations of camphor trees are laid out, which outside Formosa should also extend over Japan and eventually Korea. The experience gained in the science of forestry should be used to the greatest possible advantage; among this he reckons greater facilities in transportation. The parties interested should have placed at their disposal, for a small consideration, light portable apparatus for a rational distillation, but above all, free instruction in the cultivation, planting, distillation, etc. should be provided. Plants yielding borneol, such as *Dryobalanops aromatica, Blumea balsamifera,* etc. should also be cultivated in Japan and Formosa.

From the point of view of chemical technology, the measures which come under consideration are, a rational cultivation of plants yielding oil of turpentine, for the production of artificial camphor, and also the search for a material possibly even more suitable than turpentine oil.

Now, although artificial camphor manufactured in Japan does not exclude competition for the natural camphor, such competition could be met by a suitable extension of the Monopoly so as to include artificial camphor.

In connection with this work, the *Deutsche Japan Post* publishes a report from the Chamber of Commerce at Yokohama, wich follows here *in extenso.* Some statistical figures for 1906 (estimated) can already be found in it.

> The demand for camphor for industrial and other purposes is constantly increasing, and against this an insufficient supply makes itself felt. In the year 1867 purified camphor was sold at 16 yen per 100 kin (1 kin = 601 g.).

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[1]) Report October **1906**, 20.

[2]) Deutsche Japan-Post, Yokohama, **5** (1907), 8.

In 1899 the same quantity cost 50 yen, and in 1902 the price had increased to 88 yen. Since the introduction of the camphor monopoly, the Monopoly Department buys crude camphor at 60 to 65 yen per 100 kin, and sells the purified camphor at 115 to 123 yen. On foreign markets, however, the article costs £ 25 to £ 26 (250 to 260 yen). The commercial statistics of the last five years show the quantity and the value of the exported camphor and camphor oil as follows: —

Camphor:

1901	4165757 kin	3904923 yen
1902	3953211 „	3404832 „
1903	3985360 „	3537844 „
1904	3140800 „	3168197 „
1905	2284794 „	2566232 „

Camphor oil:

1901	1561970 kin	239933 yen
1902	630985 „	92488 „
1903	1400921 „	181919 „
1904	1189921 „	189124 „
1905	1264184 „	216122 „

The total production of camphor and camphor oil for the last few years (1906 only estimated) is contained in the following official summary: —

	Camphor:	Camphor oil:
1904	4023519 kin	3434689 kin
1905	4102362 „	3417531 „
1906	4185906 „	3484387 „

This shows that about 90% of the total production was exported. The quantities imported again into Japan in the form of celluloid during the last five years were: —

1901	383616 kin	1903	339499 kin
1902	275939 „	1904	253643 „
1905	496865 kin		

The productive capacity of Japan amounts to: —

	Camphor:	Camphor oil:
Formosa	32000000 kin	22360000 kin
Old Japan . . .	33235000 „	34290000 „

The Camphor Monopoly Department strongly recommends that great attention should be paid to the cultivation and care of camphor trees, in order to maintain the productive capacity in this staple article at the proper level.

The *Bulletin of the Imperial Institute* contains a monograph on the camphor production1). We would here only refer to this interesting treatise, as all the information worth knowing has already been dealt with in the numerous notes on this subject in our Reports.

In our last Report2) we discussed a camphor oil which had been sent to us by the Imperial Biologico-Agricultural Institute at Amani in German East Africa, and, contrary to the Japanese oil, contained no safrol, but in spite of this proved to be a very valuable and

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1) Bull. Imp. Inst. **4** (1906), 353.

2) Report October **1906**, 20.

useful product owing to its high content of camphor (75 %). The differences in the composition are probably due to the fact that the Japanese oil is distilled from the wood of the roots and the trunk, whilst the African oil was obtained from the leaves and branches. An opinion in this sense expressed by us has now been published by the above-mentioned Institute in *Der Pflanzer*[1]), simultaneously with an opinion on the same oil given by another firm, which to our surprise differs very considerably from ours and reads much less favourable. The firm in question, namely, has found in this oil a content of only 10 % camphor and little safrol, and has in consequence characterised the oil as not particularly valuable. We are at a loss to explain this striking difference from the result of our examination, but we maintain our opinion on every point, for the camphor which we found in the oil has been isolated by us as such, and must therefore have been present in the oil.

An extensive cultivation of camphor trees in the German Protectorate justifies the most sanguine hopes, and for this reason we should not hesitate (as the Imperial Biologico-Agricultural Institute justly emphasises) "to follow the example of other countries, and make ourselves independent of the Japanese production which more and more degenerates into a farming of the Monopoly."

We mentioned already in our last Report[2]) that the production of camphor in Ceylon still stood at a very low level. It goes without saying that since then no distinct progress could be made. But the interest taken by some planters there in the cultivation of the camphor tree has induced the Director of the Rangala Co., E. J. Young, to read a paper to which the *Chemist and Druggist*[3]) refers. According to this there was up to the present really only one planter in Ceylon who produced quantities of camphor worth mentioning, but he only had 10 acres under cultivation. Young, however, considers it necessary to cultivate at least 50 to 100 acres if an adequate profit is to be secured. The chief object in view must be to improve the quality of the Ceylon camphor so that it becomes equal to that of the Formosa camphor, and to extract the oil from the leaves and branches separately from the oil of the trunks of the trees, as the former has a lower commercial value. The present market conditions are favourable for new cultivation of camphor trees, but it is doubtful whether these prices will continue when the situation in Formosa has again become settled. More than one generation will pass away before the planters

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[1]) Der Pflanzer, Ratgeber für tropische Landwirtschaft, published by the *Usambara-Post* with the assistance of the Biologico-Agricultural Institute, Amani, **2** (1906), 333.

[2]) Report October **1906**, 18.

[3]) Chemist and Druggist **69** (1906), 536.

in Ceylon will be able to compete seriously with the Japanese monopoly. But at the same time, the Formosan sources of camphor are not inexhaustible; during the last 25 years the production has fallen off by 15 %, and the tree has practically dissappeared from the safe districts.

Although in Ceylon the camphor distillation has not yet led to any satisfactory results, the reason, according to the Government chemist there, Kelway Bamber[1]), is due to inexperience in the distillation. The distillation is carried out too quickly, and the cooling done badly, which naturally causes the loss of a great portion of the camphor. Various distillations made in the course of last year with shoots from districts situated at the various altitudes (below 2000 up to above 6000 feet) gave yields of 1,16 to 1,71 % camphor. When the leaves and the branches were distilled separately, it was found that the former contained three times as much camphor as the latter.

J. A. Battandier[2]) reports on the camphor tree cultivation in Algeria, and on Algerian camphor. Contrary to the views previously held, the camphor tree grown in the Mediterranean countries contains as much camphor as in the country of its origin. But in view of the large fluctuations to which here as everywhere else the various individual specimens are subject, it would be a matter of general interest to cultivate the camphor tree by selection, the more so as it grows very well from seed, and can be readily multiplied by oculation.

The present position of the camphor manufacture (natural and artificial or synthetic camphor) is dealt with in a treatise by A. Hempel[3]) to which we would only refer. As in Hempel's communication A. Hesse's work on the production of artificial camphor is also mentioned, the latter feels called upon to make various corrections. With regard to Hesse's reply[4]) and Hempel's rejoinder[5]) we content ourselves with a bare reference.

M. Demiéville, pharmaceutical chemist in Zurich, kindly called our attention to a notice in the *Gazette de Lausanne* of October 24, 1906, according to which recently in the neighbourhood of Lausanne fragments had been found in sandstone of a petrified tree which is probably identical with the camphor tree. The find consisted of one large and several smaller pieces of a trunk, and also branches and leaves. In Rivaz, in the vicinity of Lausanne, not only camphor tree leaves, but also fossil leaves of the cinnamon shrub have been discovered.

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[1]) Journal d'Agriculture Tropicale **9** (1907), 58.
[2]) Journ. de Pharm. et Chim. VI. **25** (1907), 182.
[3]) Chem. Ztg. **31** (1907), 6.
[4]) Ibidem, 101.
[5]) Ibidem, 191.

Professor Lugeon, the Director of the Geological Museum at Lausanne, where a portion of the fossils is kept, has replied to an enquiry from M. Demiéville, that it is impossible to decide from the specimen whether it is actually the trunk of a camphor tree, but that such a view is certainly supported by the presence in large numbers of fossil camphor tree leaves.

Borneo camphor. The question of the presence of camphor or borneol in the Borneo camphor trees (*Dryobalanops aromatica* Gaertn.) cultivated in the Botanical Gardens of Buitenzorg, has frequently been discussed there.[1]

A separation of camphor or borneol could not be detected in the wood of felled trees, but when a hole was bored in a living tree, a white substance separated off in the holes which consisted chiefly of borneol.

By distillation with steam there were obtained, both from the leaves and from the trunk oils which, according to their behaviour on boiling (150 to 210° and 215 to 280° respectively), did not appear to contain borneol. But in both cases only a few cc. of oil were available, so that in our opinion a decidedly more favourable result may possibly be obtained if larger quantities are worked up. The constants given here are only those of the oil from the leaves: d_{26° 0,8585; $[\alpha]_{D 26^\circ} + 2^\circ 29'$.

Caraway Oil. The tone of the Dutch caraway market is described as very quiet, and it is said that very few transactions have lately taken place. The young caraway cultivations had developed favourably by the autumn, in so far as the Northern caraway districts are concerned, and in Groningen, Friesland and North Holland their appearance could be characterised as "good". The fields in South Holland and Zeeland appeared "fairly good", but in North Brabant only "middling"; in the last-named province some areas cultivated had to be ploughed up again. In North Brabant and Zeeland the winter, which this time was very severe, has done great damage, so much so that in many cases half the fields must be turned over again and sown with rape seed. From North Holland, Groningen and Friesland no reports have been received as to how the cultivation has come through the winter, but it may be assumed that there also the consequences of the severe winter will be more or less visible.

Although at first the area cultivated with caraway was at least as large as in 1905/6, a not unimportant falling-off will have to be taken into account for the coming harvest, which may probably soon find expression in higher prices.

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[1] Verslag omtrent de te Buitenzorg gevestigde technische Afdeelingen van het Departement van Landbouw 1905. Batavia, 1906, pp. 46 and 63.

Cardamom Oil, Ceylon. See under Terpinene, p. 135.

Cassia Oil. The firmer tendency of the market which we announced in our last Report has since spread and finally an upward movement has set in, such as had not been witnessed for years for this article, which had been so long neglected. Above all, offers of 80/85 per cent. oil were for a time totally absent, and only a few weeks ago was it possible to obtain firm quotations for shipment from over there at the enormous figure of 5/6. Whether the upward race of the quotations must be really attributed to lack of supplies from the producing districts, or to speculative enterprise on the part of Chinese middlemen, is a matter on which opinions differ; on the strength of information received, though only meagre, we are inclined to accept the first-named view. Whether with the above price the highest limit has been reached is a question on which at present it would not be safe to express even conjectures.

It is not surprising that under these conditions the demand for our 100 per cent. cinnamic aldehyde free from chlorine was very brisk. Although we have nearly trebled our production, we were not always able to meet the demand from the consumers, and at the present moment we are still behindhand with large orders for America. The advantages of this preparation over natural cassia oil are so well known that we need not enter again into details on this point.

Saigon cinnamon, a cinnamon called after Saigon, the most important port of Cochin China, which in addition to Ceylon cinnamon is officinal in the American Pharmacopœia has been examined by L. Rosenthaler[1]).

According to its external habitus and its anatomical constitution, Saigon cinnamom is very closely allied to the Chinese kind; this applies very specially to the younger pieces. Rosenthaler concludes from this that Saigon cinnamon originates, if not from *Cinnamomum cassia* Bl. itself, at least from a very closely allied species.

The bark has a very fine odour and taste, and contains about 2,1 % essential oil; it therefore belongs to the cinnamon varieties richest in oil. This is already shown by the fact that the interior, when pressed with a hard object, takes a greasy lustre from expressed essential oil, the same as the cut surfaces do when the bark is cut with a knife. Rosenthaler gives no details of the properties of the oil.

Oil of Cassie blossoms. According to E. Wildeman[2]) *Acacia Farnesiana* (L.) Willd., which is so important for the French

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[1]) Inaugural publication on occasion of the inauguration of the new Pharmaceutical Institute of the Strassburg University. Strassburg, autumn 1906.

[2]) Publication de l'Etat Indépendant du Congo 1906. Notices sur des plantes utiles et intéressantes de la flore du Congo. II. Brussels, 1906, p. 105.

blossom industry, is also found in the Congo Free State. Whether the plant is there originally indigenous, is uncertain. Welwitsch is of opinion that this species belongs to the flora indigenous to Angola, and for this reason it is not impossible that it also occurs in the Congo district. *Acacia Farnesiana,* as a matter of fact, is widely distributed; apart from tropical Africa, it is also found in Egypt, India, Australia, Hawaii, the Philippines, the West Indies, and North and South America. In some districts the gum produced by this plant is collected, and used instead of gum-arabic. Seeds, blossoms and bark are frequently recommended for medicinal purposes, and various parts of the plant are used in tanning and dyeing on account of their content of tannin. In the United States this acacia is often designated with the name *Opoponax.*

In the South of France the plant is known under the names *Cassier du Levant, Casillier de Farnèse,* or simply *Cassier,* and in favourable positions it is cultivated there on a large scale.

When the plants are three years old the blossom harvest commences in the South of France. Each plant is capable of yielding 500 g. blossoms which are gathered twice weekly in the months of September, October, November and occasionally December.

In France and Algeria 150000 kilos cassie blossoms have been gathered during the last few years.

Whilst in Northern India since many years cassie pomade is prepared from the blossoms of this acacia, in the real tropics it has never been attempted to utilise the blossoms of the *Acacia Farnesiana,* although in the author's opinion the cultivation of this shrub could be tried there under certain conditions.

With regard to the physical constants and composition of oil of acacia blossoms, we would refer to our Report of April 1904, p. 23, where we have described the properties of a cassie blossom oil obtained by us from Indian pomade (from Naini Tal). In an oil of acacia blossoms which we have meanwhile isolated in the same manner from French blossom extract, the following constants were ascertained: d_{15° 1,0575, α_D — 0° 30′, n_{D22° 1,51500; acid no. 25,4, ester no. 229. The yield amounted to 5,65 % of the extract.

Cedar Leaf Oil. According to our previous observations[1]) the oil of cedar leaves of American commerce was never the oil from the leaves of *Juniperus virginiana* L., as in North America two totally different trees, *Juniperus virginiana* and *Thuja occidentalis,* are designated as "cedar". A work by Hanson and Babcock[2]) on American oils

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[1]) Report April 1894, 57; Comp. also Gildemeister and Hoffmann, The Volatile Oils, p. 278.

[2]) Journ. Amer. chem. Soc. 28 (1906), 1198.

of conifers, contains one single statement on the cedar leaf oil of *Juniperus virginiana;* the authors found a specific gravity 0,900 (16°).

Cinnamon Oil, Ceylon. The trade in this speciality of our firm was very brisk during the past half year, and although we had arranged for a large supply of cinnamon chips, we were not always able to meet the demand. Owing to the increasing demand for the crude material, also on the part of the spice industry, the prices soon hardened from 2 d to 2 $^{3}/_{16}$ d per lb., so that we could not avoid an advance in the quotations of our distillate. The following export statistics of the Chamber of Commerce in Colombo show the enormous increase in the exports of cinnamon chips: —

1906	2531614 lbs.	1901	1516083 lbs.
1905	2325514 „	1900	1863406 „
1904	2368351 „	1899	1829127 „
1903	2253269 „	1898	1414165 „
1902	1763679 „	1897	1067051 „

On the other hand, the export of cinnamon oil from Ceylon in the same period, has declined from 181536 ozs. to 158344 ozs. — a clear proof that the superiority of the European distillate over the Ceylon oil is beginning to be recognised by the consumers.

We read in the *Pharmazeutische Zeitung*1) that the American physician Ross, on the strength of a practice extending over 16 years, recommends cinnamon oil as an excellent remedy against influenza. The dose is 10 to 12 drops every two hours, until the temperature is again normal. From that moment a dose of 10 drops three times daily for one or two days is sufficient.

The essential oil from the bark of the trunk of *Cinnamomum pedunculatum* Nees (*C. japonicum* S. et Z.) known in Japan as "Yabu-nikkei"2), has been examined by S. Keimatsu and S. Asahina3). As might be expected the oil differed completely from ordinary cinnamon oil: d 0,917; $[\alpha]_D$ — 280,54′ (— 4° 40′?); acid no. 0; sap. no. 0; sap. no. after acetylation 84,6. The oil was rich in phellandrene (m. p. of the nitrite 110°) and contained also a small quantity of eugenol (m. p. of the benzoyl compound 69°), and methyl eugenol, which was identified by oxidation into veratric acid (m. p. 179°).

Citronella Oil. The firm condition of this important article, which has gradually risen to about 1/11 cif. Hamburg, is in our

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1) Pharm. Ztg. **51** (1906), 1074.

2) Not to be confounded with the Japanese cinnamon or cassia bark tree *C. Loureirii* Nees, known under the name "Nikkei". Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 391 and Report October **1904**, 96.

3) The Oriental Druggist **1** (1906), No. 3. Yokohama.

opinion explained by the fact, that the production in Ceylon is not able to keep pace with the demand which increases from year to year. The exports from Ceylon were: —

in	1904	1 133 068 lbs.
„	1905	1 309 416 „
„	1906	1 212 771 „

The year 1906 consequently closes with a deficiency of nearly 100 000 lbs. as compared with 1905, which became all the more felt, as New York was constantly on the market with orders, and not only rarely allowed the prices to come to rest, but helped to drive them up to a not inconsiderable extent in the course of a few weeks. Between October and December a certain dullness came over the market, and the prices fluctuated at first between 1/7 $^1/_4$ cif. in October and 1/8 $^1/_2$ in November and in December even for a time declined to 1/6 $^3/_4$. But this last quotation was clearly of a purely speculative character. At the beginning of January a brisk demand arose for consumption as well as for speculation, so that at the end of that month orders at 1/8 $^1/_2$ to 1/9 cif. scarcely led to business. Since that time the prices have slowy advanced further up to their present level. Although the shipments from Ceylon in 1907, up to the end of February amounted to 137 900 lbs. against 116 517 lbs. in the same period of the previous year, the reports from over there are very pessimistic, and the exporters are unanimous in declaring that the supplies are too small and that we shall have to reckon on still higher prices.

The trade in Java citronella oil has been completely paralysed by the speculative action of one interested party, as this person has secured almost the entire production at high prices. The bulk is intended for America, but we fear that the consumers are not particularly edified by the tactics of driving up the prices without cause, which the party in question has adopted.

With regard to the cultivation of citronella grass in Java, St. Smith[1]) gives some interesting information based upon a visit to one of the large plantations there, which we will briefly reproduce. If the grass is planted in a good fertile soil, and has received plenty of rain, it grows rapidly and gives a good crop, which, with four cuts in every year, amounts to about 4,8 tons per acre, which means, for 10 acres, with an oil-content of the grass of 0,5 $^0/_0$, a quantity of oil of 4,8 cwts. of a value of about £ 46.16.0. The grass has to be planted out again only after 12 years. As the cost of a distilling plant is also

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[1]) Agricultural News, vol. 5, p. 335, acc. to Bulletin of Miscellaneous Information, Royal Botanic Gardens, Kew, 1906, No. 8, p. 363.

not particularly heavy, **Smith** recommends the cultivation of the grass in Papua, in the same manner as in Java, namely between india rubber and cocoa nut trees.

We have in our Reports[1]) repeatedly alluded to the difficulties which exist in an exact differentiation of the individual Andropogon or oil grasses, and which appear almost insuperable in view of the many varieties and transition forms. These difficulties have come to the front particularly in recent times, when the oils obtained from the grasses in question meet with an increasing amount of interest, and when frequent trials are made to cultivate the grasses supplying the individual oils, both in their own habitat and also specially in other tropical countries. In view of the deficient knowledge of the individual grasses, such cultivation-trials have led to frequent disappointments, inasmuch as apparently identical plants yielded totally different oils. For this reason botanists have repeatedly endeavoured to do away with the existing contradictions, but up to the present without succeeding in actually clearing up the question.

With an industry worthy of acknowledgment, and even far more important results, Dr. Otto Stapf has now approached the solution of the problem; he has made a thorough study of the individual grasses, and has put down his observations and conclusions in a work entitled: "The Oil-Grasses of India and Ceylon"[2]). If — as Stapf himself emphasises — his work cannot lay claim to absolute completeness, as further thorough observations are needed to make it so, yet what has been so far attained, clears up many questions which had hitherto remained unanswered, and it may be taken for granted that the uncertainty which has prevailed on this subject up to the present will soon disappear completely, the more so, as the impulse given by Stapf will no doubt induce many others to take up the study of the oil-grasses. It is to be hoped that Stapf's work will have this practical result, that the oil-distillers will also acquire a more complete understanding of the individual varieties, and that more attention will be paid than hitherto to the working up of a uniform plant-material. For his examinations Stapf has had at his disposal an, if not exhaustive, at least very voluminous observation-material, and this, as well as a thorough study of the individual grasses, have had a directly decisive effect on the results of Stapf's work. The further elucidation of this question will probably be greatly assisted by the fact that Stapf has completely broken with the present nomenclature

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[1]) Reports April **1903**, 23; October **1904**, 52; April **1905**, 55.

[2]) Published in the Bulletin of Miscellaneous Information, Royal Botanic Gardens, Kew, 1906, No. 8, p. 297.

which has largely contributed to the confusion existing, and has classified the individual grasses in the following groups: —

Genus *Cymbopogon,* with 10 species
„ *Vetiveria* „ 1 „
„ *Andropogon* „ 1 „

Most interesting is the detailed discussion of the individual species. Stapf enters here in detail into the history, the habitat, the botanical characteristics, synonyms and vernacular names of the various grasses, and moreover supplies details on the oils which come under consideration. Of these particulars we reproduce here only those which appear to us necessary for our purpose, and we refer to the original work especially with regard to the very voluminous historical part and the botanical details.

1. *Cymbopogon Schoenanthus* Spreng. (Synonyms: *Andropogon Schoenanthus* L., *A. laniger* Desf., *A. Iwarancusa* subsp. *laniger* Hook. f.) Camel grass. This plant was known already in the earliest times, and was frequently employed for medicinal and cosmetic purposes. In the old pharmacopœias and herbalist's books, it appears as *Herba Schoenanthi,* but other names were also in use for it, such, for example, as *Juncus odoratus* and *Palea camelorum.* The Arabian name often used is *Izkhir.* As a characteristic desert-plant which is able to exist with the smallest possible supply of water, it is distributed over Northern Africa and Arabia, and it is also found in the Persian province of Kirman, where it grows at altitudes of 6000 feet and higher, and from South-Western Afghanistan and North-Western Beluchistan, to the Punjab.

With regard to the essential oil contained in it (camel grass oil), comp. Gildemeister and Hoffmann, The Volatile Oils, p. 299.

2. *Cymbopogon Iwarancusa* Schult. (Syn. *Andropogon Iwarancusa* Jones). The grass, which, according to Blane, is identical with the *Nardus Indica* of the Ancients, is found along the extreme mountain-zone of the Indian provinces, and here prefers the neighbourhood of streams as it requires at least at intervals, a plentiful supply of water. The natives call it *Terankus* (fever-remedy) in consequence of its beneficial action in all kinds of fever¹). The whole plant has a strongly aromatic odour, but particularly the roots, which also contain the therapeutically active constituents, and which have a burning and bitter taste when chewed. *C. Iwarancusa* differs from *C. Schoenanthus* (to which it is closely allied) by the stronger build, the long, flat, and comparatively broad leaves and the more strongly ramified panicles. At great altitudes, or in the dry parts of the Punjab, it becomes small and narrow-leaved, and then represents a transition-form to *C. Schoenanthus.*

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¹) For the rest, almost all the other species discussed here are employed for therapeutical purposes.

3. *Cymbopogon Nardus* Rendle (Syn. *Andropogon Nardus* L.), citronella grass. In this grass also various botanists suspected the *Nardus Indica* of the Ancients, and for this reason Linnaeus gave it the name *Andropogon Nardus;* from other side the grass was also connected with *Calamus aromaticus*[1]). Nicholas Grimm, a physician who lived at the end of the 17th century in Colombo, called the grass *Arundo Indica odorata.* He stated that it grows in large quantities in the neighbourhood of Colombo (probably cultivated), and that an essential oil is distilled from it. In after-days citronella grass has often been confused with lemon grass.

Citronella grass is only found cultivated; it is grown particularly in the southern part of Ceylon, and also in the Malacca peninsula and Java; in most recent times attempts have also been made to cultivate it in the West Indies. The mother-plant is very probably the wild mana grass, *Cymbopogon confertiflorus* Stapf, found in Ceylon.

It is well known that citronella grass is cultivated in two varieties: "Maha pengiri" (Maha pangiri), and "Lenabatu" (Lana batu). The first-named sort is also called "old citronella grass" or "Winter's grass", as it is now only cultivated by Winter & Son, whilst it is chiefly grown in the Malacca peninsula and in Java. It has fairly broad leaves, larger tufts than "Lenabatu", and is characterised by a rapid growth, but it is soon exhausted and dies off after 10 to 15 years. As for this reason it frequently has to be planted out afresh, it has more and more been replaced by the lenabatu variety. It yields an oil of less specific gravity, readily soluble, and rich in total geraniol (geraniol + citronellal). The statement originating from Winter[2]), that "Maha pengiri" has reached Ceylon from Malacca, must (according to Stapf) be so understood, that the grass which does not grow wild in Malacca, has been brought back to Ceylon from there as an improved race. But as "Maha pengiri" also passes for the "old or original Ceylon citronella grass", it is more probable that Winter's above statement is after all incorrect.

The variety known as "Lenabatu", also designated as "new citronella grass", which forms the bulk of Ceylon citronella grass, yields an oil of less value, which differs from the other by a higher specific gravity, lower geraniol-content, and a content of methyl eugenol.

Morphological differences between the two varieties do not exist, as Stapf proved with two specimens which, however, were not very well preserved.

4. *Cymbopogon confertiflorus* Stapf (Syn. *Andropogon confertiflorus* Steud., *A. nilagiricus* Hochst., *A. Nardus* var. *nilagiricus* Hack.). This grass is

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[1]) As Stapf mentions in another place, Royle endeavoured to prove that this name belongs to Palmarosa grass, *Cymbopogon Martini* Stapf, and for this reason proposed for the latter the designation *Andropogon Calamus aromaticus.*

[2]) Chemist and Druggist **52** (1898), 646.

found in India in the district between the Nilghiris and Ceylon, and also in Ceylon itself, where it is very characteristic for the vegetation of certain districts, and is said to grow at altitudes up to 5000 feet. It grows to a height of 5 feet and more. As already mentioned above, it is probably the wild mother-plant of citronella grass, and it has also the same odour as the latter, but it only gives a small yield of oil, of whose properties nothing is known. The Singhalese name for it is "Mana", whilst in the Nilghiris it is known as "Bambe".

5. *Cymbopogon flexuosus* Stapf (Syn. *Andropogon flexuosus* Nees ex Steud., *A. Nardus* var. *flexuosus* Hack.), Malabar or Cochin grass, is distributed in the Tinnivelli district and in Travancore. It was found there only in the wild state, and not cultivated, as erroneously stated in Gildemeister and Hoffmann's work *The Volatile Oils,* p. 285, for this plant which yields the Malabar or Travancore lemongrass oil. Only during the last few years, large areas have been planted there with this grass. According to Stapf, the oil which is known in commerce as lemongrass oil is obtained from two wholly different plants, the oil coming from the Malabar coast being produced from *C. flexuosus* Stapf, whilst the other species of lemongrass, designated as *C. citratus* Stapf, yields an oil which, though very similar, is not identical with the former; this matter is discussed more in detail further down.

C. flexuosus appears to have often been confused with citronella grass; in the *Medicinal Plants* of Bentley and Trimen, for example, it is illustrated under the name *Andropogon Nardus,* but it differs from the latter by the large, loose, grey- or slate-coloured panicles, of which the particularly thin and long diagonals are curved and frequently hanging down, and further by the less distinct spathes and the smaller and usually very thin and sharp aristæ. The sheaths of the ground-leaves are somewhat narrower than those of citronella grass, and not reddish inside.

6. *Cymbopogon coloratus* Stapf (Syn. *Andropogon coloratus* Nees, *A. Nardus* var. *coloratus* Hook. f.) is found from the Tinnivelli district to the Anamalai mountains, and also in the district Karnatik (Madras Presidency), and belongs to the lemon grasses of the Malabar district. It differs from *C. flexuosus* among others by the fact that it is much smaller. An essential oil of this plant is not known.

7. *Cymbopogon citratus* Stapf (Syn. *Andropogon citratus* D. C., *A. Schoenanthus* L., *A. citriodorum* Desf., *A. Roxburghii* Nees, *A. ceriferus* Hack., *A. Nardus* var. *ceriferus* Hack., *Schoenanthum amboinicum* Rumph.), lemon grass, in Malayan „Sereh". Contrary to Malabar grass, *C. citratus* only occurs in the cultivated state. It is found in most tropical countries, especially in Ceylon and the Straits Settlements, also in Lower Burmah and Canton, Java, Tonquin, Africa, Mexico, Brazil, the West Indies, French Guyana, Mauritius, Madagascar, New Guinea, etc.

In the Malay peninsula, and especially near Singapore, the grass is cultivated on the largest scale, and used, besides for the production of oil, chiefly for cookery purposes.

The grass blossoms very rarely, and for this reason has been very little or not at all observed by botanists; this explains why, in spite of its wide distribution, it has not yet been sufficiently identified botanically.

The oil obtained from it differs from the Malabar lemongrass oil specially by its lower solubility in alcohol and the frequently lower citral-content, for which reason it is usually less valuable than the Malabar oil.

8. *Cymbopogon Martini* Stapf (Syn. *C. Martinianus* Schult., *Andropogon Martini* Roxb., *A. pachnodes* Trin., *A. Calamus aromaticus* Royle, *A. nardoides, a,* Nees, *A. Schoenanthus* Flück. et Hanb., non L., *A. Schoenanthus* var. *genuinus* Hack., *A. Schoenanthus* var. *Martini* Hook. f.), Rusa grass, geranium grass. The vernacular name "rusa" which is largely used for this grass is probably derived from the brown-red coloration of the panicles in autumn.

Rusa grass is found from the Rajmahal mountains (on the bend of the Ganges) to the Afghan frontier, and from the sub-tropical zone of the Himalayas to the twelfth degree latitude, with the exception of the desert and the steppe region of the Punjab, the external slopes of the Westghat, and apparently a large part of Northern Karnatik.

According to Forsyth the grass commences to bud towards the end of August, and then blossoms until the end of October. During this time, namely at the commencement of the blossoming period, the destillation must be carried out, as the yield of oil later on diminishes considerably, and moreover its quality becomes quite inferior. The principal places of production of the oil are the following: Pimpalner, Akrani, Nandurbar, Shahada, and Talada, all in Khandesh; further, the districts of Nagpur, Sagar, Jabalpur, and Karnul, and of Ajmere in Rajputana. If the wide distribution of the grass is taken into consideration, the limited district of oil-production is remarkable.

A distinction is made between two varieties of the grass: "sofia" and "motia", but it is for the present undecided whether we have here to do with botanical varieties, or only with different conditions of maturity of the same species. How far in this respect opinions differ, is shown by the following lines. According to the *Pharmacographia Indica,* part III, 558, what is understood under the name "motia" or "motiya" is the young grass of which the inflorescence has a blueish-white colour; the oil obtained from it is the palmarosa oil of commerce. "Sofia", "sofiya", "sonfiya", or "sufia", on the other hand, is the name of the grass in the ripe state, in which it has a red colour; the distillate from this grass is the so-called ginger grass oil. In direct contradiction to the above is the statement by E. G. Fernandez, according to which it is a question of two different varieties. The "motia" yielding palmarosa oil is said to be usually confined to the higher slopes of the hills, whilst the "sofia" yielding the gingergrass oil is found more on the plains and the table lands of the hills; frequently, however, the two varieties are found alongside each other. Stapf has been unable to detect any morphological differences in two specimens collected by Fernandez; of these the "motia" was, moreover, just in the more developed stage[1]).

9. *Cymbopogon caesius* Stapf (Syn. *Andropogon caesius, a* et *β* Nees, *A. Schoenanthus* var. *caesius* Hack.), Kamakshi grass.

This grass is very closely allied to *C. Martini,* but yet sufficiently different; only where the two species meet, transition-forms occur which unite the two species completely. *C. caesius* grows in the largest part of Karnatik, where it is fairly common. It replaces *C. Martini* in South-Eastern India.

In the Administration Report of the Government Botanic Gardens and Parks, the Nilghiris, for 1901, p. 5, an article appears on the oil. The grass used for the distillation originated from Arni, in the North Arcot district, Madras Presidency, where it is found in large quantity. The oil-yield from the grass freshly cut at the end of December, was 0,431 $^0/_0$. Another parcel distilled at the end of April in an entirely dry state, yielded 0,711 $^0/_0$ oil. With regard to the properties of the oil, no data are available.

10. *Cymbopogon polyneuros* Stapf (Syn. *Andropogon polyneuros* Steud., *A. versicolor* Nees, *A. Schoenathus* var. *versicolor* Hack., *A. nardoides β minor,* Nees ex Steud.). *C. polyneuros* is a fairly strong grass which has a great tendency to form numerous ramifications upwards, so as to form thick clusters. It is found in the South-Western parts of India, especially in the Nilghiris, and here replaces *C. Martini.* It is also found in Ceylon, preferably at greater altitudes (up to 4500 feet), and further in the island Delft in Adams' Strait, where it is called "Delft grass" and forms a good food for horses. The odour of the rubbed leaves is said to remind of fennel or anise[2]). The oil was distilled in 1902 in Utakamand, and obtained in a yield 0,25 $^0/_0$; with regard to its properties nothing is known.

11. *Vetiveria zizanioides* Stapf (Syn. *Andropogon muricatus* Retz., *A. squarrosus* Hack., *Vetiveria muricata* Griseb. a. o.), vetiver grass, Anglo-Indian "Khas khas", a name which is probably of Hindoo origin and means "aromatic root".

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[1]) Comp. also under Palmarosa oil.

[2]) Comp. Report April **1905**, 55.

Vetiver grass occours both in the wild state and cultivated, and is much esteemed on account of its roots which are used for many purposes. In the wild state it is distributed all over British India and Ceylon, being chiefly found on the banks of rivers and on rich marshy soil up to an elevation of 1800 feet. Occasionally it is cultivated, for example in Rajputana and Chutia-Nagpur. In the Malay districts vetiver only occurs cultivated or accidentally growing wild, — the same applies to the West Indies, Brazil, and Rèunion. It is usually cultivated by dividing the tufts and transplanting them in a loose soil. The best sort of grass is found in the neighbourhood of Tutikorin which is still at the present day the most important shipping port of vetiver root. The roots were used already in early times for the manufacture of rugs and mats which were hung up in front of doors and windows, and which in hot weather were frequently sprinkled over with water and thus pleasantly cooled and perfumed the air.

The vetiver oil prepared from the root does not appear to be distilled in India itself or in the other countries with the exception of Rèunion, and this must probably be attributed to the difficulty of the manufacture. The regular export of the roots to Europe is to all appearances also of a comparatively recent date.

12. *Andropogon odoratus* Lisb. The grass was discovered in 1875 by Dymock in Thana. The oil contained in it has only a scientific interest, as it is not produced on a large scale. Whatever is known about it, is found in Gildemeister and Hoffmann's work *The Volatile Oils,* p. 299.

Although the foregoing, as already stated, gives only a rough outline of Stapf's work, it may give an idea of the importance of Stapf's researches for the knowledge of the oil-grasses. It is to be hoped that the work will everywhere in interested circles receive the attention to which it is entitled, so that very soon order may come in the chaos prevailing the present moment in this domain.

In our last Report[1]) we discussed an article relating to the citronella oil industry of Ceylon, of which as the author's name was given as A. Jayasuriya. Mr. Jayasuriya now informs us that not he is the author, but Mr. B. Samaraweera, founder of the firm "B. Samaraweera, essential oil producers and exporters" at Weligama, in Ceylon. Mr. Jayasuriya only represented Mr. Samaraweera at the Meeting of the Agricultural Society of Ceylon, and referred there to his work.

We gladly avail ourselves of this opportunity of correcting the matter, but would point out that we are innocent of the error. According to the two available sources in which this article was mentioned, (*The*

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[1]) Report October **1906**, 24.

Oil, Paint and Drug Reporter, and *The Times of Ceylon*) we were bound to consider Mr. Jayasuriya as the author.

Clove Oil. It now has the appearance as if the pessimistic among the correspondents were after all right, for since we last expressed an opinion on the harvest of 1906/7, reports have been accumulating which say that the crop only amounts to barely 60000 bales. Now, as the consumption of Europe and America alone in the course of a year is estimated at quite 60000 bales, but as the whole of the available stocks in London, New York, and Holland, are only said to amount to 41000 bales (March 1, 1907) it may be taken as probable that this quantity will not satisfy the world's requirements until the harvest 1907/8 becomes available, which at the earliest would be the case at the end of October. Very little is on the way; for instance, the shipments in the month of January 1907 only came to 5000 bales, against 18000 in January 1906, and 23000 in January 1905. Three fourths of the result of the harvest is said to have been contracted for, for shipment to Europe and America, whilst the so-called „duty cloves" representing one fourth of the production were taken off the market by an English Syndicate. The demand from India amounting to about 40000 bales, could not be covered, and it is stated that Bombay has already commenced looking out for supplies in Europe. A speculator backed up by capital appears to control there the trade in this article completely.

Under these circumstances the stocks in Europe and America will shrink considerably this year, or may possibly vanish altogether, and for the first shipments of the 1907/8 harvest, a brisk demand will have to be recorded. It would be too early at the present day to draw conclusions as to the result of this season, and it is all the less possible to form an opinion, as it cannot yet be ascertained whether the damages caused to the plantations during the harvest of 1904/5 by unsuitable picking, will make themselves further felt in a disadvantageous manner. On the whole, the opinion prevails that during the summer the prices will experience a considerable increase, and we also cannot entirely shut our eyes to the grounds which are brought forward in support of this assertion, although we are inclined to treat all reports on this subject, after our own experience, with scepticism. If it should really happen that the speculative stocks in Europe and America some day were completely absorbed by the consumption, this would at least have the effect of making it a much more simple matter to form an opinion on the market for the following season.

In 1906, no fewer than 24000 bales were imported in Hamburg, against about 19500 in 1905, about 9600 in 1904, and about 17000 in 1903. These figures give no approximate picture of the actual consumption of this article in Germany, as some of the larger firms, such as for example ourselves, cover their requirements partly on the Dutch terminal market, and those supplies reach this country mostly by land.

It is well known that clove oil is very popular as an addition to tooth-powders and mouth-washes, owing to its disinfecting properties. J. C. Webster[1]) now has found that the oil on account of its pronounced bactericide action, also constitutes an excellent disinfectant for the hands, which is distinctly preferable to mercuric dichloride. After washing and brushing the hands for about 5 minutes with warm water and soap, they are dried with a sterilised towel, and washed for 1 minute with alcohol. The hands are then rubbed in for 4 or 5 minutes with clove oil, which is finally washed off with alcohol. Bacterial cultures from hand scrapings on gelose gave in 45 cases, after applying clove oil, only 0,04 colonies, whilst by treatment with water and soap only, under otherwise similar conditions, 450 colonies were formed, and disinfection with sublimate (1:2000) still gave a mean of 21 colonies. Silk threads infected with pathogenic germs were absolutely sterile after 30 minutes' immersion in clove oil. Catgut ligatures immersed for about 8 days in clove oil were after draining, soaking in 95 per cent. alcohol for 6 to 8 hours and drying more thoroughly sterilised than by any other method. Webster characterises the results of the disinfection with clove oil as so satisfactory that all other methods were abandoned.

Oil of Copaiba. Philippine wood oils. Under this name A. M. Clover[2]) comprises liquid balsams which dry very badly, and have a high content (75 %, and above) of volatile substances. The latter consist chiefly of bodies of the sesquiterpene-group. Clover describes three different kinds of oil: —

1. Supa oil. The mother-plant, *Sindora Wallichii* Benth. (like *Copaifera* belonging to the family of the *Leguminosae*), is distributed throughout the islands.

