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KETONES FROM "MAYUR PANKHI" : SOME NEW CUPARENE-BASED SESQUITERPENOIDS

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THE essential oil from the wood of "mayur pankhi"[1] is a complex blend of sesquiterpene hydrocarbons (~ 40%), alcohols (~ 50%), ketones (~ 4%) and monoterpenic acids (~ 4%). Though the chief components of hydrocarbons, alcohols and acids are all known compounds, the ketone portion yielded six new sesquiterpenoids (Table I), and we report now on the structures of two of these (ketones IV, V). These have been shown to belong to the cuparene group of sesquiterpenoids, a new type first reported by Enzell and Erdtman in 1958[2], and of which only two members - cuparene and cuparenic acid - were known till now.

Ketone V, $C_{15}H_{20}O$, (semicarbazone, m.p. 213.5-215°) is clearly a cyclopentanone ($\nu^{c=o}$ 1746 cm^{-1}) and from its

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[1] There is some confusion in the literature as to the botanical identification of "mayur pankhi" as Thuja orientalis L. or Thuja compacta.

[2] C.Enzell and H.Erdtman, Tetrahedron 4, 361 (1958).

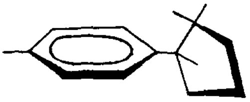
TABLE 1. **SESQUITERPENE KETONES FROM "MAYUR PANKHI"**

No.	Trivial name	% yield*	Mol.formula	No.of rings	m.p.	b.p.	n_D^{30}	$[\alpha]_D^{30}$	$\nu^{C=O}(cm^{-1})$
I	-	4	$C_{15}H_{24}O$	Tricyclic+	-	109-110°/ 3 mm	1.4977	+14.2°	1707
II	-	21	$C_{15}H_{24}O$	Tricyclic+	61-62°	-	-	+10.0°	1723
III	-	17	$C_{15}H_{24}O$	Tricyclic+	121-22°	-	-	+65.9°	1731
IV	α-Cuparenone	13	$C_{15}H_{20}O$	Bicyclic	52-53°	-	-	+177.1°	1750
V	β-Cuparenone		$C_{15}H_{20}O$	Bicyclic	-	114-115°/ 0.8 mm	1.5292	+48.0°	1746
VI	Mayurone	40	$C_{15}H_{22}O$	Tricyclic+	69.5-70°	-	-	+253.4°	1667

*Based on total ketones.

+New carbon framework.

PMR[3] (4H; 425 cps, essentially a singlet) and IR spectra (1524, 822 and 728 cm^{-1}) must contain a disubstituted benzene ring. Its PMR spectrum, further, indicated the presence of three quaternary methyls (sharp singlets at 44, 74 and 85 cps; each 3H) and one methyl (sharp singlet at 135 cps; 3H) on the aromatic ring; the placement of these signals was reminiscent of the methyl peaks of cuparene (1)[4] (33, 63, 74 and 136 cps), a component of the hydrocarbon portion of the essential oil from "mayur pankhi". These facts strongly suggested ketone V to be a derivative of cuparene. Wolff-Kishner reduction[5] of its semicarbazone yielded in 60% yield a hydrocarbon identified as cuparene. Thus ketone V should be represented by (2), (3) or (4).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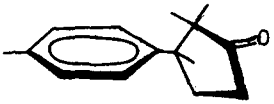
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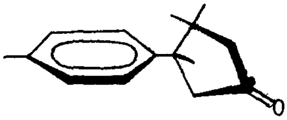
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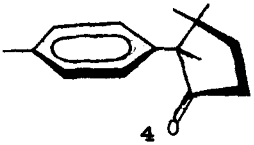
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[3] The proton magnetic resonance spectra were taken on a Varian A-60 high resolution spectrometer on ~ 20% solutions in CCl_4, using tetramethylsilane as an internal reference. The signals are reported in cps from tetramethyl silane as zero.

[4] The PMR spectra of cuparene and the related ketones show interesting features due to the anisotropy of the benzene ring and these will be discussed in the fuller paper.

[5] M.F.Grundon, H.B.Henbest and M.D.Scott, J.Chem.Soc. 1855 (1963).

The compound (2) has recently been synthesised[6] and a comparison of its infrared spectrum[7] with that of ketone V, eliminated this possibility. However, the infrared spectrum of the ketone IV turned out to be identical with that of (2), which fixes the structure of ketone IV as (2); as a matter of fact ketone IV was strongly suspected to be a cuparene derivative on the basis of its infrared (1750, 1520, 822 cm^{-1}) and PMR spectra (four aromatic protons as a multiplet centred at 427 cps; three quaternary methyls at 34, 67 and 74 cps and one methyl on an aromatic ring at 139 cps).

Ketone V is now left with two alternatives (3) and (4). A decision between these could be made by measurement of the integrated intensities of the bending frequency of the methylene group flanking the carbonyl[8,9]. Ketone V showed a clear peak at 1407 cm^{-1} assignable to such a vibration mode, while ketone IV displayed the same absorption as a sharp peak at 1419 cm^{-1}; the measured integrated intensities of these absorptions for ketone IV

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[6] W.Parker, R.Ramage and R.A.Raphael, J.Chem.Soc. 1558 (1962).

[7] We are grateful to Prof.Raphael for the infrared spectrum of the authentic material and a sample of its semicarbazone.

[8] R.N.Jones and A.R.H.Cole, J.Amer.Chem.Soc. 74, 5648 (1952); R.N.Jones, A.R.H.Cole and B.Nolin, ibid. 74, 5662 (1952).

[9] C.S.Barnes, D.H.R.Barton, A.R.H.Cole, J.S.Fawcett and B.R.Thomas, J.Chem.Soc. 573 (1953).

and ketone V were found to be in the ratio 1:1.82, clearly favouring the structure (3) for ketone V.

Thus ketones IV and V can be assigned the structures (2) and (3) respectively. In view of their relation to cuparene, (2) and (3) have been designated α-cuparenone and β-cuparenone respectively.

The chief components of the alcohol portion of the essential oil have been found to be cedrol and widdrol (accounting for over 75%). The remaining portion, which was found to be a mixture of secondary and tertiary alcohols, on chromic acid oxidation, gave besides unchanged tertiary alcohols and other products, both the cuparenones, thus showing the presence of the corresponding alcohols - cuparenols in the essential oil. These will be discussed in the fuller paper.