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SHORT COMMUNICATION

THE BARK OIL OF *EUCALYPTUS CRENULATA*[1]

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Abstract—The steam-volatile bark oil of *Eucalyptus crenulata* has been shown to contain β-phenylethyl phenylacetate, methyl 3,4,5-trimethoxybenzoate and *p*-cymene. Several minor constituents have been tentatively identified by chromatographic techniques.

IN PART III of this series an investigation of the steam-volatile leaf oil of *Eucalyptus crenulata* Blakely & de Beuzeville has been described.[2] The major components of the oil were methyl 3,4,5-trimethoxybenzoate (*ca.* 47 per cent), *p*-cymene and γ-terpinene.

Steam distillation of the bark yielded 1·5 per cent volatile oil. Gas chromatographic analysis revealed the presence of three major components and several minor components in trace amounts only. The major components were identified as β-phenylethyl phenylacetate (*ca.* 70 per cent), methyl 3,4,5-trimethoxybenzoate (*ca.* 7 per cent) and *p*-cymene (*ca.* 20 per cent). Among the minor components α-pinene, β-pinene, γ-terpinene and isovaleric aldehyde have been tentatively identified by their retention times and by cochromatography with authentic specimens. Isovaleric aldehyde was also identified by paper chromatography of its 2,4-dinitrophenylhydrazone.

Reinvestigation of the steam-volatile leaf oil by gas chromatography showed the presence of a very small amount of β-phenylethyl phenylacetate. It appears thus that the bark oil and leaf oil of *E. crenulata* are qualitatively similar although exhibiting considerable quantitative variation. Similar differences in the compositions of corresponding leaf and bark oils have been observed in *E. macarthuri*[3] and *E. bridgesiana.*[4]

It is of interest that the bark oil of *E. crenulata* resembles the leaf oil of *E. aggregata*[1] in its general composition and particularly in its high β-phenylethyl phenylacetate content.

EXPERIMENTAL

All m.ps are uncorrected. Light petroleum had b.p. 40–60°. Analytical gas–liquid chromatography (GLC) was carried out in a Perkin-Elmer 226 gas chromatograph using 150-ft Golay columns with Carbowax 20M or Castorwax as stationary phase. Preparative GLC was carried out in a Bodenseewerk Perkin-Elmer Vapor Fractometer 116 using 6 ft by ¼ in. aluminium columns packed with Carbowax 20M (15 per cent) on Celite. Silica gel used in column chromatography was Merck, particle size 0·2–0·5 mm. Paper chromatography was carried out with Whatman No. 1 paper.

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[1] Part VI in the series "The Volatile Oils of the Genus *Eucalyptus* (family Myrtaceae)"; for Part V see R. O. HELLYER, E. V. LASSAK and H. H. G. MCKERN, *Australian J. Chem.* **19**, 1765 (1966).

[2] R. O. HELLYER, H. KEYZER and H. H. G. MCKERN, *Australian J. Chem.* **17**, 283 (1964).

[3] H. G. SMITH, *Proc. R. Soc. N.S.W.* **50**, 177 (1916).

[4] R. T. BAKER and H. G. SMITH, *A Research on the Eucalypts and their Essential Oils*, 2nd edition, p. 141, Government Printer, Sydney (1920).

Isolation of Volatile Material

Freshly collected bark from a single cultivated tree growing at Pymble, N.S.W., was steam distilled with cohobation in an all-glass apparatus to yield an oil denser than water. The material came from the progeny of one of the trees used in the leaf oil investigation.[2] The crude bark oil had the following characteristics: oil yield, 1·50 per cent; n_D^{20}, 1·5251; α_D^{25}, −0·47°; d_4^{20}, 1·0225.

Identification of Constituents

A portion of the oil (1 ml) was adsorbed on a silica gel column. Elution with light petroleum (100 ml) yielded a hydrocarbon fraction (0·2 ml). This was submitted to GLC and a homogeneous fraction corresponding to a peak with the same retention time as *p*-cymene was condensed. The identification was confirmed by a comparison of its i.r. spectrum with that of an authentic specimen. The presence of traces of α-pinene, β-pinene and γ-terpinene in the hydrocarbon fraction was established by their retention times and by co-injection of authentic specimens resulting in peak enhancement. Further elution of the column with a mixture of light petroleum and diethyl ether (9:1 by vol., 200 ml) yielded β-phenylethyl phenylacetate (0·72 g), m.p. and mixed m.p. 26–27°. Elution with diethyl ether (200 ml) yielded methyl 3,4,5-trimethoxybenzoate (0·07 g,) m.p. and mixed m.p. 83°. The i.r. spectra of both aromatic esters were identical with those of authentic substances. Another portion of the oil (5 ml) was kept at 80° whilst passing a slow stream of N_2 through it. The effluent N_2 was bubbled through a solution of 2,4-dinitrophenylhydrazine reagent. The slight turbidity was filtered off and its identity established by paper chromatography against authentic isovaleric aldehyde 2,4-dinitrophenylhydrazone. Isovaleric aldehyde has also been tentatively identified in the whole crude oil by its retention time on GLC and by coinjection of an authentic specimen which resulted in peak enhancement of the isovaleric aldehyde peak.

Identification of β-Phenylethyl Phenylacetate in the Leaf Oil of E. crenulata

A portion of the oil (1 ml) used in the original leaf oil investigation was chromatographed on a silica gel column as described above. The presence of β-phenylethyl phenylacetate in the appropriate fraction was established by its retention time and by peak enhancement on coinjection of an authentic specimen.

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