Structure of Walsurenol, a New Pentacyclic Triterpene Alcohol from *Walsura tubulata*

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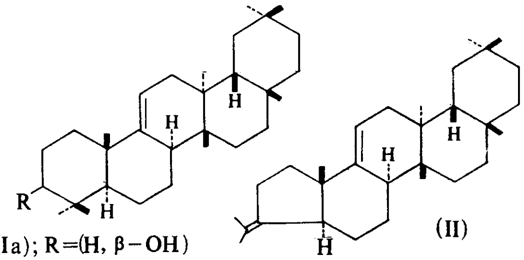
RECENT isolation of aphanamixin[1] and aphanamixol[2] in our laboratory from *Aphanamixis polystachya* Wall and Parker (Fam: *Meliaceae*) induced us to examine other *Meliaceae* species for novel chemotaxonomical information. From the leaves of *Walsura tubulata*, a member of this family, a new crystalline pentacyclic triterpene alcohol has been isolated, which we name walsurenol.

Walsurenol (Ia), $C_{30}H_{50}O$ (M^+ 426); ν_{max} 3455 (–OH), 827 (–CH=C<) cm.$^{-1}$, n.m.r. δ 0·84—1·16 (24H, 8CH_3), 3·46 (1H, m, =CH·OH) and 5·62 (1H, m, –CH=C<). The signal at δ 3·46 was shifted to δ 4·68 in the acetate (Ib), $C_{32}H_{52}O_2$ (M^+ 468), m.p. 185—187°, ν_{max} 1725, 1238 (O·CO·CH$_3$; δ 1·98, 3H, s), 827 cm.$^{-1}$ (CH=C< ; δ 5·55, 1H, m). The chemical shifts of the C(3) proton and acetate are typical of 3α-proton of triterpene 3β-acetates.

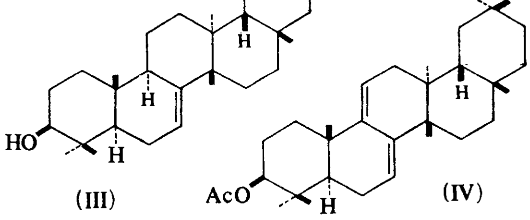
The secondary nature of the hydroxyl group was also revealed from the oxidation of (Ia) with CrO_3–pyridine to walsurenone (Ic), $C_{30}H_{48}O$, (M^+ 424), m.p. 230—232°, ν_{max} 1695 (cyclohexanone) cm.$^{-1}$. Furthermore, the presence of a 3β-oriented equatorial hydroxyl group was confirmed by the sodium borohydride reduction of (Ic) to (Ia) and the PCl_5 rearrangement of (Ia) to a hydrocarbon (II), $C_{30}H_{48}$ (M^+ 408), m.p. 185°. Reduction of (Ic) with lithium aluminium hydride furnished an epimeric product (Id) which on Sarett oxidation produced (Ic).

The trisubstituted nature of the double bond indicated that it might be 5(6), 7(8), or 9(11).



(Ia); R=(H, β–OH)
(Ib); R=(H, β–OAc)
(Ic); R=O
(Id); R=(H, α–OH)

(II)



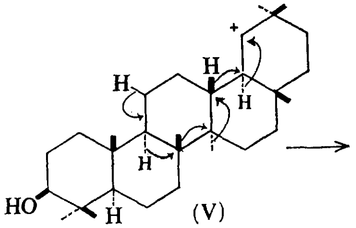
(III)

(IV)

The 5(6) position was excluded by the isolation of the retropinacolin rearranged product (II) from (Ia) (no u.v. absorption above 220 mμ). The double bond could not be at 7(8) as (Ia) is not identical with multiflorenol (III). So, the double bond, being trisubstituted and endocyclic, was assigned the 9(11) position; this was confirmed as follows. Walsurenyl acetate (Ib) was converted to a noncrystalline epoxide which on acid treatment afforded a dienylacetate (IV), $C_{32}H_{50}O_2$, m.p. 216—218° (*cf.* arundoin[3]). Compound (IV) was found to be identical with an authentic specimen of multiflora-7,9(11)-dienyl acetate[4] in all respects (m.m.p., t.l.c., rotation and superimposable i.r. spectra). This unequivocally settles the structure and stereochemistry of walsurenol as depicted in (Ia).

Biogenetically (Ia) could be derived by the degeneration of the common ion (V) or its equivalent.

We thank Dr. Bhupesh C. Das for mass and n.m.r. spectra, Dr. S. C. Pakrashi for i.r. spectra, and the Department of Health, Government of West Bengal (A.B.K.) and the C.S.I.R., India (S.C.) for financial assistance.



(V) → (Ia)

(*Received, February 12th,* 1968; *Com.* 171.)

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