

1341
Price, As. 12.]

[Vol. 9A, Part VI, pp. 133 to 148.]

JOURNAL
OF THE
Indian Institute of Science.

CONTENTS.

22 SEP 1926

THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS.
PART XIX. THE ESSENTIAL OIL FROM THE RHIZOMES OF
'KAEMPFERIA GALANGA'.

BY

Puthan Madhathil Bhaskara Panicker, B. Sanjiva Rao and John
Lionel Simonsen.

PART XX. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'CURCUMA
AROMATICA' SALISB.

BY

B. Sanjiva Rao, Vishnu Purushottam Shintre and John
Lionel Simonsen.

PART XXI. THE ESSENTIAL OIL FROM THE WOOD OF
'ERYTHROXYLON MONOGENUM', ROXB.

BY

B. Sanjiva Rao, Vishnu Purushottam Shintre and John
Lionel Simonsen.

DR. M. O. FORSTER, F.R.S., CHAIRMAN OF EDITORIAL BOARD.

JOURNAL
OF THE
INDIAN INSTITUTE OF SCIENCE.

VOLUME I.—(1914-18)

Parts I-XXI.

VOLUME II.—(1918-19).

Parts I.-XV.

VOLUME III.—(1920).

Part I.—Studies on Alcoholysis III. The Alcoholysis of Aromatic Esters and the inhibiting influence of Ortho-substituents. II.—An Automatic Separator for use in Essential Oil Distillation. III.—The Starting Conditions in Synchronous Machines. IV.—Studies in the Fermentation of Cellulose. V.—Tartaric Acid from Tamarinds. VI.—Studies in the Bio-Chemistry of the Mahua Flower. VII.—The Perishing of Paper in Indian Libraries. VIII.—The Conservation of Nitrogen with special reference to Activated Sludge. IX.—Wood Distillation. Part iii. The Distillation of Some Mysore and Baroda Woods and of Certain Waste Products: Part iv. The Tar from Coconut Shells.

VOLUME IV.—(1921).

Part I.—Research Notes on the Acetone Fermentation Process in India. II.—The Specific Gravities of Mixtures of Butyl Alcohol and Water. III.—A Suggested Method for the Extraction of Turpentine, Resin and Gum from the Gum-oleo-resin of *Boswellia Serrata* without the use of Solvents. IV.—Additive Compounds of Arylamines with Nitro-derivatives of Naphthalene. V.—The Manufacture of Thymol from Ajowan. VI.—Phase Transformation and Phase Balancing. VII.—Some experiments in the Use of Antiseptics in the Manufacture of Glue and Gelatine. VIII.—Studies relating to the Bacteria associated with Rice and other cereals. IX.—Preliminary Note on the Purification of Water by Activated Silt. X.—Additive Compounds of *m*-Dinitrobenzene. XI.—The Action of Methyl and Ethyl Alcohols on Esters of 2: 6 Dinitro- and 2: 4: 6-Trinitro-benzoic acids. XII.—Studies in Alcoholysis IV. The Alcoholysis of esters of α β -unsaturated acids and of the corresponding saturated esters. XIII.—The Bio-Chemistry of the Indigenous Indigo Dye Vat. XIV.—The Development of Chemical Industries in India. XV.—Some experiments on the production of Power Alcohol and Paper Pulp from Megasse. XVI.—Sags and Tensions of Solid Copper Overhead Conductors under Indian Conditions.

VOLUME V.—(1922).

Part I.—Studies in Acidolysis: I. The Equilibrium between Acetic Acid Trichloroacetic Acid and their Ethyl Esters; II. The Equilibrium between Acetic Acid, Trichloroacetic Acid and their Methyl Esters. II.—An Attempted Synthesis of Norpinic Acid. III.—Experiments on the influence of *s*-Trinitrobenzene on Reactions in which Arylamines are involved. IV.—Induction Motors used as Synchronous Machines. V.—The Relation Between the Iodine Values and Refractive Indices of some Hardened Vegetable Oils, Part I. VI.—Performance of Three-phase Induction Motors on Unbalanced Voltages. VII.—The Production of Barium Salts from Barytes. VIII.—The Addition of Bromine to the α - and β -Chloro- and bromocinnamic Acids and their Esters. IX.—Oil Splitting by Castor-seed Lipase. Parts V—VII. X.—Some West Coast Vegetable Oils. XI.—Utilisation of Tamarind. XII.—West Australian 'Sandalwood Oil.' XIII.—The Extraction of Caffeine. XIV.—Mechanical Tests of Some Mysore Timbers.

Price, As. 12.]

