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THE STRUCTURE OF FISSINOLIDE

D. A. H. Taylor

Department of Chemistry, University of Ibadan, Ibadan, Nigeria

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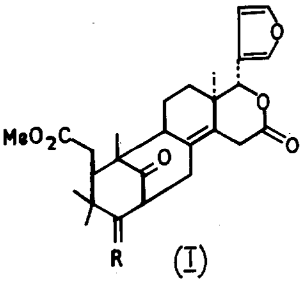
Reduction of mexicanolide (Ia) with sodium borohydride, followed by acetylation, gives an acetate,[1] also isolated as a natural product,[2] which has been assigned the structure (Ib), and named fissinolide.[2]

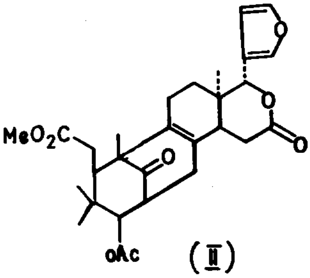
Recently, Lavie, Levy, Rosito and Zelnik[3] have claimed that fissinolide is correctly represented as (II); on the basis of the chemical shift of H-17. This is claimed to be significantly different in compounds with and without a double bond terminating at H-14. No other evidence is presented of the location of the double bond.

This analysis does not take account of the double resonance experiments which have been carried out on fissinolide,[4] which show that the two protons at C-15 resonate at δ3.76 and 3.42, and are coupled with the protons at C-.30. These latter are firmly identified by coupling with H-2, which is coupled to H-3. The chemical shift is greater than expected for protons on carbon adjacent to a lactone, but probable for protons on carbon adjacent to both a lactone and a double bond; while the coupling pattern can only be explained on the basis of an 8:14 double bond, as in (Ia). Since this double resonance evidence appears conclusive, and the new formulation of Lavie et. al. involves the assumption of a number of unlikely double bond migrations, we reject the structure (II). It appears that Lavie et. al. have overlooked the effect that substituents elsewhere in the molecule may have on the resonance frequency of H-17. It is claimed that compounds with a double bond terminating at C-14 have H-17 resonances in the range δ5.10 - δ5.30; while those without such a double bond have resonances in the range δ5.55 to δ5.70. In fact the 3-6 diketone related to swietenine (III) has an H-17 resonance at δ5.50, while the corresponding 3-β hydroxy compound and its acetate show a resonance at δ5.72; and the 6-noraldehyde shows H-17 at δ5.27.[5,6] The structures of all these compounds are firmly established by the presence of the characteristic H-30

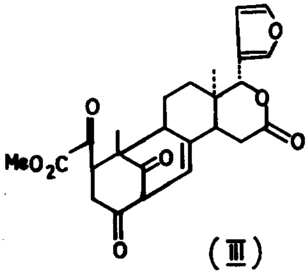


(I)

(a) R = O
(b) R = H,βOAc



(II)



(III)

resonance.

Mexicanolide already shows the H-17 resonance at δ5.30; if it should suffer a shift on reduction of the 3-ketone equal to that recorded in swietenine, H-17 in fissinolide would be at δ5.52; which is already in the region that is claimed to be diagnostic of the absence of a double bond at C-14.

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