Terpenoid Constituents of the Insect Repellant Plant *Nicandra physaloides*; X-Ray Structure of a Methyl Steroid (Nic-3)† Acetate

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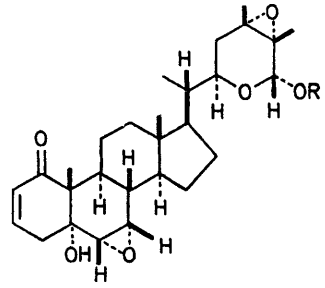
Summary *Nicandra physaloides* (Solanaceae) contains two new methyl steroids (**2**) and (**3**); the constitution of the former is demonstrated by crystallographic analysis of its acetate, using direct methods.

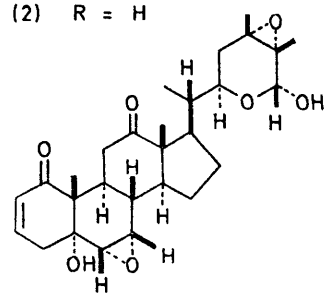
EXTRACTIVES of *Nicandra physaloides* (Solanaceae), a reputed fly repellent of Peruvian origin, have been shown to inhibit feeding of various insect species.[1] Investigation of the extractives of *Nicandra* leaves in our laboratory has so far yielded ten new terpenoids, and we now report the structures of two of them [(**1**) and (**2**)].

Nic-3, (**1**), $C_{28}H_{40}O_6$, formed an acetyl derivative $C_{30}H_{42}O_7$, m.p. 262°, crystallising in the space group $P2_12_12_1$, with unit cell dimensions $a = 6{\cdot}58$, $b = 19{\cdot}49$, and $c = 21{\cdot}76$ Å, and $Z = 4$. Intensity data were collected with Cu-K_α radiation using an automatic four-circle diffractometer, and 1783 reflections were considered observed. The structure was determined by direct methods using the Multan[2] program, and refined by block-diagonal least squares to a current R index 10·6%. The hemi-acetal (**2**) is an oxidised methyl steroid related to the withanolides[3] and physalins[4] (also from Solanaceous plants). Spectroscopic data for (**2**) and its acetate are in agreement with these structures.

Constitution (**3**) may be deduced for a second methyl steroid, Nic-7, $C_{28}H_{38}O_7$, by correlation of spectra. In the i.r., (**3**) displays two carbonyl absorptions (ν_{max} 1700, 1688 cm^{-1}) corresponding to a cyclohexanone group as well as the cyclohexenone function also present in (**2**) (ν_{max} 1693 cm^{-1}). The n.m.r. spectra show (**3**) and (**2**) to be very similar in structure; differences however appear in certain signals. Thus in (**3**), 18-Me (τ‡ 9·03, s) and 11-H_{eq} (6·15 bd, J_{gem} 11·5 Hz) resonate at significantly lower field than their counterparts in (**2**) [18-Me (9·40 s), 11-H_{eq} (7·04 bd, J_{gem} 11·5 Hz)]. The extra carbonyl function present in (**3**) must therefore be sited at C-12.



(1) R = Ac
(2) R = H



(3)

(*Received*, 15*th August* 1972; *Com.* 1432.)

† The terms Nic-3, *etc.*, are used for convenience to refer to individual members of the series of extractives.

‡ N.m.r. data at 100 MHz for C_5D_5N solutions.

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