[Vol. 2A, Part VI, pp. 133 to 148.

JOURNAL
OF THE
Indian Institute of Science.

CONTENTS.

THE CONSTITUENTS OF SOME INDIAN ESSENTIAL OILS.
PART XIX. THE ESSENTIAL OIL FROM THE RHIZOMES OF
'KAEMPFERIA GALANGA'.

BY

Puthan Madhathil Bhaskara Panicker, B. Sanjiva Rao and John
Lionel Simonsen.

PART XX. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'CURCUMA
AROMATICA' SALISB.

BY

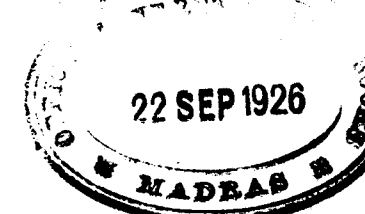
B. Sanjiva Rao, Vishnu Parashottam Shintre and John
Lionel Simonsen.

PART XXI. THE ESSENTIAL OIL FROM THE WOOD OF
'ERYTHRONYLMONOGYNUM', ROXB.

BY

B. Sanjiva Rao, Vishnu Parashottam Shintre and John
Lionel Simonsen.

F. C. M. O. FOLSTER, F.R.S., CHAIRMAN OF EDITORIAL BOARD.



PART XIX. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'KAEMPFERIA GALANGA'.

By Puthan Madhathil Bhaskara Panicker, B. Sanjiva Rao and John Lionel Simonsen.

Kaempferia galanga is grown throughout the plains of India and the Malay States. In Java the plant is cultivated, the root being used for medicinal and culinary purposes, whilst in India it would appear to be mainly utilised in the manufacture of perfumes, a small quantity also being exported.

The oil obtained by the steam-distillation of the rhizomes was first examined by van Romburgh (*Proc. K. Akad. Wetensch.*, 1900, 3, 38; 1902, 4, 618). He showed that the distillate consisted essentially of the ethyl esters of cinnamic and *p*-methoxycinnamic acids with a paraffin hydrocarbon which he considered to be *n*-pentadecane. He does not appear to have examined the terpene fraction of the oil, which, judging from the constants of the oil examined by him, must have been small in quantity.

During the course of an investigation (Hariharan and Sudborough, *This Journal*, 1925, 8A, 189) in which the rhizomes of *K. galanga* were used as a source of *p*-methoxycinnamic acid, a quantity of the non-ester fraction of the oil had accumulated, and we therefore decided to investigate it in detail. We desire to express our indebtedness to Prof. J. J. Sudborough for his assistance in the earlier stages of this work and for his consent to our completing it after his departure from Bangalore.

As will be seen from the experimental part of this paper the separation of the oil from the roots is very tedious, the material during the treatment with steam tending to form a thick magma which becomes practically impermeable. All attempts to overcome this difficulty by varying the fineness of the material distilled were unsuccessful. A satisfactory yield of the oil could only be obtained by air-drying the paste, disintegrating it and returning it to the still.

We have confirmed the presence in the oil of ethyl cinnamate and ethyl *p*-methoxycinnamate and of a paraffin hydrocarbon, whilst in the lower boiling fractions of the oil we have found camphene, *l*- Δ^3 -carene, borneol and *p*-methoxystyrene. *l*- Δ^3 -Carene has not previously been found in nature and its identity was established by the preparation of carene nitrosate (decomp. 147.5°), identical with

✓
A 117-214
N 26-9A-6

the product prepared from α - Δ^3 -carene, and by conversion into β -sylvestrene dihydrochloride. β -Sylvestrene dihydrochloride has been obtained previously only synthetically (Haworth and Perkin, *Journ. Chem. Soc.*, 1913, 103, 2285), and we were therefore unable to identify our product by the method of mixed melting point; when however it was mixed with an equal quantity of α -sylvestrene dihydrochloride and the mixture recrystallised from methyl alcohol carvestrene dihydrochloride (m.p. 52°) was obtained thus leaving no doubt as to its constitution.

The quantity of camphene present was found to be very small and only a few milligrams of isoborneol were formed when the appropriate fraction of the oil was hydrated in the usual manner. The terpene fraction consisted of nearly pure β - Δ^3 -carene since all attempts to identify other terpenes were unsuccessful.