A freshly tapped tree yields about 10 litres of the product which is obtained by hollowing out the trunk. The oil forms a mobile, homogeneous liquid with a faint yellow colour, a feeble fluorescence, and a faint but characteristic odour; $d_{30^\circ}^{30^\circ}$ 0,9202; α_{D30° — 31,3°; when cooled down below 20°, white flaky crystals separate off, which consist of a hydrocarbon of the m. p. 63 to 64°, and form about 5 % of the oil. The oil dissolves in all usual solvents except alcohol, readily absorbs oxygen from the air, and finally solidifies. When submitted to steam distillation, a colourless oil passes over, α_{D30° — 21°;

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[1]) Pharmaceutical Journal **77** (1906) 553.

[2]) Philippine Journ. of Science **1** (1906), 191.

the principal boiling temperature lies between 143 and 149° (40 mm. pressure). The distillate has $d_{30^\circ}^{30^\circ}$ 0,9053, and when again distilled at 760 mm. pressure passes over almost without residue between 255 and 267°. If the crude material, however, is at once distilled without steam *in vacuo,* the volatile oil passes over at 40 mm. pressure up to 170°, but without a constant boiling point, and consists (in addition to a small quantity of water) of about 73 % of the original specimen. This oil boils on redistillation within 7° and probably represents a mixture of sesquiterpenes, among which cadinene was isolated, in the form of cadinene hydrochloride (m. p. 117 to 118°), by the introduction of hydrochloric acid in the acetic solution of the distillate; the regenerated cadinene showed a boiling point of 164 to 165° (38 mm. pressure); α_{D30° (50 mm. tube) — 39°. The fact that neither sodium nor phosphorus pentoxide in benzene acted on the oil proved the absence of alcohol-like bodies. The residue of the vacuum-destillation had a light brown colour, became semi-solid when cooled, and dissolved in all solvents except alcohol which separated off the above-mentioned hydrocarbon. The latter neither absorbed bromine nor discoloured potassium permanganate solution when heated. Substances of a similar character (probably paraffins) frequently occur in resinous products, and also in essential oils[1]). The saponification number of the residue was 64, the acid no. 60; the amount of saponifiable substances is consequently practically nil.

2. Apitong oil (Balao). The mother-plant of this oil which is universally known among the natives is *Dipterocarpus grandifluus.* The balsam which in its composition resembles the one just described, consists chiefly of a solid resin, water, and 25 to 40 % of volatile oil. It is used for calking vessels, or as a wood varnish, and for these purposes is mixed with another solid resin, or with lime; it is also sometimes used for lighting purposes. If the resin exudes with difficulty from the tapped tree, it is set on fire; the product then rapidly running out acquires in such case a dark colour. The maximum quantity which one tree is capable of yielding per day amounts to about 1 kilo. In the fresh state the resin is white, but it gradually becomes darker, and when left standing, readily dries up in a thin film; it forms no homogeneous liquid, and contains large quantities of granular substances which do not dissolve but remain suspended in the liquid. It has a faint but characteristic odour, appears to dissolve in all solvents except alcohol, and contains water which cannot be separated off at once. Only when the balsam is mixed with an oil containing sesquiterpene, and then heated in an oil bath (above 140°), the water disappears, and if heated considerably

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[1]) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 99.

higher a clear solution is finally obtained, which on cooling again becomes semi-solid. Towards fatty oils the balsam behaves in exactly the same manner, and this property is all the more important, as it is a valuable one for the manufacture of varnishes. Whilst balao is liquid at ordinary temperature, it hardens during steam distillation, and becomes viscid to such a degree that it is impossible to obtain then more than traces of a volatile oil. Nor can the volatile substances be separated off by distillation at reduced pressure, as the mass at once begins to foam, and the residue from which the water has been removed becomes solid. It is therefore necessary to distil over a naked flame, when finally 50 % of the balsam pass over, of which about one half consists of oil, and the other half of water. The boiling temperature ranged between 200 and 300°; the bulk passed over at 260 to 264° (760 mm. pressure) or 151 to 154° (40 mm. pressure); $d^{30^\circ}_{30^\circ}$ 0,9127; α_{D30° $+78{,}5^\circ$. The distillate had a faint yellow colour and the characteristic odour of balao. Another purified sample of the same boiling temperature had $d^{30^\circ}_{30^\circ}$ 0,9131; α_{D30° $+87^\circ$. As heating over a naked flame is not favourable for the isolation of a body in the pure state, the balsam was mixed with non-volatile cocoa nut oil, and then treated with steam. The product thus obtained boiled at 149 to 152° (37 mm. pressure); $d^{30^\circ}_{30^\circ}$ 0,9140; α_{D30° $+61{,}3^\circ$; it is doubtless a sesquiterpene, but it could not be identified further.

3. Panao oil (malapaho). The mother-plant is *Dipterocarpus vernicifluus* Blanco. This oil is not used so much as balao, probably because it dries with much more difficulty. The manner of production is the same. The fresh oil is white, viscid, and has a characteristic odour which distinguishes it from similar products. It takes up oxygen from the air, and when left standing becomes darker-coloured, but it dries with difficulty even in a thin film. At 100° it becomes more liquid (contrary to balao); it dissolves in ether or chloroform with separation of water, and is also partly soluble in alcohol or benzene; none of its constituents dissolves in water. When distilled over a naked flame the balsam behaves like balao. All samples contained water (about 25 %), an oil containing sesquiterpene (about 35 %) and solid constituents (about 40 %). The sesquiterpene of malapaho boils almost completely from 256 to 261° (760 mm. pressure); $d^{30^\circ}_{30^\circ}$ 0,9165; α_{D30° -54°.

The products described greatly resemble the copaiba and gurjun balsams, and the author therefore considers it not impossible that for example supa oil might also be employed for the purpose of adulteration.

Elemi Oil. It is well known that the botanical origin of Manila elemi resin, which in the Philippines is called "brea", has up to the present not yet been determined with certainty. It was only know that the resin was obtained from the *Burseraceae,* and the suspected mother-plants were either *Icica Abilo* Blanco, or species of Canarium. We see from an article in *The Chemist and Druggist*[1]) that this question has now at last been decided on the part of the recently established Bureau of Science of the Government of the Philippine Islands, by the work of E. D. Merrill, who by a detailed examination of the botanical material has confirmed the statement first expressed by Bentley and Trimen, that elemi is obtained from a species of Canarium similar to *Canarium commune.* According to Merrill's researches, the plant yielding elemi is *Canarium luzonicum* (Miq.) A. Gray, a species peculiar to the Philippines, which is closely allied to, but not identical with *Canarium commune.* Other species of Canarium no doubt also contain elemi, but for export only the resin obtained from *Canarium luzonicum* comes under consideration. *Icica Abilo* Blanco does not yield elemi resin. No mention is unfortunately made of the source from which the statements reproduced in *The Chemist and Druggist* are derived. In *The Philippine Journal of Science* published by the Bureau of Science, in which we expected to find the original work, we only found in a study from the hand of Merrill on the flora of the Lamao Forest Reserve a short description of a few species of Canarium[2]), but no remarks regarding the above subject.

A long time ago[3]) we reported on the examination of an elemi oil fraction which was formed from the highest-boiling portions of the oil and was heavier than water. We now wish to supplement the information then given by the following results. We recently examined a fraction with the following constants: d_{15° 1,025; n_D $+2^\circ 15'$; soluble in 1,5 vol. 70 per cent. alcohol; sap. no. 2,8; sap. no. after acetylation 81,4. When fractionating it was, however, found that the fraction still contained constituents boiling below 100° (5 mm. pressure), which, in view of their high acetylation number, consisted probably chiefly of alcohols. From the first runnings on acetylation an oil with a distinct odour of spearmint could be fractionated off, which boiled at 82 to 83,5° (3 mm. pressure) and had the acetylation number 196,5. Although we were unable to confirm by positive proofs our assumption that we had here possibly to do with the acetic ester of the dihydrocumin alcohol[4])

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[1]) Chemist and Druggist **69** (1906), 678.

[2]) The Philippine Journal of Science **1** (1906), Supplement I, 71.

[3]) Report October **1896**, 29; comp. Gildemeister and Hoffmann, The Volatile Oils, p. 490.

[4]) Report April **1904**, 56.

discovered by us in ginger grass oil, we obtained, on saponifying the above-mentioned ester fraction, an oil boiling at 220 to 230°, which in the odour greatly resembled dihydrocumin alcohol. The naphthyl urethane characteristic of the latter could not be obtained. — In agreement with our earlier observations we found in the high-boiling portions a fraction distilling at 129 to 130° (4 mm. pressure) of the specific gravity 1,0467 and the optical rotation + 0° 51′. Although it boiled uniformly at 277 to 278° (ordinary pressure), it was in the course of the examination found to be a mixture of several bodies. With strong formic acid a hydrocarbon was obtained, the quantity of which was, however, insufficient for completely removing oxygenated constituents still present. The fraction of the b. p. 277 to 278° yielded, on oxidation with 2 per cent. permanganate solution, an acid of the m. p. 167,5 to 169° which crystallised from dilute alcohol in the form of needles. From benzene the compound crystallises in compact prisms. Its silver salt can be recrystallised from water and melts at 192 to 193°. The analyses of the salt and the acid point to the formula $C_{12}H_{16}O_6$: —

Acid: 0,1714 g. subst. — 0,3559 g. CO_2, 0,0962 g. H_2O.

	Found:	Calculated for $C_{12}H_{16}O_6$:
C	56,63 %	56,30 %
H	6,24 %	6,25 %.

Silver salt: 0,2628 g. subst. — 0,3848 g. CO_2, 0,1032 g. H_2O, 0,0768 g. Ag.
0,2199 g. subst. — 0,0651 g. Ag.

	Found:	Calculated for $C_{12}H_{15}AgO_6$:
C	39,93 %	39,67 %
H	4,36 %	4,13 %
Ag	29,22 %, 29,60 %	29,75 %

We will at some future time return to this subject.

Erigeron Oil. In the summer of 1904 Fr. Rabak had already distilled the fresh and the dried herb of *Erigeron canadensis* L., and in our Report of October 1905 we have referred in detail to the results[1]). Rabak[2]) has now continued these examinations, without, however, arriving at any conclusive results with regard to the composition of the oil. The odour of the new oil from fresh herb was like caraway, but reminded at the same time also of limonene; the oil formed a cloudy solution with two and more parts 90 per cent. alcohol. For

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[1]) Report October **1905**, 23; comp. also Report October **1903**, 31.

[2]) Pharm. Review **24** (1906), 326.

the sake of comparison we add here again the constants found previously: —

distilled	Spec. grav.	α_D	Acid no.	Ester no.	Sap. no.	Sap. no. after acetylation
1904	0,8614	+67° 16′	0	108	108	108
1904	0,8520	too dark	0	66	66	95
1905	0,8567	+82° 10′	0	39	39	67

The figures given for the year 1904 for α_D refer to oil from the dried herb; those for 1905 for oil from the herb in the fresh state. The latter therefore yielded an oil of greater dextrorotatory power but of lower specific gravity.

Essential Oils, Sicilian and Calabrian.

Our valued friend, Consul Eduardo Jacob, of Messina, has once more been kind enough to send us a detailed report on the position of the essence market, as follows: —

The statistics of the export of essential oils from Sicily and Calabria in the course of 1906 show that the shipments of that year have exceeded those of the previous year by 80084 kilos and 4846293 lire, i. e. by about $8^1/_3$ per cent.

Export of essential oils in the years 1905 and 1906.

	1905		1906	
	kilos	lire	kilos	lire
a) from Messina:				
to North German Ports	20227	323632	20460	409200
„ Austria-Hungary	78128	1250048	80914	1618280
„ Belgium	3239	51824	3262	65240
„ Denmark	3894	62304	2950	59000
„ France	35749	571984	34239	684780
„ Greece	545	8720	595	11900
„ the United Kingdom	212304	3396864	201567	4031340
„ the Netherlands	8818	141088	8960	179200
„ Russia	8807	140912	9253	185060
„ Scandinavia	4525	72400	7806	156120
„ Spain and Portugal	6790	108640	6729	134580
„ Turkey	1008	16128	1783	35660
„ the United States	307692	4923072	348750	6975000
„ South America	—	—	—	—
„ Australia	32039	512624	27581	551620
„ Egypt	1367	21872	1656	33120
„ India	768	12288	2568	51360
„ Italy	16572	265152	20829	416580
„ other countries	95	1520	1237	24740
Total	742567	11881072	781139	15622780

	1905		1906	
	kilos	lire	kilos	lire
b) from Reggio (Cal.):				
to North German Ports . . .	2 095	33 520	1 735	34 700
„ Austria-Hungary	19 614	313 828	28 186	563 720
„ France	21 765	348 240	31 630	632 600
„ the United Kingdom . . .	36 789	588 624	27 411	548 220
„ the Netherlands	1 210	19 360	1 800	36 000
„ the United States	11 941	191 056	20 244	404 880
„ other countries	1 905	30 480	1 777	35 540
Total	95 319	1 525 108	112 783	2 255 660
c) from Catania:				
to North German Ports . . .	460	4 600	—	—
„ Austria-Hungary	2 694	26 940	7 897	118 455
„ the United Kingdom . . .	450	4 500	350	5 250
„ other countries	713	7 130	—	—
Total	4 317	43 170	8 247	123 705
d) from Palermo:				
to North German Ports . . .	1 583	15 830	2 500	30 000
„ Austria-Hungary	3 780	37 800	3 582	42 984
„ France	3 051	30 510	3 778	45 336
„ the United Kingdom . . .	11 803	118 030	20 372	244 464
„ the United States	3 610	36 100	13 386	160 632
„ other countries	2 214	22 140	2 541	30 492
Total	26 041	260 410	46 159	553 908

Total exports in the years 1905 and 1906:

	1905		1906	
	kilos	lire	kilos	lire
from Messina	742 567	11 881 072	781 139	15 622 780
„ Reggio (Cal.)	95 319	1 525 108	112 783	2 255 660
„ Catania	4 317	43 170	8 247	123 705
„ Palermo	26 041	260 410	46 159	553 908
Total	868 244	13 709 760	948 328	18 556 053

Summary of the exports during the last ten years.

Year	kilos	lire	Year	kilos	lire
1906	948 328	18 556 053	1901	820 982	12 314 730
1905	868 244	13 709 760	1900	842 246	10 972 295
1904	1 006 103	14 758 590	1899	797 145	10 722 445
1903	864 770	11 964 839	1898	667 293	9 015 083
1902	1 085 497	15 196 958	1897	732 092	9 719 133

With regard to the individual essences, it may be said of **Bergamot Oil** that the prospects of the new harvest were neither brilliant nor bad.

The estimates made by experts did not hold out the prospect of such a good season as the previous one; on the contrary, it was thought that the harvest would be 25 to 30% smaller than the last one. In spite of this it was considered that the coming harvest could be characterised as satisfactory, and there was every reason to assume that the prices would move on a lower level than during the last few months of the preceding season. The old oil was so to speak entirely cleared out, and even up to shortly before the appearance of the new oil it still fetched a price of 21.50 marks per kilo, whilst bergamot oil was offered abroad by speculators far below this level, and was also purchased at that.

As soon as the manufacture commenced, the situation changed completely. The very first trials already made it clear that the bergamot fruit had this year a quite exceptionally small oil-content, a fact which has naturally a most important bearing on the shaping of the market. There were districts in which the yield of oil remained up to 30% behind that of the preceding year, and although the state of affairs was not equally bad everywhere, it would not be far out to estimate the deficiency in any case at least at 20%. This observation brought an immediate change over the market. The export would from this moment have to reckon upon a bad crop, instead of an average one. The manufacturers were at once placed before the fact that the new oil would cost them much more that they had expected.

The result of this was that the manufacturers, in order to recover their expenses to some extent, began to ask higher prices, and could under no circumstances be induced to make concessions, as they would then actually have lost money.

In the meantime, urgent shipping instructions arrived from abroad; the exporters, who had partly sold without cover, were compelled, in view of these demands, to commence fulfilling their obligations, and in this way the small quantities of new oil which came on the market were readily snatched up at constantly increasing prices.

In the course of December the prices advanced slowly but firmly to 23 marks; and when constantly more pressing requirements had to be met with, and the manufacturers were appealed to for goods with increasing urgency, the quotations up to the end of January jumped up rapidly to a height of 26 to 27 marks. Here the progress came to a standstill, and as at the high figures the manufacturers showed an inclination to realise, the purchasers withdrew completely from the market, in the hope of depressing the prices in this manner. As a matter of fact, a few weak manufacturers, who were possibly badly informed about the position of the market, were induced to conclude a few sales in spite of the constantly falling quotations, but larger orders at cheap prices failed owing to the firm attitude of most holders of oil.

In the first days of February the first symptoms of a new upward reaction showed themselves, and in a few days the prices had again reached their old level, at which they have since maintained themselves at the parity of 26 to 28 marks. This is an abnormally high price for bergamot oil, such as has not been paid for at least ten years, and it is therefore probable that the consumption at these high prices will shrink, and that the highest level in the quotations for this year has now about been reached. On the other hand, it would be wrong to reckon on a fall in the prices.

Although it is at the present moment impossible to obtain exact data about the stocks still held, it is believed that it may safely be assumed that they will not differ much from those held at the same time last year.

The future shaping of the prices now will depend upon the prospects of the new harvest. If the blossoms are good, and the new fruit passes victoriously through the many dangers which beset its youthful existence, a further advance in the prices of the old oil will in all probability be prevented; but if the coming harvest does not look promising, the idea of speculating for such an occurrence might easily suggest itself to the holders of prompt oil.

Lemon Oil. The position of the market of this article in September last was as follows: prompt lemon oil of the old harvest was maintained at 11 marks; new lemon oil for delivery December/March found everywhere ready buyers at 7,75 to 8,— marks. The old lemon oil which started at 5 marks, had in the course of the season advanced to 11 marks; it had been possible to buy the new forward oil from the manufacturers at first at 5,25 to 5,50 marks, but owing to the advance in the price of old oil, they also raised their quotations for new oil to about 9 marks.

In face of these high prices, the demand from abroad remained fairly passive until well in September; but when the proprietors on the approach of the new harvest decided to make small concessions to the purchasers, a brisk export business developed on the average basis of 10,50 marks, which absorbed the old stocks existing to the last drop, and would have taken more if more had been available.

It was only natural that under these circumstances the new oil came more and more to the front for interested parties of every description, and that the absolute lack of old oil gave an enhanced value to the new article.

From this it will be seen that the prices for new forward oil began to advance slowly; for the supply of very first quality oil in November about 9 marks was paid, whilst later deliveries remained at the existing level.

The manufacturers considered the prices very acceptable, and in October-November a very brisk business for forward delivery sprang up, during which the article even had to pass through occasional periods of weakness. When the first new oil appeared it was highly welcomed in view of the urgent shipping instructions from abroad, and it immediately found everywhere such a ready reception that it was not able to exert any pressure whatever on the market and its quotations. On the contrary, it soon became apparent that the manufacture could in most districts only be commenced after great delay, and that consequently the market until well in December would have to reckon with only unimportant supplies.

Under these conditions, the Union of manufacturers and landed proprietors existing in this town decided to intervene, with the definite object of driving up the price of this article to a higher basis.

It must be admitted that the schemes of the Syndicate have been executed dexterously and with a very correct appreciation of the prevailing market-conditions. A similar Association was successfully formed among the manufacturers and landed proprietors in Palermo, and since then the two Associations have hand in hand influenced the market both here and in Palermo, and regulated the supplies to these markets.

In view of the large harvest of lemons and the favourable possibilities of the manufacture, an influence on the market could only be effected by preventing an increase in the supplies beyond the demand occurring from day to day.

The following comparative statistics may give an idea of the quantities which have been shipped during the first months of the manufacturing season: —

1906 December	77742 kilos		1905 December	71734 kilos	
1907 January	144245 „		1906 January	109392 „	
1907 February	119463 „		1906 February	83300 „	
1906/1907	341450 kilos		1905/1906	264426 kilos	

This shows that in the first three producing months of the new season, already 77024 kilos more than in the same period of the previous year were sent abroad.

If it is considered that of the old harvest not a single pound had remained behind in the country, and that in spite of this, in the months of December to February, 341450 kilos could be exported, and that this has happened only with the quantity which the Syndicates were unable to withhold from the market, it is possible to obtain an idea of the magnitude of the lemon harvest and of the quantities of oil which must have been produced by the manufacturers.

Under these circumstances it will be readily understood that the majority of the exporters, in spite of the bad experience of last year, thought it an opportune time for concluding heavy engagements for export, at the average price of 8 marks which was high as compared with that of the last ten years, as the opinion prevailed generally that the bulk of the coming new oil would have a depressing effect on the above quotation. This would also have taken place, if a large portion of the new oil had not been kept away from the market and excluded from sale by artificial means, i. e. by buying up and warehousing on the part of the two Syndicates.

These Syndicates have succeeded, by their dexterous interference without consideration for others, in forcing the local speculators and the export firms, who had to cover large blank sales, to pay constantly increasing prices, by affording them no opportunity of covering more than the most urgent requirements. In this manner the two Syndicates were able to keep the prices of the new oil in December at 6 marks, to drive them up in January to 10 marks, and finally to screw them up with all sorts of despotic means in the course of February to 12 marks and at the present moment to 13,50 marks.

It is clear that this could only be done with the greatest loss to the export firms of this town. The total lack of old oil, the necessity of carrying out the engagements towards buyers abroad, had removed from the hand of the exporters every weapon with which they could have defended themselves against the intervention of the Syndicates.

The question naturally arises, whether this can and will continue, and what will become of this article?

Unfortunately this question must remain unanswered; all depends upon circumstances which do not allow of being taken into account as factors in the calculations.

The market has at its disposal a large harvest, and a large quantity of oil resulting from it, which under other circumstances could and would have been placed on the world's market at comparatively low prices.

On the one side stand the two Syndicates and many manufacturers who make common cause with them; these, excited by the results attained up to the present and by the profit already made, hold their stocks firmly and intend disposing of them only at continuously advancing prices.

On the other side, opposed to these pretensions, we see the speculators and the export firms with their requirements for uncovered sales, and possibly also the foreign buyers whose wants for the whole season may perhaps not yet be entirely covered.

As already mentioned, the shipments up to the present have been extraordinarily heavy; America has bought as much essence during the last three months as during the first five months of last year. If the foreign demand should continue to animate the market to the same extent as hitherto, the bulls will have won the game; but if the buyers abroad are in a position to exist for some time on the quantities already obtained, and to keep away from our market, and if they allow the local exporters time and put off the deliveries of the quantities which may possibly still have to be supplied, the bull party may find it hard work to maintain their present position.

Unfortunately, one thing is certain; the results attained by the Syndicate in these years of artificial influence on the local market, have made it more and more presuming. At the same, the pecuniary results have been very considerable, and in this the manufacturers, the satellites of the Syndicate, and outsiders, have shared; the latter had lost much money owing to the decline in the prices during the last ten years, and were all more or less dependent upon loans from the exporters, as soon as they wanted to commence their business for the new season.

But henceforth it will be necessary to reckon with this, that the manufacture has at its disposal — be it in the two Syndicates, or in the better financial position of the manufacturers themselves — a capital power upon which it could not rely in former times, and the lack of which formerly compelled the manufacturers to realise their goods rapidly, either by sales for forward delivery, or by disposing of their daily production.

These conditions of compulsion have now ceased to exert their price-depressing influence on the article, and it is absolutely certain that henceforth and until further it will be necessary to reckon on: —

1. a continuation of the price of lemon oil on a higher basis than formerly, and
2. on very numerous and important fluctuations in the price of the article in the future.

The chemico-physical constants of the various citrus oils have not for all fruits remained within the usual limits, probably owing to the great and prolonged heat and drought of last summer.

With regard to orange oil, nothing special can be reported; but this year's bergamot oil shows a very low specific gravity as compared with other years, a fact which is all the more remarkable, as at the same time the average ester-content must be called very high.

Lemon oil shows very striking abnormities in various respects.

In the first place, along with a very high citral-content, a comparatively low specific gravity is to be recorded, but also a quite strikingly low rotatory power of oils of every origin.

In your Report of April 1896 you mention the average rotatory power of Sicilian lemon oils as follows:

Messina and vicinity, Nizza	+ 59 to 61°
Aci-Reale, St. Teresa, St. Stefano, St. Lucia, Scaletta, Patti, St. Agata	+ 61 to 63°
Catania, Giarre, Giardini, Aci-Reale, Leontini	+ 63 to 64°
Barcellona, Siracusa	+ 64 to 67°

The lemon oils of this year's manufacture have a rotatory power which is fully two, and even three degrees lower, and they had this right from the commencement of the season. The oils of later manufacturing months will in all probability show quite abnormal rotatory powers, of 55 to at most 60°. This occurrence is all the more unpleasant for the trade of this town, as the new U. S. Pharmacopœia specifies for lemon oil a lowest rotatory power of + 60° at 25° C., a requirement which up to the present could only be met with the greatest difficulty, but which in the further course of the season it will probably not be possible to fulfil.

With regard to the solubility of this year's lemon oil, quite extraordinary conditions have also shown themselves; whilst all oils of whatever origin showed right from the first a strikingly high citral-content, although they had been pressed from quite green and not fully developed lemons, the same oils showed an inferior solubility, and on distillation also did not give the usual results.

With the increasing ripeness of the fruit, this abnormal behaviour has gradually disappeared, but it has caused much unpleasantness to the local export firms.

Now with regard to the prospects of the new harvest, the development of the trees has been retarded so much by the severe winter, that not even conjectures can be made. Yet it should not be lost sight of, that according to experience, a severe and prolonged winter with abundant rainfall and much snow (and this has been particularly plentiful this winter), usually promises a good crop.

But it would be wrong to expect from the approaching new harvest already in the summer any influence on the position of the prices of this year's oils.

Whilst in former years not unimportant stocks of old material of all oils were carried from one producing year into the other, it appears that the world's consumption has increased so much during the last 2 years that it completely uses up the production. This, clearly, is a further ground for the higher values at which during the last two years all kinds of citrus oils have kept themselves, and it is not impossible that a continued increase in the consumption of these oils may bring the prices to an even higher level, and keep them there.

Mandarin Oil. In our last Autumn Report attention was called to the approaching bad harvest of this fine species of citrus; as a matter of fact, the production of this oil has been very small, with prices which immediately set in very high.

During the producing months October/November the prices moved on a basis of 35 marks, and since then they have advanced to over 45 marks.

Orange Oil, bitter. As already stated in the last Autumn Report, the blossoms of the orange trees had turned out poorly; moreover, the prices for forward delivery of bitter oranges in cases were already during the summer of 1906 so high that only a very small production of oil was to be expected.

As a matter of fact, the prices have, with very small supplies to the market, moved slowly but steadily upwards right from the beginning of the season, and have advanced from 16.50 to 20 marks. Extremely little bitter orange oil is now left available for export.

Orange Oil, sweet. Although the orange crop has been very rich in Sicily and Calabria, there were significant reasons in favour of high, rather than for low prices of the new orange oil.

The fruit had grown last year under very favourable conditions, and promised to be of good keeping quality; this gave a prospect of a very brisk export during the winter months, and induced many landed proprietors not to sell the crop of their gardens in advance, but to await the export season and its better prices.

Under these circumstances the orange oil manufacturer found great difficulties in obtaining supplies of fruit, unless they paid prices for it which seriously increased the cost of orange oil. A further difficulty for the manufacturers was the question of labour. The constantly (epidemic-like) spreading emigration of the country people of Sicily and Calabria to America has denuded the entire provinces of the necessary labourers. Even at much higher wages than formerly it is often impossible to find the necessary workmen of any class and any trade. It goes without saying that these conditions are bound to contribute to a reduction in the production of orange oil. In any case they drive up the cost of the oil, and thereby cause a displacement upwards of the present average price level.

To these general conditions which have exerted their influence not only in the present year, but must also henceforth be always taken into account, was added this year a very small content of oil in the orange fruit.

All this led to a slow but constantly advancing tendency of this article, which, starting from 16 marks, moved during the manufacturing season up to the present level. The visible supplies are this year possibly somewhat larger than last year, and amount to about 7000 kilos.

It does not appear probable that the prices will give way in the course of the summer; on the contrary, in case of a subsequent brisk demand it is by no means impossible that they will harden again, as the available stocks are all held firm.

In German East Africa a large number of bitter oranges are used for coagulating india-rubber, and the peel of this fruit had up to the present remained unused. But, according to a communication in the *Pflanzer*[1]), the production of oil offers difficulties, which, as is well known, can only be made in a rational manner by expressing it by hand, as in Italy. In the absence of a suitable class of labourers, the adoption of an apparatus has lately been contemplated, such as is used in the West Indies for the manufacture of limette oil, and which may allow of a separation of the oil from the peel of the fruit. By means of distillation 1,4 % of oil has been obtained at Amani from the peel.

Eucalyptus Oil. Two East-Australian species of eucalyptus not yet or but little known, are described by R. T. Baker[2]), namely *Eucalyptus carnea*, sp. nov. (syn. *E. umbra* R. T. Baker, partim) and *E. Thozetiana* F. v. M. We only quote here what Baker says on the oils contained in these two plants.

Oil of *Eucalyptus carnea*. The yield of oil only amounts to 0,155 %. The oil, of which the constants are not mentioned, consists chiefly of d-pinene; of eucalyptol it only contained about 5 %, whilst phellandrene could not be detected in it at all. Baker's chemical collaborator H. G. Smith is at the moment still occupied with the examination of an ester present in the oil.

Oil of *Eucalyptus Thozetiana* F. v. M. The oil which was obtained only in an extremely small yield, is mobile, and has in the crude state a reddish colour; d_{16° 0,9257; n_{D16° 1,5026; it probably consists chiefly of ester-like compounds.

We read in the *Chemiker-Zeitung*[3]) that a factory for the production of eucalyptus oil (from *Eucalyptus Globulus*) has been started in Castelvecchio (Italy). Hooper[4]) also reports that in British India, in the Nilghiris, eucalyptus oil is manufactured. Ootakamund, Lovedale, and Coonoor come under consideration as places of production. The oil finds there a ready sale.

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[1]) Der Pflanzer, Ratgeber für tropische Landwirtschaft, published by the *Usambara-Post*, with the assistance of the Biologico-Agricultural Institute at Amani **2** (1906), 176.

[2]) Proceed. of the Linnean Soc. of N. S. W. 1906, part II, 303.

[3]) Chem. Ztg. **30** (1906), 1083.

[4]) Chemist and Druggist **70** (1907), 208.

Fennel Oil. In view of the rich fennel harvest of last autumn, and the excellent quality, we have paid particular attention during this season to the distillation of fennel oil, and thanks to our perfect installation we have worked up a considerable quantity. Our purchases of Galician, Russian, and Roumanian fennel amounted in the last few months to nearly half a million kilos, which is a striking proof that the new Customs regulations with reference to the distillation of seeds, are well adapted to bring new life into this important branch of our industry.

Geranium Oil. The trade in Algerian geranium oil during the past six months was absolutely lifeless, and the absence of any demand showed that ample advantage had been taken last summer of the opportunity of laying in cheap supplies. The rumours of the occurrence of the notorious *maladie cryptogamique* have meanwhile been denied, but it is said that the extreme drought has done severe damage to the geranium cultivations. Although the prices have nominally hardened, and a few producers talk of 30 francs per kilo, the article suffers, as already stated, from pronounced neglect.

According to the Bulletin de l'Office du Gouvernement Général de l'Algérie, the exports of geranium oil amounted last year to —

54600 kilos, value 1 639000 francs,

average value 30 francs, against in 1905, to 52600 kilos, value 1 786000 francs, average value 30 francs.

We are indebted to the kindness of M. E. Gerand, the Director of the Office de l'Algérie of Paris, in the first place for the correction of the export figures for geranium oil given in our last Report (p. 39), viz., that the definite average value per kilo in the year 1905 was 30 francs and not 34 francs (the figures given there for the years 1903 and 1904 are also definite). M. Gerand next informs us that for statistical purposes this price also applies provisionally for 1906, for such time, until the Commission algérienne des valeurs has fixed the definite price.

In the Réunion geranium oil market there was also little animation during the past 6 months. Nominally the Syndicate, supported by a considerable drop in the exchange, raised its price towards the end of the year to 31 francs cif. Marseilles, but there do not appear to have been any transactions worth mentioning, for since then the market has again fallen to 25 francs. We hear rumours of certain differences of opinion within the Organisation, and several important producers are said to have given recently notice to retire. We are inclined to think that it will soon be possible to buy at even lower prices. The exports in 1906 amounted to 39068 litres, against 47898 litres in 1905.

We abstract from the *Bulletin de l'Office du Gouvernement générat de l'Algérie*[1]) the following description of the cultivation of the geranium varieties which come under consideration for the industrial oil manufacture, after a publication by G. Bertoni which has appeared in the "Coltivatore". The principal varieties cultivated in Algeria and Réunion, and here and there also in Central Austria and South Germany (?) are *Pelargonium odoratissimum, P. capitatum,* and *P. roseum.* In Italy the cultivation of these plants is, strange to say, of no consequence, in spite of its importance for the manufacture of perfumes and its increasing consumption in the tobacco industry. *P. roseum* requires a loose, low lying soil, fresh in summer, not too damp in winter, frequently hoed, and manured in a rational manner. According to experiments made by E. Blandini at the Agricultural School at Portici, geranium cultures treated with stable-manure produced per hectare 3000 kilos blossoms with 1,98 % oil. When using a mixture of stable-manure (300 kilos per hectare) and superphosphate (400 kilos per hectare) the crop increased by 1000 kilos blossoms, and the oil-content amounted to 3,17 %. The fertilization took place in the first year, the results are those of the harvest of the following year.

When the field has been properly tilled and manured as directed, the two years old cuttings (which, however, must have been obtained from four years old mother-plants) are planted out. In hot climates this takes place from October to the beginning of February, or otherwise from August to September; the space between the individual cuttings must be 40 by 80 cm. The harvest can take place for 4 to 8 years running, but in the winter the plants must be protected from frost. Further examinations by Blandini have shown that not only the green branches and the leaves contain oil, but, as already mentioned, also the blossoms, and that in quite considerable quantities. It is said that the oil of the latter is even of excellent quality, and reminds much of rose oil. If merely the green branches and leaves are to be distilled, the harvest can take place twice or three times (in May, August, and September). This should be done in sunny unclouded weather. The crop of leaves and branches then amounts on the average in the first harvest to 16000, in the second to 3200, and in the third to 6000—8000 kilos per hectare. In the first year the best plan is to be satisfied with one single harvest, which can take place in August or September. But if only the blossoms are wanted, no definite time for the harvest can be given; it should take place either at the beginning, or towards the middle of the blossoming-period. Blandini obtained per hectare 3900 kilos blossoms yielding 7 kilos oil. On the average, branches and leaves together yield 0,1 % oil,

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[1]) Bull. de l'Off. du Gouv. de l'Alg. **12** (1906), 277.

leaves alone about 0,7 to 0,8 $^0/_0$. For this reason Blandini considers it best, from a practical point of view, to distil only the leaves. From the flowers from a two-year's cultivation, 1,5 $^0/_0$ (?) oil were obtained, and it was at the same time found that the spring-harvest gives the best yield of oil.

The French geranium, contrary to the Algerian, is an annual plant and as a consequence it can only be harvested once[1]).

According to a report from Consul J. Johnston, the production of Algerian geranium oil and also of other essential oils in Algeria, takes place chiefly in the districts immediately adjoining the township of Algiers. Boufarik in the plain of Mitidja, some 20 miles away from Algiers, is the principal market. The export to France in 1905 was valued at $ 310000, that to the other countries taken together was only a little above $ 30000.

In the East Indian geranium oils, the state of affairs this season was absolutely critical, for ginger grass oil of pure quality did not come at all on offer from India, whilst palmarosa oil gradually advanced from 5/- per lb. to 8/3, as the offers from there were by no way proportionate to the demand. Our friends report a partial failure of the harvest, but we are rather inclined to see in the increasing consumption of the article one of the principal factors of the present high prices.

The scarcity which prevails at this moment in palmarosa oil will no doubt lead to numerous adulterations. We had recently submitted to us for an expression of opinion, a substitute sold as palmarosa oil which had evidently been produced with expert skill. Although the composition was suspected on account of its peculiar odour, its constants, with the exception of the refractive index, agreed with those of palmarosa oil, as is shown by the following: —

	Palmarosa oil	Examined oil
d_{15^0}	0,887 to 0,900	0,8965
α_D	+ 6° to — 3°, usually between + 1° and — 2°	— 0° 48′
acid no.	up to 3,0	1,1
ester no.	14 to 46	16,8
ester no. after acetylation	not below 226, corresponding to a geraniol-content of at least 75 $^0/_0$	238 = 79,7 $^0/_0$ total geraniol (apparently!)
solubility	soluble in 1,5 to 3 or more vol. 70 per cent. alcohol	soluble in 1 and more vol. 70 per cent. alcohol
n_{D20^0}	1,472 to 1,476	1,46189

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[1]) Bericht Roure-Bertrand Fils, October **1906**, 28.

What was striking in the oil was the extremely low index of refraction (n_{D20° 1,46189), which in pure palmarosa oil lies between 1,472 and 1,476 (20°). The further examination now led to the surprising result that the oil contained about 20 % ethyl alcohol (compared with alcohol of 90 per cent. by vol.), and for the rest was probably a mixture of palmarosa and citronella oils, or consisted of fractions of these two oils; to this pointed on the one hand the odour, and on the other the specific gravity (d_{15° 0,9095) and refractive index (n_{D20° 1,47763) of the oil freed from alcohol, which are both too high for palmarosa oil. The small quantity of the sample at our disposal was unfortunately not sufficient to follow this matter up further, and we are consequently unable to supply a direct proof in support of the surmise expressed above.

The adulteration is interesting, above all inasmuch as we have here the rare case that it was first of all discovered merely by the abnormal index of refraction.

From a paper by D. Hooper on the manufacture and export of Indian essential oils, of which an abstract has appeared in *The Chemist and Druggist*[1]) we take the following interesting points which in a certain measure may serve as a supplement to the information given on p. 34 of the present Report.

The distillation of palmarosa oil (from *Cymbopogon Martini* Stapf) is to-day carried on in precisely the same primitive manner[2]) as 80 years ago. Each distillation lasts about 6 hours. The yield of one still in 24 hours is 1 "seer" (about 933 grams), and during the whole season 1 1/2 maunds or 80 quarts of oil. As places of distillation, only Pimpalnur came at first under consideration, subsequently Nandurbar, Shahada, and Talada; the Nimar district has always been an important centre, and the oil was called "nimar" oil directly after it. Recently the manufacture in the British Central Provinces and in Berar has increased considerably, and at present it is also carried on in the districts Hoshangabad, Betul, Mandla, and Seoni. The Forestry Department draws a considerable income from the letting of the rusa grass districts; in some districts it comes to as much as 10000 rupees. In Berar the oil distillation is carried out in the districts Akola, Ellichpur, Amraoti, Buldana, Basim, and Wun. The principal market for these oils is the town Ellichpur, whilst Bombay is the shipping port of all palmarosa oils; during the last 10 years the following quantities of oil — chiefly palmarosa oil — have been exported from there: —

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[1]) Chemist and Druggist **70** (1907), 207.

[2]) Comp. **Gildemeister** and **Hoffmann**, The Volatile Oils, p. 282.

1896/1897	8199	gallons	value	1,49,553	rupees
1897/1898	10776	„	„	2,09,691	„
1898/1899	16000	„	„	4,04,140	„
1899/1900	10400	„	„	2,78,005	„
1900/1901	12834	„	„	3,44,670	„
1901/1902	19641	„	„	6,10,783	„
1902/1903	18872	„	„	5,23,630	„
1903/1904	20680	„	„	5,38,774	„
1904/1905	18742	„	„	4,65,209	„
1905/1906	23436	„	„	5,51,425	„

The consumption was formerly chiefly in the United Kingdom, Egypt, and Turkey; nowadays Germany and France are important buyers.

Lemongrass oil, (from *Cymbopogon flexuosus* Stapf), was originally distilled only in Travancore and Cochin, where the distillation is carried out by natives. Only wild grass is worked up, and portable apparatus of a very primitive character are used which in Eastern Travancore differ somewhat from those in the West, but which consist chiefly of a copper still provided with an earthen dome. This is connected with a copper tube passing through a condenser filled with cold water, so as to condense the vapour. The water charged with oil is collected in a receiver. The individual parts of the apparatus where they are connected to each other, are closed air-tight with rags and clay. In 24 hours such an apparatus produces about 1 pint of oil.

