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CONSTITUENTS OF LABIATAE. IX.[1]

TRACHINODIOL AND TRACHINOL, TWO NEW DITERPENES FROM SIDERITIS CANARIENSIS AIT.

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The present study reports the isolation of several diterpenes from Sideritis canariensis Ait. (Labiatae), endemic to the Canary Isles,[2] and the structure elucidation of two new compounds of the trachilobane series which we name trachinodiol and trachinol.

Trachinodiol (Ia), m.p. 175-176°, $[\alpha]_D^{20}$ -10° (c, 1·22%; $CHCl_3$), has the molecular formula $C_{20}H_{32}O_2$. Its IR spectrum (KBr) reveals the presence of hydroxyl functions (3380 cm^{-1}) and a cyclopropane ring (3020 cm^{-1}), while the NMR spectrum* shows the existence of a C$\underline{H}_2$OH group (6·50 d, 1H, J = 12 Hz; 7·10 d, 1H, J = 12 Hz), a proton geminal to a secondary OH function (6·55, 1H, $w_{\frac{1}{2}}$ = 6 Hz), three tertiary methyl groups (9·33, 9·05, 8·84) and additional evidence for a cyclopropane ring (complex signal at 9·40, 2H).

Acetylation of Ia yielded the diacetate Ib, $C_{24}H_{36}O_4$, M^+ 388, m.p. 134-135°, $[\alpha]_D^{20}$ 6·4° (c, 1·56%; $CHCl_3$), the NMR spectrum of which exhibits a singlet for two acetoxyles (8·00, 6H) and another one for C$\underline{H}_2$OAc (6·34, 2H); a broad singlet at 5·27 (1H, $w_{\frac{1}{2}}$ = 6 Hz) is attributed to C$\underline{H}$OAc, and a complex signal at 9·50 (2H) to a cyclopropane ring.

Oxidation of Ia with CrO_3 in acetone afforded the ketoaldehyde II, m.p. 140-142°, $[\alpha]_D^{20}$ -22° (c, 1·64%; $CHCl_3$), IR $\nu_{max}^{CHCl_3}$ 1735, 1700 cm^{-1}, the NMR spectrum of which shows the aldehyde signal at 0·79 (1H,s), and the ketoacid IVa which was characterized as its methyl ester IVb, m.p. 110-111°, $[\alpha]_D^{20}$ -19°

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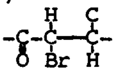
* τ-scale

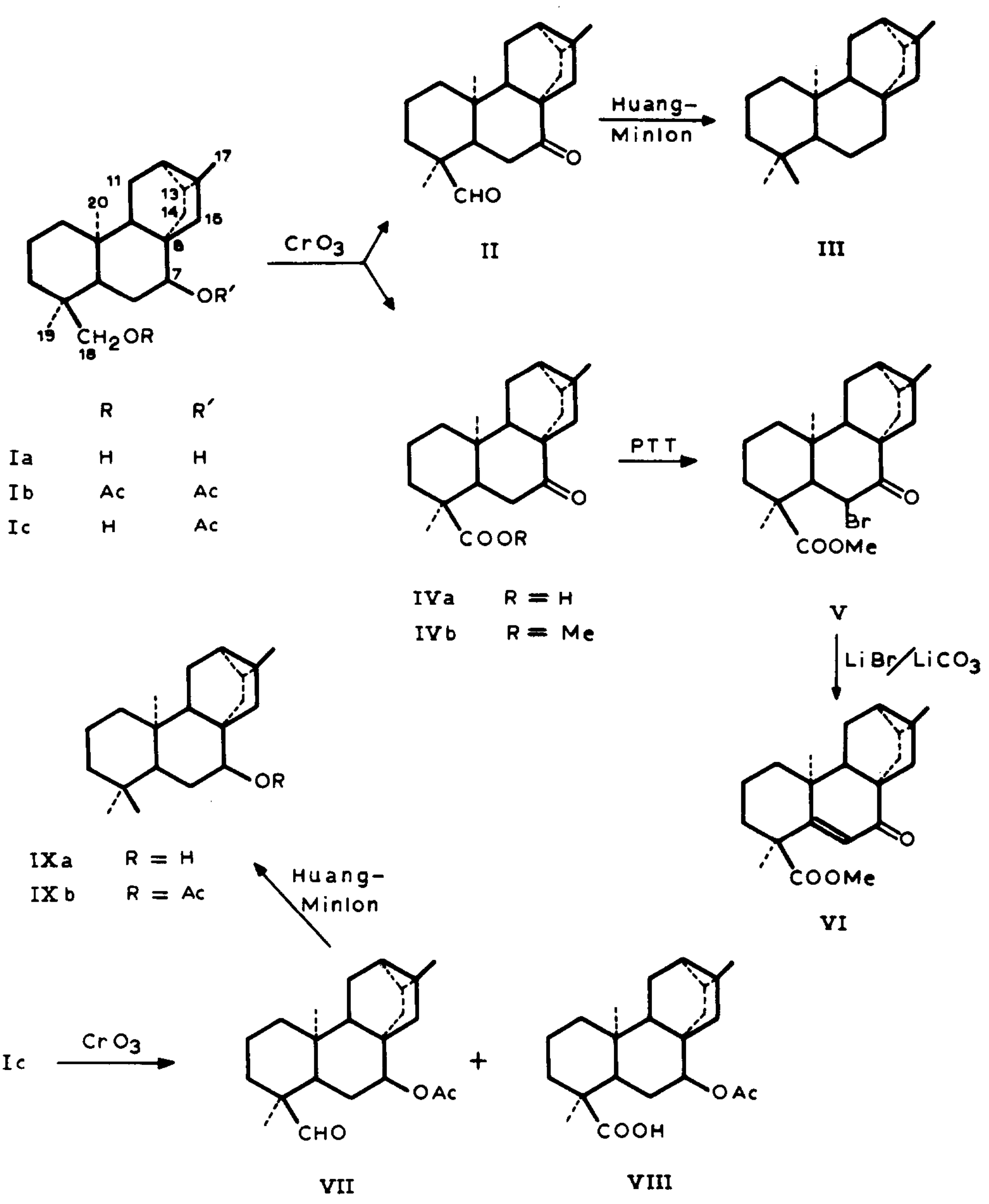
(c, 1·53%; $CHCl_3$), IR $\nu_{max}^{CS_2}$ 3020, 1724, 1703 cm^{-1}. Reduction of II by the method of Huang-Minlon gave trachilobane (III) identified by comparison with an authentic sample. The NMR data [3,4] and the lack of gem-dimethyl absorptions in the IR spectrum of Ia suggest that the primary OH function is located at C_4 of the trachilobane skeleton and that it is equatorial.