From the higher boiling fractions of the oil p -methoxystyrene was separated in considerable quantity and was identified by the preparation of the *pseudo*-nitrosate and the nitroxime (c.f. Wieland and Semper, *Annalen*, 1908, 358, 68). Although we can offer no evidence to the contrary, it appears to us extremely doubtful if p -methoxystyrene exists preformed in the oil. It has been mentioned above that the steam-distillation was very prolonged and it is therefore possible that p -methoxystyrene arises from hydrolysis of ethyl p -methoxycinnamate to p -methoxycinnamic acid, which then loses carbon dioxide with formation of p -methoxystyrene.

Van Romburgh (*loc. cit.*) considered the paraffin present in the higher boiling fraction of the oil to be identical with n -pentadecane, $C_{15}H_{32}$. Since this conclusion rests solely on a similarity of the physical constants, we are seeking a more stringent experimental proof of the constitution of this hydrocarbon.

EXPERIMENTAL.

A large number of experiments were made with the object of devising a satisfactory process for the distillation of the rhizomes since the extraction of the oil was a very prolonged and tedious process. In Table I are given the results of a number of distillations; in the first distillation the roots were crushed between rollers, in the second and third a toothed crusher was used giving largesized grains, whilst in the other experiments the roots were disintegrated and screened to $\frac{1}{4}$ " to $\frac{1}{8}$ ". It was not found possible to devise a satisfactory process for distilling the material, and it was always necessary to interrupt the distillation, dry and disintegrate the paste formed and return it to the still before all the oil could be distilled.

TABLE I.

No.	Weight of roots distilled	Moisture in roots per cent.	Yield (calculated on the dry material)	Percentage of ethyl p -methoxycinnamate	Duration of distillation in hours
1	62 lbs.	48.2	2.4	0.85	15.5
2	47.5	9.4	2.74	0.54	21.5
3	86.5	12.3	2.58	0.71	35
4	85	13.4	3.18	1.1	34
5	410	12.8	3.88	1.56	125
6	481	14.1	2.7	0.7	85 ¹

In the early stages of the distillation a clear oil passed over but later, on cooling, the distillate set to a solid crystalline cake becoming liquid again towards the end. The constants given in Table II were determined in a number of samples of the total distillate from which the crystalline ester had been removed by filtration at a temperature of 25°, except in the case of No. 3 where the oil was cooled to 15°. It will be observed that the oil had a much lower density than the Java oil examined by van Romburgh but it is not stated if the crystalline ester had been removed or whether the constants were determined in a supersaturated solution.

TABLE II.

No.	n_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Acid value	Sap. value	Sap. value after acetylation
1	0.8836	1.4773	— 4.0°	0.8	105.4	116.3
2	0.8878	1.478	— 4.5°	1.3	99.7	110.1
3	0.8792	1.4783	— 3.9°	1.2	103.4	113.8
4	0.8914	1.4855	— 2.6°	0.5	109.0	115.3
5 ²	1.0174	1.5428	— 16.0°	...	...	6

¹ Distillation not complete.

² Java oil: the density was determined at 25°.

The percentage of ethyl cinnamate and ethyl *p*-methoxycinnamate was determined in Fraction No. 3 by hydrolysing the esters present and titrating the mixture of acids obtained, when it was found to contain 15 per cent. of ethyl cinnamate and 19 per cent. of ethyl *p*-methoxycinnamate on the assumption that no other acids were present.

For the investigation of the neutral oils, the crude oil, from which the crystalline ester had been removed by filtration, was heated on the water-bath for some hours with an excess of alcoholic potassium hydroxide solution, the residual oil separated, dried over magnesium sulphate and distilled under diminished pressure when it was divided into three main fractions:—(1) up to 140°/100 mm. (7.1 per cent.), (2) 140–160°/100 mm. (3.5 per cent.) and (3) above 160°/100 mm. (46 per cent.). Prior to the distillation of Fraction 3 the pressure was reduced to 40 mm. when the bulk of the oil distilled at about 160°. In all cases the percentage yield is calculated on the total weight of the original oil.

The first two fractions were redistilled under diminished pressure using a four-pear young still-head when the following fractions resulted:—

TABLE III.

No.	B.P./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	95–105°	0.8597	1.4691	– 2.29°	2.6
2	105–115°	0.8607	1.4761	– 7.22°	2.1
3	115–135°	0.8828	1.4901	– 7.0°	1.8
4	135–160°	0.9175	1.5005	– 2.35°	1.3

A small fraction which distilled above 160°/100 mm. was added to Fraction 3 (see above). In all distillations of the higher fractions of the oil considerable polymerisation took place towards the end of the distillation with separation of an extremely viscid oil which could not be distilled. This was evidently caused by polymerisation of some *p*-methoxystyrene.

The first two fractions were subjected to repeated systematic fractionation at the ordinary pressure when three main fractions were obtained, the higher boiling oil being added to Fraction 3 (Table III).

