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STRUCTURE OF THE SESQUITERPENIC HYDROCARBON CYPERENE

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During the study of the composition of the essential oil from Cyperus rotundus L. (1) of Chinese origin we have isolated a sesquiterpenic hydrocarbon $C_{15}H_{24}$ (20%) in pure form. The sesquiterpene was identical in its chemical and physical properties with "cyperene I", a sesquiterpenic hydrocarbon of unknown structure (2). Since we have previously proved (1) that "cyperene II" is identical with β-selinene, we now propose the name "cyperene" for "cyperene I". We have established its structure to be as I.

Cyperene $C_{15}H_{24}$, m.w. 204 (mass spec.), b.p. 104°/5 mm, n_D^{20} 1.5058, d_4^{20} 0.9354, $[\alpha]_D^{20}$ -20° (in subst.) affords with osmium tetroxide a crystalline diol $C_{15}H_{26}O_2$ m.p. 147.5°, $[\alpha]_D^{20}$ ± 0°. On hydrogenation in acetic acid in the presence of platinum oxide it affords a completely saturated dihydroderivative $C_{15}H_{26}$; therefore cyperene is a tricyclic hydrocarbon. An infrared spectrum of the natural substance shows a rarely observed absorption at 1700 cm^{-1}, and in Raman spectrum a very strong peak at 1695 cm^{-1}, showing that double

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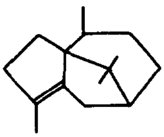
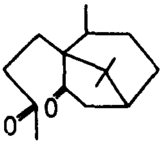
bond is tetrasubstituted.A point also brought out by NMR spectrum[++] (Fig. 1).An infrared spectrum further shows two symmetrical peaks at 1366 $\mathrm{cm^{-1}}$and 1388 $\mathrm{cm^{-1}}$ corresponding to $\genfrac{}{}{0pt}{}{\mathrm{CH_3}}{\mathrm{CH_3}}\!>\!\mathrm{C}\!<$ group which is in agreement with NMR spectrum (Fig. 1) - singlet at τ = 9.25.The signals at τ - 9.05 and 9.16 show the presence of $\mathrm{CH_3.CH}\!<$ group.The remaining fourth methyl group is situated on the double bond (τ=8.38).

In agreement with the above data the ozonisation of cyperene gave a crystalline diketone (II) m.p. 78.5° , $[\alpha]_D^{20}$ + 23.0° (monosemicarbazone m.p. 222°).An infrared spectrum showed presence of a $\mathrm{CH_3CO}$- group (1360 $\mathrm{cm^{-1}}$) and a five membered ring ketone (1735 $\mathrm{cm^{-1}}$); the absorption band at 1415 $\mathrm{cm^{-1}}$ indicated the presence of $-\mathrm{CH_2}-$ group α



I



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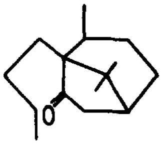

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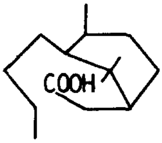

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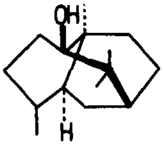

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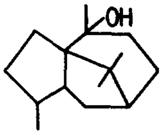

VI

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to the carbonyl group.NMR signals at τ = 7.95 (CH_3CO-), τ = 8.08 (CH_2CO-), τ = 8.83 and 9.06 ($\begin{matrix}CH_3\\CH_3\end{matrix}\!>C<$) and τ = 9.23 , 9.33 ($CH_3CH<$).

Wolff-Kishner reduction of the diketone II afforded a five membered ring ketone $C_{15}H_{26}O$ (III) ν_{max}^{CO} 1740 cm^{-1} which according to infrared spectrum had in α position $-CH_2-$ group (ν_{max} 1420 cm^{-1}).The observation that on equilibration with deuterium oxide only two hydrogen atoms were substituted by deuterium shows that the second α carbon atom must be quarternary.In agreement to this,photochemical cleavage of ketone II afforded an acid IV (methyl ester prepared (diazomethane) : ν_{max}^{CO} 1741 cm^{-1} and 1436 cm^{-1} $-COOCH_3$).

Dihydrocyperene d_4^{20} 0.9340, n_D^{20} 1.4975, $[\alpha]_D^{20}$ -61.2° was identical with the saturated hydrocarbon obtained from patchoulenone (1,3) as well as the saturated hydrocarbon obtained from patchouli alcohol (V) on hydrogenation of its isomerized dehydrated product (4,5).Identity of these compounds was further confirmed by comparison of their mass spectra.The identity of the saturated hydrocarbons and above mentioned reactions lead us to propose structure I for cyperene.

Previously mentioned structure of patchouli alcohol (VI) which was published by Büchi and co-workers (4),on the basis of chemical studies is now corrected as V after its reinvestigation by X-ray analysis (5).

It was concluded that during the pyrolysis of patchouli alcohol acetate the carbon skeleton undergoes rearrangement. No analogous rearrangement takes place during the preparation of dihydroderivative of cyperene as is evident from NMR spectrum of cyperene and its ozonisation product II which shows the presence of $CH_3CH<$ group; this could not been the case if cyperene had the carbon skeleton of patchouli alcohol (V).However,we are of the opinion that both skeletons exist in Nature; we suggest therefore the name isopatchoulane type for the skeleton of cyperene and patchoulenone.

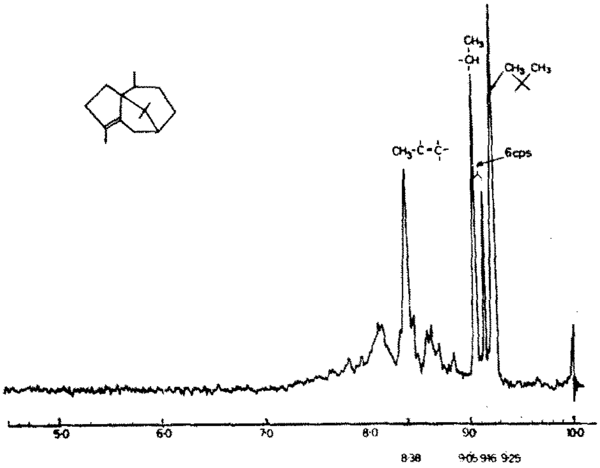

Fig.1. NMR spectrum of cyperene
(in CCl_4 using TMS as internal standard).

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