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# TERPENOIDS XC

## Khusimol, A New Sesquiterpene Alcohol*

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A systematic chemical examination of the dextrorotatory South Indian vetiver oil of the cultivated type has been undertaken in this Laboratory. Isolation and characterisation of a new cadalenic hydrocarbon from this oil has been reported.[1] From the high boiling fraction (100-140°/0.3 mm.) of the oil a new sesquiterpene alcohol has been isolated by extensive column chromatography. We propose to name it as khusimol and present evidences for its partial structure as (I).

Khusimol (I), $C_{15}H_{24}O$ (VPC and TLC pure) has the following properties, b.p. 140-45°/0.07 mm., $n_D^{24}$ 1.5183, $(\alpha)_D^{27}$ + 24.56° (c, 4.2 chloroform), IR bands (Fig.1), 3401, 1025 $cm^{-1}$ ($-CH_2OH$), 1631, 891 $cm^{-1}$ ($>C{=}CH_2$), 1370, 1353 $cm^{-1}$ ($>C<^{CH_3}_{CH_3}$ or $H_3C{-}\underset{H}{C}{-}CH_3$ ), NMR signals (Fig.2); singlet 8.99τ(6H) $>C<^{CH_3}_{CH_3}$ ; 7.5τ(1H) - OH; 6.62τ(2H) - $CH_2OH$; doublet 5.62, 5.49τ(2H) $>C{=}CH_2$. On oxidation with Jones

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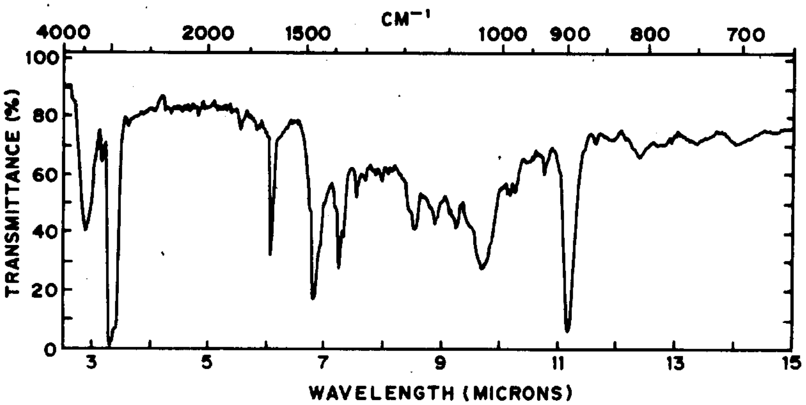

CM⁻¹
4000
2000
1500
1000
900
800
700
100
80
60
40
20
0
TRANSMITTANCE (%)
3
5
7
9
11
13
15
WAVELENGTH (MICRONS)

FIG. I.