TABLE IV.

No.	B.P./683 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	160–163°	0.8586	1.4678	– 0.25° *	0.6
2	163–166°	0.8603	1.4695	– 5.2°	1.7
3	166–170°	0.8634	1.4716	– 10.0°	1.7

Fraction (1), Camphene and 1- Δ^3 -carene.—Preliminary experiments established the absence of *d*-pinene and β -pinene in this fraction of the oil which was found to consist of a mixture of camphene and *l*- Δ^3 -carene. The presence of the latter hydrocarbon was proved by the preparation of carene nitrosate. Recrystallised from a mixture of chloroform and light petroleum the nitrosate decomposed at 147.5° and was identical in every way with the nitrosate prepared from *d*- Δ^3 -carene. (Found 12.8; calc. N, 12.3 per cent.)

On treating this fraction with a mixture of acetic and sulphuric acids a small quantity of an oil was obtained which distilled at about 140–145°/100 mm. and partially crystallised on keeping. After draining the crystals on porous porcelain they melted at 208° and after recrystallisation from light petroleum at 209–210°. There can be little doubt that this substance was *isoborneol* indicating the presence of camphene in the original oil, the quantity of material available being unfortunately insufficient for further investigation.

Fractions (2) and (3), 1- Δ^3 -carene.—These two fractions were found to consist of nearly pure *l*- Δ^3 -carene. The presence of this hydrocarbon was proved by the preparation of the nitrosate (see above) and by its conversion into *l*-sylvestrene dihydrochloride. In one experiment the terpene (15 grams) was dissolved in acetic acid (50 cc.) and the well cooled solution saturated with hydrogen chloride. After remaining overnight the deep brown solution was poured on ice, the oil extracted with ether, the ethereal solution dried and evaporated. The residual oil was distilled under diminished pressure (35 mm.) when practically the whole passed over at 143–144°. The distillate, which solidified completely when cooled in a freezing mixture, was filtered through an ice-cooled funnel and the solid after draining on porous porcelain was recrystallised from methyl alcohol when it separated in beautiful needles melting at 72°. (Found: Cl, 33.8; calc. Cl, 33.9 per cent.)

In chloroform solution (1.2016 gram in 25 cc.) $[\alpha]_D - 17.1^\circ$ was observed, which is in good agreement with the rotation of a specimen

of *d*-sylvestrene dihydrochloride ($[\alpha]_D^{20} 31$). Since direct comparison of the dihydrochloride with *l*-sylvestrene dihydrochloride was not possible, a specimen was mixed with an equal amount of *d*-sylvestrene dihydrochloride, when on crystallisation from methyl alcohol carvestrene dihydrochloride m.p. 52–53° was obtained.

When Fractions (2) and (3) of the oil were titrated in chloroform solution, only one molecule of bromine was absorbed, the sharp end-point indicating the absence of any but bicyclic terpenes in this fraction.

The presence of *L*- Δ^3 -carene having been established in the first three fractions of the oil, the main Fractions (2) and (3) were distilled over sodium, when a nearly pure specimen of *L*- Δ^3 -carene was obtained which had the following constants:—b. p. 166–167°/685 mm. $d_{30}^{30} 0.8606$, $n_D^{30} 1.4684$, $[\alpha]_D^{30} -5.72^\circ$. A sample of the dextrorotatory hydrocarbon distilled at the same temperature when determined under the same conditions.

Fractions 3 and 4 (Table III), p-Methoxystyrene.—These two fractions were carefully refractionated at 100 mm., when a large fraction was obtained which distilled fairly constantly at 135–145° the greater part boiling at 138–140°. A fraction of the oil distilling at this temperature had the following constants:— $d_{30}^{30} 0.9523$, $n_D^{30} 1.5242$,

$[\alpha]_D^{30} -0.99^\circ$. Since during the distillation of the higher fractions of the oil considerable polymerisation took place it was suspected that possibly *p*-methoxystyrene was present. This was proved by the preparation of the *pseudo*-nitrosate. (Wieland and Semper, *loc. cit.*). The oil (3 grams) dissolved in light petroleum (60 cc.) was mixed with dilute sulphuric acid (45 cc.) and to the mixture an excess of sodium nitrite solution was gradually added. The *pseudo*-nitrosate rapidly separated as a brown crystalline solid. This was collected, and washed with alcohol and ether, forming colourless leaflets decomposing at 117° (yield, 3 grams). According to Wieland and Semper the substance decomposes at 107°, but this is probably due to a misprint. (Found: N, 13.7; calc. N, 13.3 per cent.).