But the above-named producing districts were unable to meet the growing demand and the Cochin distillers now began to turn to account the rich supplies of Malabar where the value of lemongrass was totally unknown; the consequence of this was that the price of the oil increased here fourteen-fold. The hilly districts of Malabar are entirely covered with lemongrass, and large quantities of it are therefore available, but in spite of this the question of the lemongrass cultivation in suitable districts has to be considered in order to satisfy the demand. The stills used in Malabar show already a somewhat more modern construction than those in Travancore, and above all are larger; every single distillation yields 1 bottle of oil weighing about 23 oz.

The shipping port of lemon-grass oil was originally Cochin, but since the oil distillation also extends to Malabar, Cochin will probably gradually lose in importance as compared with Calicut. — At present some 2000 or 3000 cases of 12 bottles each are shipped annually from Cochin to Bombay and the various foreign ports, such as New York, Hamburg and London.

The export of essential oils (among which chiefly lemongrass oil) from Madras was from 1896 to 1906 as follows: —

1896/1897	5324	gallons,	value	79,081	rupees
1897/1898	6292	„	„	1,33,775	„
1898/1899	4278	„	„	89,745	„
1899/1900	6280	„	„	1,29,701	„
1901/1902	589	„	„	27,376	„
1902/1903	6258	„	„	2,42,319	„
1903/1904	3889	„	„	1,60,505	„
1904/1905	2721	„	„	1,41,489	„
1905/1906	2675	„	„	1,54,141	„

Hooper gives no particulars for 1900/1901.

As already mentioned in discussing Stapf's monograph on oil grasses[1]), opinions differ greatly as to whether the two rusa grasses "motia" and "sofia" are different varieties, or one and the same plant in different stages of maturity. We are now in a position to supply a further contribution to this topic, from which it will be seen to what extent the existing views on the two grasses contradict each other, and what difficulties a solution of the question presents.

We had, namely, sent to us a short time ago by some business friends three species of rusa grasses, which were designated as "motiya", "motiya ellich", and "sonfiya", with the remark that from these the real palmarosa oil is distilled.

We were at the same time informed that it had been impossible to obtain also specimens of the plant which yields ginger grass oil. Here, therefore, "sofia" is also mentioned explicitly as the mother-plant of palmarosa oil.

On the other hand, we are indebted to the kindness of J. H. Burkill, Esq., of the Indian Museum of Calcutta, for a specimen each of "sofia" and "motia" together with the essential oils belonging to them. These plants originated from the Nimar district (Central Provinces of British India).

The examination of the oils now resulted in the interesting fact that the oil distilled from "motia" was a palmarosa oil, and the other one a ginger grass oil. Both distillates possess the odours characteristic of the respective oils, and by these means could already be easily distinguished from each other.

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[1] Comp. the present Report, p. 30.

The results of the analyses follow here: —

	Motia Palmarosa oil	Sofia Ginger grass oil
Colour	bright yellow	brownish yellow
d_{15°	0,8870	0,9284
α_D	$+0^\circ 55'$	$+35^\circ$
acid no.	1,0	1,3
ester no.	39,8 = 13,9 % geranyl acetate	19,2
ester no. after acetylation	256,6 = 87,4 % total geraniol	175,0
solubility	soluble in 1,6 and more vol. 70 per cent alcohol	soluble in 2 and more vol. 70 per cent alcohol; with 10 vol. strong opalescence

These results show at once the great difference between the two oils. The ginger grass oil agrees completely with one which we had examined thoroughly before[1]), and it would therefore probably have the same chemical composition. At the moment we are still engaged in isolating the alcoholic constituents of the oil.

At our request, Dr. Stapf was kind enough to examine the above-mentioned grasses with the view of ascertaining whether we had here to do with representatives of one, or of different varieties, and he proved that the plants could not be distinguished morphologically, but both belong to the narrow-leaved form of *Cymbopogon Martini* Stapf. This result is interesting, particularly with regard to the grasses sent over by Burkill, as these yield oils which differ totally from each other. How this comes about is for the present an open question, and further reliable observations on the spot are required to clear up this mysterious behaviour of the grass.

We are greatly indebted to Dr. Stapf for the information he has so kindly supplied, and we avail ourselves of this opportunity to express to him our best thanks.

An oil which was sent to the Botanical Institute of Buitenzorg[2]), and which, judged by the odour, appeared to be palmarosa oil, contained only 49 % geraniol. The plant from which this oil had been obtained has been planted in the experimental garden at Buitenzorg, and shall later on be submitted to a detailed examination with reference to the oil it contains.

Hop Oil. In continuation of the information given by us in October last, we reproduce here a detailed statement on the cultivation

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[1]) Report April **1904**, 56.

[2]) Verslag omtrent de te Buitenzorg gevestigde technische Afdeelingen van het Departement van Landbouw 1905. Batavia, 1906, p. 46.

of hops and the estimation of the hop harvest in 1906, abstracted from the 4th Quarterly Volume of Statistics of German Empire.

> The rating of the 1361 hop-parishes, i. e. communities in which the area cultivated with hops is at least 5 hectares, showed in the fields of these parishes an area of 36459,5 hectares under cultivation, of which in the current year 1070 hectares, and in the previous year 2342,9 hectares, had been newly laid out. The older fields which only are decisive for the harvest, had an area of 33046,6 hectares. The total harvest in the hop parishes was estimated at 19825700 kilos, or an average of 540 kilos against 740 in the previous year.
>
> On the strength of the position determined for the hop parishes with the co-operation of experts in the hop cultivation, the expected harvest has then been estimated for the hop gardens situated in parishes with less than 5 hectares hop area, and for which no report on the prospect of the harvest has been received. This supplementary estimate was only required for 2401 hectares, or 6,2 % of the total area. The final result is that for the total area of 38861 hectares in September of this year a crop of 21039300 kilos was expected, distributed as follows: —

		in 1906		against 1905		
	Virgin hops	43600 ks.	= 0,2 %	197200 ks.	= 0,7 %	(Field of 1904)
	Fields of 1905	1197500 „	= 5,7 %	1434900 „	= 4,9 %	
Yield of the older fields with the remark	Very good	4328900 „	= 20,6 %	9339500 „	= 31,9 %	
	Good	10345200 „	= 49,2 %	15527300 „	= 53,1 %	
	Medium	3506100 „	= 16,7 %	2674100 „	= 9,1 %	
	Below medium	1002300 „	= 4,7 %	34400 „	= 0,1 %	
	Small	615700 „	= 2,9 %	49500 „	= 0,2 %	

The demand for hop oil last year was not particularly brisk, and even the United Kingdom, which is otherwise one of the principal consumers, showed itself very reserved. We have been unable to discover whether the slow demand is accidental, or whether the consumption itself has fallen off.

Oil of Juniper Needles. In their communications on the oils of some American conifers, R. E. Hanson and E. N. Babcock[1]) also give some particulars of the oil distilled in the beginning of May from the leaves and branches of *Juniperus communis* L. from which the berries had been removed. They obtained a bright-yellow oil in a yield of 0,15 to 0,18 % (d_{20° 0,8531) which had a characteristic juniper odour.

In connection herewith we would mention a juniper oil distilled from the berries and needles, which we recently received from Russia. It behaved as follows: d_{15° 0,8675; $\alpha_D + 8^\circ 46'$; ester no. 11,4; soluble in 6 and more vol. 90 per cent. alcohol, with slight turbidity.

It differs from the ordinary distillate from juniper berries only by the dextrorotation, and in this respect agrees with two Russian juniper

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[1]) Journ. Amer. Chem. Soc. 28 (1906), 1198; comp. also the present Report, p. 84, and Gildemeister and Hoffmann, The Volatile Oils, p. 270.

oils previously discussed by us[1]), which had therefore probably been produced from the same distillation material.

Kuromoji Oil. In our Report ot April 1904[2]) we referred to a sample of kuromoji oil sent to us from Japan, which appeared to differ distinctly in its composition from the equally-named oils[3]) which had been examined previously. In the oil analysed at that time, cineol had been detected, and the presence of linalool had been considered probable owing to the coriander-like odour.

A kuromoji oil of exactly the same properties as the one described was recently sent to us, and has been examined by us specially for linalool. The oil, which had a faint yellowish colour and an odour like coriander, showed the following constants: d_{15° 0,8942; $\alpha_D - 7^\circ 35'$; ester no. 27,3 = 9,5 % ester (calculated for geranyl acetate); soluble in 2,5 and more vol. 70 per cent. alcohol with slight opalescence which increased on dilution. When distilled *in vacuo* (4 mm. pressure), the following fractions were obtained: —

1. First runnings 35 to 40°, $\alpha_D - 22^\circ 26'$, b. p. 166 to 176° (at 761 mm. pressure), had the odour of cineol and terpenes;
2. fraction 40 to 45°, $\alpha_D - 15^\circ 44'$;
3. „ 45 „ 55°, $\alpha_D - 9^\circ 38'$;
4. „ 55 „ 66°, $\alpha_D - 1^\circ 56'$;
5. „ 66 „ 70°, $\alpha_D + 1^\circ 0'$, d_{15° 0,8767, n_{D20° 1,46427;
6. „ 70 „ 78°, $\alpha_D - 3^\circ 56'$;
7. „ 78 „ 81°, $\alpha_D - 12^\circ 37'$;
8. Residue $\alpha_D - 6^\circ 10'$.

For the detection of linalool, the fraction 5 was once more fractionated, and an oil was obtained which at 2,5 mm. pressure distilled over from 61 to 65°, and had the following properties: d_{15° 0,8767, $\alpha_D + 0^\circ 35'$, n_{D20° 1,46506. The phenyl urethane obtained from it in a very low yield crystallised from alcohol in colourless needles which melted between 62 and 63°. For detecting linalool, the oxidation to citral was next taken in hand. The linalool fraction to be oxidised had the following constants: d_{15° 0,8768; $\alpha_D + 0^\circ 48'$; n_{D20° 1,46397. By oxidation with bichromate and sulphuric acid citral was obtained (though in a low yield), and purified over the bisulphite compound. The citryl-β-naphthocinchoninic acid melted, after recrystallising it twice from alcohol, between 196 and 197° with decomposition.

The destillation-residue (No. 8) of the kuromoji oil had an ester number 97,8, corresponding to 34,2 % geranyl (or linalyl) acetate. From this was obtained by saponification an oil which distilled over at 4 mm.

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[1]) Report October **1904**, 50.

[2]) Report April **1904**, 95.

[3]) Gildemeister and Hoffmann, The Volatile Oils, p. 404.

pressure between 84 and 106°, had a distinct odour like geraniol, and reacted with calcium chloride. The alcohol contained in it was purified over the phthalic acid compound, then passed over between 90 and 94° (at 3,5 mm. pressure), and had the following constants: d_{15° 0,8856; n_{D20° 1,47724. Oxidation with chromic acid yielded citral which could by clearly recognized by the odour, whilst with diphenylcarbamine chloride, geranyl diphenyl urethane crystallising in long, colourless needles was obtained, which after recrystallisation from alcohol melted at 81,8°.

The kuromoji oil examined consequently contained, in addition to cineol and terpenes, linalool and geraniol, the latter chiefly in the form of its acetic ester.

Why the composition of this oil should differ so completely from that of the kuromoji oils previously examined we are unable to say with certainty, but we suspect that it is due to the fact that the parts of the plant used in the distillation were not the same.

Lavender Oil. As already mentioned in our last Report[1]), especially the exceptional drought of last summer had a very injurious effect on the lavender harvest, so that the prices of the oil reached a height never dreamt of. In view of the increasing consumption of this oil, it can therefore be readily understood that new sources of supply are now looked for, in order to be better able to meet the existing demand.

This purpose is served by two articles which have appeared during the last few weeks in the *Revue de Grasse*[2]). In connection with the information that this year's experiments with the cultivation of lavender shall be started in the vicinity of St. Vallier and Coursegoules, these articles endeavour to excite interest in the cultivation of lavender on a large scale. We briefly reproduce here the contents of the articles.

In consideration of the fact that both the climatic conditions and the condition of the soil of the Grasse district are the most favourable possible for lavender, the cultivation of that plant offers at present all the better prospects, as the cultivation-experiments made in 1905 on the Mont Ventoux where the conditions are about the same as at Grasse, have given most excellent results. In other countries, as for example in England, good results have even been obtained on a heathy soil in open country.

The cultivation offers no special difficulties. Decisive for a good yield is above all a proper fertilization of the soil, for which, according to Professor Zaccharewitz, of Avignon, the following mixture is most suitable: —

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1) Report October **1906**, 42.

2) La Revue de Grasse, **1907**, Nos. 8 and 10.

Sodium nitrate	20 %
Potassium chloride	20 %
Superphosphate 18/20	60 %

This manure is applied in March, at the time when the soil is first tilled, in the proportion of 500 kilos per hectare. The results obtained thereby in earlier experiments (1905 on the Mont Ventoux) were very promising. The plants were not only distinctly richer in blossoms, but the oil-content in the blossoms also increased, so that a yield of 28 kilos oil per hectare was obtained against 12 kilos oil without the manure.

This shows at once the great advantages connected with a rational cultivation of lavender, which place the latter in one line with the cultivation of cereals or potatoes, etc., the more so as for lavender a portion of the extensive areas can be utilised which at present are lying waste and give a desolate and forlorn aspect to the mountain side. In any case the cultivation of lavender offers very good prospects, and it may become for the farmers a very important source of revenue, as the use of lavender oil is constantly increasing, and a direct collapse of the prices need therefore not be feared, even with a large supply.

We can add to the foregoing that we also have commenced last year experiments in the cultivation of lavender in the district of Barrême. We are glad to say that this matter has everywhere been received with great interest, so that the cultivation of lavender there may be considered as definitely settled.

As we were able to state in our last Reports, we have succeeded in our factory situated in Barrême, Département des Basses Alpes, in producing oils of a considerably higher ester-content (about 50 %) than those known in the trade up to the present.

This fact is explained very simply by the difference in the distillation process. The method employed in the South of France for the distillation of lavender is water-distillation, in which the distillation-material is immersed in water, the latter heated direct and the oil driven over with the water vapours. For a portable distillation plant it is in all countries almost the only method in use. But for various reasons it is of all possible methods of distilling the worst. For lavender it is particularly disastrous, as its action has in a high degree the effect of saponifying the esters.

In our Barrême factory, on the other hand, we produce the lavender oil by dry steam distillation. In order to save the esters, the distillation is carried on as rapidly as possible, as the influence of the agents which have a decomposing action on the essential oils, depends in the first place on the length of time during which they are allowed to act. This, of course, means waste of steam, but also preservation of esters.

The object of our work is above all to make known in a larger circle our observations and experience gained up to the present in the lavender oil distillation, and in this manner lead to the adoption of a more suitable method of producing the oil.

With regard to the occurrence of lavender, the botanical features, and the differences and transition-forms existing between lavender and spike we would call special attention to Birckenstock's work, which we discussed already in our last Report[1]).

The distillation takes place during the time when lavender is in full bloom, i. e. from the beginning of July to the beginning of September. It is on the whole inadvisable to continue the distillation beyond that time, as the inflorescences become poorer in blossoms; along with this a decrease in the yield of oil takes place.

Not only the blossoms alone are used, but the whole inflorescence, including the upper green parts of the plant. Strictly speaking, the latter ought not to be cut off along with the rest, but it is usually done. The woody parts of the plant, on the other hand, are not employed.

The great influence of the manner of distillation on the preservation of the esters was proved in a direct way by experiments. There was an enormous difference in the ester-content of the oils, if the same material was distilled on the one hand with steam, on the other hand by the water distillation method usual in the South of France. In the latter case one of the apparatus commonly employed there was used, and the distillation carried out in the usual manner: 50 to 60 kilos blossoms were immersed in an equal quantity of water (for dry blossoms a somewhat larger proportion of water is taken), then distilled, and 16 litres distillate collected. The results thus obtained were as follows: —

		Oil yield %	d_{15°	α_D	% ester	Solubility in 70 per cent. alcohol
1.	Steam distillation	0,81	0,8894	−8° 4′	50,9	Soluble in 6 to 7 or more vol. with faint opalescence
	Water distillation	0,71	0,8871	−6°47′	44,0	Soluble in 3 and more vol.
2.	Steam distillation	0,82	0,8905	−8°	53,7	Soluble in about 7 vol. and more with faint opalescence
	Water distillation	0,75	0,8880	−6°21′	43,6	Soluble in 3,3 and more vol.

This shows that the loss of ester in the old distillation process, as compared with the steam distillation, is very considerable, and amounts in the one case to 7, in the other even to 10 $^0/_0$; further, in the steam distillation the oil yield is of course also somewhat greater.

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[1]) Report October **1906**, 42.

After these results the advantage of the steam distillation need not be pointed out specially, but the rapidity of the distillation is, for the reasons already given, also important for the preservation of the esters. This has been proved by numerous experiments. The quicker the distillation is accomplished, the larger is the content of linalyl acetate. In proportion to the rapidity of the distillation, the oils obtained from the same lavender were up to 4% richer in ester.

The observations which we have briefly reproduced here were decisive for the production of our lavender oil.

With fresh blossoms the yield of oil is 0,8%, with dried blossoms up to 1,5%. During drying the blossoms lose a great deal in weight; we have ascertained from 35 to 47%, according to the length of time occupied. Not only a portion of the water is thus lost, but also a portion of the oil, as was proved by calculating the oil yield for the fresh distillation material. As, moreover, dried lavender yields an oil of greater specific gravity and richer in ester than the same lavender in the fresh state, it follows that the blossoms thus practically only become poorer in the most volatile portions of the oil (terpenes). The following table may serve to make this clear: —

	Kind of lavender	Loss in drying	Yield of oil calculated for fresh blossoms	d_{15°	α_D	% ester	Solubility in 70 per cent. alcohol
1.	a) fresh blossoms		0,84%	0,8891	−7°20′	50,3	Soluble in 6 and more vol. with slight cloudiness, with 10 vol. still opalescent
	b) the same after drying for 1½ days	35%	0,79%	0,8905	−7°33′	51,3	
2.	a) fresh blossoms		0,87%	0,8859	−9° 4′	46,9	Soluble in about 4,5 and more vol. with opalescence
	b) the same after drying for 4 days	47%	0,79%	0,8884	−9°33′	49,2	
3.	a) fresh blossoms		0,80%	0,8875	−8°10′	47,1	Soluble in 3 and more vol.
	b) the same after drying for 5 days	47%	0,72%	0,8899	−8°44′	51,1	Soluble in 4,2 and more vol.

Small losses of ester also occur when lavender blossoms are dried, but they are only slight, and amount to between 10 and 25% of the total loss of oil.

It follows from all that has been said here on the distillation of lavender that the oil richest in ester, and at the same time the largest yield of oil, are obtained when the lavender blossoms are worked up in an entirely fresh condition, and are distilled with steam as rapidly as possible.

We have already mentioned above that the woody parts of the plant are not included in the distillation. When we distilled such a material which had purposely been cut badly, the yield of oil diminished to 0,5 %, whilst the properties and above all the ester-content of the oil itself were exactly the same as those of oils from normal distillation material: d_{15° 0,8910; α_D — 8° 13′; 51,6 % ester; soluble in about 6 and more vol. 70 per cent. alcohol with slight cloudiness. From this it may be concluded that the woody parts of the lavender plant contain very little essential oil, or none at all.

We have also found confirmed the well-known fact that lavender is not in all districts equally rich in ester¹). In our second factory, situated in Sault (Dép. Vaucluse), we obtained, in spite of absolutely the same conditions in the distillation as at Barrême, only oils with 36 to 43 % linalyl acetate.

The great difference between the steam distillation and the water distillation naturally causes a slight deviation of the oils obtained by means of steam, from the ordinary commercial oils, not only in their ester-content but also in their other properties. The requirements in force for the commercial oils are: d_{15° 0,882 to 0,895; α_D — 3 to — 9°; ester-content 30 to 45 %; soluble in 2 to 3 and more vol. 70 per cent. alcohol, sometimes with slight opalescence.

Now in the oils distilled with steam the specific gravity usually approaches more the upper value; in two cases even specific gravities of 0,8964 were observed; moreover, these oils have on the average a fairly high rotation, and mostly a distinctly lower solubility. We give below the limits of the values observed up to the present in our own distillates: —

	d_{15°	α_D	% ester	Solubility in 70 per cent. alcohol
Oils of Barrême	0,886 to 0,896	— 7° to — 9° 33′	47 to 56	Soluble in 3 to 7 and more vol., sometimes with opalescence or slight cloudiness
Oils of Sault	0,885 to 0,891	— 7° to — 8°	36 to 43	Soluble in 3 to 10 vol., mostly clear

We would still mention that particularly the Sault oils often dissolve with difficulty, a fact which is supposed to be connected with the condition of the soil. Whether and in how far this is so, is a matter on which we are unable to express an opinion.

According to a communication by C. T. Bennett²) triethyl citrate has recently been added to lavender oil in order to raise the ester-

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¹) Comp. the map given in our Report of April **1902**.

²) Chemist and Druggist **69** (1906), 691.

content. This ester is almost odourless, so that the scent is not affected, and in spite of the high density, an addition up to 5 % will scarcely be revealed by too high a specific gravity in the case of light lavender and bergamot oils; on the other hand, this small quantity suffices to give an apparent increase in the content of linalyl acetate of about 10 %, owing to the tri-basic character of the citric acid ester. This shows how dangerous an adulterant this triethyl citrate is. Bennett quotes the following constants for it: b. p. 285 to 295°; d_{15° 1,146; $\alpha_D \pm 0^\circ$; n_{D20° 1,4400; sap. no. 610. For the detection of the ester it is advisable to distil off at reduced pressure the bulk of the oil in question, then to saponify with aqueous potash liquor the residue which contains the high-boiling artificial ester, and finally to fractionate the whole saponification liquor in order to detect the ethyl alcohol. The citric acid is then left behind in the residue, and can be weighed as barium salt, which Bennett prefers to the silver salt which decomposes violently when heated.

The above communication induced us also to study the adulterations with citric acid ester. For this purpose we produced an ester of the following constants, which correspond almost completely with those given by Bennett: d_{15° 1,1422, n_{D20° 1,4471, sap. no. 615,0, b. p. 165° (7 mm. pressure) and 144 to 145° ($3^1/_2$ mm. pressure). We added this ester to lavender oils, and found that additions of even 2 % ethyl citrate can be detected with certainty. We propose the following trial test, to determine in doubtful cases whether or not it is an adulteration with citric acid ester. About 3 grams of the suspected oil are saponified with alcoholic potash liquor, the liquid neutralised with hydrochloric acid, and evaporated to dryness on the water bath. The residue is dissolved in water, then extracted with ether in order to remove the last traces of oil and resin, and filtered. The solution cleared in this manner is mixed with a concentrated solution of calcium chloride, and heated. If citric acid is present, a white precipitate of calcium citrate occurs, which on cooling disappears again.

Lemongrass Oil[1]. Our fears that the Indian producers, in view of the profitable prices of the last harvests, would be tempted to extend their plantations excessively, have unfortunately come true, and it will now probably be difficult to lift this article again to a sensible price basis. Whilst the total shipments during the season (July 1st to June 30th) of 1904/5 amounted to $1881\,^1/_2$ cases, and 1905/6 to $2269\,^5/_{12}$ cases, the export during the months July to December 1906 already amounted to $3603\,^1/_8$ cases, that is to say nearly as much as in the previous two whole years together. It is no

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[1] Comp. also under Palmarosa oil, p. 57.

wonder that in consequence of this the price fell rapidly down to 3d. per oz. and that, in spite of an unsuccessful attempt early in the year to bring some firmness in the market by withholding offers to a certain extent, there is at present no prospect of an improvement in the prices. At 3d. important sales have been made everywhere, but the tendency in purchasing has in recent times already become slightly more reserved, so that we consider a further drop in the prices by no means impossible.

The shipments from July 1st to December 31st 1906 were: —

To London	$150\,{}^{1}/_{8}$	cases
„ Havre	$1092\,{}^{5}/_{6}$	„
„ Marseilles	$1245\,{}^{1}/_{2}$	„
„ Antwerp	25	„
„ Hamburg	$638\,{}^{1}/_{2}$	„
„ New York	301	„
„ Asiatic ports	150	„
Total	$3603\,{}^{1}/_{3}$	cases

In the same period of the year 1905, only $1267\,{}^{5}/_{6}$ cases were exported, and in 1904 only $1349\,{}^{1}/_{4}$ cases. These figures are so striking that no further arguments in support of our opinion are required.

Adulterations of lemon grass oil with citronella oil, which had already been observed by Parry[1]), appear to occur lately more frequently; we have at least had before us, within very recent times, three lemon grass oils which had all been clearly adulterated with citronella oil.

These oils had the following properties: —

1. d_{15° 0,9029; α_D — 5° 38′; aldehyde-content about 33 %
2. d_{15° 0,8993; α_D — 5° 40′; aldehyde-content about 34 %
3. d_{15° 0,8995; α_D — 5° 46′; aldehyde-content about 20 %

soluble in 2 to 2,4 vol. 70 per cent. alcohol; when more alcohol was added, opalescence to cloudiness.

Unfortunately, the samples were not sufficient for a more detailed examination, but the odour of the non-aldehydic portions of the oil had a pronounced citronella character, so that it might be concluded with a fair amount of certainty that adulteration with citronella oil had taken place.

Umney and Bennett[2]) report on the examination of a West Indian lemon grass oil. This oil had a specific gravity of 0,879,

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[1]) Report April **1905**, 55.

[2]) Chemist and Druggist **70** (1907), 138.

an aldehyde content of 75%, and showed the difficult solubility characteristic of the West Indian oils. For the purpose of comparison, an East Indian oil of approximately the same aldehyde-content was taken. The fractional distillation showed that the West Indian oil contained more low-boiling portions than the East Indian oil, for while the latter only commenced to boil above 210°, 23% of the West Indian oil had already passed over up to that temperature. A comparative distillation at reduced pressure, in which the oils were split up into fractions of 20% each of the quantities employed, showed, moreover, considerable differences in the corresponding fractions, particularly with regard to the optical rotation, inasmuch as from the West Indian oil only inactive fractions were obtained, whilst those of the East Indian oil rotated between — 12° and — 2°. From various observations made by them in the aldehyde-determination by the bisulphite method, Umney and Bennett come to the conclusion that the portions of the West Indian lemon grass oil passing into the bisulphite do not consist merely of citral, and they propose to make a further publication on the subject at a later date.

We would here point out that according to our observations made both with East Indian and West Indian lemon grass oils, the aldehyde-content ascertained by the bisulphite method is always higher than the one found be the sulphite method. This difference, as we found by experiments, is explained in the case of the East Indian oil by this, that here, by means of sodium bisulphite, along with the citral also other aldehydes¹) and further a portion of the methyl heptenone are included, whilst neutral sodium sulphite only reacts with the citral. In the case of the West Indian lemon grass oil the conditions are in all probability precisely the same. There is, therefore, every reason why Burgess²) in a notice dealing with the above work, advocates the use of Sadtler's sodium sulphite method in the manner modified by him³). On the other hand, we are unable to agree with the view expressed by Umney and Bennett⁴) according to which the citral-estimation is best carried out by titration in the manner proposed by Sadtler; according to our experience this latter method gives no reliable results.

The cultivation of lemon grass in the Malay Peninsula.

The high prices which have lately been paid for lemon grass oil have induced *The Times of Malaya* to advocate the cultivation of

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¹) Report October **1905**, 44.

²) Chemist and Druggist **70** (1907), 242.

³) With regard to the most suitable manner, comp. Report April **1905**, 103.

⁴) Chemist and Druggist **70** (1907), 313.

this grass in the Malay Peninsula. We abstract from the article[1]) the following: —

As compared with the cultivation of citronella grass, that of lemon grass offers a very considerable profit. Although the latter is cut only twice yearly, against citronella grass four times, those two cuts have a value of nearly 60 times that of the citronella harvest. This enormous difference in the profitableness is due to the fact that lemon grass oil is at the present time very much in demand, and has increased in price from about 40 rupees to 58 rupees per gallon.

For the cultivation of lemon grass, a sandy clay is the best, but it also thrives excellently in a well-drained purely sandy soil. It loves a certain amount of moisture, but does not stand continual wet; for this reason rain and sunshine must be in the right proportion if a good crop is to be expected. In the third year, in the cool season, the harvest can be commenced, and at least two cuts can then be taken. The distillation must follow the harvest immediately, and is carried on in the usual primitive manner in copper stills.

Under normal conditions an annual yield of 8000 ounces oil per acre can be reckoned upon, which at a market value of 8d. per oz. would produce £ 266.13.4, so that after deducting all expenses, a net profit of at least £ 200 per acre remains. The result from 10 acres of citronella grass, however, with four cuts *per annum*, is only £ 46.16.0.

We would observe with regard to the above that in the meantime the conditions have undergone a decided change, and the prices of lemongrass oil have already gone back considerably. Many a one who may have been induced by these favourable representations to cultivate lemongrass will have a painful experience.

Linaloe Oil. The position of this article has during the last six months undergone little or no change, for the Hamburg importers keep up the monopoly now as heretofore, and by clever manipulations they are able to prevent the accumulation of any stocks worth mentioning on the European markets. The highest price obtained for larger parcels was 17 marks per kilo. But consumers appear to take up a very sceptical attitude towards such demands, for during the last few weeks a greater inclination to sell became visible; one parcel was disposed of at 16 marks. Lately the tone has again become firmer, and 16.50 marks per kilo are asked.

Oil of sweet Marjoram. See under Terpinene in the Notes on recent research work.

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[1]) Acc. to Bulletin of Miscellaneous Information, Royal Botanic Gardens, Kew, 1906, No. 8, 364.

Mustard Oil. Whilst there is now hardly any doubt about the structure of allyl cyanide, which, according to Kekulé and Rinne[1]) has not the structural formula of an allyl compound

$$CH_2 = CH - CH_2 - CN,$$

but that of crotonitrile

$$CH_3 - CH = CH - CN,$$

since F. Lippmann[2]) and F. Schindler[3]) have also supplied an unobjectionable proof in favour of the formula drawn up by Kekulé and Rinne, nothing is as yet known of the reaction mechanism during the formation of this cyanide from the allyl halogenides.

Kekulé and Rinne did not explain the re-arrangement which must be assumed to occur in the formation of allyl cyanide, and Lippmann only called attention to the analogy between the atomic displacement in this case, and the one which occurs in the conversion of safrol to isosafrol.

For this reason, C. Pomeranz[4]) has made experiments with the view of clearing up this remarkable reaction, for which he prepared the allyl cyanide according to Lippmann from allyl bromide and potassium cyanide. He then found that for the formation of crotonitrile from allyl halogenides and potassium cyanide, the presence of water is a preliminary condition, and he thus supplied a simple explanation of the reaction-mechanism. The HCN formed by hydrolysis from the potassium cyanide acts simultaneously with KCN on halogen allyl, with formation of propylene cyanide, which then further reacts with the KOH also formed by hydrolysis, when the water entering into reaction, to which in this process the part of a catalyser belongs, is continuously re-formed.

$$CH_2 : CH - CH_2Br + KCN + HCN = CH_3 - CHCN - CH_2CN + KBr$$
$$CH_3 - CHCN - CH_2CN + KOH = CH_3 - CH : CHCN + KCN + H_2O.$$

When saponifying the crotonitrile with dilute sulphuric acid, liquid isocrotonic acid is formed, which at higher temperature is converted to solid crotonic acid.

As, according to Will and Körner[5]), allyl cyanide is formed by the action of water on mustard oil, and (in accordance with what is said above) is identical with crotonitrile, it is possible that natural mustard oil is a mixture of propenyl and allyl isothiocyanate. Artificial mustard oil, which is of course obtained in a similar manner as allyl cyanide, might possibly also contain the propenyl compound $CH_3 \cdot CH : CHNCS$.

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[1]) Berl. Berichte **6** (1873), 386.
[2]) Monatsh. f. Chemie **12** (1891), 402.
[3]) Ibidem, 410.
[4]) Liebigs Annalen **351** (1907), 354.
[5]) Liebigs Annalen **125** (1863), 281.

Pomeranz supplies the proof of these possibilities only with artificial mustard oil. On oxidation he obtained in addition to much formic acid, also some acetic acid, which could only have been formed from propenyl isothiocyanate. Pomeranz is of opinion that the quantity of the propenyl compound which is formed during the synthesis of mustard oil, is much larger than that found by him, and he surmises that it remains behind in the higher boiling portions during fractionating.

Oil of Myrrh. A work by K. Lewinsohn¹) deals with the composition of myrrh oil. The author has examined three commercial oils, and one oil distilled by himself from Herabol myrrh. Not without reason Lewinsohn emphasises that the composition of myrrh oil differs according to the origin of the resin, the method of production, and the age. He suspects that in the factories, as soon as no further oil passes over with the steam, 1 °/₀₀ potassium hydroxide is added to the distillation residue for the purpose of obtaining a larger yield, and the distillation is then continued. In our works such a method is not carried out. Gildemeister and Hoffmann²) have already pointed out that during the production on a small scale, the heavier portions easily remain in the resin, and that only the lighter oil passes over. Lewinsohn has confirmed this fact again by his work. The constituents of myrrh oil identified by him are: cuminic aldehyde, $C_{10}H_{12}O$ (up to 1 %), b. p. 116° (12 mm. pressure); oxime, m. p. 56°; semicarbazone, m. p. 201°. Oxidation with permanganate yielded cuminic acid, $C_{10}H_{12}O_2$, m. p. 114 to 115°. — Acids: Of these, only acetic acid and palmitic acid (m. p. 62°) were detected with certainty. Both are present in old oils in the free state, whilst freshly distilled myrrh oil contains the acids as esters. — Phenols (about 1 %): In all 4 oils, eugenol (about 0,23 %; benzoyl compound, m. p. 69°), and a small quantity m-cresol were detected. — Hydrocarbons: Fractional distillation over sodium yielded four hydrocarbons (terpenes) of the formula $C_{10}H_{16}$ (but not simultaneously in all the examined oils), of which three were identified; pinene (nitrosochloride, m. p. 103°; nitrolbenzylamine and nitrolpiperidine); dipentene (tetrabromide, m. p. 124°); limonene (tetrabromide, m. p. 104°); the fourth hydrocarbon probably belongs also to the limonene group ($\alpha_D + 80°$, tetrabromide, m. p. 115°, and monohydrochloride, m. p. 6°) but could not be identified. — Sesquiterpenes: From old oils a resin could be separated off by petroleum ether which could be reduced to a hydrocarbon. The latter yielded a crystallising addition product of hydrochloric acid (m. p. 115 to 117°)

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¹) Thesis, Berlin 1906; Arch. der Pharm. **244** (1906), 412.

²) Gildemeister and Hoffmann, The Volatile Oils, p. 487.

which Lewinsohn suspects to be cadinene hydrochloride. The sesquiterpene boils at 163 to 168° (12 mm. pressure); d_{20° 0,926; $[\alpha]_{D20^\circ}$ + 22,75°. Another sesquiterpene of the b. p. 151 to 154° (15 mm. pressure), d_{21° 0,911, $[\alpha]_D$ + 30,4°, could not be identified at all.

Myrtle Oil. The examinations made up to the present of the low-boiling portions (from 158 to 160°) of myrtle oil have only shown the presence of pinene[1]). The high optical rotation of the fraction of the boiling point mentioned above gave rise to the belief that in addition to pinene, it also contained camphene. For this reason we have repeatedly fractionated the first runnings of French myrtle oil, and have examined the fraction boiling from 158 to 160° (α_D + 36°) in the usual manner (treatment with glacial acetic acid and sulphuric acid) for camphene. The crystals obtained, repeatedly recrystallised from petroleum ether, melted in one case at 203 to 204°, in another at 205°. In neither case could the melting point be raised. Both this fact and also the entirely borneol-like appearance of the product obtained, supported the assumption that it was not a case of pure isoborneol, but of a mixture of borneol and isoborneol. Treatment of the body with dilute sulphuric acid with the application of heat, unfortunately gave no positive result, and also pointed to a mixture. It can therefore only be said that in the first runnings of myrtle oil there is present, in addition to pinene, still another hydrocarbon which behaves like camphene, and that the possibility does not seem to be entirely excluded that a third hydrocarbon is also mixed with the others, which may give rise to the formation of borneol on treatment with glacial acetic acid and sulphuric acid.

Neroli Oil. Reports on the position of the cultivations are for the present favourable. On the whole, the trees have suffered but little from the severe cold of the past winter, and as far as can be judged up to the present, a good blossom harvest is anticipated. In view of the high prices of last year, special care has been bestowed on the trees, and if there are no further frosts, and the present drought does not continue too long, the price of the blossoms will doubtless drop to about 1 franc per kilo, i. e. half of that of 1906. The prices of neroli oil will adjust themselves proportionately in the course of the next few months.

Oil of Cretian Origanum. We had recently an opportunity of examining two origanum oils from Cyprus and also several originating from Syria, and they all corresponded to the common sort known as oil of Cretian origanum. The properties may follow here.

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[1]) Comp. **Gildemeister** and **Hoffmann**, The Volatile Oils, p. 507.

Cyprian origanum oil. 1. d_{15° 0,9624; $\alpha_D + 0^\circ 20'$; phenol-content 77 %; soluble in 2,5 to 3 and more vol. 70 per cent. alcohol. 2. d_{15° 0,9655; $\alpha_D \pm 0^\circ$; phenol-content about 70 %; soluble in 2,4 and more vol. 70 per cent. alcohol.

The oils had been sent to us for examination by the Scientific Department of the Imperial Institute of London, which has recently in its Reports[1]) also published a note on the two oils. The constants quoted there agree on the whole with those observed by us, only the phenol-content has been found higher (82,5 %) in both cases.

With regard to the mother-plant, the Imperial Institute has not been able to ascertain anything, but a request has been made to send on the respective plants so that their botanical names may still be determined. Judging from the oil, it might be a question of *Origanum hirtum* Lk., and *O. Onites* L. also occurring in Cyprus.

A welcome addition to the above information is found in a work of Saracomenos[2]), who reports on the origanum oil industry which is now since some years carried on in Cyprus. The plant used as crude material, which Saracomenos describes in detail, grows wild in the South-Western part of the island, and several specimens have now been sent to the Imperial Institute for the purpose of identification, as there exist differences of opinion on the species of the plant, which is regarded either as *Origanum hirtum*, or as *O. Onites*. Holmboe, who visited Cyprus on behalf of the University of Christiania, looks upon the plant as *O. dubium*, a sub-species of *O. Maru* L.

The distillation of the plants commences in Cyprus in July or a little earlier, when the seed is ripe, and continues until the middle of December. In order to produce one "oke" oil (= 2 2/3 lbs. or 1 quart) 30 to 45 okes origanum herb are required. The oil distilled from fresh plants has a dirty grey colour, whilst the oil obtained from plants which had been stored for a month, has a dirty red colour, which, however, the oil distilled from fresh plants also acquires in course of time.

According to analyses by Francis, Cyprian origanum oil consists chiefly of a mixture of thymol, thymene, and cymene, whilst the phenols of the oils examined by the Imperial Institute (London) and ourselves, contrary to this, were found to be carvacrol.

Saracomenos determined by gravimetric analysis the thymol-content of the oils examined by Francis, and found in the dark oil 79 %, and in the bright oil 83 % thymol.

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[1]) Bulletin of the Imperial Institute **4** (1906), 296.

[2]) Chemist and Druggist **70** (1907), 365.

Syrian origanum oil. The oils had been sent to us from Jaffa, and behaved as follows: d_{15° 0,936 to 0,960, α_D feebly to the right up to $+1^\circ 35'$, phenol-content 65 to 72%, soluble in 2 to 3 vol. 70 per cent. alcohol, when more alcohol is added opalescence to cloudiness occurs; in one case, no clear solution was formed with 70 per cent. alcohol in any proportion.

Here also the phenols consisted of carvacrol. Worthy of note is the low dextrorotation, contrary to previous observations, according to which origanum oil has a feeble lævorotation. A disadvantage of the Syrian oils is their deficient solubility.

