161. *The Chemistry of Western Australian Plants. Part VIII.** *The Essential Oil of* Eucalyptus eudesmioides *Bark.*

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The essential oil isolated from the bark of *Eucalyptus eudesmioides* by extraction and steam-distillation contains cineole, (+)-borneol, and globulol, a sesquiterpene alcohol previously obtained from *E. globulus* oil.

The bark of *Eucalyptus eudesmioides* F. Muell. has a pleasant odour but yields little volatile oil on steam-distillation. However, on extraction with light petroleum and ether, followed by steam-distillation of the extract an essential oil was obtained. From this were isolated cineole, an uncharacterised hydrocarbon fraction, (+)-borneol (as 3 : 5-dinitrobenzoate), and globulol (as 3 : 5-dinitrobenzoate).

Borneol has recently been isolated from the oil of *E. globulus* by Schmidt (Schimmel's Report, 1951, 144), and globulol from a high-boiling fraction of it (Schimmel's Report, 1904, **1**, 46; Semmler and Tobias, *Ber.*, 1913, **46**, 2030) although Ruzicka, Pontalti, and Balas (*Helv. Chim. Acta*, 1923, **6**, 861) were unable to obtain globulol crystalline. They found, however, that the corresponding fraction gave cadalene on dehydrogenation.

Experimental

The finely ground bark (10·65 kg.) of *Eucalyptus eudesmioides* from Laverton, Western Australia, was extracted by percolation with light petroleum (b. p. 60—95°; 22 l.) and then ether (50 l.). On distillation of the solvents a black gum (522 g.) remained and was distilled with steam. The volatile oil weighed 109 g. (1·02%). 71 G. were fractionated through a column (7·5 × 2·5 cm.) packed with glass helices.

Fractions 1—5 [22·1 g., b. p. up to 110°/13 mm., n_D^{17} (of centre fractions) 1·4372—1·4373] were combined and treated with an excess of 50% resorcinol solution. The solid product was washed with light petroleum (b. p. 60—80°), decomposed by alkali and steam-distilled, giving cineole (3·1 g.). It was characterised by the formation of compounds with resorcinol (m. p. 80—85°) and with *o*-cresol (m. p. 55·5°) identical with authentic specimens.

The oil obtained after removal of the light petroleum from the washings of the resorcinol compound was distilled over sodium, forming fractions (i) b. p. 158—166°, n_D^{17} 1·4690, d_4^{17} 0·853, and (ii) b. p. 164—174°, n_D^{17} 1·4690, d_4^{17} 0·855, $[\alpha]_D^{17}$ +27·5°. These hydrocarbon fractions failed to yield crystalline oxidation products indicative of the presence of α-pinene on treatment with permanganate, and were not further investigated.

0·5 G. of fraction 6 (7·3 g., b. p. 110—118°/13 mm., n_D^{17} 1·4375), 3 : 5-dinitrobenzoyl chloride (0·7 g.), and pyridine (1 ml.) were heated at 100° for 15 min., kept overnight at room temperature, and again heated at 100° for 15 min. On cooling, the mixture was washed in ether with 5% sodium hydroxide solution, water, dilute hydrochloric acid, and again water. The

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oily solid which remained after removal of the solvent was dissolved in light petroleum (b. p. 60—80°). Concentration afforded (+)-bornyl 3 : 5-dinitrobenzoate as rectangular plates, m. p. 150—151°, $[\alpha]_D^{18}$ +37° (*c*, 1·05 in $CHCl_3$) (Found : C, 59·3; H, 5·8; N, 7·85. Calc. for $C_{17}H_{20}O_6N_2$: C, 58·6; H, 5·8; N, 8·0%). The m. p. was raised to 155° on admixture with an authentic sample, m. p. 155—156°, $[\alpha]_D^{18}$ +20° (*c*, 1·09 in $CHCl_3$).

2 G. of fraction 7 (15·6 g., b. p. 120—130°/8 mm., d_4^{17} 0·939, n_D^{17} 1·4972, $[\alpha]_D^{17}$ −12·6°) in dry ether (20 ml.) treated with dry hydrogen chloride at 0° for 90 min. became dark red and on removal of the ether there remained a dark red viscous liquid from which no crystals were obtained.

0·6 G. of fraction 9 (6·2 g., b. p. 102—120°/1 mm, n_D^{17} 1·5036), 3 : 5-dinitrobenzoyl chloride (0·7 g.), and pyridine (2 ml.) were heated at 100° for 15 min. and kept overnight at room temperature. Working up as described for fraction 6 gave crystals, which formed needles of globulyl 3 : 5-dinitrobenzoate from light petroleum (b. p. 60—80°). These melted first at 139·5°, resolidified at 140° and melted again at 195—197° with decomp. Hydrolysis of the dinitrobenzoate (110 mg.) with alcohol (10 ml.) and potassium hydroxide (1 g.) for 35 min. under reflux yielded an oil (isolated by means of ether) which crystallised in fine hair-like needles. Fractions 8 (10·3 g., b. p. 130—140°/8 mm., d_4^{17} 0·949, n_D^{17} 1·5020, $[\alpha]_D^{17}$ −10·4°) and 9 were seeded with these crystals and treated with a little light petroleum. After 3 days at room temperature and a week at 0°, globulol (2·1 g.) was obtained and recrystallised from the minimum amount of light petroleum at 0° and then twice from 70% alcohol. It had m. p. 87°, $[\alpha]_D^{17}$ −42·3° (*c*, 1·0 in $CHCl_3$), gave no colour with tetranitromethane, and did not depress the m. p. of an authentic sample, m. p. 88°, $[\alpha]_D^{15}$ −41·8°, isolated from *Eucalyptus globulus* oil.

Globulyl 3 : *5-dinitrobenzoate*, prepared from authentic globulol by the above method, had m. p.s 139·5° and 196—198°, unaltered on admixture with the sample described above (Found : C, 63·5; H, 6·95; N, 6·6. $C_{22}H_{28}O_6N_2$ requires C, 63·4; H, 6·8; N, 6·7%).

Globulol (0·3 g.), pyridine (1 ml.), and phenyl *iso*cyanate (0·3 ml.) remained for 3 days at room temperature. Then 2 drops of water were added. Next day the *phenylurethane* was extracted with light petroleum (b. p. 60—80°) and crystallised from aqueous methanol in needles, m. p. 144·5°, $[\alpha]_D^{15}$ −69° (*c*, 1·84 in $COMe_2$) (Found : C, 77·8; H, 9·0; N, 4·3. $C_{22}H_{31}O_2N$ requires C, 77·4; H, 9·15; N, 4·1%).

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