

CONSTITUENTS OF CEDRUS DEODARA (DEĀR WOOD)

Part II.—Isolation of Dewardiol and Dewarenol

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An unsaturated diol, b.p. 134° C./2 mm., $n_D^{24.5}$ 1.5132, $\alpha_D^{25} + 41^\circ$ and a polyhydric aromatic unsaturated alcohol, m.p. 218° $\alpha_D^{21.5} + 6.5$ being designated as *Dewardiol* and *Dewarenol*, respectively have been isolated from Dear Wood (*Cedrus deodara*).

In the first communication¹ on the chemical constituents of *Cedrus deodara* (Dear wood), the isolation of an unsaturated hydrocarbon Dewarene and an unsaturated monohydric alcohol Dewarol had been reported. The isolation of two other compounds, designated as Dewardiol and Dewarenol is being reported in the present paper.

The alcoholic extractive of dear wood flakes was steam distilled and the non-volatile residue was extracted with ether. After washing with alkali and acid, the solvent was removed and the residue fractionally distilled. The fractions with close refractive indices were combined and the products refractionated a few times. The lower boiling fractions gave some Dewarol. The higher boiling fractions on careful distillation gave a uniform fraction b.p. 134° C./2mm. $n_D^{24.5}$ 1.5132 and $\alpha_D^{25} + 41^\circ$ (10% solution in chloroform), *Dewardiol* analysed for $C_{15}H_{24}O_2$ and showed the presence of two double bonds on microhydrogenation. Both the oxygen functions can be accounted for as alcoholic groups. The analysis showed the presence of two C-CH₃ groups.

On oxidation with chromium trioxide in glacial acetic acid, dewardiol gave a liquid ketone which had one of the alcoholic groups unattacked. It absorbed in the infra-red spectrum at 1710 cm^{-1} showing the presence of an unconjugated six membered or open chain ketone. It had I.R. maxima at 3450, 1690w, 1620w cm^{-1} which showed the presence of OH group and also unsaturation. This ketone could be acetylated to give a mono-acetyl ketone, which absorbed in the infra-red spectrum at 1735, 1710, 1690w and 1620w cm^{-1} thus showing the presence of an acetate group, open chain or six membered ketone, and unsaturation in the molecule.

The acidic fraction of ether soluble steam non-volatile fraction on chromatography over acidic

alumina with ether as eluent yielded a crystalline product, which on crystallisation from methanol-water gave *Dewarenol*, m.p. 216-8°C. The ether insoluble brown resinous mass from the steam non-volatile fraction also on column chromatography over acidic alumina according to Brockman standard gave *Dewarenol*, m.p. 218°C. identical with the sample obtained from the ether soluble fraction, described above.

The analysis for Dewarenol fits in equally well with the three following formulae $C_{21}H_{24}O_6$; $C_{22}H_{26}O_6$ and $C_{25}H_{28}O_7$. The last of the three formulae is favoured on the basis of the analysis of its oxygen functions. It shows the presence of three O-Me groups and four active hydrogen, which accounts for seven oxygen atoms. The ultraviolet spectra of this compound indicates a highly unsaturated structure for Dewarenol, λ_{max} 288i; 283; 230i; 207 $m\mu$ (ϵ 9,000; 10,000; 20,000; 99,500).

Experimental

Analyses were done by Drs. Pascher and Pascher, Microanalytical Laboratories, Bonn, West Germany. The infra-red and ultra-violet spectra were taken by Mr. A. Razzaque, Drugs and Pharmaceutical Division and Photomicrograph was taken by Mr. Ashraf Ali, Physics Division, Central Laboratories, P.C.S.I.R.

Isolation of Dewardiol.—The alcoholic extractive (486.0 g.) from dear wood flakes (5.0 kg.) was subjected to steam distillation. The steam non-volatile fraction (305.0 g.) was extracted with ether, leaving behind a brown powdery resin (47.0 g.). The ether solution was then separated into basic (2.0 g.), acidic (65.0 g.) and neutral (191.0 g.) fractions. The neutral fraction was then rectified by distillation *in vacuo* and the fractions with close refractive

indices mixed together and refractionated. After several of such rectifications a uniform fraction was collected from the higher boiling part which has been named as *Dewardiol*, b.p. 134°C./2mm. $n_D^{24.5}$ 1.5132, α_D^{25} +41° (10% solution in chloroform) (Found: C, 76.2; H, 10.45; O, 13.45; O-CH₃, 0.00; C-CH₃, 11.7; Active hydrogen, 0.658%. Mol. wt. 219. C₁₅H₂₄O₂ requires C, 76.2; H, 10.25; O, 13.55; C-CH₃ for two, 12.8; Active hydrogen for two 0.846%. Mol. wt. 236.3). On microhydrogenation over platinum catalyst in glacial acetic acid, it absorbed 1.8 moles of hydrogen. It had λ_{\max} 270i, 235j, 203.5 m μ (ϵ 1,300; 2,200; 6,000), in the ultra-violet spectrum.

