VI. ESSENTIAL OIL FROM THE RHIZOMES OF *ACORUS CALAMUS*, LINN.

By N. C. Kelkar and B. Sanjiva Rao.

Acorus Calamus, Linn, the sweet flag, one of the oldest known among the spices, is widely cultivated in many parts of the world as it thrives equally well in both temperate and tropical regions. The fragrance of the plant and its oil appears to increase when the climate in which it is cultivated is warmer, and a distinction is made between the commercial varieties from the several countries from which it is obtained. The volatile oil obtained from the rhizomes has been examined by a number of investigators, our present knowledge of the oil being mainly due to the researches of Thoms and Beckstroem (*Ber.*, 1901, **34,** 1021; 1902, **35,** 3187), Von Soden and Rojahn (*Pharm. Ztg.*, 1901, **46,** 243), Semmler and Spornitz (*Ber.*, 1913, **46,** 3700) and finally Russel (*J. Amer. Chem. Soc.*, 1915, **37,** 2387) who examined the oil from various parts of this plant. A preliminary examination of the oil a few years ago from rhizomes grown in India showed that it was not identical with the known European varieties (*Jour. Ind. Inst. Sci.*, 1925, **8A,** 150) and that it resembled the Java oils. It had also superior germicidal properties and hence a re-examination was considered desirable.

It has been found that in the Indian variety the predominating constituent is the phenolic ether, 1.2.5-trimethoxy-4-propenylbenzene called asarone (82 per cent.), terpenes and sesquiterpene derivatives being minor constituents. The usual commercial varieties contain only about 7 per cent. asarone (Finnemore, *The Essential Oils*, 1926, p. 157) and hence the higher proportion of the active constituent should enhance the value of the oil. The characteristic odour of *calamus* is not due to asarylic aldehyde or asarone but to some constituents boiling about 125–135°/11 mm., not so far identified.

EXPERIMENTAL.

On steam-distilling powdered rhizomes (100 lbs.; moisture 13·6 per cent.) an essential oil (2·4 lbs.) was obtained or 2·8 per cent. calculated on the dry rhizomes. The oil was thoroughly dried over anhydrous magnesium sulphate and was found to have the constants given in column 1, Table I, while in other columns, values recorded by other observers are given for comparison. The sample resembles Java oil.

TABLE I.

	Authors	Bangalore[1]	Semmler[2]	Russel[3]	Commercial[1] oil	Japanese[1] oil	Java[4] oil
d^{30}_{30}	1·069	..	..	..	..	..	..
d^{15}_{15}	1·076	1·0694	·9656	0·9583–0·9981	0·958–0·970	0·970 –0·995	1·0783
n^{30}_{D}	1·5461	..	1·5031	1·5022–1·5172	1·500–1·508	1·5095–1·5175	1·5464
α_D	−1·5°	+5·8°	+27°	+21·7°	+9° to +35°	−12° to +25°	+0·9°
Acid value ..	2·4	1·4	..	5·1-8·1	0·3	0·2	..
Saponification value ..	4·1	5·1	..	21·2–50·6	5–20	1–10	12
Saponification value after acetylation..	15·7	16·1	..	59·6	30–55	16–28	..
Methoxyl ..	36·7	..	..	..	..	..	..

Free acids (*palmitic and heptylic acids*).—The oil (730 g.) was dissolved in ether (2000 c.c.) and shaken with 3 per cent. sodium carbonate solution (200 c.c.). On acidifying the latter with dilute sulphuric acid an oily layer separated which on standing partially solidified. The solid acid was filtered, dried and recrystallised from acetone when it melted at 62–63°. It was confirmed as palmitic acid by the method of mixed melting point and determination of equivalent (0·2136 g. acid required 9·6 c.c. of 0·087 N sodium hydroxide, equivalent 256).

The liquid acids were subjected to steam-distillation and the volatile acids fractionally separated. The silver salts were prepared in the usual way after neutralization with ammonia. On ignition the silver salt left silver (45·2 per cent.) which approximates closely to heptylic acid (Ag, 45·5 per cent.).

