Tetrahedron Letters No. 11, pp 967 - 968.
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0040-4039/79/0308-0967$02.00/0

TETRANORTRITERPENOIDS AND RELATED COMPOUNDS PART 21.[1] THE CRYSTAL AND MOLECULAR STRUCTURE OF A REARRANGED TETRANORTRITERPENOID SPIRO-LACTONE FROM THE BARK OF CARAPA PROCERA (MELIACEAE).

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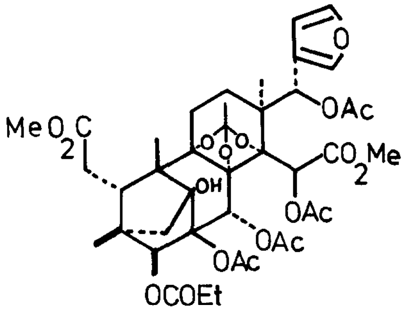
Procerin (1),[2] the major tetranortriterpenoid from the bark of Carapa procera (Meliaceae), was accompanied, in minor amount, by a second compound, $C_{26}H_{32}O_5$, which has been shown to have the rearranged spiro-lactone structure (2) by X-ray crystallographic analysis.

The spectroscopic properties of (2) revealed the characteristic β-substituted furan, five tertiary methyls [δ 0.78, 1.11, 1.48, 1.71 and 1.83], a cyclopentanone [$\nu_{max}(CCl_4)$ 1738 cm^{-1}; δ_c 219.2], a tetrasubstituted double bond [δ_c 138.8 and 130.7] and a δ-lactone [$\nu_{max}(CCl_4)$ 1738 cm^{-1}; δ_c 170.2 and 82.5 (s)]. The remaining oxygen was therefore present as a cyclic ether and attached to two secondary carbons [δ_c 80.2 and 79.3 (both d); δ_H 4.28 (2 Hm, H-1 and H-7)]. The above data indicated that the molecule was tricarbocyclic and suggested a ring A cleaved tetranortriterpenoid skeleton with a cyclopentanoid ring D.

Closer examination of the ^1H n.m.r. spectrum and the use of $Eu(fod)_3$ resulted in the identification of three ABX systems. One of these involved H-17 (δ 3.51, t, J 9.5 Hz) and together with a singlet (H-14) at δ 2.06 allowed the carbonyl group to be placed at C-15. Biogenetic reasoning suggested that the other two ABX systems were situated respectively in a ring A lactone with an oxygen substituent at C-1 and in ring B with an oxygen substituent at C-7 and no hydrogen atom on C-5. The downfield nature of three methyl signals raised the possibility of an isopropylidene group at C-5 and the ring A lactone terminus at an alternative tertiary position e.g. C-9. Thus we arrived at structure (3) as a possible solution. Lack of material prevented any chemical investigation. A crystal-structure analysis was undertaken and revealed the structure of the Carapa Compound as (2).

For the X-ray analysis, a small crystal of (2) was exposed to graphite-monochromated Mo radiation on an Enraf-Nonius CAD4 diffractometer, and the intensities of 1050 independent reflexions [$\underline{I} \geqslant 2.0\ \sigma_{\underline{I}}$] were measured using the θ,ω-scan technique in the range 2 θ 0-56°. The intensities were corrected for Lorentz and polarisation factors, but absorption effects were ignored. The structure was resolved by direct methods using the MULTAN (1976) suite of programs, and has been refined by full-matrix least-squares calculations to a final *R* value of 0.084. Since the number of data was restricted in relation to the number of atomic parameters, anisotropic thermal parameters were *not* introduced into the refinement. Positions for hydrogen atoms were determined from geometrical considerations, and these atoms were included as fixed contributors in the least-square calculations. The absolute configuration was not determined by the X-ray analysis, and is assumed to be as in (2) by analogy with other tetranortriterpenoids.

Tetranortriterpenoids with a ring A ε-lactone are not uncommon but compound (2) is the first example of a rearranged spiro-lactone in this series. Presumably it is formed from an αβ-unsaturated ε-lactone followed by Michael addition of the 7α-hydroxyl group to the conjugated system. Recently three C_{25} fungal metabolites, austin[3] and andibenin[4] with a similar ring A spiro-lactone and andilesin[5] with a ring A unsaturated ε-lactone, have been described. These fungal compounds have a mixed sesquiterpenepolyketide origin.[6]



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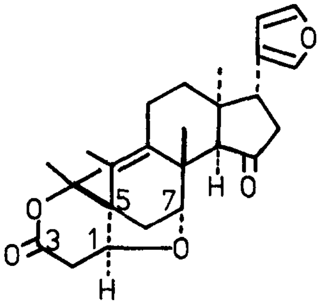

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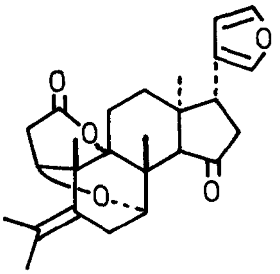

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(Received in UK 11 December 1978)