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TREVOAGENINS C AND D, DAMMARANE TRITERPENES FROM *TREVOA TRINERVIS* Miers.

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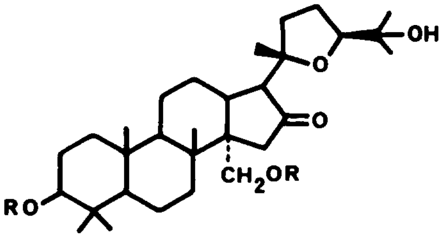
Summary.- Trevoagenins C and D are minor triterpenes isolated from Trevoa trinervis Miers. The structure of trevoagenin C was established by chemical and spectroscopic means and that of trevoagenin D by X-ray diffraction techniques.

Recently[1] we have isolated two major dammarane triterpene sapogenins, trevoagenins A and B, from Trevoa trinervis Miers. (Rhamnaceae). We now report the structure of trevoagenins C and D, two minor components of this plant.

Trevoagenin C (Ia) crystallized from acetone, mp 267-269°C, $\{\alpha\}_D$-35° (c, 0.2, dioxane). By mild acetylation it gives a diacetate (Ib), mp 171-173°C (n-hexane), $\{\alpha\}_D$-40° (c, 0.21, $CHCl_3$). The molecular formula $C_{30}H_{50}O_5$ was established for trevoagenin C by high resolution mass spectrometry (M^+ 490.3637). The ^{1}H-NMR spectrum of trevoagenin C diacetate (Ib) is almost identical with that of trevoagenin B diacetate, only the position of the two methyl groups on C_{25} being slightly different {δ ($CDCl_3$) 0.86 (s, 2x Me-C_4), 0.93 (s, Me-C_{10}), 1.13 (s, Me-C_8), 1.28 (s, Me-C_{20}), 1.09 and 1.17 (s, 2 x Me-C_{25}), 4.5 (m, $W_{\frac{1}{2}}$ 16Hz, H-C_3), 4.56 and 4.32 (AB, J = 12Hz, 2H-C_{30})}. These spectroscopic data suggest that Ia is a side chain stereoisomer of trevoagenins A and B. The lactone II was obtained by oxidation of Ib with Jones reagent, crystallized from acetone, mp 248-253°C, $\{\alpha\}_D$-26° (c, 0.17, $CHCl_3$). This lactone is identical with that prepared from trevoagenin B, thus the stereochemistry of Ia is 20S,24S.

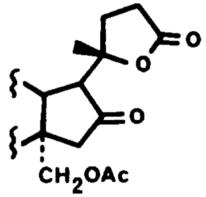
Trevoagenin D (IIIa) was obtained in a very small amount (6×10^{-3}%) by crystallization from n-hexane, mp 249-251°C, $\{\alpha\}_D$-14° (c, 0.28, $CHCl_3$). The high resolution mass spectrum established the molecular formula as $C_{30}H_{48}O_5$ (M^+ m/z 488.3527). The ^{1}H-NMR spectrum ($CDCl_3$) shows seven methyl groups {δ 0.78 (Me-C_{4a}), 0.85 (Me-C_{4b}), 0.98 (Me-C_{10}), 1.1, 1.19, 1.25, and 1.27} and four groups of protons on carbon bearing oxygen at 3.2 (m, $W_{\frac{1}{2}}$ 16Hz, H-C_3), 3.96 (m, $W_{\frac{1}{2}}$ 3Hz, 2H-C_{30}), 3.94 (dd, $J_{AX} + J_{BX}$ 16Hz, H-C_{24}), 4.83 (dd, $J_{AX} + J_{BX}$ 9Hz, H-C_{22}). A monoacetate IIIb was obtained by mild acetylation, crystallization from acetone mp 237-240°C, $\{\alpha\}_D$-8° (c, 0.26, $CHCl_3$), M^+ m/z 530. The ^{13}C-NMR spectrum of trevoagenin D was consistent with the structure, showing seven absorptions for carbon bearing oxygen at δ ($CDCl_3$) 78.8 (d, C_3), 118.9 (s, C_{16}), 87.6 (s, C_{20}), 94.5 (d, C_{22}), 85.1 (d, C_{24}), 71.3 (s, C_{25}), 65.6 (t, C_{30}) confirming the presence of an acetalic carbon at C_{16}. The electron impact mass spectrum of IIIa displays "inter alia" a fragment ion of composition $C_{27}H_{41}O_4$ at m/z 429.3022 (31%) (due to the loss of ⋌OH) and fragment {a} $C_{14}H_{23}O$ m/z 207.1750 (52%) which are consistent with this structure.



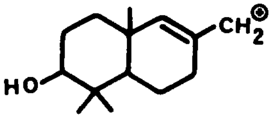
I

a R=H

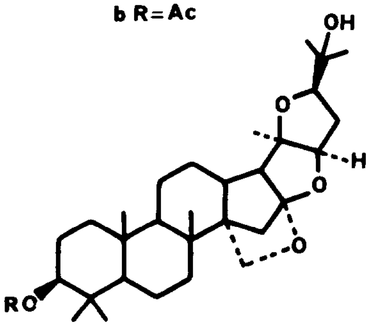
b R=Ac



II



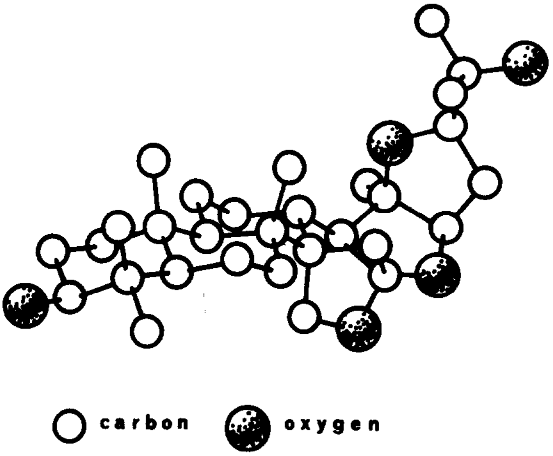
[a]



III

a R=H

b R=Ac



The structure and stereochemistry of trevoagenin D was established by crystal X-ray analysis. Crystal data: monoclinic space group $P2_1$, a = 11.58Å, b = 30.63Å, c = 8.06Å, β = 95.8°and Z = 4. A total of 4550 structural factors with $I \geqslant 2\sigma(I)$ were collected on a Philips PW1100 automatic diffractometer. The structure was solved by the Paterson search method[2] starting from a known terpene fragment of 22 atoms[3] and refinement[4] carried out by block diagonal least-squares procedures with isotropic thermal factors to a conventional value of 15%.

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References and Notes

1. A.G. González, M. Cortés and E. Suárez, *Tetrahedron Letters*, 2791 (1974).
2. B.P. Braun, J. Hornstra and J.L. Leenhouts, *Philips Research Report*, 24, 85 (1969).
3. Results to be published by the authors.
4. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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