Phenols (*Eugenol*).—The ethereal solution was then shaken with 2 per cent. potassium hydroxide solution (300 c.c.). The liberated phenol (0·9 g.) had an odour of cloves and gave a green coloration with ferric chloride. It was confirmed as eugenol by the preparation of the benzoyl derivative (m.p. 69°; mixed m.p. 69–70°) by the Schotten-Baumann process.

Acids present as esters (*palmitic and butyric acids*).—The ether was removed and the residual oil was refluxed on the water-bath with 5 per cent. alcoholic potash (200 c.c.) for 3 hours. The acids which separated consisted of palmitic acid (m.p. 62°; equivalent 256·4) and a liquid acid whose ethyl ester had a strong smell of ethyl butyrate.

Aldehydes (*Asarylic aldehyde*).—The oil after treatment with alcoholic potash was shaken with a saturated solution of potassium

---

[1] *Jour. Ind. Inst. Sci., loc. cit.*

[2] *Loc. cit.*

[3] *Loc. cit.*

[4] Finnemore, *loc. cit.*

metabisulphite (200 c.c.). The aqueous layer on acidification yielded an oil (0·1 g.) which gradually solidified (m.p. 112–113°; asarylic aldehyde melts at 114°).

Distillation of the oil.—The oil (720 g.) from which phenols, aldehydes and acids had been removed, was fractionated ten times using a 4–pear Young's column in the earlier and a 16 in. Widmer column in the later distillations, the final fractions obtained being as follows :—

TABLE II.

Fraction	B.P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{5780}$	$[\alpha]^{30}_{5461}$	$\frac{[\alpha]5461}{[\alpha]5780}$	Weight in grams	Yield per cent. on original oil	Odour	Per cent. asarone
1	70–120°	0·9131	1·4989				0·7	0·1	Camphoraceous	
2	120–125	0·9411	1·5080				0·7	0·1	Calamus like	
3	125–130	0·9661	1·5171	+17·7°	+20·7°	1·17	6·5	0.9	Strong calamus	28·2
4	130–135	0·9663	1·5178	+21·3	+25·0	1·17	5·0	0·7	,, ,,	
5	135–140	0·9965	1·5258	+12·7	+15·1	1·18	7·5	1·0	Camphoraceous	
6	140–145	1·0000	1·5282	+16·2	+19·1	1·18	7·5	1·0	,, ,,	46·0
7	145–150	1·007	1·5313	+15·5	+18·3	1·19	8·0	1·1	Faint	
8	150–154	1·025	1·5357	+10·6	+12·7	1·19	20·0	2·7	,,	
9	154–157	1·068	1·5460	+ 1·8	+ 2·1	1·19	39·5	5·4	Feeble, almost odourless	76·4
10	158–161	1·075	1·5483	+ 1·1	+ 1·3	1·17	42·5	5·8	,, ,,	
11	161–163	1·081	1·5500	+ 0·6	+ 0·7	1·17	36·5	5·0	,, ,,	
12	163	1·083	1·5511	+ 0·2	+ 0·3	1·50	9·0	1·2	,, ,,	79·0
13	,,	1·084	1·5512	,,	+ 0·2	1·00	29·0	4·0	,, ,,	
14	,,	,,	,,	0·0	0·0	..	33·0	4·5	,, ,,	
15	,,	,,	,,	,,	,,	..	55·0	7·5	,, ,,	
16	,,	,,	,,	,,	,,	..	47·5	6·5	,, ,,	81·7
17	,,	,,	,,	,,	,,	..	55·5	7·6	,, ,,	
18	,,	,,	,,	,,	,,	..	53·5	7·3	,, ,,	
19	,,	,,	,,	−0·3	−0·3	1·00	51·0	7·0	,, ,,	
20	,,	,,	,,	−0·5	−0·6	1·20	61·0	8·3	,, ,,	85·1
21	,,	,,	,,	−0·5	−0·6	1·20	25·0	3·4	,, ,,	
22	,,	,,	,,	−1·6	−1·8	1·13	61·0	8·4	,, ,,	82·5
23	,,	,,	1·5502	−1·7	−1·9	1·12	1·5	0·2	,, ,,	
24	,,	,,	1·5491	−2·7	−3·2	1·20	13·0	1·8	,, ,,	78·1