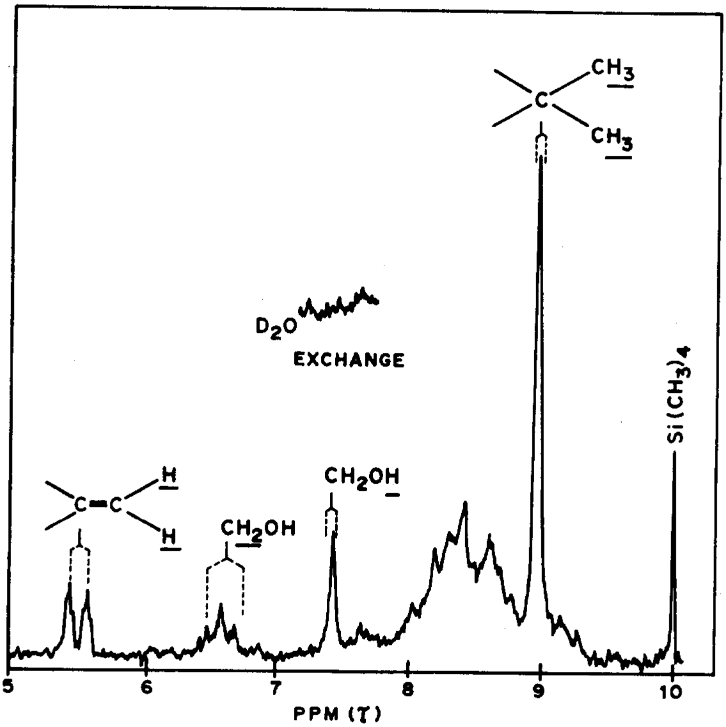

CH3
C
CH3
D2O
EXCHANGE
Si(CH3)4
H
C=C
H
CH2OH
CH2OH
5
6
7
8
9
10
PPM (τ)

FIG. II.

reagent khusimol gives an unsaturated acid (II), $C_{15}H_{22}O_2$, IR bands 3106, 1695, 1634, 1370, 1353, 891 $cm^{-1}$; cyclohexylamine salt crystallised from acetone, $C_{21}H_{33}ON$, m.p. 145°, methyl ester (III), $C_{16}H_{24}O_2$ (VPC pure), b.p. 98-100°/0.07 mm., $n_D^{26}$ 1.417; $(\alpha)_D^{26}$ + 41.7°; IR bands 1735, 1638, 891 $cm^{-1}$; NMR signals, two singlets 8.96, 8.94$\tau$(6H) $-\overset{|}{\underset{|}{C}}<^{CH_3}_{CH_3}$, singlet 6.38$\tau$(3H) - $COOCH_3$, doublet 5.45, 5.31$\tau$(2H) $>C=CH_2$. The alcohol obtained by reduction of the methyl ester (III), with LAH is identical with khusimol (I), indicating the primary nature of the alcohol. Khusimol (I), on hydrogenation with Adams catalyst in alcohol absorbs one mol of hydrogen giving a saturated alcohol (IV), $C_{15}H_{26}O$, b.p. 121-28°/0.3 mm., $n_D^{24}$ 1.507, $(\alpha)_D^{27}$ + 33.44 (c, 4.1). Khusimol containing one double bond is thus tricyclic.

Khusimol (I) on tosylation and reduction with LAH gives an unsaturated hydrocarbon (V), $C_{15}H_{24}$, b.p. 165-70°/3.5 mm., $n_D^{25}$ 1.497 $(\alpha)_D^{25}$ + 45.64° (c, 4.3), IR bands 887, 1621 $cm^{-1}$ ($\overset{|}{\underset{|}{C}} = CH_2$), 1634, 1350 $cm^{-1}$ ($>C<^{CH_3}_{CH_3}$), NMR signals, singlet 8.94 $\tau$(6H) $>C<^{CH_3}_{CH_3}$, doublet 8.75$\tau$(3H) $CH-CH_3$, doublet 5.45, 5.30 $\tau$ (2H) $>C=CH_2$. The hydrocarbon (V), on hydrogenation with Adams catalyst in alcohol, gives a saturated hydrocarbon (VI), $C_{15}H_{26}$, b.p. 165-170°/2 mm., $n_D^{28}$ 1.4912; $(\alpha)_D^{25}$ + 35.88° ; IR bands

1379, 1361, 1314, 1248, 1188, 1134, 1095, 1063, 1039, 991, 979, 932, 879, 855, 813 cm$^{-1}$. NMR signals, singlets 9.22, 9.17$\tau$ and two superimposed doublets 9.24 and 9.15 $\tau$ (J = 8 c/s) (12H) 4-$CH_3$. This hydrocarbon has been found to be different in physical properties and IR spectrum[2] from any known tricyclic hydrocarbons such as cedrane, isopatchoulane, aromadendrane, tricyclovetivane[3] and appears to have a new carbon skeleton.

Khusimol (I), the unsaturated hydrocarbon (V), and the unsaturated acid (II), on dehydrogenation with selenium, do not lead to any aromatic products.

