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A NEW DITERPENE ESTER FROM EUPHORBIA POISONII

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The latex of Euphorbia poisonii is used in a number of traditional medicinal (2,3) preparations. Other members of the genus Euphorbia have been reported (4,5,6) to contain components that are irritant to the skin and that have co-carcinogenic activity. The latex of E. poisonii in our experience shows a great deal of discomfort both during collection and during handling in the laboratory.

Recently, Evans and Schmidt published (7) the isolation, from E. poisonii, of compounds for which constitutional formulae related to phorbol, 1 were proposed. We now wish to report aspects of our long standing results of the chemical investigation of the latex of E. poisonii.

The non-triterpenoid (8) aspect of the ether soluble fraction of the cold methylated spirit extract of the latex of E. poisonii (collected from Ilorin, Kwara State, Nigeria) on column chromatography on silica gel gave a crystalline diterpene as well as a number of non-crystalline compounds. The crystalline diterpenoid "compound D" (0.3% w/v latex) m.p. 129 - 130°, analysed for $C_{31}H_{42}O_{11}$, accurate M^+ 590.2721.

It had ν_{max} (Nujol) 1730 cm^{-1}, 1220 cm^{-1} (acetate carbonyl), 1690 cm^{-1} (carbonyl), λ_{max} (MeOH) 211 (ϵ_{max} 2,600); nmr δ ($CDCl_3$ + TMS) 0.9 - 1.38 (5 methyl groups), 2.00 (3H, s, CH_3COO), 2.13 (3H, s, CH_3COO) 2.15 (6H, s, 2 x CH_3COO), 3.55 (1H, m) 4.70 (1H, d, J, 6Hz), 5.15 (2H, m) 5.50 (1H, bs), 5.60 (1H, bs) and 6.30 (1H, s).

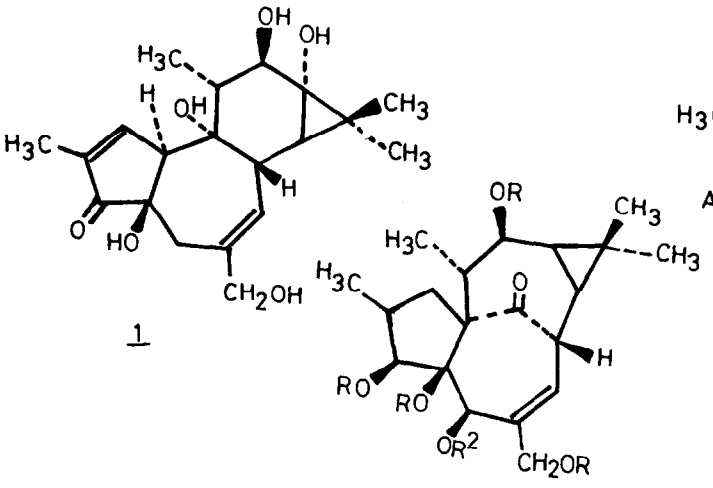
The ^1H nmr spectral properties compared well with those reported (9) for ingenol triacetate 2. The spectral and analytical properties of compound D could be accommodated in the partial and tentative structure 3 with four acetate groups and one propionate.

Compound D dissolved in methanol, and a drop of dilute sulphuric acid rapidly gave crystals of its methoxy derivative m.p. 138 - 141°. The i.r. spectrum of this derivative showed no changes in the carbonyl, acetate and hydroxyl regions. In its nmr spectrum, one of the acetate signals (at δ 1.90 in the spectrum for compound D) had disappeared and in its place, there appeared a signal (3H, s) at δ 3.40 which was due to a methoxy group while one of the low

field protons suffered an upfield shift from δ 6.27 to 4.62. The structure 3 (R^2= -OMe) also accommodated these changes.

The presence of a ketone group in the constitution of compound D was confirmed by the fact that compound D on borohydride reduction followed by acetylation with pyridine/acetic anhydride gave a crystalline pentaacetate m.p. 174 - 76° whose i.r. lacked the absorption at 1690 cm^{-1}. It had M^+ 634; nmr δ($CDCl_2$ + TMS) 2.00 (3H, s, CH_3COO), 2.10 (9H, s, 3 x CH_3COO), 2.20 (3H, s, CH_3COO), 4.60 (1H, bs), 5.04 (1H, d, J, 2Hz), 5.21 (1H, bs), 5.40 (1H, bs), 5.60 (1H, d, J, 4Hz), 5.80 (1H, bs), 6.22 (1H, s).

The properties of compound D are being further investigated to enable the complete constitutional formula to be assigned.



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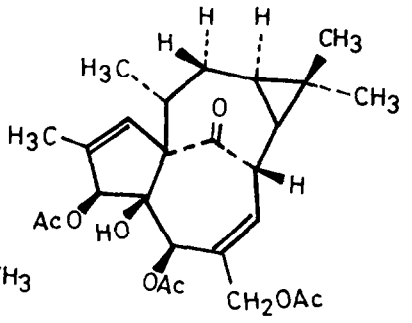

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