The curves in Fig. 1 connecting the physical constants with percentage composition rise abruptly till 13 per cent.; from 13 to 25 per cent. they are bent towards the abscissæ and from 25 per cent. onwards, are parallel to the abscissæ. The parallel portion corresponds not to pure asarone but to a constant boiling mixture rich in asarone, mixed with smaller quantities of sesquiterpenes and sesquiterpene alcohols. The optical rotation curve is more significant and shows the presence of at least six different constituents.

1.2.5–*Trimethoxy–4–propenyl-benzene* (*Asarone*).—Asarone was estimated by two processes. The methoxyl per cent. by Zeisel's method was found to be 36 in the whole oil while it amounts to 44·7 in pure asarone, showing in the oil an asarone content of 82·6 per cent. The other compounds containing methoxyl are eugenol, methyl-eugenol

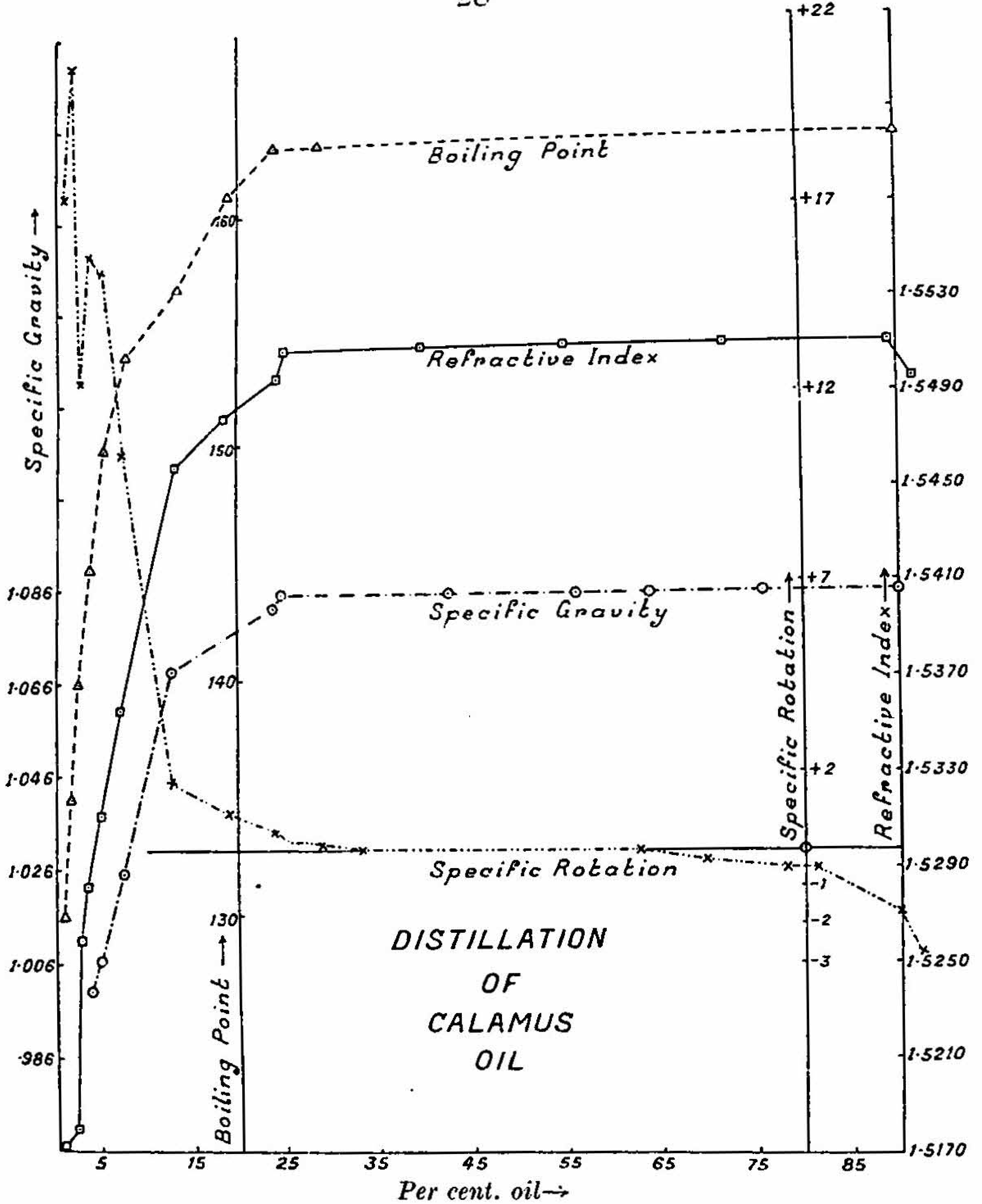

Fig. 1.

and asarylic aldehyde, all of which, however, are present in small amount. The asarone content was also determined directly by polymerisation to *para*asarone and weighing the latter. The oil (10 g.) was cooled in a freezing mixture and 90 per cent. arsenic acid (10 g.) was then added drop by drop, the mixture being kept continually stirred during the addition of the acid. The greenish paste which solidified to a hard mass was treated with cold water to remove excess of arsenic acid. The white sandy powder was then washed with petroleum ether to remove adhering oil. The *para*asarone thus obtained was further purified by dissolving in acetone and reprecipitating with water. It was dried at 100° and then weighed 8·15 g. showing an asarone content of 81·5 per cent. agreeing well with the value obtained by methoxyl estimation. The purified *para*asarone melted at 202–203° agreeing with the figure of Thoms and Beckstroem (*loc. cit.*).