Orris Oil. Our correspondents have supplied us with the following information on the orris root market: —

> Since we reported last Autumn on the Florentine orris roots, the market, owing to the brisk demand, advanced to the parity of 69/70 marks cif. Hamburg for assorted roots, and 61/63 marks cif. Hamburg for seconds, and the prices have maintained themselves with slight fluctuations at this level up to the present. But in the quotations for abroad the fluctuations were more important; for example, one of the speculators had first of all concluded blank sales, then, when he found that the prices advanced, he purchased a large quantity as a "bull", and again, when he had bought more than he could digest he disposed of the surplus of the goods to be delivered, at whatever price it would fetch. Needless to say that the regular trade suffers from such proceedings.
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> |---|---|---|
> | According to our previous statistics, the available quantity at the beginning of September 1906 was . . . . | about | 290 tons |
> | Add to this the result of the harvest . . . . | „ | 800 „ |
> | Total | about | 1090 tons |
> | If we deduct from this the shipments from the beginning of September 1906 to the end of February 1907 . . . . | about | 410 tons |
> | There are left available, at the end of February 1907 . . | about | 680 tons |
>
> Against the above 410 tons exported during the past half year, the export for the same period of the previous year, September 1905 to February 1906, amounted to 550 tons, i. e. this time about 140 tons less. The shipments during the last seasons were: —
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> | | | | | | |
> |---|---|---|---|---|---|
> | September 1902/August | 1903 | about | 840 | tons |
> | „ 1903/ | „ | 1904 | „ | 820 | „ |
> | „ 1904/ | „ | 1905 | „ | 500 | „ |
> | „ 1905/ | „ | 1906 | „ | 920 | „ |
>
> This is equal to an annual average quantity of about 770 tons. In previous years, however, the average annual export was about 900 tons. The results of the five last harvests were: —
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> | | | | |
> |---|---|---|---|
> | in 1902 | about | 1000 | tons |
> | 1903 | „ | 750 | „ |
> | 1904 | „ | 670 | „ |
> | 1905 | „ | 850 | „ |
> | 1906 | „ | 800 | „ |
>
> On a previous occasion we have already pointed out that the 1906 crop was considerably increased by the old roots which, owing to the favourable prices, had been gathered, instead of (as was apparently intended), letting them fall into oblivion. These roots were of inferior quality, but the result of the

harvest was thereby increased by fully 200 tons. With regard to the prospects of the harvest, it is generally accepted that the next crop, in view of the small quantities planted out during the last few years, will not exceed a total of 500 tons. The future course of the prices will naturally depend in the first place on the demand, but also on the manipulations of the speculators, of whom one, who has made himself repeatedly conspicuous, has already informed the proprietors that he shortly expected large orders and hoped to obtain good prices. This, of course, may equally well be fact as fancy, but it is not without its effect, where many are only too willing to ride the high horse, in anticipation of the promised mountains of gold. It would be desirable, in everybody's interest, and particularly in that of the consumers, if such manipulations were repressed by suitable means.

The crop in Verona has been small, and the prices have consequently advanced considerably, but at the present quotations of 48 to 50 marks for the so-called "mercantile" quality, no desire to buy is apparent; on the contrary so long as any of it is available buyers seem to be content with the old goods, although in respect of quality and colour it leaves something to be desired.

We have in our Reports repeatedly called attention to the fact that the liquid orris oil introduced by us into commerce, which is free from myristic acid, enjoys a large sale owing to its excellent quality. Now, as often as we have worked up in our works orris roots either into solid or liquid oil, we have observed that the oil, in addition to the actual odoriferous principle irone, also must contain still more volatile bodies which could only influence the characteristic pleasant violet odour in a disagreeable manner. In consequence of this we have now for about a year placed on the market both the liquid and the solid orris oil free from the unpleasantly smelling constituents. Now we were interested in the more detailed chemical examination of these bodies. This examination has proved how well we did in removing these constituents from the orris oil.

Tiemann and Krüger[1]) were the first to examine orris oil obtained by extraction from orris root. According to their statements, the oil contains in addition to evil-smelling substances, esters of oleic and myristic acids, which, however, are not important for the odour of orris oil. They further claim to have detected the presence of oleic acid aldehyde. But an experimental proof in support of this assertion has never been supplied.

Our examination dealt chiefly with the contituents of liquid orris oil more readily volatile than irone, viz., the evil-smelling first runnings, which are removed in the manufacture of our liquid orris oil. The oil worked up (about 100 g.) passed over between 40 and 92° (5 mm. pressure). It had a golden-yellow colour, and a disagreeable basic smell, reminding somewhat of skatol. After repeated fractionating there were obtained as a first fraction, 8 g. of an oil of the b. p. 50 to 65° (13 mm. pressure) with the constants d_{15° 0,8693, $\alpha_D + 9° 4'$.

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[1]) Berl. Berichte **26** (1893), 2675.

It boiled at atmospheric pressure between 160 and 190°. The portion boiling between 160 and 170° contained furfurol (red coloration with a solution of aniline hydrochloride in aniline). The odour and other properties of one of the next higher-boiling fractions of the b. p. 171 to 173°, pointed to the presence of a terpene, which, however, could not be identified further (d_{15° 0,8611; $\alpha_D + 10^\circ 40'$).

A fraction boiling about 60° (5 mm. pressure) yielded in small quantity a semicarbazone melting at 100 to 101°, which on heating with dilute acid gave off the characteristic orange-like odour peculiar to decylic aldehyde. A fall in the melting point of a mixture of this semicarbazone and n-decylic aldehyde semicarbazone of the m. p. 102° did not take place. The presence of n-decylic aldehyde is thus proved.

The portions boiling between 65 and 90° (4 mm. pressure) reacted with sodium bisulphite, with separation of a slimy bisulphite compound. The aldehyde ($2^1/_2$ g.) regenerated from the pure compound distilled at 80° (5 mm. pressure) and possessed the odour peculiar to the higher fatty aldehydes, which, however, reminded at the same time of cuminic aldehyde. Its semicarbazone crystallising from dilute alcohol or benzene in brilliant leaflets with a greasy feeling, melted at 167 to 168°, and on elementary analysis gave values which point to the semicarbazone of a nonylic aldehyde: —

0,1620 g. subst.: 0,3547 g. CO_2, 0,1513 g. H_2O.

	Found:	Calculated for $C_{10}H_{21}N_3O$:
C	59,71 %	60,30 %
H	10,38 %	10,55 %

The molecular weight, determined by Beckmann's method of lowering the freezing point in benzene, was, in agreement with the above formula, found to be 192,5 (calculated 199). Oxidation of the aldehyde with moist silver oxide, which took place on the water bath with decrepitation, yielded an oily acid with a smell like fatty acid, which at highly reduced temperature solidified to leafy crystals, but again melted slightly above 0°. It boiled at 128° (4 mm. pressure), at atmospheric pressure at 253 to 254°. Its silver salt, very unstable in the light, was recrystallised from hot alcohol.

0,2054 g. subst.: 0,3064 g. CO_2, 0,1220 g. H_2O.
0,2484 g. subst.: 0,0994 g. Ag.

	Found:	Calculated for $C_9H_{17}AgO_2$:
C	40,68 %	40,75 %
H	6,60 %	6,41 %
Ag	40,79 %	40,75 %

These figures also point to a nonylic acid. The zinc salt of the acid regenerated from the silver salt melted at 127 to 128°, the copper salt a little above 200°. The aldehyde in question is therefore a nonylic aldehyde, which on oxidation is converted to a nonylic acid, whose properties and salts show a great resemblance to those of pelargonic acid.

An oil of the b. p. 73 to 75° (4 mm. pressure) isolated from the non-aldehydic fractions by fractional distillation, separated off at a low temperature abundant quantities of leafy crystals, which on closer examination were found to be naphthalene. The rest of this compound which had remained dissolved in the oil, was separated off in the form of its picrate. This, after purification from alcohol, melted at 149°. From this the naphthalene was isolated by heating with soda liquor and distilling in a current of steam. In this manner we obtained about $4\frac{1}{2}$ g. of the substance. The body purified partly by sublimation, partly by crystallisation, melted at 80 to 80,5°, and on analysis gave the values required for naphthalene: —

0,1703 g. subst.: 0,5828 g. CO_2, 0,0990 g. H_2O.

	Found:	Calculated for $C_{10}H_8$:
C	93,33 %	93,75 %
H	6,46 %	6,25 %

The napththoquinone produced by oxidation with chromic acid in glacial acetic acid, melted at 125°.

This occurrence of naphthalene is particularly interesting, as this body had up to the present only been found in very isolated cases as a constituent of essential oils. To our knowledge there is in the literature only a short notice by v. Soden and Rojahn[1]) on the detection of this hydrocarbon in the oils of clove stems and storax. It is a remarkable fact that this body with such an unpleasant and characteristic odour is present in a particularly delicate and pleasant smelling essential oil. As on repeated treatment with picric acid at raised temperature a very large portion of the oil resinified, the unchanged oil was, after previous removal of any picric acid still dissolved in it, freed from the resinous constituents by distillation with steam. Attempts to identify an alcohol or a ketone in this oil boiling chiefly at 220 to 230°, were without result.

We would still mention a semicarbazone of a ketone (m. p. 217 to 218°) isolated from a fraction of the b. p. 65 to 71° (4 mm. pressure) which had not yet been treated with bisulphite. The ketone hat a mint-like odour.

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[1]) Pharm. Ztg. **47** (1902), 779; Report April **1903**, 29.

0,1393 g. subst.: 0,3166 g. CO_2, 0,1205 g. H_2O.

	Found:	Calculated for $C_{11}H_{21}N_3O$:
C	61,98 %	62,56 %
H	9,75 %	9,95 %

These values point to a ketone of the formula $C_{10}H_{18}O$. The oil also contained traces of a base, a phenol, and an alcohol reacting with phthalic anhydride.

Finally, we have established that the oleic acid aldehyde, which according to Tiemann and Krüger's statements, should be present in orris oil obtained by extraction, does not form a constituent of the distilled oil. The aldehyde produced by us for comparison, by distillation of a mixture of equal parts calcium oleate and formiate, and purified through the bisulphite compound, had the following constants: b. p. 168 to 169° (3 to 4 mm. pressure), d_{15° 0,8513, n_{D20° 1,45571. The oleic acid aldehyde $C_{18}H_{34}O$ was up to the present unknown in chemical literature. Its odour is rather faint, and resembles that of the higher fatty aldehydes. When cooled, the aldehyde congeals to a wax-like mass. Its semicarbazone melts at 87 to 89°. The analysis of the aldehyde, its oxidation to oleic acid, and the analysis of its silver salt, showed that it was here actually a question of oleic aldehyde.

Aldehyde: 0,2076 g. subst.: 0,6152 g. CO_2, 0,2430 g. H_2O.

	Found:	Calculated for $C_{18}H_{34}O$:
C	80,82 %	81,20 %
H	13,01 %	12,78 %

Silver salt of the acid: 0,2243 g. subst.: 0,0621 g. Ag.

	Found:	Calculated for $C_{18}H_{33}AgO_2$:
Ag	27,69 %	27,76 %

The acid regenerated from the silver salt boiled at 198 to 199° (3 to 4 mm. pressure) and was solid at a low temperature. The oleic acid obtained from almond oil had the same boiling point.

After this result we tested the highest boiling portions of orris oil for oleic aldehyde, and used for this purpose a fraction boiling between 140 and 180° (3 to 4 mm. pressure). In view of the facility with which oleic aldehyde combines with sodium bisulphite, a solid double compound ought to have been obtained from this fraction in case the body had been present. In spite of long-continued treatment with bisulphite liquor no solid separation could be observed. Oleic aldehyde is consequently no constituent of distilled orris oil.

Patchouli Oil. During the last few months there has been a brisk demand for our own distillate, the superiority of which over the Indian oils we have repeatedly had opportunities of proving, and the position of this article can be called firm. According to the latest reports received by mail, the plants in Sumatra have suffered much from continuous rain-fall, so that a considerable falling-off in the production is to be expected for the next few months. Owing to this the prices of first quality leaves have advanced from 26/- to 31/- per cwt., without, however, for a long time finding interested parties in view of the raised quotations. It has for the present not yet been necessary to advance the selling prices of the oil, as we are well covered for a long time to come by advantageous purchases.

With reference to our note on the three patchouli oils[1]) examined by de Jong, we may add that the oil mentioned under III was also lævorotatory, as appears from a statement to that effect published in the annual Report of the Botanical Garden of Buitenzorg[2]).

Peppermint Oil, American. In connection with what we said in October 1906, our New York friends report that the condition of the fields has been greatly improved by favourable weather during the late summer, and that in consequence a much larger quantity of oil has been obtained than had been expected. This led to a fall in the price of first grade oil from $ 3.— per lb. to about $ 2.45, and as business was very slow in the country of production, an improvement in the market can hardly be thought of for the present. It would be too early to give at this time a forecast of this year's harvest, as, owing to the late commencement of the spring, no reliable information whatever has yet been received as to how the plants have come through the winter.

Only a small number of farmers has joined the Essential Oil Department of the American Society of Equity[3]), and this movement may therefore be characterised as unsuccessful.

From an article in *The Chemist and Druggist*[4]) we learn that in recent times American peppermint oils of inferior quality have frequently been met with in commerce, which oils are very suspicious owing to their exceptionally low price. Although the chemical analysis shows that the oils are not adulterated, their odour and particularly their taste are very inferior to those of good American oils, so that for many purposes they are useless.

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[1]) Report April **1906**, 49.

[2]) Verslag omtrent de te Buitenzorg gevestigde technische Afdeelingen van het Departement van Landbouw 1905. Batavia 1906, p. 45.

[3]) See Report October **1906**, 56.

[4]) Chemist and Druggist **69** (1906), 897.

These defects are attributed to the fact that the oils have been distilled from peppermint largely intermixed with weed, for which reason they are called "weedy oils". Whereas in England the cultivation of peppermint is carried out with great care, and all weeds are immediately removed, in America frequently no attention is paid to these matters, and the consequence is an inferior oil. The weeds vary according to the year and season; of cruciferæ, small quantities already are said to affect injuriously the quality of the oil of an entire crop. It is said to be an advantage to dry the peppermint before the distillation, by means of which various weeds lose their unfavourable influence on the oil.

Peppermint Oil, English. According to E. J. Parry[1]), many peppermint oils come on the market which are offered as "English distilled peppermint oil", but which are nothing but American peppermint oil rectified in England, and to which to the utmost a small quantity of English oil has been added.

We also consider it necessary to call again the attention of all interested parties to such scandal.

Peppermint Oil, Japanese. With regard to the final result of the 1906 harvest, we have before us three estimates issued in January 1907, which differ but slightly from one another, and of which the mean may therefore no doubt be accepted as the actual result

		I.	II.	III.
Bingu Bitchiu	1st cut	12000 kin	80000 kin	80000 kin
„ „	2nd „	35000 „		
„ „	3rd „	28000 „		
Yonezawa	1st and 2nd „	12000 „	15000 „	15000 „
Hokkaido		100000 „	120000 „	90000 „
		187000 kin	215000 kin	185000 kin

Mean of three, about 195000 kin.

Particulars with regard to the quantities still available from last season fluctuate between 60000 and 100000 kin, so that the mean of 80000 kin is probably nearest the truth. There would consequently be about 275000 kin at the disposal of consumers, against about 430000 kin in 1905. Although this not unimportant deficiency by itself might give rise to an upward movement in the prices, it must not be forgotten that according to other estimates available, not less than 200000 kin were warehoused in Japan at the end of the year, of which quantity only about 30000 kin have been sold for January/February shipment. If it is also considered that the American peppermint oil market has now been completely neglected for months,

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[1]) Chemist and Druggist **70** (1907), 100.

and that from there any initiative for an upward movement can hardly be expected, one asks in vain for logical reasons for the firm tone of the Japanese, and the response with which it has recently met in the European market. The quotations of the oil have not fluctuated to any extent since our last Report; they moved between 6/- and 6/3.

The shipments of Japanese peppermint oil during the last five years were: —

in 1902	59240 kin	value 164847 yen
1903	77024 „	„ 277617 „
1904	174769 „	„ 558949 „
1905	173906 „	„ 491591 „
1906	114706 „	„ (still unknown).

The exports of peppermint oil and menthol from Japan in the year 1906 were as follows: —

	Peppermint oil	Menthol
January	240 cases	154 cases
February	233 „	114 „
March	121 „	41 „
April	286 „	200 „
May	196 „	110 „
June	107 „	94 „
July	57 „	35 „
August	127 „	122 „
September	100 „	75 „
October	106 „	89 „
November	107 „	278 „
December	156 „	184 „
	1836 cases	1496 cases

together 3332 cases,
further 486 „ menthol and oil, not specified,
3818 cases = 103086 kilos
against 194750 „ in 1905.

Peppermint Oil, Russian. A rectified Russian peppermint oil has been examined in detail by J. Schindelmeiser[1]). The oil originated from the Tambow Government where peppermint is now cultivated, and had the following properties: d_{19° 0,908; $\alpha_D - 19^\circ 48'$; 4,8 % menthyl ester, calculated as menthyl acetate; 51,22 % free menthol; 16,36 % menthone; soluble in 4 parts 70 per cent. alcohol. In a freezing mixture the oil only solidified after a prolonged time. Schindelmeiser states that a portion of the first runnings of Russian peppermint oil is removed during the rectification so as to improve

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[1]) Apotheker Ztg. **21** (1906), 927.

the odour and solubility, and that this portion is then employed for scenting plain (so-called Kasan) soap.

The bulk of the oil (85,2 %) boiled between 200 and 220°. The portions passing over below 200° contained a small quantity of a body boiling at 115 to 120° (not further determined) which is probably an aldehyde. There could also be detected in it optically inactive pinene, and a hydrocarbon which, judging from its derivatives, appeared to be identical with dipentene, but which Schindelmeiser, owing to its optical activity ($\alpha_{D20^{\circ}} - 3^{\circ}42'$), regards as a mixture of l- and d-limonene in which the former predominates. Menthene, which Andres and Andreef[1]) claim to have found in Russian peppermint oil, could not be detected, in spite of most careful tests; equally futile was the search for phellandrene which is contained in American peppermint oil. As a further constituent, cineol was discovered.

From the fraction which passed over between 208 and 210°, a lævorotatory menthone ($\alpha_D - 17^{\circ}18'$) was isolated, which Schindelmeiser for various reasons (optical behaviour, properties of the oxime and semicarbazone) considers a mixture of (more) l- and (less) d-menthone.

Menthol was present in the oil both in the free state and in the form of the esters of acetic and valeric acids. The sesquiterpene contained in the oil could not be identified further, as the fraction in question was too small.

Petitgrain Oil, Paraguay. Unfortunately, nothing of a favourable nature can be reported on this subject, as the scarcity of the supplies still continues. The prices could be reduced by a few marks, as the demand at the high quotations naturally left much to be desired, and occasionally small speculative stocks came to the light which the owners were anxious to realize at the profitable prices. Thanks to the reliability of our suppliers, we were in a position to satisfy at least the current requirements. Our correspondent recently informed us that the calamity had become in so far worse, that a terrible plague of locusts had attacked the producing district, and destroyed all leaves. In consequence of this, the distillation which had already been almost crippled by the rise in the cost of labour, had now ceased there completely, and it was now necessary to remove the manufacture to distant districts which had not been attacked by the locusts. The great expense connected with this, and especially the troublesome transport, naturally cause a corresponding increase in the cost of the distillate, of which probably not much more than a few thousand kilos can now be had. How long these abnormal conditions will last, it is, of

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[1]) Berl. Berichte **25** (1892), 609.

course, impossible to foresee; but in any case it will take many months before a return of the quotations to a normal basis can be reckoned upon.

Pine needle Oils. Although the scarcity of pure oil from Pinus montana seems at last to have come to an end, we have unfortunately to report that the lack of oil from the cones of Abies alba *(Ol. templini)* has lately made itself felt in an unpleasant manner. The modest stocks existing in Switzerland have become completely exhausted, and whatever we endeavoured to obtain from second hand showed such deviations in the constants, that we could not run the risk of offering these goods to our clients as a makeshift. A large number of our clients use Siberian pine needle oil as a welcome and cheap substitute, and we do not wish to miss this opportunity of calling again attention to the extreme usefulness of this oil both in perfumery and for technical purposes. According to the practical tests made by us, Siberian pine needle oil is very specially adapted for domestic and transparent soaps, because it possesses a pleasant aromatic and powerful odour which has a very refreshing effect. In view of the high prices of citronella oil, safrol, spike oil, camphor oil, etc., this article, which has the additional advantage of being cheap, deserves without any doubt full attention.

In the oil from the needles of *Pinus halepensis* Mill., of Algeria, E. Grimal¹), succeeded in detecting, while engaged in his work in our laboratory, phenyl ethyl alcohol, which up to the present had only been found in neroli and rose oils. Grimal had saponified the fraction of the oil passing over between 120 and 135° (10 mm. pressure), and fractionated the alcoholic constituents extracted with ether. The portions then passing over from 95 to 98° (8 mm. pressure), after treatment with phthalic anhydride, and saponification of the ester formed, yielded a liquid with a highly aromatic odour, which distilled at ordinary pressure between 218 and 220°, and had the following constants: d_{15° 1,0187; $\alpha_D \pm 0$; n_{D18° 1,52673. By elementary analysis, its behaviour on oxidation, and its phenyl urethane, the alcohol was sufficiently identified as phenyl ethyl alcohol.

R. E. Hanson and E. N. Babcock²) have examined the oils from the needles, cones and branches respectively, of some American conifers. The results are mentioned here briefly: —

Picea Mariana, "black spruce". The yield of oil from the needles amounted to 0,57 %; d_{19° 0,9274.

Tsuga canadensis, "hemlock". The needles and branches gave a yield of oil of 0,4 to 0,46 %; d_{15° 0,9238 to 0,9273.

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¹) Compt. rend. **144** (1907), 434.

²) Journ. Amer. chem. Soc. **28** (1906), 1198.

Picea canadensis, "cat spruce". Of this species, needles and cones were distilled. The former yielded 0,103 $^0/_0$ oil; d_{15° 0,9216; 25,7 $^0/_0$ ester, calculated as bornyl acetate. The odour of the oil points to the presence of limonene or dipentene. The cones yielded 0,25 $^0/_0$ of a yellow oil, also with a limonene-like odour; d_{15° 0,899 (some time after distillation).

Picea rubens, "red spruce". Of this species also the oil from the needles and cones was examined. The yield of needle oil came to 0,204 $^0/_0$; d_{16° 0,9539; 66,2 $^0/_0$ bornyl acetate; 7,76 $^0/_0$ free borneol. The odour of the cone oil resembled that of turpentine, the yield amounted to 0,38 $^0/_0$; d_{15° 0,860.

Larix Americana. The yield of the oil distilled from needles and twigs was 0,149 $^0/_0$; d_{15° 0,8816; ester-content 15,1 $^0/_0$ (calculated for bornyl acetate). The fractional distillation gave the following results. There passed over: —

from 155 to 170° = 20,0 $^0/_0$; from 170 to 180° = 38,4 $^0/_0$;
" 180 " 190° = 11,2 $^0/_0$; " 190 " 200° = 9,2 $^0/_0$;
" 200 " 240° = 14,8 $^0/_0$. Residue = 6,4 $^0/_0$.

On repeated fractional distillation, a fraction could be isolated which boiled between 155 and 162°, and in which pinene was detected, (nitrosochloride, m. p. 108° [?]). The authors conclude from their examinations that the oil consists of about 15,1 $^0/_0$ esters and for the rest largely of pinene.

Pinus rigida, "pitch pine". 12 kilos leaves and twigs yielded only 0,2 cc. of a yellow oil with an extraordinary pungent odour, which was not sufficient for analysis.

Pinus resinosa, "red pine". The quantity obtained of this oil was also too small for a chemical examination; the yield only amounted to 0,001 $^0/_0$. The colour of the oil was brownish red, the odour pungent and disagreeable.

Oil from the cones of Picea excelsa. From the one year old fruit-cones of the Norway spruce, *Picea excelsa* Lk., which had been sent to us from Thuringia, we obtained a distillate which in the rectified state had the following constants: d_{15° 0,8743; α_D — 19°15′; acid no. 1,8; ester no. 3,9 = 1,4 $^0/_0$ ester, calculated for bornyl acetate; soluble in 7 and more vol. 90 per cent. alcohol. The oil had a greenish yellow colour, and, contrary to the other conifer oils, had a somewhat stale, musty odour.

Oil of Pinus Sabiniana Douglas. On the occasion of some examinations carried out by ourselves[1]) with the oil from the turpentine of this conifer which is found in California, we summarised also the

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[1]) Report October 1906, 64.

earlier work on this oil by other investigators. Mr. W. C. Blasdale now writes to us, calling our attention to his work "A heptane from conifer woods"[1] which in the discussion at that time unfortunately escaped us. Blasdale has found that the distillates from *P. Jeffreyi* and *P. Sabiniana* boiling at 96 to 97°, consist without doubt of heptane. The two species are very widely distributed in the Sierra Nevada Mountains, and the first species is usually found only at altitudes of 4000 feet, the latter in lower districts. A large percentage of the "abietine" which was formerly placed on the market, originated from *P. Jeffreyi*; but Blasdale is unable to indicate the source of that used nowadays.

Rose Oil, Bulgarian. Owing to the large quantity of matter, the publication on the part of the Chamber of Commerce of Philippople, of the Report on the Meeting of Rose oil Manufacturers and Traders, held on July 1st last, has been further delayed, so that we are still unable to place before our readers the details which will doubtless be interesting. The proposals submitted by the Meeting have up to the present only been adopted in so far as they apply to the control of the thermometers, and the Government has also taken steps to place a control on the scales employed in the rose oil trade, so that the small producers may not be cheated when selling their oil. The other proposals formulated by the Meeting, which we mentioned in our last October Report, have for the present only been "noted".

The rose oil market has become decidedly firmer during the last few weeks, as the winter was very severe in some districts, and in consequence of this the cultivation is said to have suffered considerably here and there. But up to the present it has not been possible to ascertain anything definite on this point.

Our correspondents have sent us the following tables which are in so far particularly interesting, as it appears from them that in 1898, 1899 and 1903 much more rose oil was exported from Bulgaria than was produced, — a clear proof of the increasing adulteration. In forming an opinion on the export figures it must, of course, be taken into account, that they occasionally also include the stocks carried over from the previous year, and although the divergences may thus be explained to some extent, there remain quite considerable differences which can probably only be attributed to an "artificial extension" of the production. Although the difference between the two amounts in the year 1904 is comparatively small, we are not inclined to believe in an improvement in the situation, until further comparative data for the years 1905 and 1906 are available.

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[1] Journ. Amer. Chem. Soc. **23** (1901), 162; Chem. Centralbl. **1901**, I. 1143.

The rose-cultures and their yield of oil in the years 1898 and 1899.

District	1898					
	Area under cultivation				Yield	
	New cultures	Old cultures		Total	Flowers	Oil
		Productive cultures	Unproductive cultures			
	Décares 1)				kilos	Muscals 2)
Kotel	0,5	—	—	0,5	—	—
Sliven	—	8,0	—	8,0	926	58
Kula	1,5	—	—	1,5	—	—
Berkovitza	—	—	—	—	—	—
Vratza	—	—	—	—	—	—
Dubnitza	—	—	—	—	—	—
Kustendil	—	—	—	—	—	—
Karlovo	3240,0	13 958,1	—	17 198,1	2 951 803	173 984
Pasardchik	2,0	43,5	1,0	46,5	6 284	457
Panagurishte	175,0	187,9	—	363,7	43 395	3 144
Peshtchera	232,4	1 106,9	—	1 339,3	238 731	18 502
Philippople	554,5	3 709,6	1,5	4 265,6	645 027	39 630
Stanimaka	18,3	17,3	—	35,6	2 644	173
Nikopol	12,0	—	—	12,0	—	—
Troitan	0,7	—	—	0,7	—	—
Pirdop	1,6	—	—	1,6	—	—
Kazanlik	2663,4	18 217,9	13,8	20 895,1	2 094 960	134 079
Nova-Zagora	352,6	1 541,9	103,4	1 997,9	152 243	10 125
Stara-Zagora	592,1	1 745,1	—	2 337,2	225 119	15 198
Tchirpan	266,0	2 744,2	—	3010,2	288 175	18 034
Sevlievo	13,2	9,3	—	22,5	3 092	185
Osman-Pasar	3,5	—	—	3,5	—	—
	8130,1	43 289,7	119,7	51 539,5	6 652 399	413 569 [= about 1988 kilos
	1899					
Kotel	—	—	—	—	—	—
Sliven	8,0	—	—	8,0	—	—
Kula	—	—	—	—	—	—
Berkovitza	—	—	—	—	—	—
Vratza	—	—	—	—	—	—
Dubnitza	—	—	0,2	0,2	—	—
Kustendil	—	—	—	—	—	—
Karlovo	2665,6	14 566,5	—	17 232,1	2 676 139	161 11
Pasardchik	6,2	48,4	—	54,6	7 167	599
Panagurishte	155,9	241,2	—	397,1	41 072	2 591
Peshtchera	185,0	1 167,9	—	1 352,9	226 353	17 228
Philippople	573,7	3 878,4	5,0	4 457,1	629 629	42 071
Stanimaka	15,0	33,5	—	48,5	3 024	184
Nikopol	—	—	—	—	—	—
Troitan	—	0,7	—	0,7	63	—
Pirdop	—	—	—	—	—	—
Kazanlik	1486,3	18 469,6	343,0	20 298,9	2 487 325	176 127
Nova-Zagora	219,9	1 806,8	—	2 026,7	179 242	9399
Stara-Zagora	385,3	1 813,8	3,4	2 202,5	226 763	17 440
Tchirpan	289,1	2 544,8	—	2 833,9	294 946	18 697
Sevlievo	9,9	20,4	—	30,3	2 711	156
Osman-Pasar	—	—	—	—	—	—
	5999,9	44 592,0	351,6	50 943,5	6 774 434	445 602 [= about 2124 kilos

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1) 1 Décare = 0,247 acre. 2) 208 Muscals = 1 Kilo.

The rose-cultures and their yield of oil in the years 1903 and 1904.

District	1903					
	Area under cultivation				Yield	
	New cultures	Old cultures		Total	Flowers	Oil
		Productive cultures	Unproductive cultures			
	Décares[1]				kilos	Muscals[2]
Kotel	—	—	—	—	—	—
Sliven	—	11,2	0,5	11,7	795	45
Kula	—	—	—	—	—	—
Berkovitza	—	1,5	—	1,5	195	12
Vratza	—	—	—	—	—	—
Dubnitza	—	—	—	—	—	—
Kustendil	—	—	—	—	—	—
Karlovo	968,8	20030,5	7,6	21 006,9	4 811 596	304 091
Pasardchik	27,8	29,2	—	37,0	5 804	442
Panagurishte	50,0	343,6	—	393,6	84 964	5 847
Peshtchera	123,7	1 150,4	—	1 274,1	296 239	25 354
Philippople	523,2	5 316,5	—	5 839,7	1 216 515	95 501
Stanimaka	3,0	24,3	1,0	28,3	3 832	293
Nikopol	—	—	—	—	—	—
Troitan	—	—	—	—	—	—
Pirdop	—	—	—	—	—	—
Kazanlik	1161,0	21 250,1	—	22 411,1	4 804 507	286 514
Nova-Zagora	212,9	2 037,1	—	2 250,0	442 196	27 444
Stara-Zagora	458,3	2 438,0	—	2 896,3	467 702	33 840
Tchirpan	258,0	3 237,2	—	3 495,2	880 591	68 113
Sevlievo	3,8	36,4	—	40,2	5 711	476
Osman-Pasar	—	—	—	—	—	—
	3790,5	55 906,0	9,1	59 685,6	13 020 647	847 972
						[= about 4077 kilos
	1904					
Kotel	—	0,2	—	0,2	48	4
Sliven	—	8,0	0,5	8,5	808	42
Kula	—	—	—	—	—	—
Berkovitza	—	1,5	—	1,5	833	45
Vratza	0,7	—	—	0,7	—	—
Dubnitza	—	—	—	—	—	—
Kustendil	—	—	0,6	0,6	—	—
Karlovo	926,0	22 759,2	—	23 685,3	5 510 727	351 248
Pasardchik	22,8	66,3	0,4	89,5	14 474	1 198
Panagurishte	74,1	345,5	—	419,6	81 668	5 736
Peshtchera	100,3	987,6	—	1 087,9	217 580	19 301
Philippople	270,3	6 792,2	—	7 062,5	1 391 937	95 417
Stanimaka	5,0	25,1	—	30,1	4 327	351
Nikopol	—	—	—	—	—	—
Troitan	—	—	—	—	—	—
Pirdop	—	—	—	—	—	—
Kazanlik	539,3	23 612,8	—	24 152,1	4 367 854	288 332
Nova-Zagora	129,3	2 078,4	—	2 207,7	319 923	19 565
Stara-Zagora	193,1	2 921,8	—	3 114,9	486 113	35 308
Tchirpan	228,2	3 738,2	—	3 966,4	826 518	54 870
Sevlievo	0,1	39,8	—	39,9	11 892	677
Osman-Pasar	—	—	—	—	—	—
	2489,2	63 376,6	1,5	65 867,4	13 234 702	872 094
						[= about 4192 kilos

[1] 1 Décare = 0,247 acre. [2] 208 Muscals = 1 Kilo.

The exports of rose oil in the years 1890 to 1905, according to the Statistical figures of the Bulgarian Government.

Countries	1890		1891		1892		1893	
	kilos	%[1]	kilos	%	kilos	%	kilos	%
Austria	389	12,3	8	0,3	6	0,2	8	0,3
The United Kingdom	184	5,8	34	1,1	38	1,3	—	—
Germany	177	5,6	3	0,1	59	2,1	161	5,9
Italy	2	0,1	—	—	1	0,1	—	—
Russia	18	0,5	—	—	—	—	4	0,1
The United States	—	—	—	—	43	1,5	—	—
Turkey	1212	38,3	363	11,6	75	2,6	25	0,9
France	1180	37,3	26	0,8	216	7,6	21	0,8
Other countries	2	0,1	2696	86,1	2405	84,6	2530	92,0
	3164	100,0	3130	100,0	2843	100,0	2749	100,0
	1894		**1895**		**1896**		**1897**	
Austria	15	0,5	24	0,8	64	1,9	23	0,7
The United Kingdom	1	0,0	466	14,9	680	20,5	686	21,5
Germany	161	5,2	425	13,6	693	20,9	583	18,3
Italy	2	0,1	3	0,1	—	—	—	—
Russia	22	0,7	80	2,6	102	3,1	47	1,5
The United States	—	—	—	—	—	—	12	0,4
Turkey	154	4,9	478	15,3	495	15,0	680	21,3
France	336	10,8	1564	50,1	1271	38,4	1151	36,0
Other countries	2427	77,8	82	2,6	7	0,2	10	0,3
	3118	100,0	3122	100,0	3312	100,0	3192	100,0
	1898		**1899**		**1900**		**1901**	
Austria	23	0,7	106	2,9	93	1,7	22	0,7
The United Kingdom	707	20,6	633	17,6	1174	22,0	472	15,6
Germany	471	13,7	360	10,0	568	10,6	345	11,4
Italy	7	0,2	3	0,1	9	0,2	12	0,4
Russia	134	3,9	155	4,3	202	3,8	119	3,9
The United States	380	11,1	716	19,9	849	15,9	760	25,1
Turkey	872	25,4	582	16,2	886	16,6	564	18,6
France	761	22,2	1033	28,8	1548	28,9	728	24,1
Other countries	75	2,2	6	0,2	17	0,3	5	0,2
	3430	100,0	3594	100,0	5346	100,0	3027	100,0
	1902		**1903**		**1904**		**1905**	
Austria	38	1,0	64	1,0	23	0,5	23	0,4
The United Kingdom	521	14,2	1054	17,0	472	10,8	891	16,8
Germany	518	14,1	1027	16,5	853	19,4	714	13,4
Italy	20	0,5	36	0,6	19	0,4	20	0,4
Russia	127	3,5	272	4,4	163	3,7	238	4,5
The United States	850	23,1	1467	23,6	809	18,4	1641	30,8
Turkey	573	15,6	393	6,3	578	13,2	230	4,3
France	1011	27,5	1870	30,1	1445	32,9	1529	28,8
Other countries	18	0,5	27	0,5	32	0,7	30	0,6
	3676	100,0	6210	100,0	4394	100,0	5316	100,0

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[1]) Of the total export.

Rosemary Oil. The French oil is greatly neglected although the cheap prices ought really to stimulate interest in this article. The requirements which we put to the quality when purchasing the oil are so high, that we cannot too strongly recommend our goods to the perfumery trade as being without rival. On the other hand, pure Dalmatian oil is also one of our specialities, and this oil enjoys everywhere an appreciation which is all the greater, as owing to the severe competition the trade in this oil, which is so completely a victim of adulteration, is carried on by numerous firms in our branch only as a very subordinate business.

Sage Oil. In Gildemeister and Hoffmann's work *The Volatile Oils*, under the description of oil of sage (p. 613) it is stated *inter alia* that the saponification number determined in one oil was 107 [1]).

Contrary to this, E. J. Parry [2]) mentions that in 12 sage oils received from Spain he has observed ester numbers of only 18 to 39. Specific gravity and rotatory power also lay partly outside the limits of value given for oil of sage (d_{15° 0,915 to 0,925; α_D +10 to +25°) and came to between 0,903 and 0,927 (15°) and +7 and +25° respectively.

In so far as Parry's figures have reference to the saponification number, they agree with the observations which we also have subsequently made with oil of sage. Both in oils received by us from Dalmatia, and in our own distillates, we have found that sage has oil a very low saponification number, the values ascertained by us lying between 6 and 18. This, consequently, also applies to the Dalmatian oils to which the above-mentioned work exclusively refers.

It is not surprising that the Spanish oils examined by Parry also showed further differences, as these oils, according to their entire composition, behave more like rosemary oils than like the ordinary Dalmatian sage oil. We consider it very probable that the Spanish oil is not obtained from *Salvia officinalis* L., but from another species of salvia.

Sandalwood Oil, East Indian. Only after the closing of our October Report, we received further details by mail on the quantities of wood put up for sale by the Government, and the dates of the auctions, and these particulars may follow here by way of supplementary information.

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[1]) This was the only determination of the saponification number of sage oil which was available at the time of the publication of this work.

[2]) Chemist and Druggist **70** (1907), 263.

Date (1906)	Auction	Quantity		
		Tons	cwts.	lbs.
Nov. 17	Fraserpet	235	18	32
„ 19	Hunsur	509	11	4
„ 22	Seringapatam	303	15	28
„ 26	Bangalore	129	1	34
„ 29	Hassan	250	1	98
Dec. 3	Chikmagalur	344	1	—
„ 6	Tarikere	256	1	84
„ 8	Shimoga	530	8	14
„ 13	Sagar	175	12	—
„ 17	Tirthahalli	199	16	—
	Total:	2934	6	70

This shows that our hope has not been realized that the Government in view of the expected smaller demand from the European manufacturers, would put up for auction a correspondingly smaller quantity. If, in spite of this, the prices at the auction kept up to 20 % higher than those of the previous year, this must be solely attributed (as we know from a reliable source) to the attitude of a group of native buyers, who appeared to make this article an object of speculation. The favourable economic conditions of India have induced native capitalists to form Syndicates for raising the prices of ginger, pepper, cloves, etc., and it is believed that it was also intended to include sandalwood in the number of the various materials to which particular attention was to be paid. Of the total sales, which only amounted to about 2454 tons, about one half (1214 tons) passed into the hands of the natives, whilst about 760 tons sufficed to meet the demand from Europe and the United States. About 480 tons, i. e., more than 16 % of the quantity placed on sale, found no buyers at all, so that the Government found it necessary to invite for this remainder fresh tenders by January 5th. The fact that this delay had to be extended to the end of January, shows sufficiently that the tenders did not come in very freely.

The dreaded spike disease, the outbreak of which we first reported in October 1902, has recently again caused a stir. According to a communication from the Conservator of Forests in Mysore to our friends in Tellicherry, dated September 7th 1906, the district affected is confined to about two square miles of country in the State Mysore, in the Hassan District, near the frontier of Coorg, and has not increased during the last two years. The diseased zone comprises about one third of the sandalwood district of Mysore, and it w hoped that by the end of 1906 it would be possible to say in how far a decrease or disappearance of the disease might be reckoned upon. On November 6th a comprehensive summary of all the various reports on the spike disease[1]) was published by the Conservator, by request of the Government of the Maharajah of Mysore, and at the same time an appeal was made to scientists to devote themselves to the discovery of a remedy for which a reward of 10000 rupees was offered. It therefore appears that the situation after all gives rise to a certain amount of anxiety. Later information on the subject is not available.