The identity of this substance was confirmed by its conversion into the nitroxime by Wieland and Semper's method. It crystallised from benzene in glistening needles melting as stated by these authors at 112–113° (Found: N, 13.9; calc. N, 13.3 per cent.).

Borneol.—During some preliminary experiments a fraction distilling at 100–125°/6 mm. was separated from the oil. This on

redistillation yielded a fraction b.p. 105–110°/13 mm. having the following constants: $d_{30}^{30} 0.9287$, $n_D^{30} 1.4789$. Since from these constants the presence of an alcohol was suspected, the fraction was treated with an excess of phenyl isocyanate when on standing a crystalline urethane was deposited. This after treatment with light petroleum to remove diphenylurea was recrystallised from dilute alcohol when needles m.p. 138–139° were obtained. The identity of this substance with the phenylurethane of borneol was proved by the method of mixed melting point. The yield of phenylurethane was extremely small and it was not possible to prepare any further derivatives of this alcohol.

n-Pentadecane.—The fraction of the oil distilling above 160°/100 mm. was found to consist mainly of *n*-pentadecane. This hydrocarbon was purified by treatment with concentrated sulphuric acid until the acid no longer acquired colour on shaking. It distilled at 125–127°/6 mm., m. p. 10°, $d_{30}^{30} 0.7615$, $n_D^{25} 1.431$, these constants being in good agreement with those previously found for this hydrocarbon.



22
Dec 2, 1961
N2609A-6

PART XX. THE ESSENTIAL OIL FROM THE RHIZOMES OF 'CURCUMA AROMATICA', SALISB.

By B. Sanjiva Rao, Vishnu Purushottam Shintre and John Lionel Simonsen.

The plant *Curcuma aromatica*, Salisb., like *Kaempferia galanga*, the essential oil from the rhizomes of which forms the subject of the preceding communication, belongs to the natural order *Zingiberaceae* and is commonly known as wild turmeric. It occurs wild throughout India and is frequently cultivated especially in Mysore, Travancore, and Cochin. The rhizomes, which are light yellow in colour, are common articles of commerce in many parts of India. At one time the roots were exported for use as a dyeing material and at the present time a form of arrowroot is prepared from them in Travancore. According to Dymock (*Pharm. Ind.*, 1893, 3, 396) the roots are also used medicinally. The essential oil does not appear to have been examined.

On steam-distillation of the disintegrated roots an oil is obtained in a yield of 6.1 per cent. The oil is greenish brown in colour and has a pleasant camphoraceous smell. Examination has shown it to consist to the extent of over 65 per cent. of what appears to be a new laevorotatory monocyclic sesquiterpene for which the name *l-curcumene* is proposed. The hydrocarbon has been characterised by the preparation of the *trihydrochloride* (m.p. 84–85°), the *trihydrobromide* (m.p. 73–74°) and the *nitrosate* (m.p. 100.4°).

In a valuable series of communications Ruzicka (*Helv. Chim. Acta*, 1921, 4, 505 and subsequent papers) has applied Vesterberg's (*Ber.*, 1903, 36, 4200) sulphur method to elucidating the constitution of monocyclic and bicyclic sesquiterpenes, and has shown that in all cases one of the two naphthalene hydrocarbons, cadalene (3:8-dimethyl-5-isopropyl-naphthalene) or eudalene (1-methyl-7-isopropyl-naphthalene) results. When *l-curcumene* is treated with sulphur, although vigorous evolution of hydrogen sulphide takes place, no naphthalene derivative appears to be formed. This new monocyclic sesquiterpene behaves therefore abnormally, and we hope in a future communication to discuss its constitution.

In addition to *l-curcumene* the oil has been found to contain *d*-camphene, *d*-camphor and two sesquiterpene alcohols which are

probably tertiary and which do not yield any crystalline derivatives. The oil also contained either free or in combination a small quantity of *p*-methoxycinnamic acid.

The composition of the oil is approximately as follows:—

<i>d</i> -Camphene			0.8	per cent.
<i>d</i> -Camphor			2.5	" "
Sesquiterpenes (mainly <i>l</i> -curcumene)	...	65.5	" "	
Sesquiterpene alcohols		22.0	" "	
Acids		0.7	" "	
Unidentified		8.5	" "	

EXPERIMENTAL.

Prior to examination the oil was thoroughly dried over anhydrous magnesium sulphate, when it was found to have the following constants:— d_{30}^{30} 0.9139, n_D^{30} 1.5001, $[\alpha]_D^{30}$ -12.5°, acid value 0.9, ester value 2.03, ester value after acetylation 58.66. After treatment with an alcoholic solution of potassium hydroxide to hydrolyse the esters present the oil was distilled under diminished pressure, the results being recorded in Table I.

