

CONSTITUENTS OF CEDRUS DEODARA (DĒAR WOOD)

Part I.—Isolation of Dewarene and Dewarol

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An unsaturated hydrocarbon now designated as 'dewarene', b.p. 108°C./0.5 mm., n_D^{26} 1.5105, $[\alpha]_D^{22} + 120^\circ$, $d_{30} 0.982$ and an unsaturated alcohol now designated as 'dewarol', b.p. 130°C./1 mm., n_D^{23} 1.5141, $[\alpha]_D^{25} + 82^\circ$ have been isolated from *Cedrus deodara* locally called 'dear' wood.

Cedrus deodara (locally called 'dear', or 'deodar' wood) is grown extensively in the northern part of Pakistan and India. It is a soft wood with characteristic sweet odour and is extensively used for making furniture in Pakistan. The crude exudate obtained by heating the wood in the absence of air has been claimed to be active against leprosy by Dr. Baden Powell.¹ Other authors have also reported the oily exudation obtained from the tree to be active against this disease.² The wood chips, which are usually wasted by burning, were investigated for the extraction of some useful chemicals out of it. Some Indian workers have reported the isolation of α - and β -himachalene from Himalayan deodar.³ The hydrocarbons have b_{10} 124°, d_{27} 0.9241, $[\alpha]_D^{27}$ 86.54°, n_D^{27} 1.5070 and b_{10} 132°, d_{27} 0.9264, $[\alpha]_D^{27} + 196.78^\circ$, n_D^{27} 1.5130, respectively.

The present investigation was carried out with thin flakes obtained from the wood. The flakes were extracted with alcohol followed by diluted alcohol and the combined extractive freed of the solvent *in vacuo*. The semi-solid mass was then steam distilled and the steam distillate extracted with ether. The ethereal extractive yielded on repeated fractional distillation *in vacuo* a hydrocarbon which has been named as 'dewarene'. The steam non-volatile residue was extracted with ether. The ethereal layer could be separated into an acidic, a basic and a neutral fraction. The neutral fraction on repeated fractionation gave an alcohol, designated as 'dewarol' and an ester fraction which on hydrolysis gave this alcohol and an acid similar to that obtained from the acidic fraction of the ethereal extract. All these fractions are under investigation.

The hydrocarbon 'dewarene' was obtained as a colourless oil, with a pleasant smell similar to that of the raw wood. It is a terpene b.p. 108°C./0.5 mm., n_D^{26} 1.5105, $[\alpha]_D^{22} + 120^\circ$ (liquid phase), d_{30} 0.982 and analysed for $C_{15}H_{24}$. It further showed the presence of two double bonds

(microhydrogenation) and at least one C-CH₃.

Its ultraviolet absorption spectrum shows maxima at 214 and 243 m μ (ϵ 7,800 and 625) in cyclohexane. It reacts avidly with bromine in carbon tetrachloride solution producing hydrobromic acid gas and gives a dibromo derivative, which absorbs three moles of hydrogen on microhydrogenation. Its ultraviolet absorption spectra shows three maxima at 202, 240 and 270 m μ (ϵ 22,500; 9,600 and 6,000) in ethanol. This in the presence of alkali shifts to λ_{max} 211.5 and 264 m μ (ϵ 22,500 and 6,900) in ethanol.

The alcohol, 'dewarol,' is also terpenic in nature and most likely differs from 'dewarene' in having one of the hydrogen substituted by a hydroxyl group. It has b. p. 130°/1 mm., n_D^{23} 1.5141, and $[\alpha]_D^{23} + 82^\circ$ (10% solution in chloroform). It analyses for $C_{15}H_{24}O$ with one active H⁺ and at least one C-CH₃ and absorbs two moles hydrogen on microhydrogenation. The alcohol also reacts with bromine giving off hydrobromic acid gas. In alcoholic solution 'dewarol' shows ultraviolet absorption maxima at 223.5 and 245 m μ (ϵ 5,200 and 1,700).

On oxidation with chromium trioxide, dewarol gives a ketone $C_{15}H_{22}O$ which shows infrared absorption maxima at 1710 cm.⁻¹ (unconjugated ketone) and ultraviolet absorption maxima at 212 and 233.81 m μ (ϵ 3,500 and 1,800) in alcohol. Further work on the elucidation of the structures of dewarene and dewarol is in progress.