On the strength of observations with 13 East Indian sandal oils, which they have distilled from various kinds of wood imported by themselves, A. L. R. Dohme and H. Engelhardt[2]) proved that the specific gravity $d\frac{25^\circ}{25^\circ}$ 0,965 to 0,975 required for sandal oil by the U. S. Pharmacopœia, does not agree with the fact that many sandal oils have a specific gravity up to 0,980.

A good oil further, should contain 91 to 92 % total santalol[3]) and at 25° make a clear solution with 5 vol. 70 per cent. alcohol. Optical rotation, acid and ester numbers, are, in Dohme's and Engelhardt's opinion, of no importance for judging a sandal oil.

The yields of oil varied, according to the character of the distillation material, from 3,95 to 6,18 %, but from sawdust it only amounted to 2,26 %.

We would mention with regard to the above statements, that in discussing the U. S. Pharmacopœia[4]) we already pointed out that the upper limit of specific gravity there required ($d\frac{25^\circ}{25^\circ}$ 0,975) should be raised to 0,980. Contrary to Dohme and Engelhardt, we consider the optical rotation and also the acid and ester numbers, very useful factors in judging the oil; the rotation particularly supplies frequently important information as to whether and with what substance an oil is adulterated.

Sandarac Oil. A good many years ago already Tschirch in conjunction with Balzer[5]) had attempted the examination of this

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[1]) Selections from reports and notes on spike disease in Sandal. Cola Lodge 1906. A number of copies of this publication have been placed at our disposal, and we shall be pleased to send them to interested parties.

[2]) American Druggist and Pharmaceutical Record **49** (1906), 145.

[3]) Unfortunately it is not said on what formula the santalol-content is based. If it is calculated on $C_{15}H_{24}O$, a minimum of 90 % should be required. It should also be taken into consideration that oils with more than 92 % santalol are also met with.

[4]) Report April **1906**, 76.

[5]) Arch. der Pharm. **234** (1896), 310; Report October **1901**, 49.

oil. But the yield which these investigators obtained by treating the non-pulverised resin with steam under pressure, was so small, that the intended examination could not be carried out. Now recently A. Tschirch, jointly with M. Wolff¹), has again taken up this study. The oil obtained on distillation with steam in a yield of 1,3 %, was colourless, and had a pleasant odour. The bulk passed over between 152 and 159°, and but a small portion distilled only between 260 and 280°. No further details are given with regard to the physical constants of the essential oil.

Sassafras Oil. With a brisk demand, and supported by the high prices of safrol, the quotations have advanced slowly. In view of the higher cost of labour in the producing districts, and the increase in the price of the raw material the present value appears to us to be justified.

Savin Oil. In consequence of the note contained in our last Report²), that the oil of *Juniperus thurifera* var. *gallica* De Coincy might possibly also be used as a substitute or for the adulteration of genuine savin oil, Professor Dr. P. Guigues, of Beyrout (Syria), was kind enough to call our attention to a study³) from his hand on this species of *Juniperus*. Unfortunately we are unable to enter in detail into this very interesting study, at it is a work of purely botanical character and consequently lies outside the scope of these Reports. According to the observations of Professor Guigues, who has also worked up the plant material for oil, it possesses a toxic action, which manifested itself, for example in the persons occupied in the distillation, in severe diuresis.

Professor Guigues kindly sent us at our request the sample of this oil which was still in his possession; but its quantity was so small (about 1,5 cc.) that it is impossible to form an opinion on the oil. It had a yellowish colour and a pleasant aromatic odour, which, however, had only a faint savin character. The specific gravity which we ascertained as 0,9246 (15°) agreed with that of genuine oil of savin, but the rotation was very considerably lower and only amounted to between +1 and +2°.

We avail ourselves of this opportunity to express our sincere thanks to Professor Guigues for his kind attention towards us.

From a further work on the same subject, originating from E. Perrot and Mongin⁴), which has also a purely botanical con-

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¹) Arch. der Pharm. **244** (1906), 709.

²) Report October **1906**, 72.

³) P. Guigues, Une forêt de Sabines dans les Hautes-Alpes. Bull. des Sciences pharmacologiques, No. 2, February **1902**, 33.

⁴) A propos de la Sabine et des espèces botaniques de *Juniperus* fournissant la drogue commerciale. Bull. des Sciences pharmacologiques, No. 2, February **1902**, 38. According to a reprint kindly sent to us by Professor Perrot.

tent, we find that the drug which in France is met with in commerce as savin, is a mixture of the tops of the branches of *Juniperus Sabina*, *J. phoenicea*, and *J. thurifera* var. *gallica*, of which by far the largest part consists of *J. phoenicea*. Owing to its inactivity, this species particularly must be regarded as a direct adulterant of the official drug, whilst *Juniperus thurifera* var. *gallica* is said to be a substitute of equal value. In how far these statements apply, must be proved by further studies.

Umney and Bennett[1]) reported some time ago on the oil of *Juniperus phoenicea* L., which in the South of France frequently occupies the place of the genuine savin oil derived from *J. Sabina* L. A further contribution to the knowledge of this oil is supplied by J. Rodié[2]). The material from which the oil examined by Rodié had been prepared, consisted chiefly of branches partly in flower, without berries, and was therefore in the first stage of development. As a consequence, the oil, obtained in a yield of 0,45 to 0,50 %, was particularly rich in terpenes and had a very low specific gravity. The constants of five different distillates were: d_{15° 0,867 to 0,868; $\alpha_D + 2^\circ 54'$ to $+ 4^\circ 10'$; soluble in 4 to 5 vol. 90 per cent. alcohol. The oil had a bright greenish-yellow colour and a peculiar odour, which, however, was more like that of oil of juniper berries than that of genuine savin.

The further examination showed that more than 90 % of the oil was represented by terpenes, the bulk of which consisted of pinene, as already detected by Umney and Bennett. The pinene fraction (87,5 % of the original oil; $\alpha_D + 4^\circ 31'$) passed over between 154 and 156°; the other terpenes between 156 and 176°; of the latter, those detected with certainty were l-camphene and phellandrene, the nitrate of which showed the m. p. 101°. But the quantities of these terpenes present in the oil are very small; Rodié estimates that of camphene at scarcely 0,1 %.

Rodié is still engaged on the examination of the further constituents of the oil boiling above 180°.

We may add to the foregoing that we have observed entirely similar properties in two distillates of *Juniperus phoenicea* L. sent to us from Cannes. The oils, obtained by water distillation, behaved as follows: —

1. d_{15° 0,8634; $\alpha_D + 2^\circ 30'$; ester no. 0; ester no. after acetylation 4,7; soluble in 6 to 6,5 and more vol. 90 per cent. alcohol.
2. d_{15° 0,8723; $\alpha_D + 2^\circ$; ester no. 2,1; ester no. after acetylation 11,0; soluble in 5 to 6 and more vol. 90 per cent. alcohol, with minute opalescence.

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[1]) Pharmaceutical Journal **75** (1905), 827; Report April **1906**, 62.

[2]) Bull. Soc. Chim. III. **35** (1906), 922.

The oils, therefore, have also a very low specific gravity[1]), and contain moreover no ester, or only very little, and quite unimportant quantities of alcoholic constituents. Here, also, the distillation material which originated from the Département Bouches-du-Rhône, was in a comparatively early stage of development.

Professor Perrot of Paris, who is an excellent authority on the *Juniperus* species, was kind enough to establish the identity of the material worked up with *Juniperus phoenicea* L.

Spearmint Oil. The last harvest was very abundant and as the demand was only moderate, the prices fell back in proportion. It appears that fairly important stocks of this article have accumulated, and that these depress the market.

Spoonwort Oil. As the German Pharmacopœia prescribes a spoonwort spirit containing 0,06 to 0,07 % of butyl mustard oil, it is only possible to use a material which yields 0,3 to 0,35 % mustard oil. On a previous occasion we mentioned already that Urban[2]) obtained a distillate which agreed with the requirements of the Pharmacopœia, by using as crude material not the herb, but the seed of the plant. Of a mixture consisting of 200 g. pulverised seed freed from fatty oil, 50 g. white mustard flour, 3000 g. water, and 1125 g. 90 per cent. alcohol, he distilled off 1,5 kilo. The identity of the essential oil obtained from the seed with that obtained from the herb, was proved by conversion of the oil in secondary butyl thio-carbamate (m. p. 137°).

E. Lücker[3]) has now found after repeated trials, that also from quite fresh herb, according to the directions of the German Pharmacopœia III, a spoonwort spirit is obtained which answers the requirements of the Pharmacopœia. Lücker himself had cultivated the plants, and although they are said to thrive usually only on the seaside and near salt springs, he obtained in his own garden excellent yields; the radical leaves had a length of 20 to 25 cm.

The fresh herb (8 parts) was pounded to a uniform paste, macerated for 12 hours with alcohol (3 parts) and water (3 parts) and then submitted to distillation. The distillate produced according to the directions had a specific gravity of 0,908. Now, whilst a commercial preparation, or one prepared according to the German Pharmacopœia IV, only contained 0,026 and 0,027 % butyl mustard oil respectively, instead of 0,0575 %, Lücker obtained in 100 g. distillate from 100 g. fresh herb, a content of mustard oil of 0,0512 g. From the distillate obtained from the fresh herb, Lücker was able to produce

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[1]) Comp. for the rest also oil described by us in our last Report, p. 72.

[2]) Arch. der Pharm. **242** (1904), 51; Report April **1904**, 83.

[3]) Apotheker Ztg. **21** (1906), 1006.

without difficulty butyl thio-carbamate (m. p. 134 to 135°). Lücker concludes from his experiments that spoonwort spirit belongs to those preparations which it should be the duty of every chemist to prepare himself.

Star-Anise Oil. Like in the case of cassia oil also with this staple article, reliable reports by mail now come very rarely to Europe, and it is greatly to be regretted that there is little prospect of ever obtaining authoritative statistics of the production. In the export lists of China firms, star-anise oil is always mentioned jointly with cassia oil, so that the figures of the quantities have no informatory value whatever either for the one article or for the other. Thanks to the excellent watch kept over the arrivals at Hong Kong on the part of the export firms, on account of our well-known method of examination, inferior oil is now rarely shipped, and although it was now and then necessary to object to individual parcels, it was almost without exception a question of lots which had been thrown about for years by speculators, had drifted about in London and Hamburg, and of which the normal condition had suffered from partial oxidation. We can only caution consumers strongly against the purchase of such usually cheap parcels. The prices have maintained themselves with slight fluctuations at about 5/- cif. Hamburg, although it was occasionally possible to buy a little cheaper. The neglected condition of the market mentioned in our last Report, has for this reason continued.

As *De Indische Mercuur*[1]) informs us, *Illicium verum,* the mother-plant of star-anise, suffers in the course of its development from numerous injurious influences. In its early age the principal enemy of the plant is the locust, which is represented in China by numerous varieties of *Orthoptera.* If the tree grows up, it falls a victim to the game; a species of caterpillar not described more in detail also damages the plant considerably. But the tree suffers most from the irrational manner in which it is treated by the inhabitants of that country. When the fruit is gathered, so many branches are broken and pulled down that it takes years before the tree has recovered. For this reason it is estimated in Cochin China that there is a good harvest only once in every three years. The average yield of fruit from a tree between 10 and 20 years old, amounts to about 30 to 35 kilos, and from a tree above 20 years old from 40 to 45 kilos. 40 kilos fruit yield about 0,7 kilo oil. Up to the present day the distilling plant in China is still of a very primitive character.[2])

Oil of Sweet Marjoram. See under Terpinene, in the Notes on recent research work.

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[1]) De Indische Mercuur **29** (1906), 715.

[2]) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 356.

Turpentine Oil. From a report[1] of the German Consulate-General at Calcutta in the *Reichsanzeiger* we abstract the following on the production of turpentine in India: During the working year 1904/05 about 62000 trees in the Forestry District Naini-Tal were tapped; the yield of crude resin amounted to 4260 maunds[2] from which 6000 gallons turpentine and 3300 maunds colophony were obtained. The cost of production came to about 14000 rupees, and the proceeds to about 30000 rupees. Owing to the good demand, great hopes are entertained for the development of this new branch of industry. With regard to the influence of the boxing of the trees on their growth, and also on the quality and the weight of the wood, further experience will have to be obtained, also with regard to the intensity with which the extraction of the balsam may be carried on.

Another report on the turpentine production in India[3] on the whole agrees with the above; it may still be stated that in another district 6811 maunds crude resin were obtained, which yielded roughly 10000 gallons oil and 4000 maunds colophonium. The oil is said to be of such good quality that it is partly preferred to American and English brands. The Forest Department which keeps the management in its own hands, and will continue to do so, expects an annual yield of 10000 to 11000 gallons oil, but hopes to raise the production further if the demand increases.

Under the direction of the Conservator of Forests in Eastern Bengal and Assam, trials have recently been commenced there on a small scale for the production of turpentine etc. from *Pinus Khasya,* a species of conifer which is found in the neighbourhood of Shillong[4]. But the yield of turpentine per tree did not yet come to one ounce, and the attempt had therefore to be characterised as a failure. The bad result is attributed chiefly to the time of the year in which the trees were tapped. This had, namely, been done during the rainy season, instead of in the spring, and it is now intended to repeat the experiments this spring under more suitable conditions.

Japanese turpentine (from *Pinus Thunbergii*) has been submitted by M. Burchhardt[5] to an examination, in which he obtained 10% of an essential oil which was fractionated for the purpose of purification. The bulk of the oil passed over at 165°; the individual fractions boiled between 157 and 292°. Unfortunately no details whatever are given of the physical constants of the oil.

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[1] Acc. to Chem. Zeitschrift **5** (1906), 428.

[2] 1 maund = 82,287 lbs.

[3] Chem. Ztg. **30** (1906), 888.

[4] Chemist and Druggist **69** (1906), 961.

[5] Thesis, Berne 1906, 22.

G. Weigel[1]) has recently examined a sample of a turpentine from Eastern Asia. This showed the usual viscid consistency, a brownish yellow colour, and the characteristic pinene odour; acid no. 145,45; sap. no. 149,38. On steam-distillation it yielded about 14,5 % oil, $\alpha_D + 39° 9'$[2]).

The granular-crystalline Mexican turpentine has, according to the same author, a faint lemon-yellow colour, and a limonene-like odour; acid no. 107,54; sap. no. 115,12. When distilled with water vapour, it yielded about 14 % oil with a pleasant aroma, $\alpha_D + 33° 44'$.

In view of the steadily increasing consumption of turpentine oil, a work by G. B. Frankforter[3]) on the pitch and the terpenes from the Norway pine *(Pinus resinosa)* and the Douglas fir *(Pseudotsuga taxifolia)* is of particular interest. These two conifers, which are largely distributed chiefly in the North and West of North America, are up to the present only used as lumber. Wood containing too much turpentine is either burnt, or simply thrown aside. The utilisation of such waste products for the manufacture of turpentine has not yet been found sufficiently remunerative in those districts, and for this reason almost all the turpentine oil used in the North and West must be obtained elsewhere. The box-system universally employed in the South for the production of turpentine is not appliable in the North and West. It was therefore necessary to work out first of all a method for the industrial utilisation of the waste products suitable for the prevailing conditions. Frankforter has in his studies come to the following results: —

1. *Pinus resinosa.* The water-white turpentine had been obtained partly by the box-system, and partly from stumps of trees and other waste material, by means of extraction, distillation by steam and dry distillation. The examinations showed that the working up of these waste products is remunerative, not only for the production of oil of turpentine, but also of tar and other by-products. Lean wood yielded on the average 6,2 %, average quality 8,6 % turpentine. Stumps yielded 19,4, pitchy wood 39,1, and very pitchy wood even 42,6 % turpentine. Its constants were: $d_{20°}$ 0,8137 (erratum?); $[\alpha]_{D20°} + 4°$; n_D 1,47869; it contained 22,1 % oil of turpentine, 77,3 % colophony, and 0,6 % water, and on being left standing it became in one or two months' time either semi-solid or solid, according to the content of oil.

2. Douglas Fir. The turpentine-content was, in very lean wood 11,6 %, in lean wood 13,5 %, medium quality 19,8 %, rich

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[1]) Pharm. Centralh. **47** (1906), 866.

[2]) Comp. Reports April **1905**, 78; October **1905**, 67; also Gildemeister and Hoffmann, The Volatile Oils, p. 253.

[3]) Journ. Amer. chem. Soc. **28** (1906), 1467.

wood 40,7 %, and very rich wood 42,4 %. On the whole the balsam was water-white and very mobile; but it became darker on exposure to the air, and gradually became viscid. In the fresh state it had a peculiar aromatic odour; d_{20° 0,9821; $[\alpha]_D$ — 8,82°; n_{D20° 1,51745; the yield of oil was 22 %.

The oils from the two species of wood show fairly large differences according to the manner of production, whether by extraction and steam distillation, or by dry distillation. The last-named method yields apparently more complicated products which distil within wide boiling limits. The following table shows the influence of dry distillation on compounds with the same boiling point: —

	Terpene from *P. resinosa:*		Terpene from the Douglas fir:	
	steam distillation	destructive distillation	steam distillation	destructive distillation
b. p.	153 to 154°	158 to 160°	153,5 to 154°	157 to 160°
d_{20°	0,8636	0,8666	0,8621	0,8662
$[\alpha]_D$	+ 17,39°	— 7,56°	— 47,2°	— 29,4°
n_{D20°	1,47127	1,47160	1,47299	1,47246

M. Vèzes and M. Mouline have continued, in conjunction with R. Bridon[1]), their studies on the mutual solubility of oil of turpentine and dilute alcohol. In our note on the first work[2]) of Vèzes and Mouline, we had called attention to the fact that it is important in such examinations, also to give details of the character and the properties of the turpentine oil used. The authors state that the object of examination in the trials under discussion was French turpentine oil, three times rectified, from the Département des Landes, which had the following constants: d_{25° 0,8580; α_D —33,1°; n_{D25° 1,4665. The conditions of the tests were on the whole the same as in the earlier tests, and the results confirm or amplify those previously obtained. The more dilute the alcohol used for the mixture, the more necessary it is to raise the temperature in order to bring about a homogeneous mixture with the turpentine oil. The authors have summed up their results in a number of tables, and give the separation-curves for a large number of mixtures of turpentine and alcohol, for alcohols of various degrees of concentration. One curve illustrates the preparation of those mixtures, of which it is certain that the turpentine-alcohol mixtures produced in accordance therewith with alcohols of different strength, do not become cloudy even when strongly cooled (several degrees below 0°).

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[1]) Reprint from the Procès-Verbaux des Séances de la Soc. des sc. phys. et nat. de Bordeaux, June 28, 1906.

[2]) Bull. Soc. Chim. III. **31** (1904), 1043; Report April **1905**, 76.

From Professor E. Sundvik[1]) we received an interesting publication on the turpentine oil (pine tar oil) produced by destructive distillation. In Finland and also in Sweden, the two kinds of oil, viz., the turpentine oil obtained by distillation with steam, and the pine tar oil produced by destructive distillation, are both called "turpentine", whilst our turpentine is in the North called turpentine balsam (Pinus balsam). Now, although turpentine oil is one of the most important domestic remedies over there, pine tar oil is, in the existing confusion among the names, in spite of this, quite openly sold as turpentine oil.

According to Sundvik pine tar oil differs from turpentine oil — apart from the smell — by its very low capacity of oxidising, and also by the absence of the decrepitation with iodine, and of the formation of vapours with chlorine. The first-named difference may possibly be due to the presence of oxidation-preventing bodies which themselves absorb oxygen preventing its becoming attached to the principal constituents of the oil. The negative reactions with the halogens in question must perhaps be attributed to the peculiar structure of the two principal constituents of pine tar oil, sylvestrene and dipentene. For the purpose of elucidating these possibilities, Sundvik examined several samples of pine tar oil of various origin as to their missing oxidation-capacity, the peculiar behaviour of a terpene contained in pine tar oil, and the presence of oxidation-preventing bodies. By treating about 10 litres oil with bisulphite, furfurol (5 g.) could be detected. In the oil freed from the latter, the phenols were determined. The total quantity of these amounted to 30 cc., whose fraction boiling at about 200° (d 1,12) yielded guaiacol ($50\,^{0}/_{0}$). In the lower boiling fractions phenol was detected.

The odour of the oil from which the aldehydes, ketones and phenols have been removed, although more pleasant than that of the original oil, does not by a long way come up to that of the French turpentine oil.

The distillation-residue represents a resin of a topaze-yellow colour. The easy resinification of the purified pine tar oil on renewed steam distillation is in Sundvik's opinion due to the content of sylvestrene and dipentene in the oil; the resinification occurs most readily when shaking the oil with sulphuric acid.

All the pine tar oils examined by Sundvik give Herzfeld's reaction in an excellent manner, also after removal of the aldehydes and phenols, but this is not the case with the resin remaining behind in the steam-distillation when dissolved in French oil of turpentine. Sundvik has arranged the results of his experiments in tabular form. The

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[1]) Reprint from the *Festschrift für* Olof Hammersten. Upsala **1906**.

French turpentine oils examined by him all rotate to the right, whilst this oil is usually lævorotatory[1]. The figures for Finnish pine tar oil agree with those of other authors (Flawitzky, for Polish pine tar oil, $\alpha_D + 15^\circ 24'$ to $+ 24^\circ$; Atterberg, for Swedish pine tar oil $\alpha_D + 14^\circ 48'$). The boiling point of pine tar oils (160 to 170°) lies somewhat higher than that of good turpentine oils. A few of the oils examined contained methyl alcohol, acetone, and acids, and one oil was adulterated with 30 to 40 % petroleum.

Verbena Oil. Under the name "*Thyme lemon oil*" we recently received an oil from Spain, on the botanical origin of which we were unable to obtain any information, but of which we wish to mention the properties here, as meanwhile a communication from Parry and Bennett dealing with a similar oil has also made its appearance.

The oil examined by us had an orange-yellow colour, and an odour like lemon oil with a suspicion of thyme oil; d_{15° 0,9085; $\alpha_D + 9^\circ 45'$; soluble in 1 and more vol. 80 per cent alcohol, but of 70 per cent. alcohol not even 15 vol. sufficed for a complete solution. Unfortunately we had only a few grams of this oil at our disposal, so that we had to content ourselves with the determination of the above constants.

A somewhat more detailed examination now is found in the above-mentioned work of Parry and Bennett[2]. The thyme lemon oil here described agrees fairly well with ours: d_{15° 0,901, $\alpha_D + 18^\circ 30'$, not soluble in 70 per cent. alcohol, soluble in 2 vol. 80 per cent. alcohol. The oil contained about 20 % aldehydes, which consisted chiefly of citral. 5 per cent. potash liquor absorbed about 10 % of the oil, from which a corresponding phenol-content was assumed. A closer examination, however, showed that the portion combined with the liquor was more of a resiniferous character, and gave only a feeble reaction with ferric chloride. From the behaviour of the oil in boiling (b. p. 175°, the bulk passes over below 230°) Parry and Bennett conclude that of terpenes chiefly limonene is present, and that pinene is probably not contained at all in the oil. The portions boiling above 230° contain clearly a sesquiterpene, as may be assumed from the high index of refraction (1,50).

Parry and Bennett also say that the oil, according to the distillers, originates from *Lippia citriodora* Kth. (*Verbena triphylla* L.), and would therefore be a genuine verbena oil. This does not quite agree with previous observations according to which verbena oil is lævorotatory, more difficulty soluble, and also contains more citral;

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[1] We ourselves have never yet had a dextrorotatory French oil of turpentine in hand.

[2] Chemist and Druggist **69** (1906), 481.

but such differences may be due to the source of supply and the manner of distillation. Parry and Bennett hope at some future time to give further details on this oil.

Vetiver Oil. In one of our previous Reports[1] we discussed a vetiver oil originating from German East Africa, which we had received from the Imperial Biologico-Agricultural Institute at Amani. The oil proved to be a normal product, but it showed differences as compared with distillates produced in Germany, which we attributed solely to the distillation-material. We have now, however, convinced ourselves that the differences must also be due to the method of distillation. The Director of the Botanical Department of the above-mentioned Institute, Professor Zimmermann, was kind enough to send us vetiver roots which we have distilled here ourselves. The oil obtained in a yield of 2,2 % had a brown colour and powerful odour; d_{15° 1,0166; $\alpha_D + 36^\circ 35'$; acid no. 40,0; ester no. 22,8; soluble in 1 to 1,5 and more vol. 80 per cent. alcohol.

These results show that the East African vetiver root yields a useful oil which is equal in value to the products obtained in Germany from roots of a different origin.

Wintergreen Oil. Owing to the new Food and Drugs Act (see Introduction) which has come into force in the United States, the use of the natural oil has lately been taken up again more largely in that country, whereas up to the present the artificial oil had been chiefly employed for flavouring, as the latter possessed in the first place the great advantage of cheapness. Owing to the demand, the quotations of the genuine oil have advanced considerably, a fact which was bound to find expression in our price-lists.

Wormseed Oil, American. In our last Report[2] we mentioned already that on the strength of extensive pharmacological studies by H. Brüning, the American or Baltimore wormseed oil has been proved to be an anthelmintic at least equal in value to santonin, and that the body $C_{10}H_{16}O_2$ found by us in wormseed oil is probably the active constituent of this oil. Brüning[3] now has determined the physiological action of wormseed oil on various living beings, and also its action on blood, raw cow's milk, solutions of egg-albumin, and bacteria cultures.

The deadly dose for frogs is 0,5 cc. oil per kilogr. body weight; fish die within 12 hours with a dilution of the oil to 1 : 8000; for guinea pigs the fatal dose is 0,6 cc. per kilogr. weight, for hens 0,5 cc. oil per kilogr. weight. In dogs 0,2 cc. oil per kilogr. body weight, when

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[1] Report April **1905**, 84.

[2] Report October **1906**, 81.

[3] Ztschr. f. exp. Pathol. u. Therap. **3** (1906), 564.

applied hypodermically, have a fatal action, in rabbits 0,3 cc. Combined glycuronic acids could not be detected in the urine.

In the blood of rabbits, guinea pigs, dogs and calves, wormseed oil in suitable concentration develops methemoglobin- and cathemoglobin-forming properties; in suspensions of blood corpuscles in physiological solution of common salt, it effects a strong hematolysis.

Wormseed oil prevents the milk becoming sour, or curdling, by its action on the bacteria. In solutions of egg-albumin it effects precipitation of the albuminoids. Even when diluted to 1 : 200, the oil has a retarding action on the development of bacteria cultures.

All these effects of wormseed oil were also shown by the body $C_{10}H_{16}O_2$ present in it, which was discovered by us. With regard to its action on man, no results are as yet available, but it is probable that this constituent of the oil when suitably diluted, will show the same action.

Brüning¹) discussed furthermore at the 30th Meeting of the Mecklenburg Society of Physicians, the treatment of ascaridiasis with Baltimore wormseed oil. His statements may be summarised as follows: The remedy, in a suitable form, is taken without objection even by children. It showed no disagreeable secondary symptoms, and the action itself was absolutely reliable. On the manner of administration we have already reported on a previous occasion.²)

Wormwood Oil. It appears that it is now intended to take energetic measures in France against the use of absinth and similar liqueurs, by placing as many difficulties as possible in the way of the manufacture and the sale of these products and the essential oils used for that purpose. This, at least, appears from a law enacted January 30th, 1907, which has caused a great sensation in interested circles. According to this, the manufacture not only of absinth and similar liqueurs, but also of the oils required therefor, such as wormwood oil, etc., is to be subject to the continuous control of the Board of Revenue. The cost of this, which is annually fixed by the Treasury Department according to the number and pay of the officers employed, has to be borne by the manufactures. On the alcohol used for the beverages in question, a special additional tax of 50 francs per hectolitre is levied, and in addition to this, the maximum content of wormwood oil and essential oils generally in the beverages shall be determined by special decree. The substitution of natural essential oils by artificial chemical products of any kind is prohibited, as well as the trade in liqueurs which have been prepared with such substitutes.

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¹) Centralbl. f. die ges. Therapie **24** (1906), 81.

²) Comp. Report October **1906**, 81.

The products in question may only be forwarded in cases, boxes, or bottles, which have been numbered and sealed by the officials, and must be accompanied by a permit indicating the number, and also the weight of the contents and the packing.

The stocks in hand at the time of the publication of this Act are already subject to these conditions. Contraventions are punished with seizure of the products and severe fines, and in addition to this an amount equal to five times the duty has to be paid.

From Switzerland it is reported that similar measures are impending.

For the detection of wormwood oil and oil of tansy in absinth liqueur, L. Cuniasse[1]) recommends various reactions which are all based upon the detection of the thujone contained in the above-named oils. We content ourselves with a reference to this work.

Ylang Ylang Oil, "Sartorius". The demand has been so brisk that we were compelled to ask our friends in Manila to make a considerable increase in their production. We hope that we shall now be able to meet the whole of the demand from the consumers.

P. Kettenhofen[2]) has studied the action of ylang ylang oil (which we had placed at his disposal for the purpose) on micro-organisms, colourless blood-cells, cold-blooded and warm-blooded animals, and also the influence on the respiration-capacity and the blood-pressure, and the action in normal and in increased reflex-excitability, and has thereby arrived at the following results. Ylang ylang oil injures, or destroys, micro-organisms, and prevents decay and fermentation owing to its paralysing effect on the protoplasma of the ferments of putrefaction and decomposition. Towards colourless blood-cells it has an analogous action; the cells are paralysed, and unable to leave the circulatory system, thus suppressing a commencing ulceration. In the organism of cold-blooded animals, ylang ylang oil causes already in a small dose general paralysis, which with increased doses ends fatally. In the case of warm-blooded animals, a passing diminution of the functions occurs, which does not, however, cause any serious injury to the organism. Pulsation and frequency of respiration become less, breathing and blood-pressure more feeble; the animals show a somewhat apathetic behaviour. In a reflex-excitability increased by convulsion-producing poisons, the excitability becomes less when ylang ylang oil is administered, and the convulsions cease. If it were desired to transfer these results to man, no symptoms of any serious affection would in Kettenhofen's opinion be produced, apart from those already mentioned, if the doses were not too large. The normal reflex-

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[1]) Journ. de Pharm. et Chim. **25** (1907), 180.

[2]) Thesis, Bonn 1906

excitability is first of all lowered, and ceases entirely with sufficiently large doses of the oil.

In the treatment of malaria it might be used as a substitute of quinine in cases where the latter is not tolerated, or for definite reasons cannot be given.

New essential oils.

In our last Report we mentioned on pages 82—83 two new oils — of **Evodia simplex** and **Pilea** — which had been sent to us by the Syndicat du Géranium Bourbon. Of a third oil, which we had received at the same time, we did not then give a description, as that oil was described simply as oil of "une espèce nouvelle". Since then we have heard from Réunion that the oil is obtained from a shrub belonging to the *Rutaceæ* which de Cordemoy has described under the name of *Evodia aubertia,* but which is said to have been known already for a long time under the name *Xanthoxylum aubertia.* This plant is known in Réunion under the name "Catafaille blanc", and is highly esteemed there as a very active remedy for wounds, but is also employed as a diaphoretic and a blood-purifying remedy. Unfortunately we found no description of this variety in the botanical works which we have at our disposal; we are also unable to say from what part of the plant the oil has been obtained. It represents a yellowish-green liquid with a pronounced odour like parsley; d_{15° 0,9052; α_D — 62° 10′; acid no. 1,3; ester no. 7,3; ester no. after acetylation 51,0. The solubility in 90 per cent. alcohol is not complete, and even with 10 vol. alcohol only a very cloudy solution is obtained; in 95 per cent. alcohol the oil makes first of all a clear solution, but when more than 2 vol. are added opalescence occurs owing to separation of paraffin.

A test for phellandrene which we suspected to find in the oil had a negative result. It appears from the ester and acetylation numbers that the oil contains only very small quantities of ester-like and alcoholic constituents.

A second sample of oil from the same species, which we received a short time ago, had also the characteristic parsley-like odour of the former oil, but differed considerably from the latter in respect of specific gravity and rotation, and showed in these properties a remarkable agreement with the oil of *Evodia simplex*[1]). The constants were as follows: d_{15° 0,9708; α_D — 19° 20′; acid no. 1,1; ester no. 8,7; ester no. after acetylation 33,0. The solubility of this oil was also

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[1]) Comp. Report October 1906, 82.

better than that of the one received before, as it dissolved in every proportion in 90 per cent. alcohol; when highly diluted (1:10) a faint opalescence occurred. With 10 vol. 80 per cent. alcohol it did not form a clear solution.

Whether these differences between the two oils must be attributed to various methods of distillation, or to different stages of development of the plants due to the time of the year, we are unable to say.

Along with the oil just discussed we also received another sample of the pilea oil already described in detail in our last Report[1]. The oil now received showed a greenish tinge, and had a considerably higher rotation, $\alpha_D + 58^\circ 20'$; for the rest it agreed with the previous oil; d_{15° 0,8520; n_{D20° 1,46902; acid no. 0; ester no. 7,7; ester no. after acetylation 34,4; soluble in 3,8 and more vol. 90 per cent. alcohol.

From the **buds of the Black Currant** (*Ribes nigrum* L.), which had been sent to us from Russia, we obtained in a yield of 0,75 % an essential oil of the following constants: d_{15° 0,8741; $\alpha_D + 2^\circ 30'$; n_{D20° 1,48585; acid no. 0; ester no. 5,6; soluble in 6,5 and more vol. 90 per cent. alcohol with slight cloudiness, which disappears on greater dilution (1:10). The oil had a pale greenish colour and, judging from the odour, appeared to contain among others cymene. As we only had a few grams of oil at our disposal, we must content ourselves with the enumeration of the foregoing data.

Ayapana Oil. The oil of *Eupatorium triplinerve* Vahl (*E. Ayapana* Vent), a composite indigenous to equatorial Africa, which in other tropical districts is often growing wild, but in the East Indies is cultivated as a tea-plant, was sent to us from Mayotte, one of the Comoro islands, in the Straits of Mozambique, under the name of "essence d'ayapana".

The oil has a pale-green colour and a peculiar odour; d_{15° 0,9808; $\alpha_D + 3^\circ 10'$; ester no. 8,0; ester no. after acetylation 23,4. It forms a clear solution with $1^1/_2$ times its vol. 90 per cent. alcohol, but is practically insoluble in 80 per cent. alcohol. On fractional distillation at 3,5 mm. pressure it was found that, apart from a small quantity first runnings with a terpene-like odour, and an equally unimportant residue, the oil boiled almost uniformly. We obtained three fractions with the following properties:

1.	40 to 104°	5,6 %	d_{15° 0,9680	$\alpha_D + 10^\circ 40'$
2.	104°	51,8 %	d_{15° 0,9825	$\alpha_D + 1^\circ 35'$
3.	104 to 105°	28,0 %	d_{15° 0,9848	$\alpha_D + 3^\circ 5'$
	residue:	15,9 %		

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[1] Report October 1906, 83.

When once more distilled over metallic sodium, the bulk was obtained almost unchanged with the following constants: b. p. 237 to 238° (750 mm. pressure), d_{15° 0,9891; α_D + 0° 40′; miscible in every proportion with 90 per cent. alcohol.

An attempt to arrive by means of potassium permanganate at an oxidation-product led to an acid, readily soluble in alcohol and ether, but with difficulty in water, which, after repeated recrystallisation from aqueous alcohol, melted at 93°. But even at the temperature of the water-bath, only about 25 % of the oil could be oxidised, whilst 75 % remained behind almost unchanged. The results show that the oil consists chiefly of a uniform body.

Oil of Mentha rotundifolia L. A small sample of oil from *Mentha rotundifolia* L. which was sent to us from Algeria, had a dark orange-yellow colour and a musty, faint, somewhat pungent odour, which distantly resembled the odour of spearmint oil. The constants were as follows: d_{15° 0,9777; α_D — 37° 30′; acid no. 1,5; ester no. 71,2; ester no. after acetylation 209. The oil was miscible in all proportions with 90 per cent. alcohol and dissolved in 1 vol. 80 per cent. alcohol; on dilution strong cloudiness and separation of small oil drops occurred immediately.

Pharmacopœias.

Dutch Pharmacopœia.

In continuation of our discussion of the Dutch Pharmacopœia[1]) we would still mention that in the meantime a supplement has been issued which corrects various errors, such as for example the statement on the behaviour in boiling of mace oil, which now reads as follows: "At least half the oil shall pass over between 160 and 175°; of the remainder, one portion distils from 175 to 200°, and another portion only above 235°".

British Pharmacopœia.

In order to avoid as much as possible omissions and errors in the publication of a new Pharmacopœia, the British Pharmacopœia Commission has issued proposals for altering the tests of a large number of official drugs and preparations, which have among others been published in the *Pharmaceutical Journal*[2]). This publication has the object of making the improvements intended as widely known as possible, and submitting them to discussion. The points dealing with essential oils are briefly discussed in the following lines, in the same

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[1]) Report October 1906, 84.

[2]) Pharmaceutical Journal 77 (1906), 632.

manner as has been the case with the previous pharmacopœia discussions.

Anise Oil (*Oleum anisi*). M. p. not below + 15°; soluble in 3 vol. 90 per cent. alcohol.

Cajeput Oil (*Oleum cajuputi*)[1]. Cineol-content not below 50 %, the determination must be carried out by the phosphoric acid method.[2]

[1] The lower limit for the specific gravity of cajeput oil is given too high in the Pharmacopœia, viz., 0,922; it should read: d_{15° 0,919 to 0,930.

[2] We have convinced ourselves that the phosphoric acid method does not give reliable results, and for this reason we cannot recommend it as useful. Comp. Report April **1906**, 72, Cajeput oil, note 1.

Caraway Oil (*Oleum carui*). At least 40 % of the oil must pass over above 200°; $\alpha_D + 74$ to $+ 78°$[1].

[1] The rotation of normal oil lies between 70 and 80°.

Cinnamon Oil, Ceylon (*Oleum cinnamomi*). Aldehyde-content at least 68 %.

Clove Oil (*Oleum caryophylli*). Minimum-content of eugenol 80 %; test for solubility in 70 per cent. alcohol[1].

[1] 2 vol. 70 per cent. alcohol are required to make a solution.

Copaiba Oil (*Oleum copaivae*). Definite proposals are wanting. Comp. our Report, April **1903**, 29.

Coriander Oil (*Oleum coriandri*). $\alpha_D - 7$ to $- 14°$[1].

[1] Coriander oil is dextrorotatory, $\alpha_D + 8$ to $+ 13°$.

Cubeb Oil (*Oleum cubebae*). $\alpha_D - 30$ to $- 40°$[1].

[1] The lower limit should be fixed at $- 25°$.

Dill Oil (*Oleum anethi*). A minimum-content of 45 % carvone should be required, which should be determined by fractional distillation[1].

[1] For the determination of carvone it is best to employ the sodium sulphite method in the manner proposed by Burgess. For the most suitable way of carrying it out see our Report April **1905**, 103.

Eucalyptus Oil (*Oleum eucalypti*). Cineol-content not below 55 %[1], the specific gravity should be raised to 0,910[2].

[1] With regard to the cineol-determination, comp. Report April **1906**, 72, Cajeput oil, note 1.

[2] This proposal is inexplicable, as the British Pharmacopœia gives 0,910 as lowest limit of value.

Peppermint Oil (*Oleum menthae piperitae*). Excepting Japanese oil, all peppermint oils should be official, and the menthol, both free and combined, determined by the usual processes.

Pimenta Oil (*Oleum pimentae*). Eugenol-content at least 65 %.

Sandalwood Oil (*Oleum santali*). A determination of the santalol-content should be included, and this should not be below 94%[1]).

[1]) The requirement of such a high santalol-content is not justified. In the case of good oils, it is not below 90%, calculated for the formula $C_{15}H_{24}O$.

Chemical preparations and drugs.

Civet. According to reports from the British Vice Consuls at Addis Abeba and Harrar, the export of civet is constantly declining, — it is said, because an artificial civet perfume has been invented in Europe which is prepared from coal tar, and is very cheap. (?) Only France is said to consume still small parcels. The total export in 1905 is estimated at 4800 oz., value £ 9600.

We are not inclined to take quite such a pessimistic view of the situation, for up to the present we have not yet been able to obtain any information on the existence of a really useful artificial civet. Our well-assorted stock enjoyed even a very brisk demand last year, and up to present we have not noticed any falling-off in the demand. Our sales of this important drug in the year 1906 were, on the contrary, larger than ever.