Isolation of Dewarenol.—The brown resinous solid (100 g.) described above was dissolved in methanol and treated with charcoal and the

C₂₂H₂₆O₆ requires C, 68.35; H, 6.75; 24.85%. Mol. wt. 386.5.

C₂₁H₂₄O₆ requires C, 67.75; H, 6.5; O, 25.95% Mol. wt. 372.5.

The acidic fraction obtained from ether soluble steam non-volatile residue, when similarly chromatographed on acidic alumina also gave *Dewarenol*, m.p. 218° mixed m.p. with above undepressed. (Found: C, 67.78; H, 6.61; O, 25.06; O-CH₃, 23.84; C-CH₃, 1.56; Active hydrogen 0.979%, Mol. wt. (rast), 378).

The infra-red spectra of the two samples mentioned above were also identical in all respect.

Oxidation of Dewardiol.—The alcohol (0.2 g.) was oxidized with chromium trioxide (0.2 g.) in glacial acetic acid (2 ml). After 24 hrs. at room

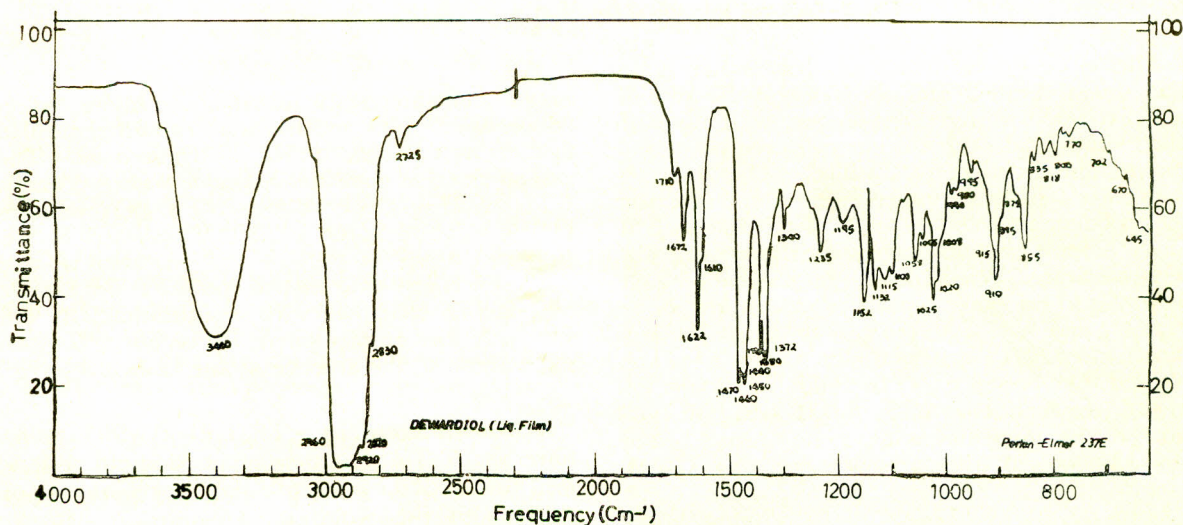


Fig. 1.—Infra-red spectrum of Dewardiol (liquid film).

solvent removed *in vacuo*. It (85.0 g.) was redissolved in a small amount of methanol and evaporated with acidic alumina (Ca~200 g.). The dry powdery mass was transferred with dry benzene onto a column of acidic alumina (2 kg.) in benzene. The benzene-ether (3:1) elute gave a white crystalline powder, which on crystallisation from methanol containing a little water gave octahedral crystals, *Dewarenol*, m.p. 216-8°C., $\alpha_D^{21.5}$ +6.5°. (Found: C, 68.09; H, 6.65; O, 25.01; O-CH₃, 23.5; C-CH₃, 4.81; Active hydrogen 1.07%; Mol. wt. (rast) 412. C₂₅H₂₈O₇ requires, C, 68.15; H, 6.4; O, 25.45; for three O-CH₃, 21.2; for one C-CH₃, 3.45; for four active hydrogen, 0.91%. Mol. wt. 440).

temperature it was made alkaline (cooling) with 50% caustic soda and extracted with ether. The ether extract was dried (anhyd. sodium sulphate) and after removal of solvent the residue was distilled *in vacuo* in a micro distillation set at 2.5 mm. of Hg pressure. The *Oxidised Dewardiol* (Found: C, 74.75; H, 9.7; O, 15.2; Active hydrogen 0.65%, C₁₅H₂₂O₂ requires C, 76.85; H, 9.45; O, 13.7; for one active hydrogen, 0.43%) absorbed in the infra-red spectrum at 3450 (m), 1710 (s) and 1620 (w) cm⁻¹ showing the presence of hydroxyl and ketonic group together with unsaturation.

