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SPATHELIN - A SECO-RING A TETRANORTRITERPENE FROM SPATHELIA SORBIFOLIA

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Several genera of the Rutaceae have yielded tetranortriterpenes of the limonin type (limonoids) (1). We have examined *Spathelia sorbifolia* (Rutaceae, subfamily Spathelioideae) and have recently reported on a novel chromone from young trees (2). This communication deals with the structure of a seco-ring A limonoid isolated from an old plant. Benzene extraction of the roots followed by chromatography gave spathelin, $C_{29}H_{34}O_{10}$, m.p. 178.5-180°, $[\alpha]_D^{25}$ -7°, for which we propose the constitution (I).

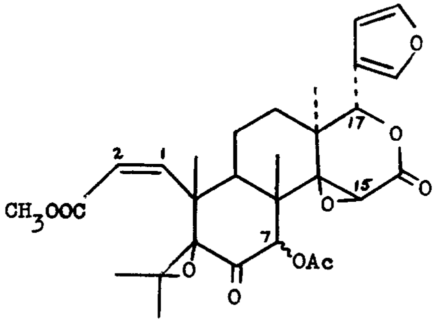
The i.r. spectrum showed, in addition to furan absorption at 3080, 1500 and 877 cm.$^{-1}$, carbonyl bands at 1748 (sh), 1742, 1727 and 1712 cm.$^{-1}$ and olefinic absorption at 1634 cm.$^{-1}$, while the u.v. spectrum ($\lambda_{max.}$ 206 nm., ε 11,500) indicated the summation of the furan and another chromophore. The n.m.r. spectrum (δ values) showed the presence of five tertiary C-methyls [0.85, 1.23 (2), 1.27, 1.33], an acetate (2.28), a methyl ester (3.72), and an AB quartet (6.22, 5.83, J = 12.5 Hz) for H-1 and H-2, as well as the furan signals. In addition, singlets at 3.83, 5.50 and 6.25 were assigned to H-15, H-17 and the hydrogen on carbon bearing acetate (H-7) respectively (3). The low field position of this latter proton is in consonance with the presence of an adjacent diamagnetically anisotropic group.

Subjection of spathelin (I) to lactone titration conditions indicated three hydrolysable groups and furnished the diosphenol acid (II), $C_{26}H_{30}O_9$, m.p. 288-291°, $\lambda_{max.}$ 205 and 276 nm. (ε 5400 and 8600), the latter band shifting in base to 332 nm. (ε 5950), $\nu_{max.}$ 3350, 1745, 1712, 1686 and 1664 $cm.^{-1}$ The non-crystalline methyl ester (III), whose n.m.r. spectrum was in full accord with its structure, was converted by treatment with sodium methoxide in methanol to the amorphous C-1 epimeric acid (IV). The identity of this acid (IV) with that obtained (4) from autoxidation of isoobacunoic acid (V) was confirmed by t.l.c. and i.r. and n.m.r. spectral comparison of the acids and their methyl esters. A comparison of the chemical shifts and multiplicities of H-1 in methyl isoobacunoate (VI) (3.94, broad triplet, J = 5.8 Hz) and the derived diosphenol (VII) (3.97, triplet, J = 6.0 Hz) with those in veprisone (VIII) (4.30, quartet, J = 5, 10 Hz) (5) and the related diosphenol (III) (4.35, quartet, J = 6.5, 8.5 Hz) supports the configuration assigned at C-1 in (III).

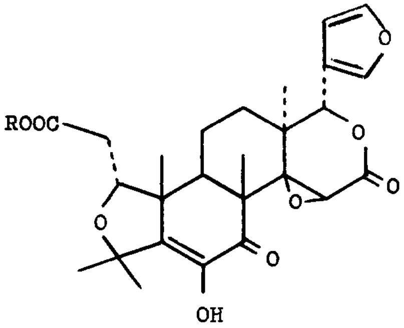
The evidence cited defines the structure of spathelin except for the arrangement of the ketone and acetate groups in ring B. This was shown by chromous chloride reduction of spathelin which gave the cisoid α,β-unsaturated ketone (IX), $C_{27}H_{32}O_6$, m.p. 167-170°, $\lambda_{max.}$ 211 and 250 (sh) nm. (ε 15,700 and 7700), $\nu_{max.}$ 1721 (ester and lactone) and 1661 (ketone) $cm.^{-1}$, whose n.m.r. spectrum fully supported the structure, revealing, *inter alia*, two vinylic methyls (1.71, 1.94), and two singlets at 5.03 and 5.96 assigned to H-17 and H-15 respectively. These positions are consistent with the ene lactone system of (IX): in particular, the chemical shift of H-15 demonstrates the absence of a 7-ketone (6) and is consistent with the presence of a 7-methylene [cf. odoratin (7)].

Further work to define the configuration at C-5 and C-7 of spathelin is in progress.

The isolation of spathelin from *Spathelia sorbifolia* supports its inclusion in the Rutaceae since this is the only family from which seco-ring A limonoids have been obtained.

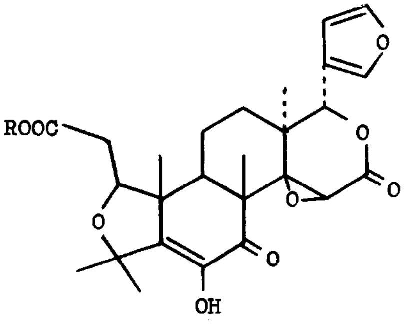


I



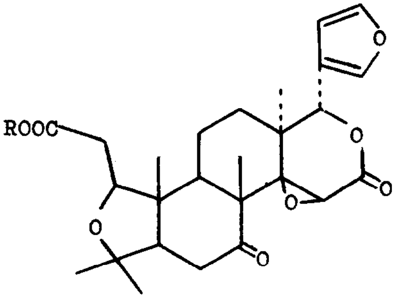
II R = H

III R = $\mathrm{CH_3}$



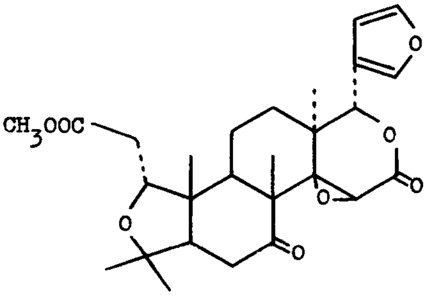
IV R = H

VII R = $\mathrm{CH_3}$

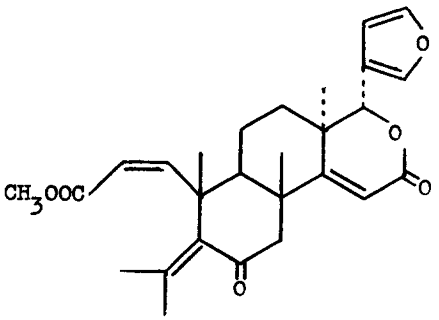


V R = H

VI R = $\mathrm{CH_3}$



VIII



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