TABLE I.

No.	B.P./100 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent
1	70–140°	0.8988	1.4709	30.8°	3.0
2	140–170°	0.8898	1.4951	- 17.9°	60.7
3	170–185°	0.9131	1.5022	..	3.7
4	185–200°	0.9576	1.5166	...	24.2
	Residue and loss	...	...	...	8.4

* These four fractions were subjected to a prolonged systematic fractionation when ultimately eleven fractions were obtained.

¹ This was the yield of camphor separated from the appropriate fraction after draining on porous porcelain. The other fractions of the oil contained considerable quantities of the ketone but there does not appear to be any satisfactory method for estimating camphor in essential oils, the ordinary methods for the estimation of ketones, such as Kleber's phenylhydrazine method, giving very low results. The value must therefore be regarded as only approximate.

TABLE II.

No.	B.P./10 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	45-65°	0.8634	1.46	49.4°	0.5
2	65-75°	0.8892	1.4671	39.7°	0.5
3	75-85°	...	...	...	1.25
4	85-105°	0.8998	1.4822	...	0.3
5	105-125°	0.8979	1.4897	-11.1°	1.7
6	125-131°	0.8857	1.4939	-16.8°	23.7
7	131-133°	0.8863	1.4947	-16.5°	35.5
8	133-150°	0.9131	1.4998	... ¹	3.1
9	150-153°	0.9272	1.5051	... ¹	8.9
10	153-158°	0.9667	1.5198	... ¹	13.4
11	158-161°	0.9691	1.5246	... ¹	2.5

Fractions 1 and 2, d-Camphene.—The two fractions were redistilled at the ordinary pressure using a four-pear Young still-head, when a terpene fraction with the following constants was separated:—b.p. 152-155°/687 mm., d_{30}^{30} 0.8597, n_D^{30} 1.4569, $[\alpha]_D^{30}$ 50.6°. These constants indicated the presence of *d*-camphene and this was established by the preparation of the hydrochloride, m.p. 149-150°, the identity being confirmed by the method of mixed melting point. No α -pinene could be detected in this fraction of the oil.

Fraction 3, d-Camphor.—This fraction, which partially solidified in the condenser during distillation, had a strong camphoraceous smell and crystallised almost completely on keeping. The solid was collected and purified by crystallisation from alcohol, when it was found to melt at 175°, and this melting point was not depressed on admixture with a specimen of *d*-camphor from another source. The rotation was found to be 43.6° which is in agreement with that recorded for *d*-camphor, namely, 44°. The identity was further confirmed by the preparation of the oxime which melted at 118°.

Fractions 4 and 5.—These two fractions were found to be a mixture of *d*-camphor and sesquiterpenes; the alcohol-content ($C_{10}H_{16}O$) as determined by acetylation was less than three per cent.

¹ Owing to the green colour of these fractions the rotation could not be determined.

Fractions 6 and 7, l-Curcumene.—Fractions 6 and 7 which formed the bulk of the distillate, consisted essentially of *l*-curcumene. The hydrocarbon was purified by repeated distillation over sodium, when it boiled at 127-129°/6 mm. and had the following constant:— d_{30}^{30} 0.8760, n_D^{30} 1.4929, $[\alpha]_D^{30}$ -21.5°, $[R_L]_D$ 67.67, calc. 67.76 (Found: C, 88.1; H, 11.9; $C_{15}H_{24}$ requires C, 88.2; H, 11.8 per cent.).

l-Curcumene is a faintly yellow oil with a slight and not unpleasant smell. When dissolved in acetic anhydride and treated with a drop of sulphuric acid a bright pink colour develops which becomes dark red on warming.

l-Curcumene trihydrochloride was readily obtained when an acetic acid solution of the hydrocarbon was treated with hydrogen chloride. It separated from methyl alcohol in hexagonal plates, m.p. 84-85° (Found: Cl, 33.6; $C_{15}H_{24}Cl_3$ requires Cl, 34.1 per cent.). It is dextrorotatory, having $[\alpha]_D^{30}$ 26.04° in chloroform.

l-Curcumene trihydrobromide crystallised from methyl alcohol in needles, m.p. 73-74°.

l-Curcumene nitrosate was obtained in poor yield when amyl nitrite and nitric acid were added to an acetic acid solution of the hydrocarbon. It crystallised from light petroleum in rectangular prisms, m.p. 100.4° (Found: N, 9.5; $C_{15}H_{24}O_4N_2$ requires N, 9.5 per cent.).

