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TERPENOIDS CXVII - STRUCTURES OF CYPERENOL AND PATCHOULENOL. TWO NEW SESQUITERPENE ALCOHOLS FROM THE OIL OF CYPERUS SCARIOSUS*

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In continuation of our previous work[1], two new crystalline sesquiterpene alcohols have been isolated in pure form (TLC and GLC) from the alcoholic fraction of the essential oil obtained from the tubers of Cyperus scariosus. We propose to name them as cyperenol (I) and patchoulenol (II).

Cyperenol (I)

Cyperenol (I), $C_{15}H_{24}O$, m.p. 94°, $(\alpha)_D^{30}$ - 12.1° (C, 4.3, $CHCl_3$), UV: ε_{210} 10,470, shows IR bands at 3333, 1379, 1361, 1018 and 980 cm^{-1}. Cyperenol, on oxidation with Jones' reagent, gives an α,β-unsaturated acid, $C_{15}H_{22}O_2$, UV: λ_{max} 230 mμ, ε 2,340 and IR band at 1704 cm^{-1}, indicating the allylic nature of the primary alcohol.

NMR spectrum of cyperenol does not show any signals due to the presence of vinyl protons, thus the only double bond present in the alcohol is tetrasubstituted and this is supported by the high UV end absorption. It further shows a triplet at 9.05, 9.12 and 9.22τ corresponding to 9 protons (one gemdimethyl group and one secondary methyl group). No signal in the NMR spectrum of the alcohol is attributable to a methyl on a double bond. A clearly discernible signal at 5.91τ represents the two protons of the primary alcoholic group (CH_2OH) and a signal at 7.69τ accounts for the hydrogen of the hydroxyl group which disappears after D_2O exchange. Cyperenol is, thus, a monoethenoid tricyclic sesquiterpene primary alcohol.

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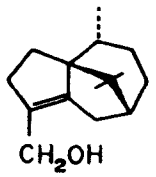
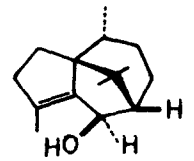
The tosyl derivative of cyperenol on reduction with LAH affords an unsaturated hydrocarbon (III), $C_{15}H_{24}$, b.p. 78°(bath)/0.2 mm., n_D^{30} 1.5017, $(\alpha)_D^{30}$ - 19.73°. This hydrocarbon has been identified as cyperene[2] (III) (GLC, rotation and IR spectrum).

The stereochemistry of cyperene represented by structure III has been established by the Japanese workers[3]. On the basis of these evidences, the stereoformula I represents the structure and stereochemistry of cyperenol.



(I)



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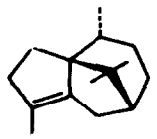
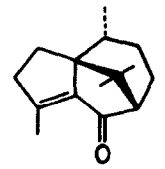


(III)



(IV)

Patchoulenol (II)

Patchoulenol (II), $C_{15}H_{24}O$, m.p. 74°, $(\alpha)_D^{30}$ - 54.23° (C, 3.8, $CHCl_3$), UV: ε_{210} 10,340, shows IR bands at 3333, 1379, 1361, 1064, 1053 and 1020 cm^{-1}. Patchoulenol on oxidation with Jones' reagent gives an α,β-unsaturated ketone, $C_{15}H_{22}O$, m.p. 53°, $(\alpha)_D^{36}$ - 93.73°, (C, 3.51, $CHCl_3$) λ_{max} 263 mμ, ε 9198 and IR band at 1712 cm^{-1}, indicating the allylic nature of the secondary alcohol.

The only double bond in the alcohol is tetrasubstituted as the NMR spectrum of patchoulenol does not show any signal due to the presence of olefinic protons. The NMR spectrum further shows a quartet between 9.02 and 9.32τ corresponding to 9 protons (one gemdimethyl group and one secondary methyl group). A singlet at 8.22τ accounts for a methyl group on a double bond. Another singlet at 8.45τ represents the proton of the hydroxyl group as it disappears on D_2O exchange. A singlet at 5.68τ accounts for one proton on an asymmetric carbon atom carrying hydroxyl group. Thus patchoulenol is a monoethenoid tricyclic sesquiterpene secondary alcohol.

Patchoulenol on reduction with LAH and $AlCl_3$ gives an unsaturated hydrocarbon $C_{15}H_{24}$, $(\alpha)_D^{30}$ - 21°, n_D^{30} 1.5020. This hydrocarbon is found to be identical with cyperene[2] (III) (GLC, rotation and IR spectrum). The α,β-unsaturated ketone, $C_{15}H_{22}O$, m.p. 53°, obtained by oxidation of patchoulenol with Jones' reagent is also identical with patchoulenone[4] (IV) (GLC, mixed m.p., rotation, UV and IR spectra).

The proton on the asymmetric carbon atom carrying hydroxyl group appears to be axial as it shows a singlet at 5.68τ in the NMR spectrum. Patchoulenol has, therefore, been represented by structure II.

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