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

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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 the product prepared from *d*-Δ^3-carene, and by conversion into *l*-sylvestrene dihydrochloride. *l*-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 *d*-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 *iso*borneol were formed when the appropriate fraction of the oil was hydrated in the usual manner. The terpene fraction consisted of nearly pure *l*-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*-methoxy-cinnamate	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.	$d_{30^\circ}^{30^\circ}$	$n_D^{30^\circ}$	$[\alpha]_D^{30^\circ}$	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.	$d_{30^\circ}^{30^\circ}$	$n_D^{30^\circ}$	$[\alpha]_D^{30^\circ}$	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.	$d_{30^\circ}^{30^\circ}$	$n_D^{30^\circ}$	$[\alpha]_D^{30^\circ}$	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 l-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 *iso*borneol indicating the presence of camphene in the original oil, the quantity of material available being unfortunately insufficient for further investigation.

Fractions (2) and (3), l-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 (35mm.) 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 goo dagreement 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, $n^{30°}_{D}$ 1·4684, $[\alpha]^{30°}_{D}$ $-5·72^0$. 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, $n^{30°}_{D}$ 1·5242, $[\alpha]^{30°}_{D}$ $-0·99^0$. 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, $n^{30°}_{D}$ 1·4789. Since from these constants the presence of an alcohol was suspected, the fraction was treated with an excess of phenyl *iso*cyanate 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, $n^{25°}_{D}$ 1·431, these constants being in good agreement with those previously found for this hydrocarbon.