Experimental

Analyses were done by Pascher and Pascher, Microanalytical Laboratories, Bonn, West Germany, and the infrared and ultraviolet spectra were recorded by Mr. A. Razzaque Qureshi, Central Laboratories, P. C. S. I. R., Karachi.

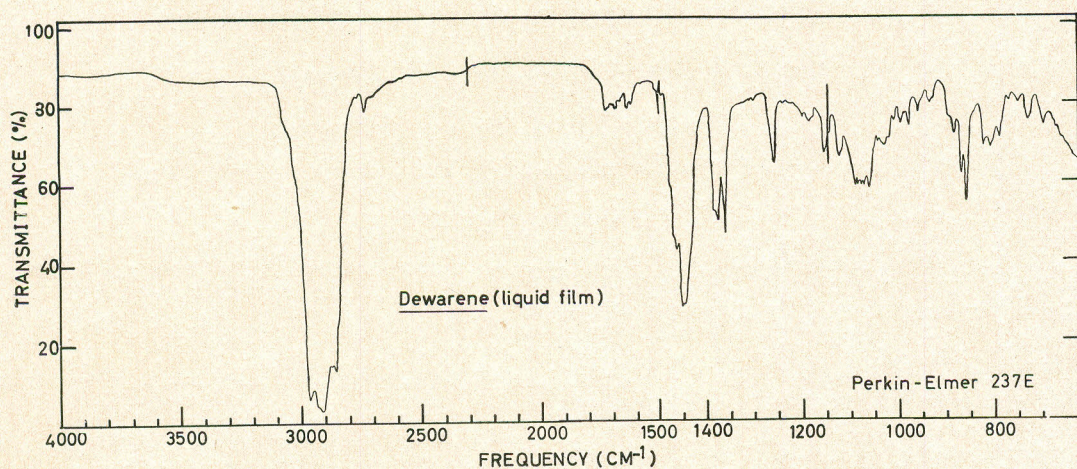


Fig. 1.—Infrared spectrum of 'dewarene', $C_{15}H_{24}$ (liquid film).

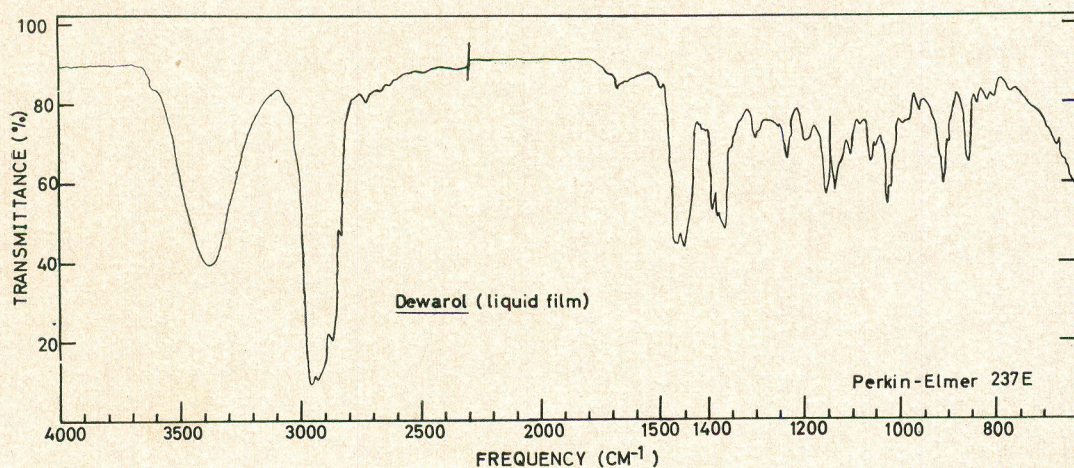


Fig. 2.—Infrared spectrum of 'dewarol', $C_{15}H_{24}O$ (liquid film)

Extraction of Dear Wood.—Small pieces of the wood were mechanically flaked into thin slices. These chips (5 kg; moisture content, 8.2%; ash 29.1%) were extracted with ethanol (12.3 l.) by soaking it in aspirator bottles for 2-3 days. The extraction was repeated 3-4 times with dilute ethanol (80% and then 70%). The residual wood chips did not give any sooty flame on ignition and the ash content was also considerably reduced (12.7%). The combined percolates were freed of solvent in cyclone evaporator below 30°C. (486 g.).