Balsam of Hardwickia Pinnata Roxb. (*Kingiodendron pinnatum* [Roxb.] Harms). Some time ago[1]) we reported on a balsam alleged to have been derived from *Hardwickia binata* Roxb. Recently G. Weigel[2]) and also D. Hooper[3]) have published further interesting information on this balsam, which we discuss more in detail in the following.

It should be stated at once that the mother-plant is not *Hardwickia binata* Roxb., which, according to Hooper, does not yield any balsam at all, and serves only as an ornamental tree in streets and gardens, but *Hardwickia pinnata* Roxb.[4]) It is a stately tree, closely allied to the Copaifera species, and is found in British India. The balsam contained in it is used both for medicinal and technical purposes (for painting the woodwork of houses) and, according to Hooper, is obtained in South Canara as follows: About 3 feet above the ground a deep cavity is cut down to the heart of the trunk, after which the

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[1]) Report April **1905**, 85.

[2]) Pharm. Centralh. **47** (1906), 773.

[3]) Pharmaceutical Journal **78** (1907), 4.

[4]) In Engler's "Pflanzenfamilien" the species *Kingiodendron* is still separated from the species *Hardwickia*, and for the original designation *Hardwickia pinnata* Roxb., the name *Kingiodendron pinnatum* (Roxb.) Harms is introduced. In order to avoid confusion we consider the exclusive use of the last name advisable. Comp. A. Engler, Die natürlichen Pflanzenfamilien, supplement, p. 194.

balsam soon begins to exude. Only the stronger trees of at least 5 to 6 feet circumference are tapped. The trees are exhausted completely, which is accomplished in about 4 days; a healthy, strong tree of 8 feet circumference may yield about 12 gallons balsam.

With regard to the properties, the data given by Weigel as well as those of Hooper agree on the whole with our own observations.

	Weigel	Hooper		Schimmel & Co.
d_{15°	0,977	1,0124	1,0068	1,0021
acid no.	73,28	97,2	99,8	96,2
ester no.	9,66	9,0	12,6	12,3
content of volatile oil	48,5 %	41,1 %	39,5 %	44 %

The balsam dissolves readily in the usual solvents such as alcohol, ether, chloroform, petroleum ether, etc., only with methyl alcohol it does not make a clear solution; the ammoniacal solution is slightly cloudy, and gelatinises finally.

As Weigel observes, the balsams are sometimes more, and sometimes less viscid, which also explains their varying content of essential oil, which fluctuates between 25 and 50 %.

Weigel isolated the following constituents: 48,5 % essential oil (colourless; d_{15° 0,9045; $\alpha_D - 8^\circ 24'$), also a resin acid (hardwickia acid) and an unsaponifiable resin body (hardwickia resene). Hardwickia acid represents 48,3 % of the balsam, and in the purified state is a white, amorphous, odourless powder.

To distinguish hardwickia balsam from copaiba and gurjun balsams, a colour-reaction already recommended by Broughton is, according to Weigel, useful; by this method 1 drop balsam is dissolved in 19 drops carbon disulphide, and 1 drop each sulphuric acid and nitric acid added to the solution. Whilst copaiba balsam then produces a reddish-brown, and gurjun balsam an intense violet-red colour, no special colour appears in the case of hardwickia balsam.

Hooper also recommends the colour-reaction with glacial acetic acid and sulphuric acid indicated by L. van Itallie and C. H. Nieuwland[1]) for copaiba balsams, in which copaiba balsam produces a blue, hardwickia balsam a brick-red coloration.

We would still mention that the statements made both by Weigel and by Hooper, according to which large quantities of the balsam could be obtained in Hamburg, now no longer apply, as in spite of the greatest exertion we were unable to receive even a small quantity of the balsam.

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[1]) Comp. Report April 1905, 25.

Honduras Balsam. We were able to place a small quantity of this balsam (of whose origin and production nothing could be ascertained) at the disposal of M. Burchhardt[1]), who in his examinations arrived at the following results: The balsam was a yellow, turbid, syrupy liquid with a pronounced storax odour; d_{15° 1,082. The following constituents have been isolated and identified: 1. Free cinnamic acid, m. p. 133°. 2. The cinnamic acid ester of honduroresinol, m. p. 160 to 165°. In its percentage composition this body corresponds with Lüdy's benzoresinol[2]), with van Itallie's storesinol[3]), and with Hellström's styresinol[4]), although the melting points indicated by the various authors show partly considerable differences. 3. The cinnamic acid esters of cinnamic alcohol, of phenyl propyl alcohol, and other (not identified) aromatic alcohols. 4. Honduroresene, m. p. indistinctly at 200 to 210°. 5. A body insoluble in alcohol.

From his examinations Burchhardt draws the conclusion that Honduras balsam has practically nothing in common with Peru balsam or white Peru balsam.

Menthol. The speculators have not succeeded in maintaining the prices at the level of 10/-, which was reached in September for goods for shipment, and since that time the market has, with slight interruptions and feeble reactions, declined to about 8/2. There is very little demand, and the European stocks appear to be very considerable. According to the Financial and Economic Year Book of Japan, the total value of the menthol exports in 1899 to 1905 was as follows: —

	1899	1900	1901	1902	1903	1904	1905
British India . . .	16096	20875	18807	11698	23020	63955	42470
France	19522	4950	25212	22565	43317	141075	128991
Germany	43926	46391	100040	71045	193729	159496	110649
The United Kingdom	29607	62995	9706	90833	155406	229685	301569
Hong Kong	42759	13964	163884	127369	219189	156775	59193
The United States	43442	23000	111130	126525	162754	326784	149565
Other countries . .	73	326	8273	13684	6987	12973	5188
Total	195424	172501	437051	463719	804401	1090742	797624

With regard to the quantities shipped in 1906, we would refer to p. 82 of the present Report.

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[1]) Thesis, Berne 1906, 30; Arch. der Pharm. **243** (1905), 218.
[2]) Arch. der Pharm. **231** (1893), 64.
[3]) Ibidem **239** (1901), 506.
[4]) Ibidem **243** (1905), 218.

Musk, Tonkin. The season commenced at the end of October under the impression of a brisk demand, as during the summer months numerous orders had accumulated in Shanghai, and particularly the Japanese purchasers showed great interest, especially for Sawko musk which fetched enormous prices. When the Japanese demand had been satisfied, the market calmed down somewhat, but now inquiries commenced also to come in from New York and Paris, and in view of the very small supplies, the prices advanced considerably. The position as regards quality is not unfavourable this season, although the "blue skin" musk, which we prefer for exvesicating, is unfortunately very scarce. According to the latest information to the end of January received by mail, the prices move between 290 and 298 taels per catty, which in comparison with the previous year's values must be called very high, the more so as the exchange is now also considerably higher. The number of Chinese Merchants engaged in the musk trade is said to be continuously diminishing, and an attempt on the part of the European musk exporters to depress the prices would undoubtedly be soon followed by a stoppage in the supplies.

We have still at our disposal a considerable stock of first class goods exvesicated by ourselves, but we have already been compelled to raise our quotations somewhat, so as to bring them in harmony with the market.

Musk export from Shanghai in the year 1906.

Year	Paris	London	New York	Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1906	670	8	414	45	**1137***)
		against:			
1905	378	73	386	40	**877**
1904	722	76	366	52	**1216**
1903	772	157	324	73	**1326**
1902	751	191	360	116	**1418**
1901	599	154	314	105	**1172**
1900	790	43	219	52	**1104**
1899	873	180	290	148	**1491**

Safrol. We can confine ourselves chiefly to a reference to our detailed information on camphor oil, page 15, and to the statement

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1) Of which about 85 % Tonkin, 15 % Sawko, Tampi, and Cabardine.

that the price has gradually advanced up to 4 marks per kilo. Even at this quotation there was a brisk demand, especially on the part of the heliotropin manufacturers for whom this article has gradually become the indispensable raw material. We are now without any competition in safrol, but are naturally bound to put certain restrictions to the offers made by us, as the limited supplies of camphor oil are not by any means sufficient to satisfy the demand from every side. The safrol manufacture in Japan, to which we have referred on various occasions, has ceased completely.

Thymol. The quotations for ajowan seed have declined under the pressure of the new harvest, which is now in progress and is said to have a normal result, to about 12/- per cwt. The absurd price-cutting which was practised formerly in thymol by some competing firms, has again been started vigorously. Quite recently we heard of a price of 13 marks per kilo, which we could only treat with ridicule, in view of the fact that almost everywhere we are paid for our quality the full price asked by us.

Vanillin. E. O. v. Lippmann¹) reports on a peculiar occurrence of vanillin. In an attempt to detect in dahlia tubers in various stages of development, in addition to inulin, also fructose, large quantities of alcoholic-ethereal extracts were obtained which left behind a syrupy, vanilla-like smelling residue, which, however, could not be brought to crystallise. Now, after more than 10 years' standing, the formation of beautiful needles arranged in the form of stars was observed, which after re-crystallisation from ligroin could be identified as vanillin (m. p. 81°). v. Lippmann points out at the same time, that Payen²) already in 1823 called attention to a vanilla-like aroma in the tubers of dahlias.

Notes on recent research work concerning terpenes and terpene derivatives.

General.

In her Thesis³) *The relations between structure and smell in organic compounds,* Gertrud Woker attributes to the multiple bonds which are present in the majority of the odoriferous compounds (taken in the broadest sense), a special influence on the capacity of developing

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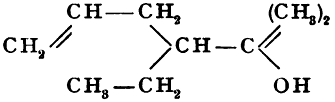
¹) Berl. Berichte **39** (1906), 4147.

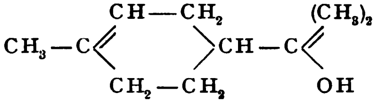
²) Annales de Chimie **24** (1823), 209.

³) Thesis, Berne 1906; according to the English translation in the Journ. of phys. Chem. **10** (1906), 455.

smell. The double or triple linking need not always exist between two carbon atoms; groups such as C:O and C:N or C⋮N are in the same manner important as compared with the less strongly smelling compounds with the groups C•O and C•N. As a proof, Miss Woker mentions on the one hand the aldehydes, ketones and acids, and also the nitriles, and on the other the alcohols and amines. In connection with the C—N derivatives the authoress discusses the difference in the odour between nitriles and the isomeric carbylamines, which, compared with the former, are still less saturated. The more powerful influence of two double linkings in comparison with a triple linking, is exemplified by the odoriferous properties of the iso (-thio-) cyanic esters and the normal esters. Important is the entrance of sulphur in the place of oxygen in the thio alcohols and esters, and in the place of the group — CH:CH — in the thiophene derivatives. An accumulation of the same atoms or atom complexes (in the case of the terpene derivatives, chiefly of CH_3-groups) increases not only the intensity of the odour, but also the volatility of the compounds, for example, it is well known that of the isomeric butyl alcohols, the one with the largest number of methyl groups, i. e. the tertiary butyl alcohol, has the lowest boiling point. Ring-closure of an aliphatic into a hydroaromatic body is said to exert no special influence on the odour. The example citral—pulegone taken from the terpene series is, however, not a very happy one, and it would perhaps have been better if the authoress had substituted for it the comparison, originating from Perkin jun., of his aliphatic terpineol



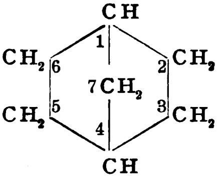
with cyclic α-terpineol

 .

If, on the other hand, double linkings disappear during the ring-formation, as, for example, in the formation of trithio aldehydes, cyanuric acid derivatives, and similar polymerisations, the smell also disappears. Under certain conditions, several factors influencing the smell are able to neutralise each other, as is proved for instance by uric acid, in which three CO-groups, the ethylene groups, and four multiple-linked N-atoms, yield a completely odourless body.

The comparisons made by the authoress are drawn from bodies which she has not studied herself, but taken from Krafft's Text-book of Organic Chemistry. It is, however, a well-known fact that the odour is just that property which in text-books, like in publications in general, is described least correctly, partly because it does not lend itself well to a description, and partly because the description is frequently based on old and unreliable statements. The data on the smell in the tables are of a very general character and are not particularly suitable for giving a clear conception of the degree of influence. It would not be devoid of interest to examine systematically, with definite examples which might perhaps be taken from the terpene series, what influence is exerted by the entry of double linkings, or by their saturation, by the substitution of sulphur, the addition of phenyl-rests, etc. not only on the odour generally, but particularly on its degree of intensity. The numerous easily accessible and well-studied derivatives of the carvone and the camphor series would be specially suitable for this purpose.

Owing to the close relationship between the bornyl and the fenchyl derivatives, which belong to the pentaceangroup, I. Kondakow1) proposes for these compounds the introduction of a nomenclature which makes the relationship of these bodies as methylated derivatives of bicycloheptane easily understood. According to this, nor-camphane would be dimethyl-7, 7-bicycloheptane; camphane = o-trimethyl-1, 7, 7-bicycloheptane; dihydrofenchane = m-trimethyl-2, 7, 7-bicycloheptane; nor-isocamphane = dimethyl-6, 6-bicycloheptane. From the last-named hydrocarbon are derived 2 ortho-, 2 meta- and 1 para-derivative, viz., o-trimethyl-1, 2, 2-bicycloheptane and isocamphane = o-trimethyl-2, 2, 3-bicycloheptane = o-2, 2-dimethyl-m-3-methylbicycloheptane; fenchane = m-trimethyl-2, 2, 4-bicycloheptane; m-trimethyl-2, 2, 6-bicycloheptane; isofenchane = p-trimethyl-2, 2, 5-bicycloheptane. All methylated ortho-, meta- and para-derivatives can be explained by the formula of bicycloheptane: —



We reported already last year2) on Harries' ozonides of terpene compounds, and we now add to what we then said a short note regarding an ozonide, the production of which was described by Harries and Weil in a work3) published some time ago. This is the ozonide of an unsaturated cyclic hydrocarbon 1, 1, 3-trimethylcyclohexene-3

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1) Journ. f. prakt. Chem. II. **74** (1906), 420.

2) Report April **1906**, 98.

3) Berl. Berichte **37** (1904), 845.

(cyclogeraniolene). This body — contrary to analogous derivatives with open chain and those of the aromatic series — is attacked by water only with difficulty. Further, cyclogeraniolene does apparently not react with one molecule ozone (O_3), but, according to Harries and Weil, with O_4, as the body on analysis showed the composition $C_9H_{16}O_4$, and the cryoscopic determination showed the double molecular volume. According to a new work by Harries and Neresheimer[1]) the same takes place in lower homologues of cyclogeraniolene; but with tetrahydrobenzene the values ascertained for the ozonide still corresponded more or less with those calculated for the normal compound. Tetrahydrotoluene already behaves like cyclogeraniolene. Tetrahydrobenzene ozonide has probably the composition $C_6H_{10}O_3$; when split up with water, it yields little adipic dialdehyde and much adipic acid, m. p. 148 to 149°. m-Dihydroxylene diozonide, $(CH_3)_2C_6H_6(O_3)_2$ yielded only on reduction with aluminium amalgam in ethereal solution, levulic aldehyde, b. p. 77 to 80° (15 mm. pressure).

Bibliographical notes.

J. W. Brandel[2]) has completed his abstracts on the volatile oils in 1904, and commenced a report on the publications in this domain during the year 1905. We would not fail to call attention also to these continuations.

Analytical notes.

For the determination of citral in lemon oil, a whole number of methods[3]) has already been recommended, of which, however, not one has up to the present been found to answer in practice, as they all give results which are not so accurate as is required in view of the small quantity of citral contained in lemon oil. Now, a method has recently been published by Edward Mac Kay Chace[4]), which is said to be very useful for the estimation of small quantities of citral. It is based on the property of fuchsin sulphurous acid of acquiring a red colour in the presence of aldehydes, and that more or less strongly according to the quantity of aldehyde present. By means of comparative tests with solutions of a known aldehyde-content, the quantity of the latter in the oil to be examined is ascertained.

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[1]) Berl. Berichte **39** (1906), 2846.

[2]) Pharm. Review **24** (1906), 112, 149, 317, 344, 375; **25** (1907), 58; comp. also Reports April **1906**, 101, and October **1906**, 102.

[3]) Reports April **1900**, 22, October **1900**, 25, April **1904**, 47, October **1904**, 121, April **1905**, 35, October **1905**, 29.

[4]) A method for the determination of citral in lemon oils and extracts. Journ. Amer. chem. Soc. **28** (1906), 1472.

For carrying out the determination there are required:

1. Fuchsinsulphurous acid: 0,5 g. fuchsin (magenta) are dissolved in 100 cc. water, and a solution of sulphurous acid added which contains 16 g. SO_2. This is left standing until discolored, and then made up to 1 litre. The solution must be renewed every 2 or 3 days, as it deteriorates very rapidly.

2. Alcohol of 95 per cent. by volume, absolutely free from aldehyde. In order to free the alcohol from aldehyde down to the smallest trace, it is left standing for several days over alkali, then distilled off, and the distillate boiled for several hours in a reflux condenser with m-phenylenediamine hydrochloride, 25 g. per litre; the alcohol is next again distilled off, and is then ready for use.

3. A standard citral solution, i. e., a 0,1 per cent. solution of citral in 50 per cent. alcohol free from aldehyde.

All these, and also the following solutions, are used exactly at 15°, and all determinations are also carried out at that temperature, by placing the vessels, before making the comparative tests, for 10 minutes in a water bath of 15°. A higher temperature must be particularly avoided.

The procedure now is as follows: 2 g. of each of the lemon oils to be examined, or 20 to 30 g. of the lemon extracts, are diluted with alcohol free from aldehyde to 100 cc. Of each of these solutions, 4 cc. is placed in vessels of exactly equal capacity; 20 cc. alcohol free from aldehyde are added, and next 20 cc. fuchsin sulphurous acid, and finally alcohol is added up to 50 cc. and the whole well mixed. By means of the above-mentioned standard solution, comparative samples of known citral-content are prepared in the same manner. All solutions are left for 10 minutes in the water bath, and they are then compared, either direct, or by means of a colorimeter.

Chace proved by tests with mixtures of known citral-content that this method gives very exact results, both with mixtures of citral and limonene, and with lemon extracts, in which the values found differed on the average by not more than 0,2 % from the actual content of citral. With lemon oils the results were less favourable, but in spite of this the limit of error was here also mostly below 0,5 %.

In testing this method, where the only object we had in view was to ascertain its usefulness for lemon oils, we did not employ a colorimeter, but determined the shades of colour by direct comparison. We proceeded as follows: by means of the normal solution we prepared in the above-described manner with fuchsin sulphurous acid and alcohol, eight different samples, of which each following sample contained 1 cc. solution = 1 mg. citral more than the previous one; the first vessel contained 1 cc. normal solution = 1 mg. citral; the eighth 8 cc. solution = 8 mg. citral. We then found that the individual solutions up to a content of 5 mg. citral still showed distinct differences in colour from milligram to milligram, whilst with a content of more than 5 mg. citral the coloration became so intense that differences could no longer be observed. Smaller differences than 1 mg. in the content of the solutions could only be detected by us (by simple comparison and without colorimeter), in the case of very weak solutions — up to about 2 mg. citral-content.

This, however, only applies to alcoholic solutions of citral, and also to mixtures of citral and limonene, in which the citral-content could be correctly determined by comparison with correspondingly strong normal solutions, although it follows from what we have just said, that we did not in every case arrive at such exact results as Chace.

But with lemon oils, as Chace has already observed, the citral-content cannot be determined with the same certainty; this is due to the fact that, owing to the wax-like constituents contained in lemon oil, the solution is here slightly turbid, which renders it impossible to determine the tint of the red coloration with absolute precision. This, however, may lead to considerable errors. If namely the proportionate quantities indicated by Chace are taken as basis, the citral-quantity found by the colour test must be multiplied with 1250 in order to express the percentage of citral in the oil. Now, if there is any doubt as to whether the tint indicates a citral-content of 3 mg. or one of 4 mg. (more exact distinctions it is, as a matter of fact, impossible to make with lemon oil), it follows that the percentage of citral in the oil is calculated either as $0{,}003 \cdot 1250 = 3{,}75$, or as $0{,}004 \cdot 1250 = 5{,}0$, i. e., results which differ by 1,25 %. In view of the slight content of citral in lemon oils, this margin is too large to recommend the method (which is undoubtedly very useful for the citral-determination in lemon extracts) also for lemon oils, — an opinion to which, for the rest, Chace himself has given expression in his work. We have made no tests to ascertain whether more exact results are obtained in lemon oil by means of a colorimeter, but in view of the observations already made, we must doubt this.

Determination of phenols. Of the methods proposed for the determination of phenols, the extraction with 5 per cent. soda liquor indicated by Gildemeister[1]) for thyme oil, has given the best results in practice, as it is a method readily carried out and sufficiently exact for practical purposes. Umney[2]) subsequently extended the process to clove oil, with the application of a 10 per cent. potash liquor. But the results then obtained were too high by 10 to 12 %, because

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[1]) Hager-Fischer-Hartwich, Kommentar zum Arzneibuch für das Deutsche Reich, 3rd Ed. 1892, Vol. II. p. 377.

[2]) Pharmaceutical Journal 55 (1895), 951.

the strong liquor also dissolved a portion of the other constituents of clove oil. The determinations become more correct if a 5 per cent. soda liquor[1]) is employed, but in the case of clove oils very rich in eugenol (about 95 %) this method is also unsuitable, as such oils dissolve completely in the lye. This is shown, in an even more striking manner with pimenta oil and terpeneless bay oil; in the case of the former, the results obtained with 5 per cent. lye were by 11 to 13 % too high, and terpeneless bay oil with about 80 % eugenol dissolves readily in 5 per cent. liquor.

In one of our previous Reports[2]) we have already mentioned that these drawbacks in the case of clove oil are obviated by the use of a 3 per cent. soda liquor, and we have made the same observation with the two other oils, so that now we determine the eugenol in all oils containing this body, exclusively with 3 per cent. soda liquor, by adding to 10 cc. oil in a cassia flask of 100 cc. capacity, so much liquor that the flask is filled for about three-fourths, and repeatedly shaking the mixture strongly. The further determination is accomplished in the usual manner. In the case of clove oils we heat at the same time for 10 minutes in the water bath, in order to be quite sure that the acetoeugenol contained in them is completely saponified[3]), as this is of equal importance as the free eugenol in valueing clove oils.

The phenol-content of oils containing thymol and carvacrol however, such as oils of thyme and Cretian origanum, we continue to determine (with the use of a burette) with 5 per cent. liquor, which, as experience has shown, absorbs the phenols of these oils better than 3 per cent. liquor.

We would still mention that in the oils containing eugenol referred to above, the 5 per cent. liquor has a dissolving action on the non-phenols only on account of its content of eugenol sodium, and acts in the first place on their oxygenated portions. If the eugenol is previously removed from the oil by means of 3 per cent. liquor, the 5 per cent. liquor is practically incapable of dissolving anything further from the non-phenols. An exception to this is of course aceto-eugenol, on which the liquor has a saponifying action.

Determination of alcohols. For the quantitative determination of linalool, terpineol, and tertiary alcohols generally, which, as is well-known, cannot be determined quantitatively by the usual acetylation

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[1]) We wish to state specially that it is immaterial whether soda liquor is employed, or potash liquor of the same percentage.

[2]) Report October **1903**, 30.

[3]) In the cold this occurs only after prolonged shaking; when proceeding in the usual manner, the saponification is only complete in the case of oils very rich in eugenol. Comp. Report October **1903**, 29.

method, owing to the partial decomposition which occurs during the process, V. Boulez[1]) recommends a method which apparently gives good results. Boulez endeavours to prevent the decomposition of the alcohols by diluting them with an indifferent substance (for example, oil of turpentine), and acetylating the mixture. In the case of linalool he proceeds as follows: 5 g. linalool are diluted with 25 g. oil of turpentine, whose acetylation number must be previously ascertained, then 40 g. acetic anhydride and about 3 to 4 g. sodium acetate are added, and the whole boiled for three hours. After washing and drying, he saponifies about 1 g. of the acetylated mixture with 25 cc. alcoholic $^1/_4$ n. potash liquor, and in this manner ascertains the acetylation number. From this Boulez calculates, with due regard to the acetylation number of the turpentine oil, the linalool-content of the mixture; but he here commits the error that in his calculation he identifies the percentage composition of the original oil with that of the acetylated oil, and calculates the ester numbers of the acetylated substance straightway as those of the original oil, which is naturally bound to give incorrect results. Boulez namely calculates as follows: If 100 g. of the original oil mixture contain 83,3 g. turpentine oil of the ascertained acetylation number 10,5, the portion of the total alkali quantity belonging to the turpentine oil, which has been ascertained by the saponification of the acetylated oil mixture, amounts to 0,874 g., corresponding to the formula $\frac{1{,}05 \times 83{,}3}{100}$, and this figure is deducted from the total alkali quantity referred to, in order to find the alkali quantity corresponding to the 16,7 g. acetylated linalool.

The error in this calculation is at once apparent, if it is considered that the proportionate figures 16,7 g. linalool: 83,3 g. turpentine oil relate to the original not yet acetylated oil mixture, and that this ratio after the acetylation is of course completely changed by the entry of an acetyl-group in the alcoholic body, and that in such manner, that if 1 g. original oil mixture consisted of 0,167 g. linalool and 0,833 g. solvent, 1 g. of the same oil mixture after the acetylation consists of 0,203 g. linalyl acetate and 0,797 g. solvent.

Now, for the correct calculation the following considerations should apply: if x grams of the acetylated oil mixture require a cc. normal potash liquor for saponification, the corresponding quantity of alcohol calculated for 100 g. original oil amounts to $\frac{a \times 15{,}4}{x-(a \times 0{,}042)}$. The number 15,4 is $^1/_{10}$ th of the molecular weight of the alcohol in question (linalool = 154), and the number 0,042 represents the acetic acid equivalent corresponding to 1 cc. normal liquor, by which an

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[1]) Les corps gras **33** (1907), 178; Bull. Soc. Chim. IV. **1** (1907), 117.

alcohol molecule has become heavier during the acetylation, and by which the denominator of the above fraction of the alkali quantity must be reduced in order to obtain correct results. By means of this formula the alcohol quantity in the oil mixture corresponding to the acetylation number is obtained, from which, however, the portion appertaining to the diluent must still be deducted. The remainder corresponds to the alcohol quantity which was to be ascertained, and which as value found must then be in proportion to the quantity employed.

We have made a whole series of tests in order to arrive at Boulez's favourable results; in the first instance we kept strictly to the author's arrangement of tests, but subsequently we have also used other diluents, such as toluene and xylene, and moreover altered the duration of the acetylation. In analogous experiments, corresponding strictly to Boulez's conditions, we have only been able to find back 85,5 $^0/_0$ linalool and 98 $^0/_0$ terpineol; but during these tests we made the astonishing observation that just these corresponding tests Nos. 2 and 3 also apparently gave 100 $^0/_0$ linalool if we calculated the result according to Boulez, i. e. incorrectly. All further details are found in the following tables. These show particularly that a maximum yield of ester is obtained with an acetylation lasting about 7 hours, and that if this period is prolonged, both the linalool and the terpinyl acetates appear to be decomposed, a fact which need cause no surprise in view of the labile character of the molecules of these alcohols, and which must rather be regarded as a confirmation of earlier experiments made by us with terpineol, according to which, after submitting undiluted terpineol for two hours to the action of acetic anhydride, only about 78 $^0/_0$ terpineol were recovered, whilst previously in $^3/_4$ hours' acetylation about 85 $^0/_0$ alcohol had been found.

1. Turpentine oil.

Duration of acetylation:	1 hour	3 hours
Ester no.:	6,7	6,7

2. 16,67 $^0/_0$ linalool in turpentine oil.

Duration of acetylation:	1 hour	3 hours
Ester no.:	43,8	53,5
$^0/_0$ $C_{10}H_{18}O$:	10,9	13,7
Found per 100 parts alcohol used:	65,4	82,7

3. 20,00 $^0/_0$ linalool in turpentine oil.

Duration of acetylation:	3 hours	5 hours
Ester no.:	64,3	69,6
$^0/_0$ $C_{10}H_{18}O$:	17,1	18,7
Found per 100 parts alcohol used:	85,5	93,5

4. 16,67 % linalool in toluene.

Duration of acetylation:	1 hour	5 hours (20 % linalool)
Ester no.:	28,5	55,2
% $C_{10}H_{18}O$:	8,0	15,8
Found per 100 parts alcohol used:	48,0	79,0

5. 16,67 % linalool in xylene.

Duration of acetylation:	1 hour	3 hours
Ester no.:	30,8	46,7
% $C_{10}H_{18}O$:	8,7	13,3
Found per 100 parts alcohol used:	52,1	79,9

6. 20 % linalool in xylene.

Duration of acetylation:	3 hours	5 hours	7 hours	12 hours	20 hours
Ester no.:	53,3	60,4	63,0	63,3	51,6
% $C_{10}H_{18}O$:	15,3	17,4	18,2	18,3	14,75
Found per 100 parts alcohol used:	76,5	87,0	91,0	91,5	73,8

7. 20 % terpineol in xylene.

Duration of acetylation:	3 hours¹)	4 hours	5 hours	7 hours	12 hours
Ester no.:	55,2	67,7	68,8	68,1	65,1
% $C_{10}H_{18}O$:	15,8	19,6	19,95	19,75	18,8
Found per 100 parts alcohol used:	94,6	98,0	99,8	98,8	94,0

It is a well-known fact that linalool during boiling with acetic anhydride (or acetic acid), is partly converted in terpineol, geraniol and nerol. Even the use of diluents does not completely arrest this conversion, as was proved when the acetate, obtained after 6 hours' boiling of 2 parts linalool with 3 parts acetic anhydride and 10 parts xylene, was further examined. On fractionating the ester, a fraction with the odour of geranyl acetate could be separated off from the higher-boiling portions, which on saponification yielded geraniol whose diphenyl urethane melted at 80°.

G. Bruylants²) describes two methods for the determination of essential oils in liqueurs. The one, based upon the capacity of absorbing bromine of the essential oils dissolved in petroleum ether, is employed in the case of liqueurs in which only one essential oil, or several of the same group, are used (anisette, caraway liqueur, Curaçao, peppermint liqueur). The other method (by gravimetric analysis) is suitable for liqueurs containing essential oils of different groups

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¹) The mixture used for this test contained only 16,67 % terpineol.

²) Ann. de pharm. **12** (1906), 397.

(Chartreuse, Benedictine liqueur, etc.). In both cases 200 cc. of the liqueur are diluted with water to 300 cc., and of this mixture 200 cc. are distilled off, on the one hand to separate it off from the sugar, and on the other to estimate the alcohol-content.

1. **Titration method with bromine liquor.** Required are: $^1/_{20}{}^{th}$ normal bromine solution (4 g. bromine to 1 liter water containing 40 g. potassium bromide); petroleum ether of the spec. grav. 0,680 previously treated with bromine and washed; further, comparative solutions of oils with the same alcohol-content as the distillate of the liqueur to be analysed and a definite quantity (at most 1 g. per litre) oil. 100 cc. of the distillate and 100 cc. of the comparative solution are each placed in a graduated stoppered tube; 15 cc. of the above petroleum ether and sufficient water are added to bring the alcohol-content to about 25° Gay-Lussac; the mixture is then repeatedly strongly shaken, and left standing. After adding about 20 g. common salt the aqueous layer is carefully separated from the petroleum ether. Every 10 cc. of the petroleum liquids are now placed in stoppered flasks of 50 cc. capacity, 10 cc. water added, and titrated with the above-mentioned bromine solution. In addition to this a blind test is made with petroleum ether and water alone, and the result calculated.

2. **Method by gravimetric analysis:** 15 cc. petroleum ether boiling between 25 and 35° are used; the extraction is the same as with the titrimetric process, except that as a precaution the mixture is also cooled. 10 cc. of the petroleum ether extract are placed in a weighed Erlenmeyer flask of 30 cc. capacity, the flask put in a vacuum desiccator provided with lime and in which is placed a thermometer graduated into $^1/_{10}{}^{th}$ degrees; it is evacuated, and the cock closed when the thermometer again indicates the original temperature. After half an hour, dry air is admitted into the apparatus, and the substance weighed. By multiplying the weight of the residue of the petroleum ether with $\frac{3}{2}$, and the product with 10, the quantity of oil per litre liqueur is found.

Physical notes.

On the strength of J. W. Brühl's researches regarding the influence of multiple linkings on the capacity of refraction and dispersion of organic bodies, the molecular refraction has frequently been employed for clearing up the situation of the linkings in the molecule. In view of the definite conclusions which Brühl's figures enable us to draw on the structural conditions, K. Auwers¹) now explains the abnormally high refraction and dispersion of certain bodies by a special

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¹) Berl. Berichte **39** (1906), 3753.

influence exerted on these constants by conjugated double-linkings which may possibly be present. Whereas, for example, in the meta-series of the menthadienes, sylvestrene and the closely allied carvestrene show a refractive power corresponding to the theoretical one (45,24) [Wallach 45,22 for sylvestrene1), Kondakow and Schindelmeiser 45,10 for carvestrene2)], Harries and Antoni3) observed a considerably higher refraction (45,94) in an **m**-menthadiene obtained synthetically. The formulæ propounded for this body by the two investigators both show a system of conjugated double-linkings. The conditions in the more accurately known menthadienes of the p-series are entirely similar. The limonene and dipentene groups without conjugated double-linking behave optically normally; a p-menthadiene produced by Harries4) from dihydrocarvylamine shows considerably higher refraction, and also contains a conjugated double-linking (d-limonene MR_C 44,76; 44,69 instead of 44,97 calculated; l-limonene MR_D 45,23 instead of 45,24 calculated; dipentene MR_C 45,04; 44,82 instead of 44,97 calculated; MR_D 45,43; 45,03 instead of 45,24; p-menthadiene from dihydrocarvylamine according to Harries MR_D 46,17 instead of 45,24). A further example is the p-menthadine (MR_D 46,98 instead of 45,24) produced by Mahla5) from a nitrosohydroxyamino-menthene; the remaining menthadienes (terpinolene, terpinene, etc.) have not yet been examined with respect to their physical constants with sufficient certainty. Yet it is probable that the two phellandrenes also contain conjugated double-linkings, although Wallach's observations on preparations produced from essential oils, gave a refractive power which was absolutely normal. Anyhow in the case of phellandrene from Δ_6-menthenone-2, Harries and Johnson6) observed distinctly higher values. An explanation of these divergent results is still to be looked for.

Pharmacologico-physiological notes.

The opinion prevails that the secondary actions observed in the employment of balsams, must be attributed to adulterations. In consequence of this, pharmacologico-chemical examinations have been made with various balsams, and on the strength thereof H. Vieth7), in a paper read before the Versammlung Deutscher Naturforscher und Ärzte

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1) Liebig's Annalen **252** (1889), 149.

2) Journ. f. prakt. Chem. II. **68** (1903), 190.

3) Liebig's Annalen **328** (1903), 104, 119.

4) Ibidem, 322.

5) Berl. Berichte **36** (1903), 489.

6) Ibidem **38** (1905), 1832.

7) Verh. d. Ges. Deutsch. Naturforscher und Ärzte. Meran, **1905**. II. Vol. 2d part, p. 364. Acc. to Chem. Centralbl. **1906**, II. 1448; comp. also Weiss, The Balsams, Chemist and Druggist **69** (1906), 839.

at Meran, gives the following summary as to the chemical composition of the principal balsams:

	Turpentine Oil %	Terpin hydrate %	Colophonium %	Copaiba balsam %	Para balsam %	Gurjun balsam %	Sandalwood oil, East Ind. %	Sandalwood oil, West Ind. %	Cedar oil %	Juniper berry oil %
Terpenes, or sesquiterpenes	100	—	—	55	65	70	6	35	80	90
Terpene alcohols	—	100	—	—	—	—	94	65	20	10
Resinic acids	—	—	90	40	30	5	—	—	—	—
Resins	—	—	10	5	5	25	—	—	—	—

Now it has been found that from the composition of a balsam, a conclusion can be drawn as to its pharmacological action. Balsams rich in terpenes, although otherwise of good therapeutic value, are said to produce comparatively readily irritation; resinic acids administered in larger doses cause diarrhœa. The urine acquires albumin-coagulating properties after the administration of balsams. The products of assimilation of the four different classes of bodies in the organism are the same; this explains why they have the same therapeutic effect. The resins show no disagreeable secondary actions. By conversion of the terpene alcohols and resinic acids in ester-like compounds, it is hoped to do away with the secondary actions of the balsams on the stomach and intestine.

For the treatment of catarrhs of the respiratory passages and the lungs with medicated vapours, Dr. M. Saenger[1]) recommends a medicinal vaporising apparatus constructed by Gentsch according to his directions. It consists chiefly of a small steam boiler of about 300 cc. capacity into which is built a flat receptacle, not communicating with the boiler, for receiving the inhalation remedies. The boiler (which is provided with a spring safety valve), and the open receptacle for the medicine, both end in a system of narrow tubes, which in the manner of the well-known vaporisers, are arranged at right angles. When the boiler is heated with a spirit lamp, the medicine is heated at the same time, and the vapour issuing from the horizontal member of the vaporiser draws out of the receptacle a warm current of air laden with the vapours of the medicament, with which it combines. The vapour is received in a funnel, at the narrow end of which the patient inhales it.

This handy little apparatus, which is specially intended for the inhalation of essential oils (Ol. tereb., Ol. cupress., eucalyptol, menthol etc.),

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[1]) Reprint from Wien. Klin. Rundschau, **1904**, No. 34/35. Publ. by Gentsch, Magdeburg.

has, according to our experience, a satisfactory action and appears to answer its purpose.

We read in the Diplomatic and Consular Report[1]) on Belgium, issued by the British Government, that wintergreen oil and eucalyptus oil (from *E. Globulus*) have recently also been used with good results, besides male fern, as prophylactics against worm-disease of the miners in that country. The remedy is administered in the following form: wintergreen oil 4 g., chloroform 3 g., castor oil 40 g.; or eucalyptus oil 2 g., chloroform 3 g., castor oil 40 g.

With regard to the pharmacological and physiological action of ylang ylang oil, comp. what is said under that heading, p. 104.

Phyto-physiological notes.

Roure-Bertrand Fils[2]) have recently extended their experiments on the formation and distribution of the essential oil and the terpene compounds in the various organs of the plants, — to which we have already repeatedly called attention[3]), — also to a perennial plant, which, in addition to compounds of an alcoholic character, also contains an aldehyde. A suitable experimential plant was found in *Verbena triphylla* L., the oil of which had already been examined formerly[4]) for its constituents by the firm in question. In the case of *Verbena* also, the fact previously observed is confirmed, that a migration of odoriferous substances takes place from the leaf to the inflorescence. Further, the quantity of essential oil occurring in the twigs carrying blossoms, is proportionate to the quantity of oil present in the stem. It would, therefore, appeart hat the leaf, in which the odorous substances originate, is connected canal-like with the blossom in which they are again partly consumed.

The examination of the constituents of the oil of the various organs of the plant showed that the oil of the inflorescences contains more citral than the oil of the leaves. The mechanism of the formation of odoriferous substances in *Verbena* is consequently dependent in the first place on the partial esterification of the geraniol formed in the green parts of the plant, and its simultaneous oxidation into citral. The comparatively readily soluble substances formed in this manner diffuse in the inflorescences, in which therefore also a more readily

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[1]) Diplomatic and Consular Reports. Miscellaneous Series. No. 656. Belgium. February 1907.

[2]) Berichte von Roure-Bertrand Fils, October **1906**, 1.

[3]) Our Reports April **1906**, 105; October **1906**, 106.

[4]) Berichte von Roure-Bertrand Fils, April **1906**, 38; comp. our Reports October **1900**, 64; April **1903**, 76; October **1906**, 80.

soluble oil occurs than that remaining behind in the leaves. During the fructification (what is meant is doubtless "during the development of the fruit"), a portion of the odoriferous substances is used up; the energy required for this act is supplied chiefly by citral.

The work published by E. Charabot and G. Laloue¹) on the formation and distribution of the essential oil, and on the gradual distribution of the terpene compounds, in *Artemisia absynthium* L., has already been discussed by us in our last Report²).