Fraction 8 consisted of a mixture of sesquiterpenes and sesquiterpene alcohols.

Fractions 9, 10 and 11, were refractionated, when two main fractions were obtained; (i) b.p. 142-144°/7 mm., d_{30}^{30} 0.9586, n_D^{30} 1.5135 (Found: C, 81.9; H, 10.3; $C_{15}H_{24}O$ requires C, 81.8; H, 10.9 per cent.); (ii) b.p. 152-154°/7 mm., d_{30}^{30} 0.9701, n_D^{30} 1.5208 (Found: C, 81.5; H, 10.4 per cent.).

Both fractions were coloured (i) being light green whilst (ii) was deep blue when freshly distilled, the colour however changing to a brownish green on keeping. Since the molecular refractive index was 69.0, both fractions appear to be monocyclic. All attempts to prepare crystalline derivatives by treatment with phthalic anhydride and

p-nitrobenzoyl chloride were unsuccessful and from their marked stability to dehydrating agents it may be concluded that they are tertiary alcohols.

Free and Combined Acids.—The alkaline solution separated from the treatment of the original oil with an alcoholic solution of potassium hydroxide (p. 141) was, after removal of the alcohol, acidified with sulphuric acid and distilled in steam. An analysis of the silver salts of the volatile acids indicated the presence of caprylic acid (Found: Ag, 42.9; calc. Ag, 43.0 per cent.). The residual liquid from the steam-distillation on keeping deposited a crystalline solid which was collected and purified by crystallisation from hot water, when it was found to melt at 170° and was identified as *p*-methoxycinnamic acid by the method of mixed melting point.

PART XXI. THE ESSENTIAL OIL FROM THE WOOD OF 'ERYTHROXYLON MONOGYNUM', ROXB.

By B. Sanjiva Rao, Vishnu Purushottam Shintre and
John Lionel Simonsen.

The number of wood oils, the constituents of which have been studied, is somewhat limited and in view of the attention which has been directed in these laboratories to the chemistry of sandalwood oil (from *Santalum album*, L.), we welcomed the opportunity of studying the oil from the wood of *Erythroxylon monogynum*, Roxb., which is occasionally known as the 'bastard sandal' or 'red cedar'.

E. monogynum is a small tree or shrub found in considerable quantity in all parts of the Mysore State, the hilly parts of the Indian Peninsula and in Ceylon (Cameron, *The Forest Trees of Mysore and Coorg*, 1894, 44; Hooker, *Flora British India*, 1875, I, 414). The timber is in large demand and according to Gamble (*A Manual of Indian Timbers*, 1922, 116) it is one of the most useful trees in the dry evergreen forests. The fruit and leaves are edible, whilst according to Watt (*The Commercial Products of India*, 1908, 525) the leaves and bark are also used medicinally.

The oil obtained by the steam distillation of the wood does not appear to have been used technically, but in Ceylon the crude oil obtained by the destructive distillation of the wood has been used in the preservation of timber and is known locally as 'dummele'.

The oil isolated by steam-distillation of the wood has been the subject of two previous investigations. Schimmel and Co. (*Berichte*, 1904 (April), 100; *J. Soc. Chem. Ind.*, 1905, 23A, 679) obtained an oil in a yield of 2.56 per cent., from which a crystalline alcohol $C_{25}H_{32}O$, m.p. 117–118°, was separated, whilst more recently Shastry (*Quart. J. Mysore For. Assoc.*, 1923, 5, 7) has shown that the Mysore wood yields 1.15 per cent. of an oil the average constants of which are given in Table I. Mr. Shastry very kindly placed a quantity of the oil obtained by him at our disposal for further investigation.

An examination of the oil has shown it to consist of a mixture of sesquiterpenes and sesquiterpene alcohols. In the sesquiterpene fraction the presence of bisabolene was established by the preparation of the characteristic trihydrochloride and trihydrobromide, whilst the colour reactions indicated the presence of cadinene, although unfortunately we were not able to confirm the presence of this hydrocarbon by

the preparation of derivatives. The quantity of sesquiterpene alcohols obtained was very small, and we were unable to find any indication of the existence of the crystalline alcohol described by Schimmel and Co. So it is unlikely that this alcohol is present in the oil separated from wood grown in Mysore.

EXPERIMENTAL.

The oil examined was very viscid and deep reddish-brown in colour; it had the constants given in column 1 of Table I, whilst in columns 2 and 3 are given the constants observed by Schimmel and Co. and Shastry, respectively.