Acetylation of Oxidised Dewardiol.—The oxidised product (0.1 g.) was acetylated with acetic

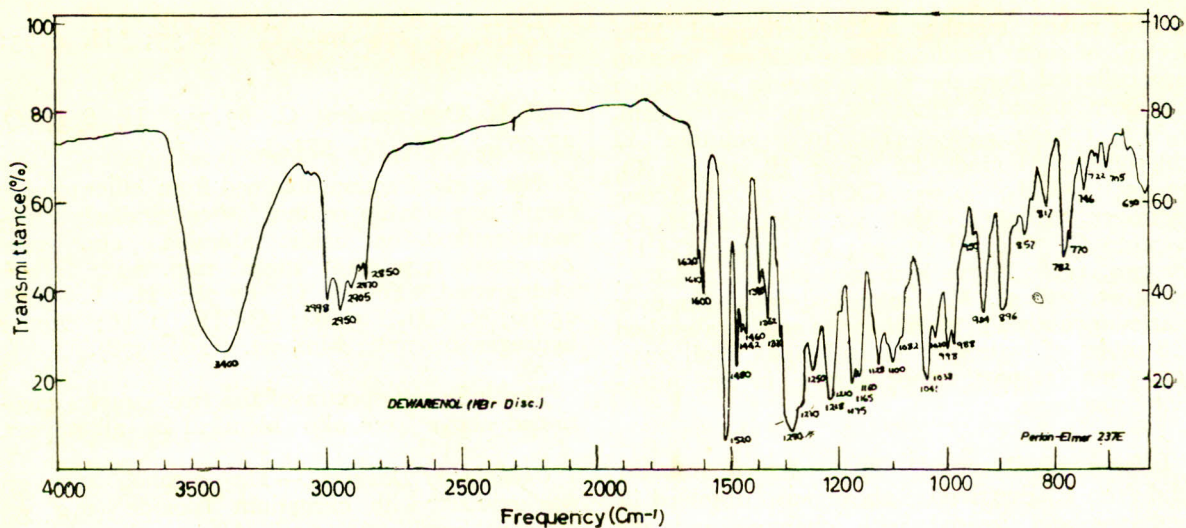


Fig. 2.—Infra-red spectrum of *Dewarenol* (in potassium bromide pellet).

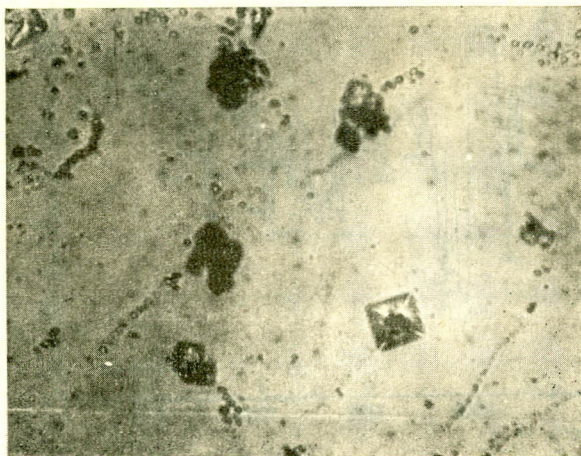


Fig. 3.—Photomicrograph of *Dewarenol*

anhydride (1 ml.) with one drop of acetyl chloride. After leaving overnight at room temperature the

excess acetic anhydride was removed under reduced pressure. The residue was carefully distilled *in vacuo* at 1.9 mm. of Hg, in a micro set. The second fraction gave the *acetylated product* (Found: C, 74.2; H, 9.5; O, 15.7%. $C_{17}H_{24}O_3$ requires C, 73.9; H, 8.8; O, 17.35%) absorbed in the infra-red region at 1735(s), 1710(s), 1690(w) and 1620(w) cm^{-1} showing the presence of acetate and ketone together with unsaturation. It did not have any absorption in the region 3500-3000 cm^{-1} showing the absence of any hydroxyl group.

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Reference

1. M. Manzoor-i-Khuda and M.A. Saleque, *Pakistan J. Sci. Ind. Research*, **6**, 201 (1963).