Steam Distillation of the Extract.—The above extractive (486 g.) was subjected to exhaustive steam distillation and the distillate was extracted with ether. The ether layer was dried over sodium sulphate and freed of solvent, when it gave a pleasant smelling oil which showed appreciable

drying qualities.

The residue left after steam distillation was extracted with ether and the ethereal layer shaken with 2N hydrochloric acid, from which a small amount of base could be liberated. On extraction with caustic soda it also gave an acidic fraction leaving behind a neutral mass (A). The ether insoluble mass gave a dark brown resinous mass partly soluble in alkali. All these products are under further investigation.

Isolation of Dewarene.—The steam volatile oil which was found to be neutral in character was fractionally distilled *in vacuo* (ca. ~ 1 mm.). Of the twelve fractions collected, those of middle boiling range which showed similar refractive indices were taken together and refractionated *in vacuo*. Following this procedure, a uniform frac-

tion was finally obtained which on further fractionation gave cuts with very close optical rotation values. On being subjected to gas chromatography also, it showed evidence of its uniformity and was designated as *dewarene*, b.p. 108°C./0.5 mm., n_D^{26} 1.5105, $[\alpha]_D^{22} + 120^\circ$ (liquid phase), d_{30} 0.982 (Found: C, 87.6; H, 11.7; C-CH₃, 6.7; O-CH₃, 0.00% mol. wt., 204; microhydrogenation 1.95 double bonds; C₁₅H₂₄ requires: C, 88.15; H, 11.85; C-CH₃ 7.35%; mol. wt., 204).

Isolation of Dewarol.—The neutral fraction from the residue of steam distillate referred to above as (A) was repeatedly fractionated *in vacuo*. The middle boiling fractions finally gave an alcohol which has been named as dewarol, b.p., 146-48°C./4mm., $n_D^{24.5}$ 1.5156 (Found: C, 80.9; H, 11.0%; microhydrogenation 1.7 double bonds. C₁₅H₂₄O requires C, 81.75; H, 11.0%). The neutral fraction mentioned above when refluxed with 10% alcoholic caustic potash for six hours; on working up and distillation *in vacuo* gave dewarol, as the middle fractions, b.p. 130°C./1 mm., n_D^{23} 1.5141 and $[\alpha]_D^{23} + 82^\circ$ (10% solution in chloroform). (Found: C, 81.0; H, 11.2; O, 7.6; C-CH₃, 8.8 and 9.15; active H⁺, 0.47; O-CH₃, 0.00%; mol. wt., 200; microhydrogenation, 1.7 double bonds. C₁₅H₂₄O requires: C, 81.75; H, 11.0; O, 7.25; C-CH₃, 6.8; active H⁺, 0.46%; mol. wt., 220).

Bromo Derivative of Dewarene.—The hydrocarbon was dissolved in carbon tetrachloride and excess of bromine in carbon tetrachloride added on to

it when hydrobromic acid gas evolved profusely during the reaction. After slight warming the solvent was removed and the liquid residue distilled *in vacuo* in a Hickmann still. The colourless product obtained, analysed as C₁₅H₂₀Br₂. (Found: Br, 40.9. C₁₅H₂₀Br₂ requires: Br, 44.3). On microhydrogenation it absorbed 2.7 moles of hydrogen.

Oxidation of Dewarol.—The alcohol (5 g.) was oxidized with chromium trioxide (5 g.) in glacial acetic acid (50 ml.). After 29 hours at room temperature it was made alkaline and extracted with ether. The ethereal extract was dried over sodium sulphate and after removal of the solvent, the liquid residue was distilled *in vacuo* to give a pleasant smelling ketone, b.p. 132°-38°C./1.8 mm., n_D^{26} 1.5073. (Found: C, 81.90; H, 10.85; O, 7.5; C-CH₃, 9.80%; mol. wt., 202. C₁₅H₂₂O requires: C, 82.5; H, 10.2; O, 7.35; C-CH₃, 6.9; mol. wt. 218).

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