of $HN_3$, makes the present method unsuitable for studying the dissociation constant of, *e. g.*, $H_3N_3^{++}$. Similar effects have recently been reported by Deno and Perizzolo [7].

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# The Chemistry of the Natural Order Cupressales

## XIX *. The Occurrence of Manool in *Cupressus sempervirens* L.

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During routine examinations of the heartwood extractives of the conifers belonging to the genera *Cupressus* and *Chamaecyparis*, the heartwood of the Mediterranean cypress *Cupressus sempervirens* has been subjected to a brief study. Like Di Modica and Rossi [1] we have found that the main neutral constituents are carvacrol methyl ether and cedrol. The high boiling material, rather surprisingly gave manool [2](I). This diterpene alcohol is characteristic of a section of the genus *Dacrydium*, N. O. Podocarpales, and this is the first time it has been found in another genus of the conifers. Minor neutral constituents of the wood extractives are *d*-borneol, *d*-bornyl acetate and sesquiterpenes. From the acid material carvacrol, $\beta$-thujaplicin and nootkatin were isolated.

*Experimental.* Melting points were taken on the Koflerblock. Only upper limits of b.p. range of the fractions are given.

Finely divided heartwood (4.8 kg, from Le Lavandou, Provence, S. France) was extracted with acetone for 48 h. The acetone was removed and the residue poured, with vigorous stirring, into a tenfold volume of ether, which was filtered, concentrated and similarly poured into light petroleum. The filtered solution was successively shaken with 5 % aqueous potassium hydroxide, 10 % ethanolic potassium hydroxide and water. The alkaline fractions were combined, washed with light petroleum, acidified and extracted with light petroleum. The combined neutral solutions and the acid solution were dried ($Na_2SO_4$) and the solvent evaporated. The neutral fraction yielded 276 g (5.8 %) of a slightly coloured oil (N) and the acid fraction 20.4 g (0.4 %) of a yellow brown oil (A).

*The neutral oil, N,* (166 g) was fractionally distilled through a vacuum jacketed, packed column. Pressure 26 mm. Back pressure 10 mm. Fraction $N_1$, b. p. up to 104°, 1.9 g; $N_2$, 109°, 11.4 g; $N_3$, 110°, 70.0 g; $N_4$, 140°, 16.6 g; $N_5$, 162°, 9.6 g; $N_6$, 172°, 15.2 g; $N_7$, 178°, 2.1 g; $N_8$ (at lower pressure), 5.0 g. The remainder, after a simple distillation at lower pressure, yielded a distillate $N_9$ (31.9 g) and a residue (2.3 g, discarded).

Fractions $N_{1-2}$ deposited a solid (2.5 g) which was recrystallized from ligroin and from nitromethane and sublimed. M. p. and mixed m. p. with *d*-borneol 204—207° (sealed tube, uncorr.), $[\alpha]_D^{22}$ +36.5° ($CHCl_3$; *c* 1.7).

Judging from the distillation curve the non-crystalline part of $N_2$ and fraction $N_3$ (total 79 g) contained the same compound, namely carvacrol methylether. Demethylation with HBr followed by etherification with chloroacetic acid yielded carvacroxy acetic acid, m. p. and mixed m. p. 150—152°. Fraction $N_4$ and the non-crystalline part of $N_5$ (see below) were combined (23.7 g) and distilled through a spinning band column. Pressure 26 mm.

Fraction $N_{41}$, b. p. up to 118°, 3.24 g, $[\alpha]_D^{22}$ +6.6°, $n_D^{21}$ 1.4973; $N_{42}$, 120°, 3.59 g, +18.0°, 1.4882; $N_{43}$, 120°, 3.03 g, +29.5°, 1.4716; $N_{44}$, 128°, 2.31 g, +18.3°, 1.4800; $N_{45}$, 142°, 2.16 g, —7.7°, 1.4968; $N_{46}$, 144°, 2.96 g, —17.8°, 1.5003; $N_{47}$, 156°, 1.17 g, —22.8°, 1.5029; $N_{48}$, 173°, 2.76 g, —17.8°, 1.5071; $N_{49}$, tailings/10 mm 1.31 g, +8.5°; Residue 1.25 g.

