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TERPENOIDS LXXXVIII. ISOLATION OF FERNENOL, A NEW PENTACYCLIC ALCOHOL FROM ARTEMISIA VULGARIS L.*

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The petroleum ether extract of the plant *Artemisia vulgaris* furnished in 0.0013% yield a new crystalline pentacyclic triterpene alcohol, fernenol, m.p. 194°, $(\alpha)_D$ - 24° (c, 0.64; $CHCl_3$), $\nu_{max.}^{CHCl_3}$ 3650 cm^{-1}; NMR[1] signals at 4.75 τ (1H, vinyl proton; trisubstituted double bond), 6.90 τ (1H, $\underline{\underline{H}} - C\overset{/}{\underset{\backslash}{-}} OH$) and 8.95, 9.05, 9.13, 9.17, 9.25, 9.28 τ (24H, eight $C\underline{\underline{H_3}}$ groups) (Found: C, 84.41; H, 11.79. Mol.Wt.[2] 426; $C_{30}H_{50}O$ requires: C, 84.17; H, 11.81% and Mol.wt. 426). Investigations described below show that it has the fernane carbon skeleton and is represented by structure (I).

On acetylation fernenol furnished the acetate (II), m.p. 215-16°, $(\alpha)_D$ - 10° (c, 0.69; $CHCl_3$) $\nu_{max.}$ 1740, 1250 cm^{-1} (Found: C, 82.02; H, 11.22; Molwt.[2] 468; $C_{32}H_{52}O_2$ requires: C, 81.99; H, 11.18% and Mol.wt. 468).

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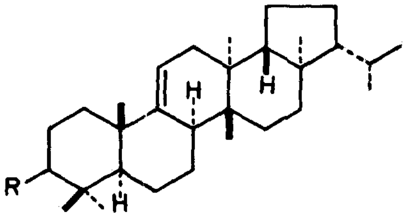
On chromic acid axidation fernenol (I) furnished the ketone (III), m.p.187-88°, $(\alpha)_D$ - 43.2° (c, 1.8, $CHCl_3$) $\nu^{KBr}_{max.}$ 1700 cm^{-1} with a negative cotton effect ORD curve (trough: $[\phi]^{MeOH}_{311}$ - 2310, peak: $[\phi]_{276}$ mμ - 320) of amplitude -20 (Found: Mol.wt.[2] 424. $C_{30}H_{48}O$ requires: Mol.wt. 424).

The presence of a β-oriented equatorial hydroxyl group at the customary 3-position was indicated by the $NaBH_4$ reduction of the ketone (III) to fernenol (I) and the PCl_5 rearrangement of fernenol (I) to the hydrocarbon (IV), m.p. 161-62°, $(\alpha)_D$ - 31° (c, 1.1. $CHCl_3$). NMR[1] signals at 9.08, 9.12, 9.15, 9.18, 9.24 τ (18H, only six CH_3- groups) (Found: Mol.wt.[2] 408. $C_{30}H_{48}$ requires Mol.wt. 408). Conversion of the hydrocarbon (IV) to the diol (V) m.p.182-83° with osmium tetraxide and subsequent oxidation with lead tetraacetate furnished acetone and the ketone (VI) ($\nu_{max.}$ 1750 cm^{-1}, C=0 group in five membered ring).

The position of double bond in fernenol was revealed by the mass spectra of the acetate (II), ketone (III) and hydrocarbon (IV) which exhibited characteristic base peaks at M + - 167.[3] Chromic acid oxidation of the acetate (II) furnished the α,β- unsaturated ketone (VII) m.p. 253°, $\nu_{max.}$ 1750, 1690 cm^{-1} $\lambda^{EtOH}_{max.}$ 244 mμ, ε 9,500, with a positive cotton effect ORD curve (peak: $[\phi]^{MeOH}_{358}$ + 2530, trough: $[\phi]_{307}$ -6850) of amplitude a + 94, comparable with the ORD curve of 12-keto methyl davallate,[3e] (positive cotton effect) having 13α, 14β-methyl groups, but not with the ORD curve of 12-keto-arborinolacetate (negative cotton effect curve), having 13β, 14α-methyl groups at C/D ring junction. The circular dichroism curve of the ketone (VII) showed maxima at 340 ($\Delta\epsilon$ + 2.06) and 271 mμ ($\Delta\epsilon$+ 0.41).

The above data are compatible with structure (I) for fernenol and correlation with a suitable member of the fernane series was considered. Methylation of fernenol (I) with potassium and methyl iodide[4] in benzene furnished the corresponding methylether which was identified as arundoin[5] (VIII) by direct comparison (mixed m.p.) with an authentic sample, kindly furnished by Professor S. Natori.

Prof. S. Natori has kindly informed us that he has isolated fern-9 (11)-en-3β-ol, m.p.192-93°, $(\alpha)_D$ - 19°$(CHCl_3)$ from the rhizomes of Imperata cylindrica P. Beauv var.media Hubbard (Gramineae) and established its structure.[6] We have retained the name fernenol, suggested by Prof.Natori for this alcohol.



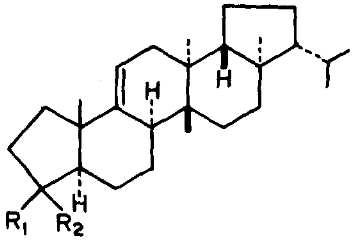
I , R = β-OH

II , R = β-OAc

III , R = O

VII , R = β-OAc and 12-keto

VIII , R β-OMe



IV , R_1, R_2 = $\mathrm{C}\langle^{\mathrm{Me}}_{\mathrm{Me}}$

V , R_1 = OH ; R_2 = $\underset{\mathrm{OH}}{\mathrm{C}}\langle^{\mathrm{Me}}_{\mathrm{Me}}$

VI , R_1, R_2 = O

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