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TERPENOIDS LXXVII. STRUCTURE OF ISOPATCHOULENONE, A NEW SESQUITERPENE KETONE FROM THE OIL OF CYPERUS SCARIOSUS*

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A new crystalline sesquiterpene ketone, $C_{15}H_{22}O$, m.p. 48°, $(\alpha)_D$ + 39.9° (c, 3.1) (positive tetranitromethane test) has been isolated in a pure form (TLC and VPC) from the carbonyl fraction of the essential oil obtained from the tubers of *Cyperus scariosus*. We propose to name it as isopatchoulenone (I) because of its structural similarity to patchoulenone[1] (II).

Infrared spectrum of isopatchoulenone shows two bands of almost equal intensity at 1663 and 1706 cm^{-1}, which on the basis of its ultraviolet spectrum ($\lambda_{max.}$ 243 mμ, ε 14,235) are evidently due to the presence of a conjugated enone chromophore. Isopatchoulenone, however, did not form any semicarbazone or a 2,4-dinitrophenylhydrazone.

On catalytic hydrogenation (Pt/acetic acid) it absorbs one mole of hydrogen to give the saturated, crystalline, dihydroisopatchoulenone, $C_{15}H_{24}O$, m.p. 74°, $(\alpha)_D$ - 28.4° (c, 3.3), which does not give any colour

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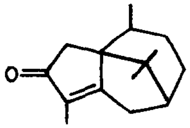
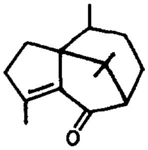
with tetranitromethane. Isopatchoulenone is thus monoolefinic and is tricyclic. The dihydroisopatchoulenone in its infrared spectrum shows an intense band at 1742 cm^{-1} indicating the presence of the ketonic function on a five-membered ring.

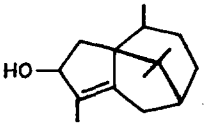
NMR spectrum of isopatchoulenone does not show any signals due to the presence of vinyl protons, thus the double bond in the ketone is tetrasubstituted. It further shows a doublet at $\tau = 9.36$ (3H, $J = 7$ c/s) corresponding to a secondary methyl group, two signals at $\tau = 9.2$ (3H) and 8.87 (3H) corresponding to a gem dimethyl group and a signal at $\tau = 8.32$ (3H) due to a methyl group on a double bond. A clearly discernible AB quartet at $\tau = 7.62$ represents the two α protons to the carbonyl group. Reduction of iso-patchoulenone with lithium aluminium hydride gives the corresponding crystalline alcohol, $C_{15}H_{24}O$, isopatchoulenol (III), m.p. 140°, $(\alpha)_D - 53^\circ$ (c, 2.0); infrared band at 3226 cm^{-1} (-OH). Wolff-Kishner reduction of dihydroisopatchoulenone gives a saturated hydrocarbon, $C_{15}H_{26}$, $(\alpha)_D - 76^\circ$ (c, 4.1), which according to its infrared spectrum (intense bands at: 1124, 975, 930 and 848 cm^{-1}) was identical with patchoulane[2] (intense bands at: 1125, 970, 937 and 850 cm^{-1}), prepared by the reduction of α-patchoulene. On the basis of this data, only two structures (I) & (II), follow for isopatchoulenone.



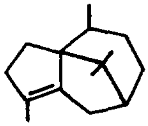
I



II.



III



IV

Structure (II), however, represents patchoulenone,[1] m.p. 52.5°, $(\alpha)_D$ - 97.1° (c, 8.2), recently characterised by Sorm *etal*. Isopatchoulenone is, therefore, represented by (I). In conformity with this a sharp infrared absorption band at 1416 cm^{-1} in isopatchoulenone and at 1422 cm^{-1} in its dihydroproduct show the presence of a methylene group in α position to the carbonyl group.

Further chemical evidence for the confirmation of structure I was obtained by the oxidation of the sesquiterpene hydrocarbon cyperene[1] (IV), $(\alpha)_D$- 21° (c, 4.0), b.p. 94° (bath)/1 mm., isolated by us[+] from the present oil in a pure form (TLC & VPC) with t-butyl chromate. Among the products of oxidation (TLC, 4 spots) isopatchoulenone was found to be present from a comparative TLC study with the natural isopatchoulenone. The oxidation product was reduced with lithium aluminium hydride to afford the crystalline alcohol, identical with isopatchoulenol (III), m.p. and mixed m.p. 140°. Oxidation of this crystalline alcohol with Jones reagent gives a ketone, m.p. and mixed m.p. 48°, $(\alpha)_D$ + 38° (c, 2.1), identical in all respects with the natural isopatcheulenone (I).

References

1. B. Trevedi, O. Motl, V.Herout and F.Sorm, Coll.Chem.Comm., 29, 1675 (1964).
2. J. Pliva, M.Horak, V.Herout and F.Sorm, Die Terpene, Sammlung der Spektren Und Physikalischen Konstanten. Teil 1: Seskviterpene. Akademie Verlag, Berlin 1960.

All compounds described gave satisfactory analysis and $(\alpha)_D$ are for $CHCl_3$.

+ This hydrocarbon was initially isolated and partially characterised in this laboratory and presented in the Ph.D. thesis (1960)- Agra University by the guest worker Dr. I.C. Nigam (now in Ottawa, Canada). He also carried out oxidation of cyperene with chromic acid in acetic acid but could not fully characterise the products.