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For the fractions $N_{41-44}$ the above data, the carbonyl absorption in the I.R. and the odour indicated *d*-bornylacetate. Saponification and back titration showed the presence of 45 % of the ester. *d*-Borneol was easily isolated by chromatography from the hydrolysate. M. p. and mixed m. p. 204—207° (sealed tube, uncorr.) $[\alpha]_D^{22}$ +36.3° ($CHCl_3$, *c* 3.2). Fractions $N_{45-48}$ showed carbon-carbon double bond absorptions in I.R. and the main part behaved chromatographically as a hydrocarbon while $N_{49}$ was fairly pure cedrol. The hydrocarbon, boiling between bornylacetate and cedrol, may therefore possibly be a mixture of cedrenes.

Fractions $N_{6-7}$ and the crystalline material from $N_5$ were combined (19.9 g), recrystallized from aqueous methanol and sublimed *in vacuo*. M. p. and mixed m. p. with cedrol 87.5—88° $[\alpha]_D^{22}$ +10.0° ($CHCl_3$, *c* 1.1).

Fraction $N_9$ (31.9 g) was distilled through the spinning band column. Pressure 14 mm.

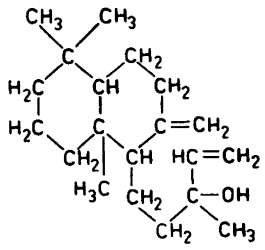
Fraction $N_{91}$, b. p. up to 110°, 0.45 g, $[\alpha]_D^{22}$ —8.5°, $n_D^{21}$ 1.5029; $N_{92}$, 184°, 3.61 g, —6.5°, 1.5136; $N_{93}$, 189°, 2.4 g, +20°, 1.5178; $N_{94}$, 190°, 3.61 g, +29°, 1.5160; $N_{95}$, 192°, 3.40 g, +30°, 1.5148; $N_{96}$, 192°, 2.13 g, +28°, 1.5147; $N_{97}$, 198°, 2.83 g, +30°, 1.5139; $N_{98}$, 210°, 1.86 g, +30°, 1.5167; $N_{99}$, 217°, 1.42 g, +32°, 1.5273; $N_{910}$, 224°, 0.71 g, +23°, 1.5344; $N_{911}$, 229°, 2.34 g, +16°, 1.5348; $N_{912}$, 233°, 0.83 g, +25°, 1.5412; Residue 6.3 g.

Fractions $N_{94-97}$ (12 g or 0.3 %) distilled at fairly constant temperature. Molecular weight determinations (Rast, 289, 292), optical rotation, refractive index and I.R. absorption properties indicated manool. When the thick oily material was seeded with authentic manool it immediately started to crystallise. The solid was recrystallized from light petroleum, m. p. and mixed m. p. 53—53.5°. The infra red absorption spectra were identical.

*The acid fraction A* on standing deposited nootkatin (0.2 g). The remaining oil was distilled at low pressure yielding 13.9 g volatile material, which was subjected to a fractional distillation in the spinning band column. Pressure 27 mm.

Fraction $A_1$, b. p. up to 129°, 1.44 g; $A_2$, 129°, 1.33 g; $A_3$, 156°, 0.86 g; $A_4$, 175°, 0.94 g; $A_5$, 175°, 0.43 g; $A_6$, 216°, 2.46 g; tailings/13 mm, 1.03 g. Residue 5.7 g. The rotation of all fractions was close to zero.

Fractions $A_1$ and $A_2$ according to I. R. data and paper chromatography (in light petroleum, on dimethyl sulphoxide impregnated paper)[3] contained carvacrol and etherification with chloracetic acid gave carvacroxy acetic acid, m. p. and mixed m. p. 150—2°. Fractions $A_3$ and $A_4$, according to paper chromatographic results [4] contained β-thujaplicin (0.5 g), which crystallized when seeded with this compound. M. p. and mixed m. p. 51.5—52.0°. The solid fractions $A_6$ and $A_7$ were largely nootkatin, identified by paper chromatography [4], m. p. and mixed m. p. 95—96°.



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## Syntheses of Nonan-1,2-diol and Nonan-1,3-diol

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During the investigation of the structure of some natural products two diols hitherto not prepared *viz.* nonan-1,2-diol and nonan-1,3-diol have been synthesised. The two diols are, when solid, white, odorless and waxy products, soluble in all the common organic solvents. They react with 3,5-dinitrobenzoyl chloride and yield, under mild conditions, mono-dinitroben-