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A NEW HEXACYCLIC TETRANORTRITERPENOID

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Vilasinin, a new hexacyclic tetranortriterpenoid has been isolated from the green leaves of the neem tree and its structure determined. It appears to be a biogenetic precursor of salanin and nimbin.

The alcohol extract of the green leaves of the neem tree (Azadirachta indica) after the removal of chlorophyll, on extensive chromatography on neutral alumina, gave, besides known products, a new crystalline compound, vilasinin (III) (0.1%), m.p.255°, $(\alpha)_D$-4° (py), $C_{26}H_{36}O_5$, (M^+428), ν_{max} 3400 and 3200 cm^{-1} (bonded OH), 1498 and 788 cm^{-1} (β-substituted furan ring) and 878 cm^{-1} (trisubstituted double bond) and absence of absorption in the carbonyl region. It forms a triacetate (IV), m.p.220°, $(\alpha)_D$-26° ($CHCl_3$), or a tribenzoate, m.p.255°, both hydrolysable back to vilasinin. The IR spectrum of (IV) $C_{32}H_{42}O_8$, (M^+554), was transparent in the hydroxyl region and showed absorptions for the acetates (1725, 1245 cm^{-1}), besides those for the furan ring and the double bond, the latter being further confirmed by a strong positive TNM test.

The PMR spectrum of (IV) in $CDCl_3$ was revealing that it showed the features of the A,B-rings of salanin (I)[1] and of C_7 and the C,D-rings of azadirone (II)[2,3], both previously isolated from neem seeds. Thus (IV) showed the presence of only four quaternary methyl groups at δ 0.83(C_{24}), 1.03(C_{25}) and 1.2(C_{22},C_{26}) and the characteristic narrow triplets centred at δ 4.93 and 4.73, J = 3 Hz, 1H each, due to the C_1 and C_3β-protons respectively[4] coupled with the two C_2-protons as in salanin. PMR signals due to the protons on the C_5-C_6-C_7-carbon chain closely resembled those of salanin and nimbin[5] in their coupling pattern as axial, axial, equatorial, with H_6 as a quartet centred at δ 4.13, J = 13 and 3 Hz, H_7 as a doublet centred at δ 5.52, J = 3 Hz and H_5 as a doublet centred at δ 2.58, J = 13 Hz. The signal of H_7 is at low field in (IV) due to the acetate there, but is at about the same place as in azadirone, and is superimposed on the signal of the vinyl proton most probably at C_{15}. The two α-furan protons appear at δ 7.4 and 7.34 and the one β-furan proton at δ 6.3 as in azadirone. The fifth methyl group absent in the new compound has to be engaged in an ether linkage at C_{23}-C_6-α, as in salanin since the PMR spectrum shows two mutually coupled protons centred at δ 3.42 and 3.51, J = 8 Hz, (C_{23}-H_2).

These assignments are fully confirmed by double irradiation experiments with a 100 MHz NMR spectrometer. Irradiation at the C_5-H doublet centred at δ 2.58

simplifies the C_6-H quartet centred at δ 4.13 to a narrow doublet J = 3 Hz and irradiation at the multiplet signal at δ 5.5 containing the C_7-H, reduces the same quartet to a doublet J = 13 Hz. Finally, irradiation at the C_6-H quartet at δ 4.13 simplifies the multiplet centred at about δ 5.5 to a singlet at δ 5.52. This singlet is superimposed on a triplet due to the C_{15}-H, centred at about δ 5.5, J = 3 Hz. Irradiation at the C_2-methylene group at δ 2.3, reduces the triplets at δ 4.73 and 4.93 to singlets. Also irradiation at the C_{22}-methyl signal at δ 1.2 significantly increases the height of the $C_{23}\alpha$-proton doublet centred at δ 3.42, showing thereby that there is long range W-coupling between the $C_{22}\beta$-methyl and the $C_{23}\alpha$-H as in the case of salanin.

The new compound, vilasinin, is therefore assigned structure (III) and appears to be a biogenetic precursor of salanin and nimbin, both obtained from the fruits of the same tree, but having their C-ring oxidized and broken.

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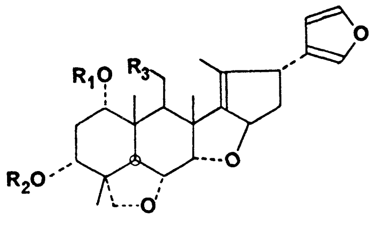
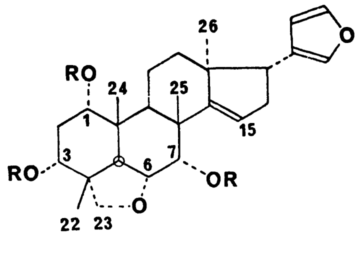
References

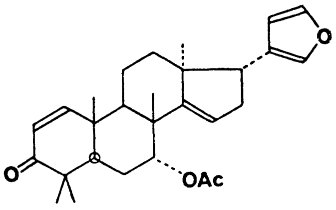
1. R. Henderson, R. McCrindle, A. Malera and K.H. Overton, Tetrahedron, 24, 1525 (1968).
2. D. Lavie and M.K. Jain, Chem. Comm., 278 (1967).
3. Azadirone described as an oil by Lavie and Jain[2] is crystallized from ether-methanol, m.p.136°, $(\alpha)_D$ +24°, to give sharp spectral features; B.M. Sawant, Ph.D.Thesis, Poona University (1970), p.81.
4. C.R. Narayanan, R.V. Pachapurkar, B.M. Sawant and M.S. Wadia, Indian J. Chem., 7, 187 (1969).
5. C.R. Narayanan, R.V. Pachapurkar, S.K. Pradhan, and V.R. Sha, Chem. and Ind. (London), 322, 324 (1964) ; Tetrahedron Letters, 4333 (1965), 533 (1966) ; M. Harris, R. Henderson, R. McCrindle, K.H. Overton and D.W. Turner, Tetrahedron, 24, 1517 (1968).



I, salanin, R_1 = COC_4H_7
R_2 = $COCH_3$
R_3 = CO_2CH_3



III, vilasinin, R = H
IV, R = Ac



II, azadirone

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