TABLE I.

—	1	2	3
d_{30}^{30} }	0.9499	less than 1	$\{ d_{20}^{20} 0.918-0.927$
n_D^{30} }	1.4998	...	$\{ n_D^{20} 1.4955-1.498$
$[\alpha]_D^{30}$ }	-43.9°	...	-59.0°-51.0°
Acid value	5.7	6.8	...
Ester value	22.7	1.56	5.4-12.1
Ester value after acetylation...	74.7	131.0	45.1-60.9

Prior to fractionation the oil was heated for some hours with an excess of an alcoholic solution of potassium hydroxide to hydrolyse any esters present, the alkaline solution being reserved for later investigation (p. 148). After two distillations under diminished pressure the following fractions were obtained, monocyclic terpenes being apparently completely absent.

TABLE II.

No.	B.P. 10 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Yield per cent.
1	113-134°	...	...	...	0.5
2	134-136°	0.8944	1.4909	-65.5°	54.2
3	136-150°	...	...	...	0.3
4	150-160°	0.9414	1.4987	...	6.6
5	160-170°	0.9686	1.5034	...	6.0

The main fraction (Fraction 2) was distilled twice over sodium, when it boiled at 118-120°/8 mm. and was shown by analysis to have the formula $C_{15}H_{24}$ (Found: C, 88.2, H, 11.9; calc. C, 88.2, H, 11.8 per cent.) The purified terpene had the following constants:— d_{30}^{30} 0.8911, n_D^{30} 1.4909, $[\alpha]_D^{30}$ -71.1°. When dissolved in acetic anhydride and treated with a drop of sulphuric acid a purple coloration developed which gradually changed to indigo-blue and finally became green on warming. These colour reactions are stated to be characteristic of cadinene but, as has already been mentioned, all attempts to prepare crystalline derivatives of this hydrocarbon failed, and if present it can only be in very small amount.

On treatment of an acetic acid solution of the terpene with hydrogen chloride a liquid hydrochloride was formed which on keeping partially crystallised (2.5 grams crystalline hydrochloride from 10 grams of terpene). The hydrochloride separated from methyl alcohol in glistening leaflets, m.p. 79-80° and was shown by analysis to be a trihydrochloride (Found: Cl, 34.4; calc. Cl, 34.0 per cent.). A solution of the hydrochloride in chloroform was optically inactive. It appeared probable that the hydrochloride was bisabolene trihydrochloride which melts at the above-mentioned temperature, and confirmation was afforded by the preparation of the trihydrobromide, m.p. 84° (*Annalen*, 1909, 368, 19. Found: Br, 54.2; calc. Br, 53.7 per cent.).

In view of the very low yield of the crystalline trihydrochloride it was clear that the sesquiterpene was a mixture and it was therefore carefully refractionated using a four-pear Young still-head. Ten fractions distilling between 119° and 125°/8 mm. were obtained, and as will be seen from the constants of the extreme fractions (Table III) there was a marked difference in their physical properties.

TABLE III.

No.	B.P./8 mm.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$
1	119-121°	0.894	1.491	-70.1°
10	123-125°	0.8853	1.4896	-49.1°

Both fractions gave on treatment with hydrogen chloride bisabolene trihydrochloride; but bisabolene was present in much larger amount in the final fraction, the yield of trihydrochloride being more than three times that obtained from the first fraction. All

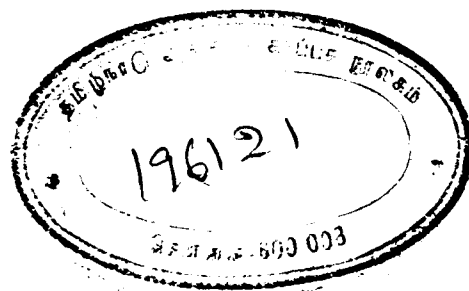
attempts to prepare additional crystalline derivatives were unsuccessful and the nature of the other sesquiterpenes present could not be determined.

Fractions 4 and 5 (Table II) consisted entirely of sesquiterpene alcohols, but owing to the small quantity of material available they could not be purified and no crystalline derivatives were obtained.

The alkaline solution remaining on hydrolysis of the original oil was, after removal of the alcohol, acidified with sulphuric acid and distilled in steam. The silver salt prepared from the distillate was analysed and indicated the presence of capric acid (Found : Ag, 38.8; calc. Ag, 38.7 per cent.).

*Department of Organic Chemistry,
Indian Institute of Science,
Bangalore.*

[Accepted, 1-7-26.]



22
Am 2. 1926
N 26. 9. 1926