A. Goris and J. Ducher³) have published some interesting studies on the volatile constituents of the roots of *Primula officinalis* Jacq. When rubbing the fresh roots of this plant between the fingers, an anise-like smell is developed, which soon however more and more approaches the aroma of methyl ester of salicylic acid. Whilst this anise odour occurs very strongly in *Primula officinalis*, *Primula elatior* Hill. shows it but very faintly, and with *Primula grandiflora* Lam. an odour like methyl salicylate can be recognised at once. The same thing was found to occur with the reddish parts of the base of the leaf of these plants. As the odour is only transitory, it is believed to belong to a body formed by fermentative decomposition. This view has been confirmed by suitable experiments.

In our last Report⁴) we referred already to a summary published by M. Greshoff, of all plants in which prussic acid has been detected. In a fresh publication Greshoff⁵) adds a further 15 genera to this table.

According to F. Weehuizen⁶), another prussic acid plant is *Merremia vitifolia* (family of *Convolvulaceae*), whose leaves have already a distinct odour of bitter almond oil. They contain 0,04 $^0/_0$ prussic acid, which, in addition to benzylaldehyde cyanohydrin, can be split off enzymatically.

L. Guignard⁷) next reports on about 20 species of *Rosaceae*, in which he had detected prussic acid. In the leaves and branches, and also in the roots in case the plants had not been grafted, 0,002 to 0,115 $^0/_0$ prussic acid was found.

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¹) Compt. rend. **144** (1907), 152.

²) Report October **1906**, 106.

³) Bull. des Sciences pharm. **13** (1906), 536. Acc. to Pharm. Ztg. **51** (1906), 1104, and Pharmaceutical Journal **77** (1906), 627.

⁴) Report October **1906**, 107.

⁵) Arch. der Pharm. **244** (1906), 665.

⁶) Pharm. Weekblad **43** (1906), 907. Acc. to a reprint kindly sent to us.

⁷) Compt. rend. **143** (1906), 451; comp. also Reports October **1905**, 110, and April **1900**, 48.

H. Hérissey[1]) has etablished that in the seeds of *Eryobotrya Japonica*, amygdalin is the only glucoside which can be split up by emulsin; the quantities found amounted to 1,0 to 1,1 %.

In a second work Hérissey[2]) reports on the presence of prulaurasin in *Cotoneaster microphylla* Wall. The glucoside melted at 120 to 122°; α_D (in 6,67 per cent. solution) — 52,4°. By means of emulsin it was split up into glucose, prussic acid, and benzylaldehyde, the latter being identified by the phenylhydrazone.

In the distillation waters of some plants indigenous to Belgium, P. Jitschy[3]) has found prussic acid, namely in *Ranunculus repens* and *R. arvensis* (*Ranunculaceae*), *Gynerium argenteum*, *Melica altissima*, *M. nutans*, *M. uniflora*, and *M. ciliata* (*Gramineae*). The quantity of prussic acid detected fluctuated between 0,0071 and 0,0231 %.

A. Hébert[4]) found in the upper portions of *Viscachera pucara* 0,02 % prussic acid, and an emulsin-like enzyme.

A new prussic acid glucoside, "vicianin" has been isolated by G. Bertrand[5]) from the seed of the vetch, *Vicia angustifolia* Roth. The melting point of the glucoside lies at about 160°; the prussic acid can be split off by emulsin. 1 kilo seed yields about 0,750 g. prussic acid.

Hydrocarbons.

Pinene. W. A. Tilden and F. G. Shepheard[6]) report on the production and properties of dihydropinylamine (pinocamphylamine). This body forms the principal product of the reduction of nitrosopinene with sodium and amyl alcohol. The free base is colourless, liquid, and possesses a pinylamine-like odour. It boils at 198 to 199°, and absorbs hydrochloric acid. Wallach[7]) had already produced pinocamphylamine by the action of zinc and acetic acid on nitrosopinene and identified it by the carbamide (m. p. 204°) and the acetyl compound (m. p. 120°). Tilden and Shepheard, however, found the melting point of the latter at 108 to 110°, and for the carbamide the same as Wallach. They also produced the platinum salt, the picrate (m. p. 208°), the nitrate (m. p. 180°), the oxalate (m. p. 275°), and the benzoyl compound (m. p. 144°). The boiling point determined previously by Smythe[8]) for pinocampheol, 104 to 105° (pressure

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[1]) Journ. de Pharm. et Chim. VI. **24** (1906), 350.

[2]) Ibidem, 537.

[3]) Ibidem, 355.

[4]) Bull. Soc. Chim. III. **35** (1906), 919.

[5]) Compt. rend. **143** (1906), 832.

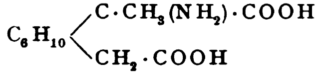
[6]) Proceed. chem. Soc. **22** (1906), 235; Journ. chem. Soc. **89** (1906), 1560.

[7]) Liebig's Annalen **300** (1898), 266; Report October **1898**, 41; Liebig's Annalen **313** (1900), 367.

[8]) Smythe, Thesis, Göttingen 1898, 19.

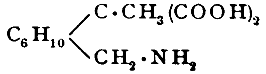
not given), was found by Tilden and Shepheard at 103° (pressure 15 mm.). The former produced pinocampheol by reduction of pinocamphone; the latter obtained it by the action of sodium nitrite on pinocamphylamine hydrochloride.

An amidocarboxylic acid derived from pinene had already been obtained by Tilden and Burrows[1]. In a further work by Tilden and Blyther[2], the production of this acid and a number of its derivates is described. Of the formulæ coming under consideration:



$$C_6H_{10}\left\langle\begin{array}{l}C\cdot CH_3(NH_2)\cdot COOH\\ CH_2\cdot COOH\end{array}\right.$$

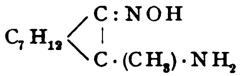
and



$$C_6H_{10}\left\langle\begin{array}{l}C\cdot CH_3(COOH)_2\\ CH_2\cdot NH_2\end{array}\right.$$

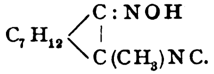
the former may be taken as the more probable one, but the examination is continued. The acid melts at 273° with escape of carbon dioxide.

If pinene nitrosochloride is treated at 45 to 50° with ammonia and alcohol, there is formed the well-crystallising nitrolamine



$$C_7H_{12}\left\langle\begin{array}{l}C:NOH\\ \,|\\ C\cdot(CH_3)\cdot NH_2\end{array}\right.$$

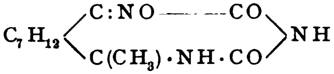
which melts indistinctly at 123 to 125°, but when heated further, melts again, with evolution of gas, at 129 to 131°, and which contains approximately $^1/_2$ molecule water. F. P. Leach[3] has produced this body and identified it by various derivatives. Pinene nitrolamine yields with benzaldehyde a benzylidene compound of the m. p. 162°, analogous bodies with salicylic aldehyde of the m. p. 128°, and with furfurol of the m. p. 164°. When heated with chloroform and alkalis, nitrolamine gives off an odour like an isonitrile of the probable formula



$$C_7H_{12}\left\langle\begin{array}{l}C:NOH\\ \,|\\ C(CH_3)NC.\end{array}\right.$$

Reducing agents either do not act all on pinene nitrolamine, or yield, by elimination of the amido-group, Wallach's pinocamphone (oxime, m. p. 86°)[4].

Leach[5] further produced a pseudo-semicarbazide from pinene. Potassium cyanate and pinene nitrosochloride yield in alcoholic solution a compound $C_{12}H_{17}O_3N_3$ having the constitution



$$C_7H_{12}\left\langle\begin{array}{l}C:NO\text{——}CO\\ C(CH_3)\cdot NH\cdot CO\end{array}\right\rangle NH$$

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[1] Comp. Proceed. chem. Soc. **18** (1902), 161; Report October **1902**, 88; Journ. chem. Soc. **87** (1905), 344; Report October **1905**, 96.

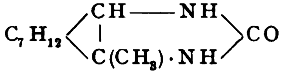
[2] Journ. chem. Soc. **89** (1906), 1563.

[3] Proceed. chem. Soc. **22** (1906), 304; Journ. chem. Soc. **91** (1907), 1.

[4] Comp. Report October **1906**, 110.

[5] Proceed. chem. Soc. **22** (1906), 304; Journ. chem. Soc. **91** (1907), 10.

and the m. p. 238 to 240°. When this body is reduced with zinc and dilute acetic acid, there is obtained a pseudo carbamide



$$C_7H_{12}\left\langle\begin{array}{l}CH\text{——}NH \\ | \\ C(CH_3)\cdot NH\end{array}\right\rangle CO$$

melting at 224°. The latter is converted by the action of nitrous acid in a corresponding nitroso compound, which melts at 161°, and on reduction yields the pseudo-semicarbazide melting at 209°, from which, by means of some aldehydes and ketones, ψ-semicarbazones could be produced and identified.

G. B. Frankforter and F. C. Frary[1]) have published a work on the production of several chloro-hydrochlorides of pinene and firpene. The pinene used for the experiments had been produced by steam-distillation from common oil of turpentine, and had the following constants: b. p. 156 to 157°, $d_{20°}$ 0,8647, $n_{D20°}$ 1,46336, $[\alpha]_D + 14{,}34°$. The crude material preparing for the chlorohydrochlorides was pinene hydrochloride, the process was as follows: A definite quantity of hydrochloride is dissolved in five parts by weight chloroform, and whilst stirring an equal quantity of water is added, then the same quantity potassium permanganate, and finally with care hydrochloric acid (d 1,2). The two last-named reagents are added again from time to time; an excess of chlorine must always be present. After allowing the action to proceed for one week, the chloroform is driven off, the amorphous solid residue allowed to crystallise from alcohol, and purified in the usual manner. The reaction-product resembles in its crystal-form pinene hydrochloride; it melts at 173 to 174° (corr.) and, according to analysis, is a body of the formula $C_{10}H_{11}Cl_5 \cdot HCl$, i. e., pinene pentachlorohydrochloride. This compound could not be obtained directly from pinene.

By suitable modifications of the conditions of the reaction, the hydrochlorides of pinene hexa- and nonachloride were obtained.

Bromine by itself had scarcely any action on pinene hydrochloride; only prolonged treatment of the hydrochloride with hydrobromic acid in the presence of potassium permanganate and sulphuric acid yielded an aromatic oil which appeared to be a bromide, but which could not be obtained sufficiently pure in analytical form.

Firpene. The firpene of G. B. Frankforter and F. C. Frary mentioned in the above treatise was obtained by steam-distillation of the crude turpentine of the so-called "Western fir". According to elementary analysis and determination of molecular weight, the terpene corresponded to the formula $C_{10}H_{16}$. Firpene differs in its odour and

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[1]) Journ. Amer. chem. Soc. 28 (1906), 1461.

its chemical and physical properties from pure pinene; its constants are as follows: b.p. 152 to 153,5°; d_{20° 0,8598; n_{D20° 1,47299; $[\alpha]_D$ —47,2°. Firpene hydrochloride melted after repeated recrystallisation from alcohol at 130 to 131°, and has consequently the same melting point as pinene hydrochloride according to Long. It is, however, more volatile and more readily soluble than the latter, and has a somewhat different odour. But the principal difference lies in its totally different behaviour towards chlorine. Whereas pinene hydrochloride shows no inclination to form a dichlorohydrochloride, firpene hydrochloride yields such a product; on the other hand, no crystalline higher chlorides could be produced. The hydrobromide of firpene melts at 102°, pinene hydrobromide at 90°. The feathery crystals of the former are very volatile, and soluble in almost all organic solvents.

Pinene and firpene also behave differently towards nitrosylchloride. The former, as is well known, yields without difficulty a beautifully crystallising nitrosochloride. From firpene, however, no crystallising nitrosochloride could be obtained with nitrosylchloride. This reaction is clearly the characteristic distinguishing feature between the two terpenes.

Dipentene. The boiling point of dipentene had long ago been given by Wallach¹) as 178 to 180°. Semmler²) attributes this high boiling point to the presence of terpinene, and is of opinion that under all circumstances, according to every experience, dipentene must boil at the same point where active limonene boils, i. e. 174 to 175°. Wallach³) replies to this, that he has never stated that he had obtained forthwith pure dipentene, and he then indicates a detailed method for the production and purification, which yields the purest dipentene which it has up to the present been possible to produce. It boils from 177 to 178°, that is to say about 2° higher than active limonene, or inactive limonene obtained by mixing the active bodies. For the purpose of comparison the tetrabromides of dipentene and of inactive limonene were employed. From 10 g. of the former 10 g. bromide were obtained, from 10 g. of the latter 8,5 g. bromide. In these 8,5 g. the bromide of any other terpene could not be detected. From the higher-boiling portions (180 to 185°) of crude dipentene also, only dipentene tetrabromide could be obtained, and no terpinolene-bromide. No fraction of the crude dipentene used (50 g.) gave the terpinene reaction. On the strength of this experiment Wallach concludes that in the dipentene fraction (b. p. 177 to 178°) a terpene which can be detected by the reactions hitherto known could hardly be

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¹) Liebig's Annalen **227** (1885), 239, 301; **239** (1887), 12.

²) Semmler, The Volatile Oils, vol. II, 309; Berl. Berichte **39** (1906), 4427.

³) Berl. Berichte **40** (1907), 600.

present in such quantity as to influence the boiling point of inactive limonene to such an extent. Wallach considers it probable that the increase in the boiling point is due to another hydrocarbon which is difficult to separate from dipentene even by repeated fractionating. For practical purposes it is in any case clear that in searching for dipentene in mixtures of hydrocarbons, now as before the fractions boiling somewhat higher than limonene must be taken into consideration.

J. W. Brühl[1]) reports on the relations between the physical constants of d- and l- and also i-limonene, which he compares with the constants of Perkin's and Kay's[2]) $\Delta_{3,8(9)}$-menthadiene. The limonenes had been produced by us from caraway oil and templin oil respectively. The l-limonene had a somewhat lower rotation than the d-limonene, but could not be purified further by fractional distillation.

The constants given by Brühl are: —

	Boiling point (763 mm. press., corr.)	d	α_D	n_D	$M_D/\overline{\overline{2}}$	$M_D/\overline{\overline{2}}$ calculated
d-limonene	175,5 to 176,5°	0,8402 at $\frac{21^\circ}{4^\circ}$	$+104^\circ 15'$ at 19,5°	1,47428 at 21°	45,51	45,24
l-limonene	175,5 to 176,5°	0,8407 at $\frac{20{,}5^\circ}{4^\circ}$	$-101^\circ 30'$ at 19,5°	1,47468 at 20,5°	45,52	45,24
d- and l-limonene in equal parts	175,5 to 176,5°	0,8409 at $\frac{20{,}7^\circ}{4^\circ}$	$+1^\circ 29'$ at 19°	1,47448 at 20,7°	45,49	45,24
d- and so much l-limonene that the mixture was inactive	175,5 to 176,5°	0,8402 at $\frac{20{,}85^\circ}{4^\circ}$	$\pm 0^\circ$ at 20°	1,47443 at 20,85°	45,53	45,24

As d- and (d+l)-$\Delta_{3,8(9)}$-p-menthadienes of Kay and Perkin show considerable differences in these constants, they cannot stand in the same relation to each other, as d- and l-limonene on the one side to dipentene on the other. For it will be seen from the table that these bodies correspond completely in their properties. It is more probable that (d+l)-$\Delta_{3,8(9)}$-p-menthadiene is a racemic body.

Our view (which we communicated to Mr. Brühl), that the l-limonene was not absolutely pure, is based upon the lower rotation as compared with d-limonene. Now if Brühl finds a further proof for the impurity in this, that a mixture of equal parts of d-limonene ($\alpha_D + 104^\circ 15'$) and l-limonene ($\alpha_D - 101^\circ 30'$) only rotates $+1^\circ 29'$,

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[1]) Journ. chem. Soc. **91** (1907), 120.

[2]) Journ. chem. Soc. **89** (1906), 839; Report October **1906**, 107.

instead of, as he calculates, $+104^\circ 15' - 101^\circ 30' = +2^\circ 45'$, it should be pointed out that the mixture of two components whose rotatory powers are not equally strong, gives the arithmetic mean, in this case $\frac{+104^\circ 15' - 101^\circ 30'}{2} = +1^\circ 22{,}5'$, — a value which corresponds well with the value found.

Sabinene. With regard to the relationship of sabinene towards terpinene, see under terpinene, p. 137.

Thujene. For the relations between thujene and terpinene, see under terpinene, p. 138.

Terpinene. On the subject of terpinene and its derivatives, and also on its relationship towards sabinene and thujene, we have before us several treatises by Wallach and by Semmler, on which we report in a connected form as follows.

In the course of the last few years we have repeatedly had occasion to discuss[1]) works on the chemical behaviour of terpinene, but only the last work of Wallach[2]) on this important hydrocarbon brings the results hitherto obtained more or less to a conclusion. The only derivative characteristic for terpinene was the nitrosite $C_{10}H_{16}N_2O_3$ (m. p. 155°); on the other hand, very little was known with regard to the hydrohalogen addition products. These now Wallach has examined again, and he has thereby come to the result that terpinene yields crystallised halogen derivatives which are very similar to those of dipentene, and can easily be mistaken for the latter. They also occur in cis- and trans-form, and even if they have been produced from active material they are optically inactive. A comparative review of the melting points of the trans-forms of the terpinene and dipentene series is given below: —

	from terpinene	from dipentene
$C_{10}H_{16} \cdot 2HCl$	51 to 52°	49 to 50°
$C_{10}H_{16} \cdot 2HBr$	58 to 59°	64°
$C_{10}H_{16} \cdot 2HI$	76°	77° and 78 to 79°
$C_{10}H_{18}(OH)_2$	135 to 136°	156°

As a result of his experiments, Wallach proposes as crude material for the trans-terpinene compounds, sabinene and the terpineol of oil of sweet marjoram (see p. 135). But the hydrohalogen compounds, for

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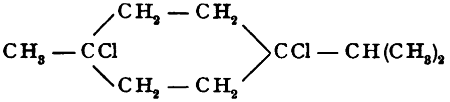
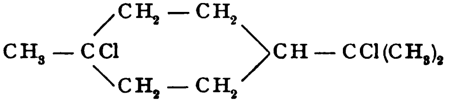
[1]) Report April **1901**, 67; October **1901**, 61; April **1902**, 88; October **1905**, 100; April **1906**, 115.

[2]) Liebig's Annalen **350** (1906), 141.

example, can also be produced from the crude terpinene which is obtained when treating terpin hydrate with dilute sulphuric acid (1 : 7), by introducing into it hydrohalogen dissolved in glacial acetic acid. The presence of dipentene renders the separation extremely difficult, and for this reason the characteristic addition-products of terpinene have long been overlooked. The constitution of the hydrochlorides is found on the one hand from the regeneration of terpinene, on the other from their easy manner of production from sabinene and thujene, and from v. Baeyer's terpineol of the m. p. 69°. Wallach accepts the following formula, and for the sake of comparison the formula of dipentene dihydrochloride has been placed below it: —



Terpinene dihydrochloride (1, 4-dichlorohexahydro-p-cymene)

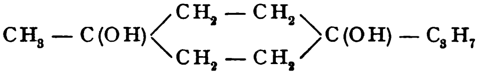


Dipentene dihydrochloride (1, 8-dichlorohexahydro-p-cymene)

From the hydrochloride or the hydrobromide, terpinene can be produced in the pure state in the following manner: 10 g. terpinene hydrochloride are heated with 20 cc. aniline until reaction begins, and after adding 20 cc. glacial acetic acid, are distilled over with steam The distillate is shaken with oxalic acid, and again treated with steam, which operation is repeated until the distillate has been freed from aniline. Pure terpinene boils between 179 and 181° (d_{20° 0,846; n_D 1,4789), yields without difficulty the nitrosite (m. p. 155°), and readily absorbs hydrohalogen acids. When terpinene dihydrobromide (m. p. 58°) is treated with silver acetate in solution of glacial acetic acid, there is obtained, after saponification of the acetate formed, *α*-terpineol (m. p. 35°), but in addition to this, cis-terpin (m. p. 117°) and trans-terpin (m. p. 156 to 157°). The view that according to this result the hydrochlorides of terpinene could yet be identical with the corresponding compounds of dipentene, and that only physical isomerides might here be present, is contradicted by the following experimental results.

Whilst dipentene dihydrochloride, when shaken with 2 per cent. aqueous potash liquor at 50°, readily yields, besides dipentene, *α*-terpineol, cis-terpin (m. p. 117°), and trans-terpin (m. p. 156°), there is formed during the same treatment of terpinene dihydrochloride at 100°, much more slowly, in addition to a large quantity of pure terpinene, a new terpineol of the following constants: b. p. 212 to 214°;

d 0,9290; n_D 1,4803. This, however, when treated with hydrochloric acid, does not yield back dipentene dihydrochloride, but terpinene dihydrochloride (m. p. 52°). The study of the constitution of this new terpineol has not yet been completed. In addition to this terpineol, there was discovered in the non-volatile products of conversion of terpinene hydrochloride, a new terpin, which is more soluble than its isomerides, and after crystallisation from acetic ester and ligroin melts at 136,5 to 137,5°. But strange to say, there was also found both ordinary cis- and trans-terpin. When the new terpin was treated with glacial acetic acid and hydrobromic acid, it yielded terpinene dihydrobromide (m. p. 58°). The old terpin formula



belongs to it.

Wallach makes use of the previously mentioned dissimilar behaviour of terpinene and dipentene dihydrochlorides towards aqueous alkali, in order to detect the two bodies alongside each other. Terpinene hydrochloride, which resists the action of the alkali longer, can, namely, be separated by fractional steam distillation from the dipentene and α-terpineol formed from dipentene hydrochloride. Wallach explains this behaviour thus, that the chlorine atoms in the terpinene compound (comp. the formulæ p. 134) are both situated in the nucleus, and are consequently more firmly attached than the one chlorine atom in the isopropyl group of the dipentene compound.

By earlier studies of the constituents of Ceylon cardamom oil (from long Ceylon cardamoms), carried out conjointly with E. Weber, Wallach[1]) had already demonstrated that this oil contains terpinene and a terpineol not identical with ordinary terpineol. More recent examinations[2]), for which we again supplied the material, also showed the presence of terpinene and a d-terpineol which yielded terpinene dihydrochloride (m. p. 52°), the corresponding bromide (m. p. 59°), and iodide (m. p. 76°). In oil of sweet marjoram Wallach was also able to detect this terpineol, in addition to α-terpineol already found by Biltz[3]). The new terpineol when treated with hydrohalogen acids does not yield dipentene compounds, but gives a very good yield of the above-described terpinene compounds. When oxidised with potassium permanganate it yields a glycerol which, recrystallised from chloroform, forms needles melting at 114 to 116°; when heated carefully, water separates off, and a product sublimes which melts at about 129°.

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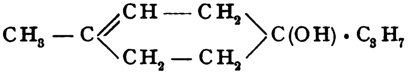
[1]) Liebig's Annalen **238** (1887), 98.

[2]) Liebig's Annalen **350** (1906), 168.

[3]) Berl. Berichte **32** (1899), 995.

On further oxidation with chromic acid the glycerol does not yield the ketolactone $C_{10}H_{16}O_3$ melting at 62° which is obtained from α-terpineol. In the further course of the examination, Wallach and Boedecker[1]) were then able to demonstrate that the above-mentioned terpineol of cardamom and sweet marjoram oils, and the alcohol which is formed by shaking sabinene with sulphuric acid (see page 140), are identical with the terpineol which is obtained by the action of aqueous alkali on terpinene dihydrochloride (see above). Wallach designates it as terpinenol, to distinguish it from the known terpineols, and in order to give expression to the relationship between the body and terpinene. All terpinenols of various origin yield with hydrohalogen terpinene hydrohalogenides, with dilute sulphuric acid the new terpin melting at 137°, and when treated with oxidising agents the same oxidation products. The glycerol $C_{10}H_{17}(OH)_3$ which, in addition to a not yet examined ketone, is formed on treatment with potassium permanganate, is more difficultly soluble in chloroform, and crystallises in a manner different from that of the isomeride prepared from α-terpineol. When distilled with aqueous hydrochloric acid it yields carvenone, besides cymene. The oxidation products of the two isomeric glycerols show a distinct difference. When the glycerol from the terpineol is oxidised, an acid $C_{10}H_{18}O_6$ is obtained, which occurs in two modifications (m. p. 205 to 206° and 188 to 189° respectively). Both are readily converted in crystallised lactones $C_{10}H_{14}O_4$, volatile with steam, if they are heated by themselves or in solution, under the influence of suitable reagents. The one corresponding to the higher-melting acid melts at 63 to 64°, the one which corresponds to the lower-melting acid, at 72 to 73°. The former has nearly the same melting point as the ketolactone $C_{10}H_{16}O_3$ from the glycerol from α-terpineol. Now, as the detection of the latter in oil of sweet marjoram by Biltz is based solely upon an oxidation-product of the m. p. 61°, which was obtained in a small quantity, might possibly not have been quite pure and for that reason have had a lower melting point, and which moreover was not analysed, — it is clear that Semmler's opinion that the presence of α-terpineol in oil of sweet marjoram were established beyond doubt, must be accepted only with caution. If the fraction of oil of sweet marjoram which contains the terpineol is shaken with sulphuric acid, there is formed ordinary cis-terpin hydrate, and terpinene terpin melting at 137°. For the present Wallach gives to terpinenol the following formula:



$$CH_3-C\left\langle\begin{array}{l}CH-CH_2\\ CH_2-CH_2\end{array}\right\rangle C(OH)\cdot C_3H_7$$

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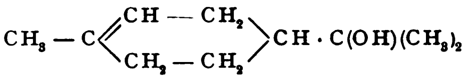
[1]) Berl. Berichte **40** (1907), 596.

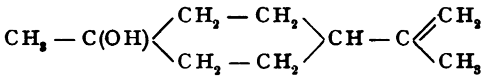
With regard to the behaviour of the terpineols and terpins known up to the present, towards hydrohalogen acids, Wallach[1]) communicates the following:

α-terpineol (m. p. 35°)

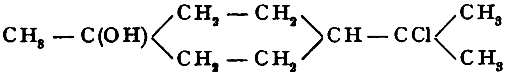


yields with hydrohalogen acids the common dipentene derivatives.

β-terpineol (m. p. 32°)

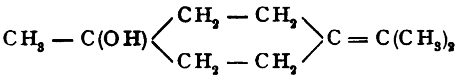


yields the same compounds as α-terpineol. But under certain conditions the hitherto unknown chlorohydrin



(m. p. 74 to 75°) can be obtained. With 2 per cent. potash liquor it yields cis-terpin.

γ-terpineol (v. Baeyer, m. p. 69°)



yields with glacial acetic and hydrochloric acids a mixture of dipentene and terpinene dihydrochlorides.

Cis- and trans-terpin (m. p. 117 and 156° resp.) yield dipentene derivatives.

The optically active terpinenols of oils of cardamom and sweet marjoram yield the inactive terpinene hydrohalogen compounds.

The relationship between sabinene and terpinene is also of the greatest interest. The observations of Kondakow and Skworzow[2]) regarding the convertability of sabinene into derivatives of the limonene-group are, according to Wallach[3]), incorrect; on the contrary, the action of glacial acetic and hydrohalogen acids produces not a trace of a dipentene compound, but only terpinene compounds, and of these, principally the high-melting trans-forms. Wallach even considers sabinene a very good crude material for such compounds. The process which takes place during the reaction speaks not only well for the

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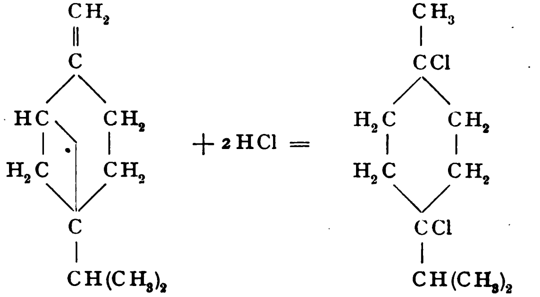
[1]) Liebig's Annalen **350** (1906), 157.

[2]) Journ. f. prakt. Chem. II. **69** (1904), 170.

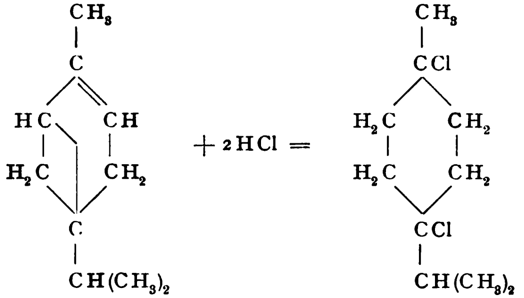
[3] Liebig's Annalen **350** (1906), 162.

correctness of Semmler's sabinene formula[1]), but also for the formula given for the terpinene hydrohalogen addition products:


sabinene terpinene dihydrochloride

Contrary to Semmler[2]), Wallach was able to convert sabinene readily by treatment with dilute sulphuric acid (1 : 7) into terpinene, which was identified by the nitrosite and the dihydrochloride.

On account of the relationship between thujene and sabinene, the former was also submitted to examination, and contrary to the results obtained by Kondakow[3]) and Tschugaeff[4]) Wallach has found that also from thujene, by treatment with hydrohalogen acids, not dipentene, but compounds of terpinene hydrohalogenide are formed:


α-thujene terpinene dihydrochloride

These examinations of Wallach render the thujene formula accepted by Kondakow illusory.

Semmler[5]) also expresses himself on the relationship of sabinene and thujene towards terpinene. The conversion of sabinene in terpinene

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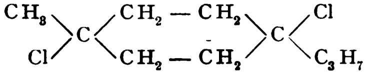
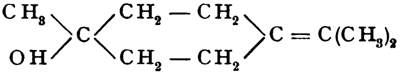
[1]) Comp. Report October **1902**, 91.
[2]) Semmler, Die ätherischen Öle, vol. II, 289.
[3]) Chem. Ztg. **26** (1902), 722.
[4]) Berl. Berichte **37** (1904), 1483.
[5]) Berl. Berichte **39** (1906), 4416.

has been shown both by himself and also by Kondakow and Skworzow[1], but this conversion should not be utilised for the determination of the constitution, as all terpenes of the menthane-series can be converted in terpinene. No doubt the conversion of sabinene, or thujene, in limonene hydrohalogen addition-products according to Kondakow and Skworzow, and also according to Tschugaeff[2], could only be explained from his (Semmler's) formulæ by rearrangement, but a rearrangement could in this case be readily explained, as glacial acetic acid and hydrohalogen had been employed. Semmler considers that the hydrohalogen addition-products cannot be utilised at all for constitution determinations, and for this reason he also objects to the above-discussed work of Wallach on the conversion of sabinene and thujene in terpinene dihydrochloride, the uniformity of which he doubts. The whole process of this reaction appears to Semmler to be wanting in lucidity, the more so as the terpinene dihydrochloride on treatment with alkali, yielded the common terpin (1,8) as well as the other.

The explanation of this behaviour is given by Wallach[3] in the following manner: If the chloride melting at 52° has the formula



it can on the one hand yield a new terpin by substituting OH for Cl, and on the other, by splitting off HCl and substitution of the second chloride atom by OH, be converted among others in v. Baeyer's γ-terpineol,



rendering subsequently ordinary terpin.

As a matter of fact, Wallach was able to establish by experiment the conversion of γ-terpineol in the common cis- and trans-terpins, under the conditions determined for the conversion of terpinene dihydrochloride to terpinenol. The terpinene-terpin could now also be obtained with great facility by treating the terpinenols with dilute sulphuric acid. It melts at 137 to 138°, and boils at 250° with traces of decomposition. It can be recrystallised from boiling water or dilute methyl alcohol, and is inactive. When treated with hydrogen chloride, it changes easily into terpinene dihydrochloride.

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[1] Journ. f. prakt. Chemie II. **69** (1904), 176; Report October **1904**, 112; Chem. Ztg. **26** (1902), 722.

[2] Berl. Berichte **37** (1904), 1483; Report October **1904**, 113.

[3] Berl. Berichte **40** (1907), 577.

The priority claimed by Semmler[1]) with regard to the inversion of sabinene to terpinene, is objected to by Wallach[2]), as Semmler had only given theoretical speculations, but not supplied experimental proofs. He also considers Semmler wrong in his opinion that the intermediate products occurring in this process cannot be separated. Wallach proves this by isolating the products obtained by shaking sabinene with dilute sulphuric acid, particularly terpinenol and terpinene-terpin, during which not a trace of the common terpins occurs. The last-named fact may serve as a proof that sabinene, — contrary to the opinion represented by Semmler — has little inclination when in contact with acids to pass over into compounds of the limonene series. The terpinenol obtained from sabinene is chemically and physically identical with that from the oils of cardamom and sweet marjoram (see p. 135), and is the optically active modification of the one obtained from terpinene dihydrochloride and alkali.

Some time ago Wallach[3]) had already called attention to the abnormally high molecular refraction of sabinene, and on that occasion corrected the figures calculated by Semmler, which agreed with those found by experiment. In face of the reply by Semmler[4]) who holds out a prospect of further communications regarding the high dispersion of sabinene, Wallach[5]) maintains the abnormal refraction of sabinene.

By treating sabinene with glacial acetic acid alone, or with glacial acetic and sulphuric acids, Semmler[6]) obtained an acetate in addition to a mixture of hydrocarbons. When shaking sabinene with aqueous hydrochloric acid, there were obtained besides a dichloride (m. p. 52°), monochlorides which Semmler considers partly as semicyclic, whilst on introducing hydrochloric acid in the solution of sabinene in absolute ether at —18°, a dichloride of the m. p. 53 to 54° was formed, in addition to the terpinene dichloride (m. p. 51 to 52°) of Wallach, and monochlorides which appear to be semicyclic. The action of glacial acetic acid and hydrochloric acid, on the other hand, yielded a dichloride (m. p. 52°) besides semicyclic monochlorides. Semmler concludes from the formation of semicyclic bodies that the hydrochloric acid is absorbed more difficultly by the semicyclic double linking than by the double linkings in the nucleus or in the side-chain.

These observations of Semmler agree only in part with Wallach's results, who, however, considers Semmler's dihydrochloride of the

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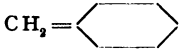
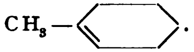
[1]) Berl. Berichte **39** (1906), 4418.
[2]) Berl. Berichte **40** (1907), 592.
[3]) Liebig's Annalen **347** (1906), 319.
[4]) loc. cit.
[5]) Berl. Berichte **40** (1907), 585.
[6]) Berl. Berichte **39** (1906), 4419.

m. p. 53 to 54° as certainly identical with his own of the m. p. 51 to 52°. The slight difference might be explained by a difference in the manner of determining the melting point. According to Wallach's[1]) examinations, the dihydrochloride is not formed at all if moisture is carefully excluded, but only a monohydrochloride, which therefore is best obtained in a solution of carbon disulphide. It has the following properties: b. p. 87 to 92° (12 mm. pressure); d 0,982; n_{D20° 1,4842. It could not be obtained in the solid form, and contrary to limonene monochloride, formed no difficultly soluble nitrosate, but a nitrosochloride. By adding hydrogen chloride it is converted in the dichloride of the m. p. 52°. In a study dealing with the formula of the monochloride, Wallach comes to the conclusion that he is unable to confirm Semmler's proposition that the double linking of the pseudo-form



adds hydrohalogen with much greater difficulty, than the ortho-form



When treating sabinene with formic acid at a highly reduced temperature, and saponifying the resulting formiate, Semmler[2]) obtained an alcohol $C_{10}H_{18}O$ (b. p. 93 to 96°, at 11 mm. pressure; d_{20° 0,926; n_D 1,48033; $\alpha_D + 14^\circ$), which by the action of glacial acetic acid and hydrochloric acid yielded a dichloride of the m. p. 51 to 52°. Semmler considers this provisionally as identical with the terpinene dihydrochloride of Wallach, and compares his alcohol with the one discovered by Wallach in oil of sweet marjoram, for which Semmler proposes the name origanol. The synthetic alcohol, when oxidised with potassium permanganate, yields a glycerol which Wallach obtained from the alcohol of oil of sweet marjoram. If the formiate of the alcohol from sabinene is heated with quinoline to 230°, there results a terpene $C_{10}H_{16}$ (b. p. 174 to 177°); d_{20° 0,839; n_D 1,479; $\alpha_D + 4^\circ 12'$) which gives a feeble terpinene reaction. When treating the alcohol with phosphorus pentachloride, with the application of heat, a terpene is obtained which gives a powerful terpinene reaction. A urethane or any ester of the alcohol could not be obtained.

The treatment of this alcohol with glacial acetic acid and hydrogen chloride, which Semmler carried out for the determination of its constitution gives Wallach[3]) an opportunity of criticising the abovementioned view of Semmler, that the addition products of hydrogen

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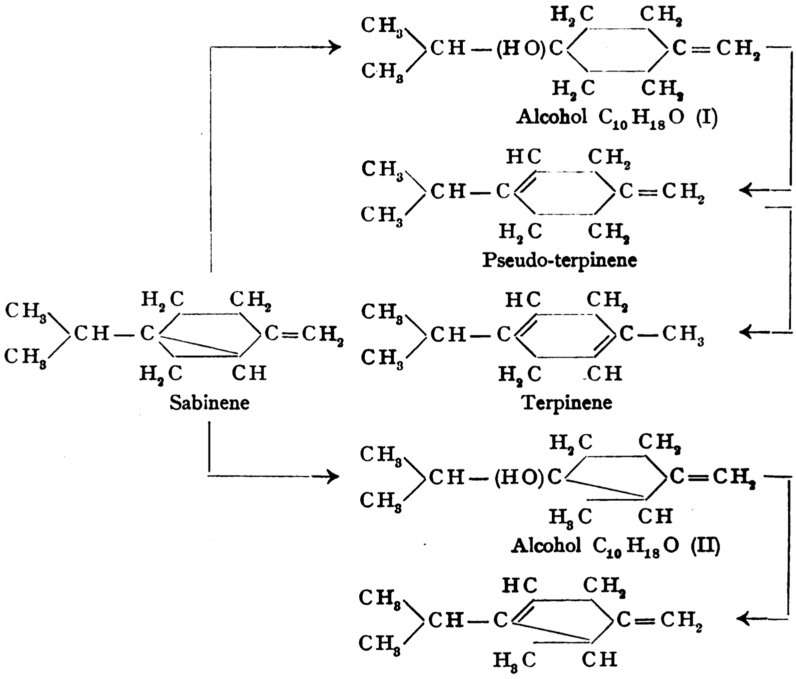
[1]) Berl. Berichte **40** (1907), 588.
[2]) Berl. Berichte **39** (1906), 4421.
[3]) Berl. Berichte **40** (1907), 595.

chloride were absolutely useless for constitution-determinations, and were not suitable for identifying purposes.

In addition to the alcohol $C_{10}H_{18}O$, Semmler obtained by the action of formic acid on sabinene a terpene $C_{10}H_{16}$ (b. p. 169 to 173°; $d_{20°}$ 0,829 to 0,831; α_D + 13 to + 14°; n_D 1,471), which, on the strength of its physical properties, he considers a pentamethylene derivative. There would then have taken place in this reaction a disruption of the three-membered ring in sabinene, and the semicyclic linking would have remained intact. Attempts made to attach formic acid to the hydrocarbons camphene and β-(pseudo-) phellandrene which contain such a linking, appear to confirm this view, as these bodies did not attach formic acid.

Semmler gives a representation of the reactions described above in the following formulæ: —



The production of terpinene nitrosite has already been described by Wallach[1]) on a previous occasion. The behaviour of this body towards alcoholic potash had led him to entirely different (not yet

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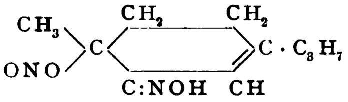
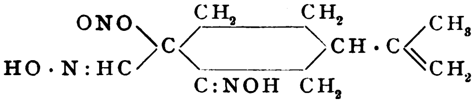
[1]) Liebig's Annalen **239** (1888), 35.

published) results than Semmler[1]. In a subsequent examination the earlier results were confirmed. By the action of equal molecules of nitrosite and sodium methylate or ethylate, alcoholic or aqueous potash, there was formed, with separation of sodium nitrite, a body $C_{20}H_{31}N_3O_4$, m. p. 163 to 164°; benzoyl derivative, m. p. 127°. Semmler, who allowed two mol. potash to act on one mol. nitrite, received, on the other hand, a body $C_{10}H_{15}NO_2$, of the m. p. 85°. Wallach, working under conditions such as Semmler, did not obtain the body melting at 85°, but, in addition to resinous substances, the body melting at 163 to 164°. The observation made by Amenomiya[2], that the reduction of terpinene nitrosite with zinc in acetic solution yields carvenone, confirms Wallach's assumption that under such conditions carvone derivatives are formed. In repeating these experiments carvenone and tetrahydrocarvylamine were found as reaction-products. Good yields of carvenone were obtained when the body (m. p. 163°) formed from the nitrosite by means of alcoholic potash, or when terpinene nitrol-piperidide (m. p. 154°) were reduced in glacial acetic acid solution, first at 0°, and then at the temperature of the waterbath. The hydrochloride of terpinene nitrol-piperidide yielded on dry distillation carvacrylamine. On the strength of the now known facts, Wallach assumes that the nitrosite reacts according to the formula

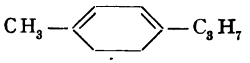


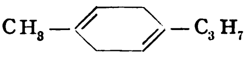
whilst the formula accepted by Semmler,

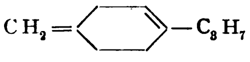


has been completely disproved.