The asarone in the various fractions in Table II was calculated from methoxyl values, 12·7, 20·6, 34·4, 35·6, 36·5, 38·1, 36·9 and 34·9 the corresponding percentage of asarone being given in last column in Table II. The percentage of asarone increases in the higher fractions upto 85 per cent. in fraction 20. None of the fractions yielded any solid asarone on cooling. An attempt to isolate asarone by slow cooling of the fractions from −10° to −25° in an ether bath using solid carbon dioxide only increased the viscosity and the product instead of freezing to crystals gave a syrupy glass-like substance which could be pulled into long threads.

The asarone in fractions 2–8 was converted into *para*asarone by addition of 90 per cent. arsenic acid. The purified *para*asarone (10 g.) was distilled at 14 mm. when a light coloured distillate (3·2 g.) was obtained. The latter solidified on keeping in the ice-chest and was found to be crystalline asarone melting at 62–63° after recrystallising from alcohol (Found : C, 69·1 ; H, 7·5. $C_{12}H_{16}O_3$ (asarone) requires, C, 69·23 ; H, 7·69 per cent.).

Asaronic acid.—A solution of potassium permanganate (11·5 g.) in water (150 c.c.) was added drop by drop to the boiling mixture of fraction 20 (5 g.), sodium carbonate (14 g.) in water (200 c.c.) during half an hour. The manganese dioxide was filtered and washed repeatedly with hot water. The filtrate on being washed with ether and acidified, gave a white precipitate (1·7 g.) which after recrystallising from alcohol melted at 143–144°, thus confirming the presence of asarone.

Fractions 1 *and* 2 (*α–pinene*).—The first two fractions on distillation over sodium gave a colourless oil (0·6 c.c.). On treating the fraction (0·3 c.c.) with amyl nitrite and hydrochloric acid, a small quantity of nitrosochloride (m.p. 105°) was obtained. Though the liquid had an odour of camphene, its presence could not be confirmed by any derivatives.

