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A REINVESTIGATION OF THE ESSENTIAL OIL OF *AFRAMOMUM MALA* (ZINGIBERACEAE)

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Abstract—A gas chromatographic investigation of the essential oil of *Aframomum mala* (Zingiberaceae) has revealed that the constituents are predominantly monoterpenoid. The C_{16} hydrocarbons, α- and β-kayene, reputed to be present in this oil could not be detected.

INTRODUCTION

Two "modifications" of an unusual hydrocarbon, $C_{16}H_{28}$, were described by Worsley[1] as occurring in the essential oil of the seeds of *Aframomum mala* (Zingiberaceae). The essential oil had been separated by distillation into several fractions, one of which Worsley treated with resorcinol to remove cineole. The liquid which remained he fractionally distilled over sodium and under a current of hydrogen to give the two "modifications" which he termed α- and β-kayene. On the basis of molecular refraction data, α- and β-kayenes were said to contain a cyclobutane and a cyclopropane ring respectively. The current interest in small-ring compounds prompted the present reinvestigation of the essential oil of *A. mala*. It was found in fact that the monoterpenoid fraction of this species contains α-pinene, β-pinene, sabinene, α-phellandrene, limonene, and 1,8-cineole.

RESULTS AND DISCUSSION

Consideration of the boiling points given by Worsley[1] for the kayenes and the fact that these hydrocarbons were said to distill in the same fraction as cineole, suggested that the kayenes were monoterpenoid rather than sesquiterpenoid. In fact, the present study of the essential oil of *Aframomum mala* by gas–liquid chromatography (GLC) has not disclosed the presence of a compound, $C_{16}H_{28}$, in the proportion suggested by Worsley, since distillation showed that the monoterpene fraction accounted for 85 per cent by weight of the essential oil. The mole percentage composition of the monoterpene fraction of the essential oil was determined by both "marker" and "internal normalization" techniques[2] as α-pinene (10%), β-pinene (21%), sabinene (14%), α-phellandrene (1%), limonene (15%), 1,8-cineole (39%) and an unknown (1%). The quantity of cineole in the essential oil was also determined by the method of Cross, Gunn and Stevens[3] in which the optical densities for the principal C–O stretching absorption at 1085 cm^{-1} in the i.r. were measured for a series of CS_2-cineole mixtures of known concentration and then for a CS_2 solution of the essential oil; the weight percentage of cineole was again found to be close to 39 per cent. It seems possible that the two "modifications", α- and β-kayene, claimed by Worsley[1] were partially separated mixtures of β-pinene and sabinene.

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[2] A. I. M. KEULEMANS, *Gas Chromatography* (2nd Ed.), Reinhold, New York (1959).

[3] A. H. J. CROSS, A. H. GUNN and S. G. E. STEVENS, *Perfumery and Essent. Oil Record* **49**, 226 (1958).

As suggested by von Rudloff,[4] chemotaxonomic investigations based on GLC examinations of essential oils should become widespread, and it is interesting to note that there is a general similarity in the monoterpene constituents of the essential oils of *A. mala*, *A. angustifolium*[5] and *Elettaria cardamomum*[5] (Zingiberaceae).

EXPERIMENTAL

Seeds of *Aframomum mala* which had been macerated in water for 2 min, were steam distilled to give an oil which was extracted from the water layer with light petroleum (b.p. 40–60°). This extract was dried with sodium sulphate, filtered and the solvent removed under reduced pressure to give the essential oil (1·5 per cent, n_D^{23} 1·4663; Worsley reported 3·2 per cent, n_D^{20} 1·4693). The essential oil was analysed by gas-liquid chromatography on a Pye Argon Chromatograph as in Table 1.

TABLE 1. GAS-LIQUID CHROMATOGRAPHIC RELATIVE RETENTION TIMES OF ESSENTIAL OIL CONSTITUENTS

	Column (temp. in parentheses)					
Constituent	25% Silicone (80°)	20% T.T.P. (88°)	20% Ap.L (107°)	5% Ap.L (73°)	20% P.E.G. 600 (148°)	5% P.E.G. 600 (50°)
α-Pinene	1·00 (28)*	1·00 (10)*	1·00 (6·1)*	1·00 (4·7)*	1·00 (8·0)*	1·00 (2·3)*
β-Pinene	1·26	1·78	1·38	1·46	1·43	1·87
Sabinene			1·23	1·30		2·08
α-Phellandrene		2·37		1·78	2·00	3·12
Limonene	1·68	2·90	1·98	2·30	2·33	3·56
Cineole	1·68	3·40	1·80	2·18		4·43
Unknown			2·00	2·38		6·42

Columns (46 in. × $\frac{1}{8}$ in.): Silicone—Silicone oil, T.T.P.—tritolyl phosphate, Ap.L—Apiezon "L" and P.E.G. 600—polyethylene glycol, M.W. 600, all on Celite, 100–120 mesh.

* Retention time for α-pinene, in min.

The essential oil was also chromatographed on a preparative scale GLC column (120 in × $\frac{3}{4}$ in.) of firebrick coated with 20% silicone oil at 155° and several fractions were collected in traps cooled with liquid air. The first fraction had n_D^{23} 1·4650, b.p. 154–155° at 760 mm (pure α-pinene had n_D^{23} 1·4658, b.p. 154° at 760 mm) and an i.r. absorption spectrum identical with that of α-pinene. GLC analysis of the second fraction whose i.r. absorption bands at 3080, 1650 and 790 cm^{-1} were consistent with an exomethylene group, showed the presence of two components. Ozonolysis of this fraction gave a mixture of ketones whose GLC retention times were identical with those of nopinone and sabina ketone, indicating that the components of the second fraction were β-pinene and sabinene. The physical properties of the third fraction (n_D^{24} 1·4722, b.p. 174–176° at 760 mm) were identical with those of pure limonene (n_D 1·4775, b.p. 176–176·5° at 760 mm). The i.r. spectrum of the fourth fraction (n_D^{22} 1·4625, b.p. 176° at 760 mm) was identical with that of cineole (n_D^{22} 1·4562, b.p. 176° at 760 mm). A resorcinol complex was formed (m.p. 78°) by mixing a saturated solution of resorcinol with fraction 4.

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