The compounds I, III and V on ozonolysis give formaldehyde in the volatile fraction. The non-volatile neutral portion in each case shows IR bands at ~1701-1709 cm$^{-1}$ indicating that the exomethylene group is situated on a six or seven membered ring.

The saturated acid (VII), $C_{15}H_{24}O_2$, $(\alpha)_D$ + 31.84° obtained by hydrogenation of the acid (II), on treatment with methyl lithium gives a methyl ketone (VIII), $C_{16}H_{26}O$, b.p. 150-55°/0.02 mm., $n_D^{26}$ 1.502, IR bands 1706 cm$^{-1}$. The methyl ketone (VIII), on oxidation with perbenzoic acid followed by hydrolysis, gives a crystalline alcohol (IX), $C_{14}H_{24}O$, m.p.136-137°, IR bands 3401, 1059 cm$^{-1}$. This alcohol (IX), on oxidation with Jones reagent forms a ketone, $C_{14}H_{22}O$ (X), b.p.135-136°/0.5 mm., $(\alpha)_D^{27}$ - 127.7°, IR bands

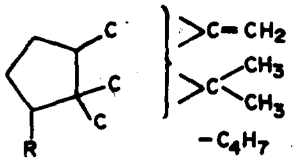
1733, 1410, 1389, 1364 cm-$^{1}$ indicating the presence of a carbonyl group in a five membered ring having an adjacent methylene group. Thus the alcohol group in khusimol (I), is attached to a five membered ring.

The ketone (X), on treatment with perbenzoic acid furnishes a crystalline $\delta$ -lactone (XI), $C_{14}H_{22}O_2$ m.p.102°, IR bands 1737, 1389, 1372 cm-$^{1}$, which on hydrolysis and acidification regenerates the $\delta$ -lactone. On reduction with LAH, the $\delta$ -lactone (XI), gives a diol (XII), $C_{14}H_{26}O_2$, IR bands 3390 very strong, 1045, 1385, 1361 cm-$^{1}$. The diol (XII) on acetylation under mild conditions forms a monoacetate (XIII), $C_{16}H_{28}O_3$, IR bands 3509, 1047, 1748, 1235, 1389, 1361 cm-$^{1}$ indicating the presence of a tertiary alcoholic group in the diol(XII). This is further confirmed by the resistance of the monoacetate (XIII) to oxidation with Jones reagent. This suggests that the carbonyl group in the five membered ring is flanked on one side by a tertiary carbon atom and a methylene group on the other side. The absence of any proton attached to carbon atom carrying lactone oxygen is shown by the fact that the NMR spectrum of this compound shows no signal below 7.5$\tau$.

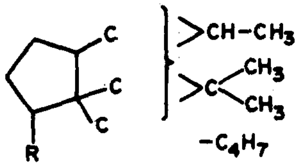
Provisional structures (XIVa) and (XIVb) which would confirm to the data presented have may be assigned to the alcohol. Out of these (XIVa) appears feasible from biogenetic consideration. This carbon skeleton was formerly suggested for cedrane.[4]

Further work on elucidation of structure of khusimol is in progress.

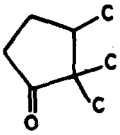
All compounds give satisfactory analyses.



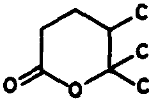
I R = $CH_2OH$
II R = COOH
III R = $COOCH_3$
V R = $CH_3$



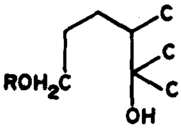
IV R = $CH_2OH$
VI R = $CH_3$
VII R = COOH
VIII R = $COCH_3$
IX R = OH



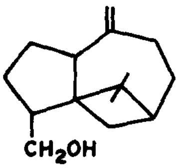
X



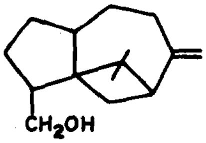
XI



XII R = H
XIII R = $COCH_3$



XIV a



XIV b

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