With regard to the constitution of terpinene, Wallach considers that this question, although not yet solved, has yet been brought near its solution. He considers Semmler's terpinene formula[3] as well as the formula proposed by v. Baeyer[4], as out of the question. The following come under consideration for illustrating the ready formation of the terpinene hydrohalogen compounds: —







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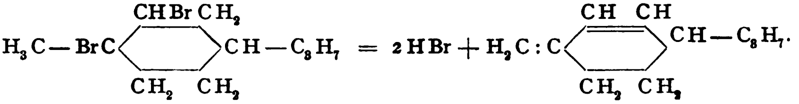
[1] Berl. Berichte **34** (1901), 715; Report October **1901**, 62.
[2] Berl. Berichte **38** (1905), 2730; Report April **1906**, 115.
[3] Berl. Berichte **34** (1901), 715; Report October **1901**, 62.
[4] Berl. Berichte **27** (1894), 453.

The first originates from Wallach (1891), the second from Harries[1], and the last has up to the present not yet been taken into account, but comes to the front owing to the relationship between sabinene and terpinene. This formula would not, however, explain the derivation of the nitrosite from a semicyclic methene hydrocarbon, as in such case the reduction should yield an aldehyde, and not a ketone of the carvone series. The situation would become clear if, as Wallach accepts, there were several modifications of terpinene.

To Semmler's statement that previous to the discovery of terpinene dihydrochloride it was possible to form exactly the same picture of the relations of sabinene, Wallach[2] replies that not theoretical discussions, but only the experimental realisation enable one to form a clear idea of a reaction.

A further communication by Semmler[3] regarding the constitution of terpinene, origanol, sabinene, dipentene, and their derivatives, deals only with the above-mentioned works of Wallach, and supplies no fresh experimental material. Semmler endeavours to defend his views, and to put an end to differences of opinion which have arisen.

Phellandrene. As a supplement to their work[4] on the synthesis of phellandrene from carvomenthene dibromide, Kondakow and Schindelmeiser[5] state that they have obtained from their inactive hydrocarbon two nitrites whose melting points (102 to 103,5°, and 94 to 95°) very nearly agree with those of the β-phellandrene nitrites[6]. The formation of phellandrene from carvomenthene dibromide proceeds therefore as follows: —



From the previously obtained chlorides of β-phellandrene from oil of water fennel, there were produced, by means of further purification, two solid chlorides, viz., dipentene dihydrochloride (m. p. 50°), and pinene hydrochloride (m. p. 126°). But the manner of identifying these bodies is not mentioned. The intermediate fraction obtained in the

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[1] Berl. Berichte **35** (1902), 1169.

[2] Berl. Berichte **40** (1907), 584.

[3] Berl. Berichte **40** (1907), 751.

[4] Journ. f. prakt. Chem. II. **72** (1905), 193; Report April **1906**, 113.

[5] Journ. f. prakt. Chem. II. **75** (1907), 141.

[6] Instead of the designations pseudo- and β-phellandrene which Kondakow and Schindelmeiser use in turn, the uniform name β-phellandrene may be recommended.

distillation of the two chlorides, when treated with alcoholic potash liquor, gave a mixture of monochloride and a hydrocarbon (b. p. 177 to 185°; d 0,845; n_D 1,4718; $\alpha_D \pm 0°$; MR 45,15), which yielded no nitrosite, but a crystalline bromine compound. Kondakow and Schindelmeiser therefore believe it to be dipentene.

In their opinion the formation of pinene hydrochloride can be attributed to the presence of pinene in the oil of water fennel, or to a conversion of the phellandrene. Although the presence of pinene in oil of water fennel has not yet been proved, various circumstances indicated more in detail by the authors, allow of such a conclusion being drawn. If it should not be found possible to detect pinene in oil of water fennel, the formation of pinene hydrochloride would probably be due to a conversion of the phellandrene. In a theoretical study on the constitution of the chlorides obtained, such a possibility is discussed more in detail.

Carvestrene. W. H. Perkin jun. and G. Tattersall¹) publish a preliminary communication on the synthesis of carvestrene. If m-hydroxybenzoic acid is reduced with sodium and alcohol, hexahydro-m-hydroxybenzoic acid is formed, which is oxidised by bichromate and sulphuric acid to γ-ketohexahydrobenzoic acid (b. p. 210° [25 mm. pressure]; m. p. 75 to 76°). This yields a semicarbazone melting at 182 to 183° with decomposition. The ethyl ester of γ-ketohexahydrobenzoic acid, when treated with magnesium methyl iodide, is converted in the lactone of γ-hydroxyhexahydro-m-toluic acid (b. p. 145° [20 mm. pressure]). When the latter is heated with hydrobromic acid, it yields γ-bromohexahydro-m-toluic acid, which is converted by treatment with pyridine in tetrahydro-m-toluic acid (b. p. 142 to 144° [15 mm. pressure]). If magnesium methyl iodide is allowed to act on the ester of this acid, there is formed Δ_1-m-menthenol-8 (b. p. 110 to 112° [30 mm. pressure]), and this yields, when heated with potassium bisulphate, with. loss of water, carvestrene (b. p. 179 to 180°), which was identified by the dihydrochloride (m. p. 52,5°) and the dihydrobromide (m. p. 48°).

Alcohols.

For the production of glycols, the materials employed are frequently either the corresponding bromides or unsaturated alcohols, or occasionally also diamines, chlorohydrins, etc. The trouble, costliness, and comparatively small yield of these methods have induced F. W. Semmler²) to look for a more rational method for the production of the glycols of terpene derivatives, and he succeeded in producing γ-, δ- and ε-glycols

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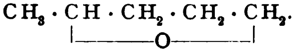
¹) Proceed. chem. Soc. **22** (1906), 268.

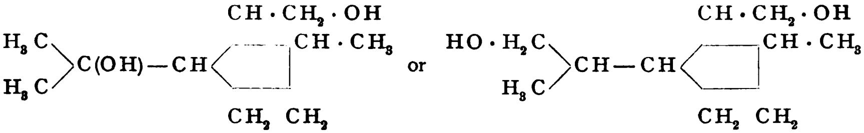
²) Berl. Berichte **39** (1906), 2851.

from the corresponding aliphatic, hydroaromatic, and aromatic lactones by reducing these with sodium and alcohol. The yields fluctuate between 20 and 60%. The reduction of γ-valerolactone yielded, besides the glycol (pentane-1,4-diol, $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$), the corresponding hydroxyvaleric acid, which with concentrated sulphuric acid can be reconverted in the lactone. After treatment with alcoholic hydrochloric acid in a sealed tube (3 hours at 150°), the glycol yielded γ-pentylene oxide

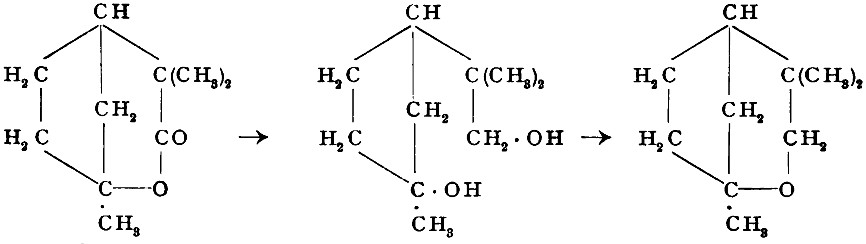


$$\underbrace{CH_3 \cdot CH \cdot CH_2 \cdot CH_2 \cdot CH_2}_{O}.$$

Wallach's pulegenic acid lactone gave, in a yield of about 40%, the glycol $C_{10}H_{20}O_2$ [1] (b. p. 137 to 140° [10 mm. pressure]; d_{20° 0,9945; n_{D20° 1,4715), which could be converted by alcoholic hydrochloric or sulphuric acid in an oxide $C_{10}H_{18}O$, and which may possibly be a γ- oder δ-glycol of the following constitution: —



The glycol of α-fencholenic acid lactone (m. p. 77 to 78°), which latter was designated by Cockburn [2] as α-fencholenic acid, but which Semmler has now identified as a lactone by conversion in an acid $C_{10}H_{18}O_3$ by means of alkalis, boils at 158 to 161° (11 mm. pressure), and melts at 59 to 60°. Boiling with dilute sulphuric acid produces in a yield of 60%, an oxide $C_{10}H_{18}O$ (d_{20° 0,918; n_D 1,46012), which Semmler considers identical with Wallach's [3] fenchenol from fencholenic alcohol. The following graphic formulæ explain the conversion from lactone to oxide: —



lactone glycol oxide (fenchenol)

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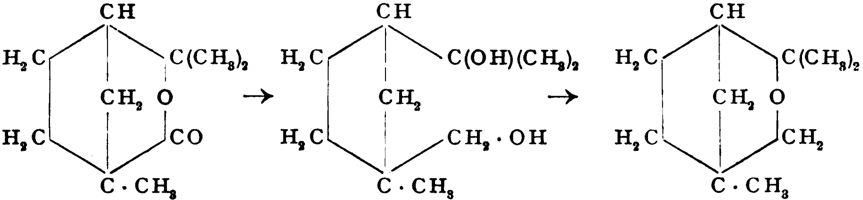
[1] Berl. Berichte **38** (1905), 146; Report April **1905**, 114.

[2] Journ. chem. Soc. **75** (1899), 506.

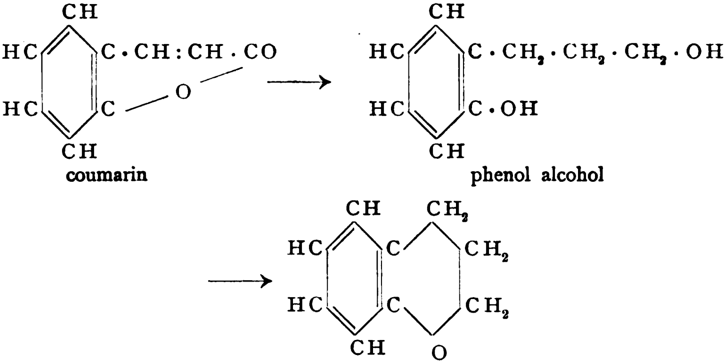
[3] Liebig's Annalen **284** (1894), 338; **300** (1898), 321.

β-Fencholenic acid lactone (b. p. 116 to 118° [8 mm. pressure]; m. p. 68 to 69°; d_{25° 1,0343; n_D 1,46757 [cooled below the solidifying point!]), when treated with sodium and alcohol, passes over in the corresponding glycol of the b. p. 142 to 143° (8 to 9 mm. pressure), which also yields an oxide: —



lactone glycol oxide

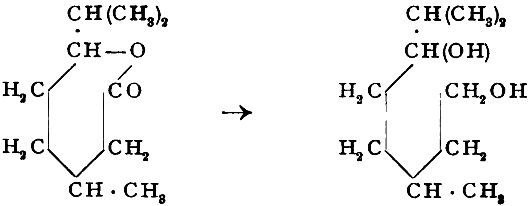
The reduction of a δ-lactone (coumarin) yielded, besides α-hydroxy-dihydrocinnamic acid, a hitherto unknown phenol alcohol, o-hydroxy-dihydrocinnamic alcohol $C_9H_{12}O_2$ (b. p. 177 to 178° [8 mm. pressure]; d_{20° 1,1293; n_D 1,55984), of which Semmler produced in quantitative yield the corresponding oxide, chromane. The alcohol yields with benzoyl chloride a benzoyl compound of the m. p. 99 to 100°.



coumarin phenol alcohol

chromane

When reducing the ε-lactone of 2,6-dimethyl-octane-3-ol acid from menthene, Semmler obtained a glycol $C_{10}H_{22}O_2$, b. p: 147° (10 mm. pressure); the conversion is as follows: —



ε-lactone dimethyl-2, 6-octanediol-3, 8

On reducing phthalide, Semmler observed the primary formation of phthalic alcohol which is not stable towards alcoholic potash.

He explains the formation of these glycols by the ether-like linking of the oxygen atom with two carbon atoms in one ring. In the first instance an alcohol aldehyde is formed with addition of nascent hydrogen, and from this, by further action of the nascent hydrogen, the glycol. The ring-formation has doubtless some influence on the comparatively good yields.

Terpineol. With regard to the constitution of the various terpineols and their behaviour towards hydrohalogen acids, see under terpinene (p. 137).

Terpinenol. See under terpinene (p. 136).

Borneol. In our last Report we made a communication with reference to a work by W. Borsche and W. Lange¹) on the production of thioborneol from pinene hydrochloride. The authors make a somewhat belated reference to a previous work (which they had overlooked at the time) by W. Wuyts²), who had produced thioborneol by a different method. The same subject has been studied by J. Houben and H. Doescher³) who succeeded in producing hydropinene sulphinic acid, hydropinene carbithio acid, thioborneol, and thiocamphor, and whose results on most points agree with those of the above-mentioned authors. The thioborneol obtained by Houben and Doescher by the action of sulphur on hydropinene magnesium chloride melts at 63°, and boils at 94 to 95° (12,5 mm. pressure). The oily distillation residue consists of hydrodicamphor, bornyldisulphide, and small quantities of a body still richer in sulphur; when extracted with ether, it yields in the fractional distillation *in vacuo* thioborneol and thiocamphor, — results which previously had also been obtained by Wuyts. Oxidation of thioborneol with chromic acid yielded bornyldisulphide (m. p. 178°). Although the bornyldisulphide obtained by Borsche and Lange showed the m. p. 121°, a product obtained by Wuyts from camphor again melted at 175 to 176°. If a sufficiently high temperature is employed, almost the whole quantity of the sulphur-containing products formed from sulphur and hydropinene magnesium chloride is converted in thiocamphor, which, however, oxidises already when simply left standing exposed to air. The thiocamphor obtained by distillation

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¹) Berl. Berichte **39** (1906), 2346; Report October **1906**, 121.

²) Berl. Berichte **36** (1903), 869.

³) Ibidem **39** (1906), 3503.

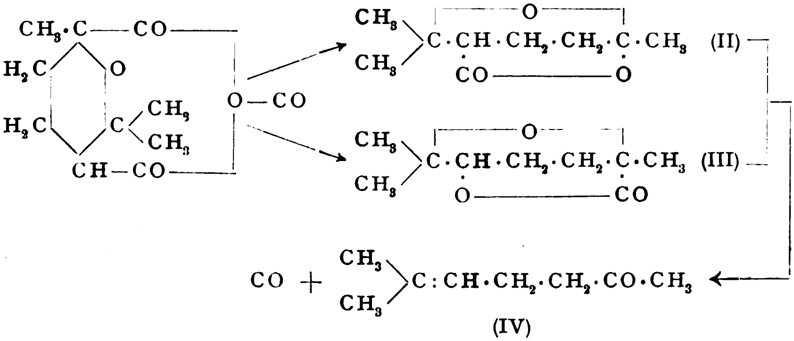
(12 mm. pressure) from pinene hydrochloride magnesium and the sulphurated reaction-products non-volatile with water vapour, was identified by conversion in camphoroxime (m. p. 117 to 119°).

Oxides.

Cineol. We have already on several occasions reported[1]) on Rupe's work regarding the behaviour of cineolic acid from a chemical as well as from a physical point of view. Further experiments carried out by Rupe conjointly with W. Lotz[2]), deal with the effect of bromine on cineolic acid anhydride. Cineolic acid itself is not attacked by bromine; on the other hand, the latter acts on the anhydride of the acid with a violence similar to an explosion. The authors obtained one liquid and also two solid crystallising bromine derivatives. The two solid bodies which can be separated by fractional crystallisation from methyl alcohol, are isomeric, and have the rough formula $C_9H_{11}O_3Br_3$.

The bromide A crystallises from methyl alcohol in white needles or brilliant crystals, but also as a granular crystal powder; the melting point lies at 156 to 157°. The bromide B melts after recrystallisation from alcohol at 129°, and crystallises from methyl alcohol in large tablets. Both bromides show the character of lactones; halogen is best split off by treatment with zinc dust and alcohol. The body resulting from this has the properties of a δ-lactone, which on slow distillation at 170° (ordinary pressure), is converted, with loss of carbonic acid, in methyl heptenone (IV) (b. p. 173°); the latter was identified by its semicarbazone (m. p. 134°).

The course of the reaction, i. e. the splitting off of CO from cineolic acid anhydride, is conceivable in two directions, whereby the substitution of the H-atoms by bromine need not for the present be taken into account. The following formulæ explain the reaction: —



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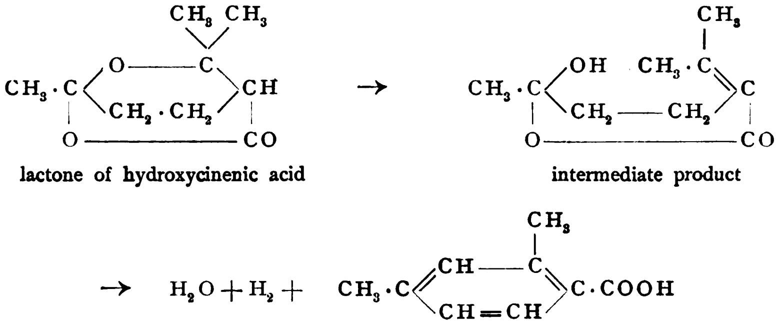
[1]) Reports October **1900**, 76; April **1901**, 70; October **1905**, 109.
[2]) Berl. Berichte **39** (1906), 4076.

As a matter of fact, there was formed, by splitting off the carbonyl-group situated at the tertiary carbon atom, as might be expected, the compound II, the lactone of an as yet unknown hydroxycinenic acid, which was proved by the conversion of the latter in 1, 3-dimethylbenzoic acid-4[1]; this speaks against the formation of compound III.

With regard to the position of the bromine atoms in the substitution products, Rupe and Lotz do not express any definite opinion.

The hydroxycinenic acid lactone just described is formed by treating[2] cineolic acid, or better still its anhydride, with concentrated sulphuric acid in the cold, which reaction is also accompanied by loss of carbon oxide. The loss takes place, as above, at the tertiary carbon atom. If the lactone melting at 50 to 51° is heated with concentrated sulphuric acid, or if cineolic acid or its anhydride are heated directly with oil of vitriol, the above-mentioned 1, 3-dimethylbenzoic acid-4 (m. p. 125 to 126°) is obtained: —



dimethylbenzoic acid

It will be seen from the formulæ that the sulphuric acid has a condensing as well as an oxidising action. But from an attempt to arrive at dihydrodimethylbenzoic acid, in a manner analogous to the formation of dihydro-m-xylene from cineolic acid according to Wallach and Gildemeister[3], by melting the above-described lactone with zinc chloride, it would appear that the intermediary formation of the acid is not impossible. Dihydro-m-xylene boiled at 132 to 134,5° (according to Wallach and Gildemeister at 132 to 134°); n_{D20° 1,46867; the dinitroxylene produced from it melted at 90 to 91°.

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[1] Comp. hereafter the action of sulphuric acid on cineolic acid.

[2] Berl. Berichte **39** (1906), 4083.

[3] Liebig's Annalen **246** (1888), 268.

Aldehydes.

In the electrolytic reduction of aromatic aldehydes, H. D. Law[1]) obtained compounds of the hydrobenzoin type. The reduction is accomplished according to the equation $2\,R \cdot CHO + 2\,H = R \cdot CH(OH) \cdot CH(OH) \cdot R$. The introduction of $-OH$-, $-OCH_3$- and $= O_2CH_2$-groups has no influence on the reaction. In the experiments the anode and cathode compartments were separated by a diaphragm. The excess of hydrogen evolved in the cathode compartment was collected in the usual manner, and the intensity of the current was moreover measured with a hydrogen coulombmeter. Bodies which could in this manner be reduced without difficulty, were cuminaldehyde, piperonal, vanillin, anisaldehyde, salicylaldehyde; further, anisoin, cuminoin, and piperonyloin. The mixtures of the hydro- and isohydrobenzoins formed can in every case be separated.

Unsaturated aldehydes, such as furfurol and cinnamaldehyde, yielded only resins on electrolytic reduction.

Ketones.

We have already referred[2]) to the synthesis of the three menthanones (m-menthanone-2,-3, and -4) perfected by A. Kötz and his collaborators. The crude material for these experiments is o-, m- and p-cresol, which were transformed over the corresponding methylcyclohexanones and their oxalic and carboxylic esters, finally into the methyl isopropyl cyclohexanone carboxylic esters.

In a quite analogous manner A. Kötz and A. Michels[3]) have now, starting from phenol, produced isopropyl-1-cyclohexanone-2, after having first obtained cyclohexanone-2-oxalic ester and the corresponding carboxylic ester. Isopropyl-1-cyclohexanone-2 (by splitting the ketone from the corresponding carboxylic ester), boils at 92° (15 mm. pressure); its semicarbazone melts at 187°. With regard to the production of methyl-1-isopropyl-3-hexanone-2, (m-menthanone-2, m-menthone) from the diester, we refer to our last Report, p. 148, as the methods are analogous.

A. Kötz[4]) also makes a communication regarding the experiments for producing dicarboxylic esters from cyclic monoketones. Such esters are generally formed by conversion of chloro-formic ester or chloroacetic ester, with the sodium compounds of cyclic β-ketonic acid esters. Some esters of this class were produced by Kötz and Michels in the

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[1]) Journ. chem. Soc. **89** (1906), 1512.

[2]) Report April **1906**, 126; October **1906**, 148.

[3]) Liebig's Annalen **350** (1906), 204.

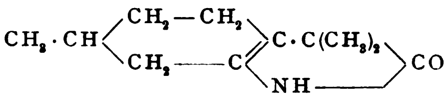
[4]) Ibidem, 229.

course of the work referred to above and also some other dicarboxylic esters whose two carboxethyl groups are in some cases linked to the same carbon atom, and sometimes to different carbon atoms in different distances from each other. When heated with alcohol, the esters were partly split up into aliphatic tricarboxylic esters.

In connection with the above work, Kötz and Michels report on the differences in the easiness with which semicarbazones are formed in the case of cyclohexanones.

Carvone. As already described in our last Report, A. Lapworth¹) obtained by hydrolysis of cyanodihydrocarvone, two stereo isomeric acids. The neutralised β-acid yields with prussic acid a cyanohydrin. This now, like the cyanodihydrocarvone cyanohydrin formed from HCN and cyanodihydrocarvone, can, according to Lapworth's²) further studies, be readily hydrolysed by mineral acids, and finally be converted in 2-methyl-5-isopropenyl-Δ_2-tetrahydroisophthalic acid, which on reduction yields a mixture of isomeric 2-methyl-5-isopropenyl-hexahydrophthalic acids. Although these latter are unsaturated, they cannot be further reduced by sodium amalgam. The addition products of cyanodihydrocarvone with hydrohalogen acids are well-characterised crystalline bodies. The hydroiodide can be reduced with zinc and methyl alcohol to a mixture of cyanodihydrocarvone and cyanocarvomenthone, of which the last-named is converted by the action of acids in carvomenthonecarboxylic acid, and by alkalis in carvotanacetone.

Pulegone. A. Lapworth³) has conjointly with W. L. Clarke, studied the action of potassium cyanide on pulegone. The body $C_{11}H_{17}ON$ formed in this reaction, can according to Hann and Lapworth⁴) by readily converted in menthonecarboxylic acid (m. p. 120 to 121°). When treated with acetyl chloride, or heated with mineral acids, this yields an unsaturated lactone $C_{11}H_{16}O_2$, from which by shaking with ammonia the original body $C_{11}H_{17}ON$, can be regenerated. This body had long been wrongly regarded as cyanomenthone; in reality it represents an anhydramide of the following constitution: —



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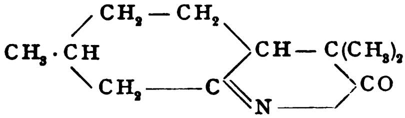
¹) Proceed. chem. Soc. **22** (1906), 164; Report October **1906**, 132.
²) Proceed. chem. Soc. **22** (1906), 285; Journ. chem. Soc. **89** (1906), 1819.
³) Proceed. chem. Soc. **22** (1906), 285; Journ. chem. Soc. **89** (1906), 1869.
⁴) Proceed. chem. Soc. **20** (1904), 54.

or



and it is formed in all cases in which, according to the previous opinion, cyanomenthone is to be expected. The optical rotation of the anhydramide in a 200 mm. tube was $[\alpha]_D + 66,6^\circ$ (in absolute alcohol).

Fenchone. Jointly with K. Bartelt, F. W. Semmler[1]) publishes two papers on the determination of the constitution in isomeric fencholenic acids. The β-acid is formed by saponification of the corresponding nitrile, which can be produced from fenchone oxime. The assumption that the reaction-mechanism proceeds in a manner analogous to the production of α- and β-campholenic nitrile from camphor oxime, where the first-named nitrile can be converted in the last-named, could not be upheld. On the contrary, the two fencholenic nitriles are formed primarily alongside each other, and up to the present it has not yet been possible to convert the one in the other.

β-Fencholenic acid forms a difficultly soluble silver salt, which yields with methyl iodide a methyl ester $C_9H_{15} \cdot COOCH_3$ (b. p. 97 to 99°; d_{22° 0,9808; n_{D20° 1,46459). The latter can be reduced with sodium and alcohol to the corresponding alcohol $C_{10}H_{18}O$ (b. p. 106 to 108°; d_{22° 0,9272; n_{D20° 1,48033).

When β-fencholenic acid is treated with concentrated sulphuric acid, the corresponding lactone is formed, as already mentioned on another page[2]). This, when shaken with dilute soda liquor in the cold, yields hydroxyhydrofencholenic acid $C_{10}H_{18}O_3$ of the m. p. 110°.

If β-fencholenic acid is diluted with equal quantities of benzene and water, and a powerful current of ozone is passed through the mixture, a solid ketonic acid $C_7H_{10}O_3$ is formed; b. p. 166 to 170° (12 mm. pressure); d_{16° 1,1533; $[\alpha]_D + 13,15^\circ$ (in 50 per cent. alcoholic solution); n_D 1,472. Semicarbazone, m. p. 198 to 199°; oxime m. p. 145°. When treated with permanganate in neutral or weak alkaline solution, this ketonic acid is split up into a not yet identified tricarboxylic acid $C_7H_{10}O_6$ very readily soluble in water, on whose distillation *in vacuo*, with loss of carbonic acid, an acid passes over which Semmler regards as α-methyl glutaric acid (b. p. 205 to 208° [12 mm. pressure]; m. p. 77 to 78°).

The melting point of the β-fencholenic acid which is formed from the comparatively readily saponifyable β-nitrile, is at 72 to

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[1]) Berl. Berichte **39** (1906), 3960, and **40** (1907), 432.

[2]) See present Report p. 146.

73°; α-fencholenic nitrile, however, is very difficult to saponify; the α-fencholenic acid thereby formed is liquid; $\alpha_D + 32° 35'$. The authors now attempted, on the strength of earlier examinations by Czerny¹) to produce α-fencholenic acid from bromofenchone by the action of alcoholic potash. The resulting acid, however, could not be looked upon as α-fencholenic acid, although the properties of most of its derivatives agreed with those of the α-acid. There was, rather, formed in the first place a new γ-fencholenic acid. The principal difference between the two acids lies in the rotatory power (α-acid $\alpha_D + 32° 35'$, γ-acid $\alpha_D + 52° 30'$) and in the formation of a ketonic acid $C_8H_{12}O_3$, which was only obtained from the γ-fencholenic acid. The amides (m. p. 113 to 114°) and the hydrochlorides (m. p. 90°) of both acids, however, have the same melting points respectively. The lactones obtained by treating the acids with concentrated sulphuric acid, as well as the glycols formed by their reduction with sodium and alcohol, are identical, and it may therefore be taken for granted that the γ-acid is extraordinarily easily converted into the α-acid. The lactone $C_{10}H_{16}O_2$ of the b. p. 122 to 123° (9 mm. pressure) melts at 77 to 78°; the glycol $C_{10}H_{20}O_2$ boils between 158 to 161° (11 mm. pressure) and melts at 58 to 60°. Finally, the oxide $C_{10}H_{18}O$ produced from the glycol of the γ-acid was also identical with the glycol of the α-acid.

Diosphenol. As mentioned by us in our last Report²), Semmler and McKenzie have by their examinations established the degradation and the synthesis of diosphenol. Against this in our opinion entirely justified claim of these two authors, I. Kondakow³) attempts in two long articles to assert his priority, by characterising the results obtained by Semmler and his collaborator, with a reference to his (Kondakow's) earlier work, as almost wholly a confirmation of his own experiments. Kondakow only admits as really new the formation of α-isopropyl-α'-methyl-n-adipic acid by oxidation of the glycol $C_{10}H_{20}O_2$. To Kondakow's reproach that Semmler had, moreover, without justification entered a strange working sphere, the latter emphasises in his reply⁴), that the last work of the Russian scientist on buchu camphor⁵) dates from the year 1901. When subsequently, in 1905, that is to say fully 4 years afterwards, a work of Kondakow on menthols⁶) was published, (in which certainly buchu oil had partly served as crude material), the synthesis of buchu camphor

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¹) Berl. Berichte **33** (1900), 2287; Report April **1901**, 69.
²) Report October **1906**, 140.
³) Chem. Ztg. **30** (1906), 1090, 1100.
⁴) Ibidem, 1208.
⁵) Acta et commentationes Imp. Universitatis Jurievensis (olim Dorpatensis), **1901**.
⁶) Journ. f. prakt. Chem. II. **72** (1905), 186.

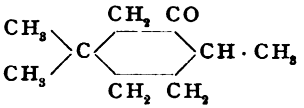
accomplished by Semmler jointly with McKenzie was (as Semmler declares) already completed. A comparison of Kondakow's and Semmler's formulæ, the derivatives produced by Semmler and McKenzie, and finally also the synthesis of diosphenol, speak for themselves in favour of Semmler's claim, which is not shaken by a reiterated reply of Kondakow[1]).

Cyclohexanone and allied bodies. Part IX of the terpene syntheses of W. H. Perkin jun.[2]) deals with the production of cyclopentanone-4-carboxylic acid and cyclohexanone-4-carboxylic acid (δ-ketohexahydrobenzoic acid). We would refer to the original work, and also to Wallach's[3]) experiments with the condensation products of cyclohexanone with hydrochloric acid, and finally to a work by C. Mannich[4]) on the condensation of cyclohexanone with methyl alcoholic sulphuric acid.

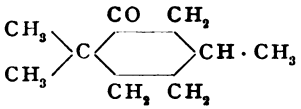
If the anhydrides of 3, 3-dimethyl- or 3, 3, 6-trimethyl pimelic acids are distilled slowly at ordinary pressure, according to G. Blanc[5]), they are converted quantitatively, with loss of carbonic acid and ring-closure, in the corresponding cyclohexanones. 3, 3-Dimethyl cyclohexanone possesses a menthone-like odour, boils at 173°, and yields a semicarbazone of the m. p. 203°.

3, 3, 6-Trimethyl cyclohexanone (I) which in its constitution is closely allied to the pulenone (II) produced by Wallach and Kempe[6]), (as shown by the following formulæ), has a powerful menthone odour, and boils at 186°; its semicarbazone melts at 170°.

I.



II.



Acids.

By his previous experiments E. Erlenmeyer jun.[7]) had found that a salt melting at 135°, whose 1 per cent. solution is inactive, is always formed in alcoholic solution from molecular quantities of brucine and natural cinnamic acid, but under suitable conditions

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[1]) Chem. Ztg. **31** (1907), 90.

[2]) Journ. chem. Soc. **89** (1906), 1640; comp. ibidem **85** (1904), 418: also Berl. Berichte **27** (1894), 102, 965.

[3]) Berl. Berichte **40** (1907), 70.

[4]) Ibidem, 153.

[5]) Compt. rend. **144** (1907), 143.

[6]) Liebig's Annalen **329** (1903), 82; Report April **1904**, 121.

[7]) Berl. Berichte **39** (1906), 285, 1570; Report October **1906**, 152.

also from synthetic cinnamic acid. W. Marckwald and R. Meth¹) now have severally proved that Erlenmeyer's inactive salt cannot consist of equal molecules of brucine and cinnamic acid, as they always obtained under the same conditions solutions of $[\alpha]_D$ —19,5°. Mixtures of cinnamic acid and brucine in the molecular proportion of 2 : 1 also still gave a specific rotation of —4,2°; the melting point of the mixture lay, however, also at 135°. The true neutral brucine salt of storax cinnamic acid, on the other hand, melted indistinctly between 107 and 113°, and contained 1 mol. crystal-alcohol.

In his last work, published in conjunction with Barkow and Herz, Erlenmeyer jun.²) states that there are at least six different cinnamic acids in existence. Five of these can be distinguished from each other by the crystal-form, which has been examined in detail, and also by the differences in melting point and solubility. The acids are: —

1. Isocinnamic acid of Erlenmeyer sen.; m. p. 37 to 38°;
2. Allocinnamic acid of Liebermann; m. p. 68°;
3. Isocinnamic acid of Liebermann; m. p. 59°;
4. *α*-cinnamic acid from Storax, m. p. 134 to 135°;
5. *β*-cinnamic acid prepared from *α*-acid by rearrangement, m. p. 132 to 133°.

   To these acids which have all been examined in detail must be added: —

6. Isocinnamic acid of Erlenmeyer jun. and Allen; m. p. 59°;
7. New, triclinic cinnamic acid, m. p. 127 to 128°.

The acid mentioned under 6. was obtained from the second, more readily soluble amorphous brucine salt, which is formed from anhydrous brucine and allocinnamic acid in absolute alcohol. The crystal-form is the same as that of the acid under 3., but there are differences in the development.

The triclinic acid was obtained:

1. from the brucine salt of the m. p. 151° from allocinnamic acid; 2. from synthetic cinnamic acid by means of frequently repeated recrystallisation from 75 per cent. alcohol, and evaporation to dryness and recrystallisation of the residue of the mother liquor in each case. The crystals separating off from the solutions were identical with storax cinnamic acid.

Marckwald's statements with regard to the composition of the brucine salt (m. p. 135°) of storax cinnamic acid, were confirmed.

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¹) Berl. Berichte **38** (1905), 3499; **39** (1906), 1176, 1966, 2598.

²) Berl. Berichte **40** (1907), 653.

Phenols and Phenol ethers.

In conjunction with his collaborators A. Blumenthal and K. Kowerski, C. A. Bischoff1) has studied the conversion of the carvacryl and thymyl esters of α-bromo-fatty acids with sodium carvacrylate and thymylate respectively, and obtained products with a normal chain. The above-mentioned esters were produced in the usual manner by conversion of the bromides of α-bromo-propionic, butyric, isobutyric, and isovaleric acids with thymol and with carvacrol, or preferably its sodium compound. The α-brominated esters obtained, when again treated with the sodium salts of the phenols in question, yielded carvacryl esters of the α-carvacroxy fatty acids, and thymyl esters of the α-thymoxy acids respectively.

Anethol. J. Th. Henrard2) found that anethol and methyl chavicol, on reduction with nickel and hydrogen, are quantitatively converted in p-propylanisol (b. p. 213,5 to 214,5°, corr.).

Apiol. For the elucidation of the constitution of apiol we are indebted to Ciamician and Silber, and also to Thoms3). Both apiols are converted by alcoholic potash liquor or sodium ethylate in the corresponding isoapiols, the nitrosites of which are described in a work just published by E. Rimini and F. Olivari4). The nitrosite of dill apiol $C_{12}H_{14}O_7N_2$ is a fine yellowish powder melting at 134° with decomposition, and yields with piperidine, suspended in alcohol, when carbonic acid is passed through the filtrate, the corresponding β-nitroisoapiol, $C_{12}H_{13}O_6N$, m. p. 94 to 95°. The β-nitroisoapiol from parsley apiol, produced in an analogous manner, melts at 96°. In aqueous-alcoholic solution this body is converted with hydroxylamine hydrochloride and soda, in apiolaldoxime of the m. p. 160°. By the action of piperidine on the nitrosites, small quantities of an aldehyde are formed, no doubt owing to secondary influences of the piperidine on the nitro compounds.

Asarone. According to R. Fabinyi and T. Széki5), asarone cannot be nitrated, as it then resinifies. But the authors were able to produce a nitro body by nitrating asaronic acid with glacial acetic acid and nitric acid; the carboxyl-group is thereby split off and substituted by the nitro-group. If the 1, 2, 5-trimethoxy-4-nitrobenzene, $(CH_3O)_3 \cdot C_6H_2NO_2$, m. p. 130°, which is thus formed, is reduced

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1) Berl. Berichte **39** (1906), 3840.

2) Chem. Weekblad **3** (1906), 761. Acc. to Chem. Centralbl. **1907**, I. 343.

3) Berl. Berichte **36** (1903), 1714; Report October **1903**, 99.

4) Atti R. Accad. dei Lincei Roma **15** (1906), 138. Acc. to Chem. Centralbl. **1906**, II. 1125.

5) Berl. Berichte **39** (1906), 3679.

with tin and hydrochloric acid, asarylamine (1, 2, 5-trimethoxy-4-amidobenzene), $(CH_3O)_3 \cdot C_6H_2NH_2$, m. p. 95°, is obtained. The benzoyl compound produced for identification melts at 138°; from the asarylamine is formed with asaryl aldehyde a Schiff's base, trimethoxybenzylidene trimethoxyamidobenzene (asarylidene-asarylamine) of the m. p. 142,5°.

When asaronic acid is boiled with sodium nitrite, not only the carboxyl-group is split off, but also a methoxyl-group, and they are replaced by a hydroxyl- and nitroso-group, or a quinone- and oxime-group respectively. The process yields extremely stable bodies, which condense with amines and amidophenols to quinone-imide dyes.

Eugenol. On the 5-azoeugenols and the constitution of the so-called o-oxyazo compounds, a communication has been published by G. Oddo and E. Puxeddu[1]). If diazonium salts are allowed to act on solutions of eugenol in alkalis, there are formed azoeugenols which must be regarded as pseudo acids, as they cannot be accepted as azophenols owing to their stronger acid properties. The alkyl ethers of azoeugenol are true oxyazo bodies; the acetyl derivatives on the other hand contain the acetyl linked to the nitrogen.

E. Puxeddu[2]) has also conjointly with M. Comella, produced nitroisoeugenol. This body, of the formula $C_{10}H_{11}O_4N$, decomposes without melting at 150°. It can be acetylised, and then yields a body $C_{12}H_{13}O_5N$ which on being heated above 200° decomposes.

Thymol. Whilst it was formerly believed that a combination of phenols and trichloracetic acid was impossible, a recent notice[3]) states that *Thymylum trichloraceticum* can be produced in a comparatively simple manner. When experimenting in accordance with the directions, O. Anselmino[4]), however, obtained regularly a product free from chlorine, which was identified as unchanged thymol. Only by thymol sodium with trichloracetylchloride in petroleum ether, a body was obtained which left no doubt as to its identity with the thymol ester of trichloracetic acid. The ester boiled at 12 mm. pressure at 110 to 111°, but could only be produced in liquid form. It was readily saponifiable, and when digested with aniline yielded thymol and the trichloracetanilide melting at 95°.

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[1]) Gazz. chim. ital. **36** (1906), 1. Acc. to Chem. Centralbl. **1906**, II. 1191; comp. also Gazz. chim. ital. **35** (1905), 55. Acc. to Chem. Centralbl. **1905**, I. 1238; — further G. Oddo, Paper read before the VI. Internat. Congress for Applied Chemistry, Rome, **1906**; Chem. Centralbl. **1906**, II. 1811.

[2]) Gazz. chim. ital. **36** (1906), 450; acc. to Chem. Centralbl. **1906**, II. 1607.

[3]) Pharm. Centralh. **46** (1905), 684.

[4]) Berichte d. Deutsch. Pharm. Ges. **16** (1906), 390.

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