Fractions 3–8 (*Calamene and eugenol-methyl-ether*).—The residual liquid remaining from the mixture of fractions after asarone was removed as *para*asarone gave the following results on distillation at 11 mm. :—

Fraction	B. P.	d_{30}^{30}	n_D^{30}	$[\alpha]_D^{30}$	Weight in grams	C	H
A	−137°	0·9445	1·5094	+23·9	2·0		
B	143–146	0·9566	1·5143	+28·9	5·0	83·3	10·9
C	146–160	0·9851	1·5222	+22·5	2·0		

These fractions reacted very slightly with sodium. Hence they were mixed together and distilled over sodium at 8 mm. twice, the following two fractions being obtained :

Fraction	B. P.	d^{30}_{30}	n^{30}_{D}	$[\alpha]^{30}_{D}$	Weight in grams	C	H
D	124–129	0·9438	1·5184	+18·1	2·5	86·1	10·7
E	129–132	0·9704	1·5278	+14·5	3·0	78·7	9·1
$C_{15}H_{24}$ requires						88·2	11·8
$C_{11}H_{14}O_2$ (methyl-eugenol) requires						74·2	7·9

The physical constants and the analysis showed that the fractions were not pure hydrocarbons but were mixed with ethers.

When a few drops of concentrated sulphuric acid were added to a glacial acetic acid solution of fraction D, a green coloration was observed indicating the presence of the sesquiterpene calamene (*Apoth.-Ztg.*, 1906, **21**, 879). No nitrosate or hydrochloride was obtained as calamene does not yield any crystalline derivatives. On treating a well-cooled ethereal solution of fraction E (1 g.) with an ethereal solution of bromine (0·5 c.c.) and allowing to stand, a few crystals separated along with an oil which after recrystallisation from alcohol melted at 78–79° showing the presence of eugenol-methyl-ether tribromide (Wassermann, *Ber.*, 1877, **10**, 236).

Fractions 12–18 (*Calamenenol*, $C_{15}H_{24}O$).—These were mixed and treated twice with arsenic acid to separate the asarone completely. The oil, after distilling twice and rejecting the first fraction, had the following constants, b.p. 140–146°/8 mm., d^{30}_{30} 0·9391, n^{30}_{D} 1·5004, α^{30}_{D} +1·8° (Found: C, 82·2; H, 11·2. $C_{15}H_{24}O$ requires C, 81·8; H, 10·9 per cent.). It was thus probably a sesquiterpene alcohol.

Fractions 19–22 (*Calameone*).—After removal of asarone from these fractions a yellowish brown oil was obtained. The oil (10 g.) was dissolved in chloroform cooled in a freezing mixture and petrol-ether gradually added with stirring, when, after some time, a brownish pasty substance separated. The supernatant liquid was removed and the deposit was washed a number of times with petrol when a white powder was obtained. After recrystallising four times from alcohol, it melted at 167–168° (Found: C, 75·5; H, 11·1. $C_{15}H_{26}O_2$ requires C, 75·6; H, 10·9 per cent.).

SUMMARY.

1. The difference between the Indian and the commercial varieties of calamus oil is not due to the presence of any new constituents but due to the predominance of asarone in the Indian oil.

2. The Indian oil contains 82 per cent. of asarone while the usual commercial varieties have only about 7 per cent. of the same constituent.

3. The characteristic odour of calamus which appears to be pronounced in the fraction 125–135°/11 mm. is not due to any of the constituents so far isolated from the oil.

4. The percentage composition of the oil is approximately as follows:—α-pinene and camphene, 0·2; eugenol, 0·3; eugenol-methyl-ether, 1·0; asarone 82·0; calamene, 4·0; calamenenol, 5·0; calameone, 1·0.

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

[Accepted, 30-10-1933.]

2298-33.—Printed at The Bangalore Press, Bangalore City, by T. Subramania Aiyar, Superintendent.