Bromination of IVb with trimethylphenylammonium tribromide yielded the liquid bromoketone V, $[\alpha]_D^{20}$ -3·3° (c, 1·82%; $CHCl_3$), IR $\nu_{max}^{CS_2}$ 3020, 1730, 1708 cm^{-1}, the NMR spectrum of which shows a typical AX pattern for the partial formula  $-\underset{O}{C}-\underset{Br}{\overset{H}{C}}-\underset{H}{\overset{C}{C}}-C-$ (5·51 d, 1H, J = 10 Hz, proton geminal to Br; and 7·38 d, 1H, J = 10 Hz, tertiary H). Only a C_7 ketone accounts for these assignations.

Dehydrobromination of V with LiBr/$LiCO_3$ gave the enone VI, m.p. 140-142°, UV λ_{max}^{EtOH} 245 nm, IR ν_{max}^{KBr} 3020, 1655, 1603 cm^{-1}; its NMR spectrum shows a singlet at 4·26 corresponding to one vinyl proton.

The conformation of ring B in V requires some comment: the fact that the C=O stretching frequency appears at the same position in the ketone IVb and the bromoketone V indicates that the bromine is axial.[5] The coupling constants observed in the AX system of V suggest a dihedral angle of 140° between C_5-H and C_6-H; consequently, ring B must have a slightly deformed boat conformation due to which the C_{10}-Me suffers a diamagnetic shift (0·14 ppm) in relation to IVb because it falls into the shielding cone of the carbonyl at C_7. Finally, the secondary OH group at C_7 in Ia must have axial (β) configuration because the $w_{\frac{1}{2}}$-value found for the geminal proton precludes axial-axial interactions.

The second diterpene, trachinol (IXa) has the molecular formula $C_{20}H_{32}O$, m.p. 105-106°, $[\alpha]_D^{20}$ 4° (c, 1·66%; $CHCl_3$), IR ν_{max}^{KBr} 3480, 3020, 1390, 1373 cm^{-1}, and forms the monoacetate IXb, $C_{22}H_{34}O_2$, M^+ 330, m.p. 148-149°, $[\alpha]_D^{20}$ 1·4° (c, 1·82%; $CHCl_3$). Its NMR spectrum is similar to that of trachinodiol except that it shows four tertiary methyl groups (singlets at 8·85, 9·07, 9·17, 9·21) and does not exhibit signals for a $C\underline{H}_2OH$ group. It was correlated with Ia as follows. Partial saponification of Ib gave a mixture of Ia and the monoacetate Ic. The latter, m.p. 157-160°, $[\alpha]_D^{20}$ 7·6° (c, 1·71%; $CHCl_3$), was oxidized with CrO_3 to the aldehyde VII (NMR: 0·72 s, 1H; 5·22, 1H, $w_{\frac{1}{2}}$ = 6 Hz; 7·92 s, 3H; 8·73, 8·86



and 8·96, singlets, 3H each) and the acetoxy acid VIII (m.p. 245-246°; IR ν_{max}^{KBr} 3500-2600, 1730, 1680 cm^{-1}; NMR: 5·34, 1H, $w_{\frac{1}{2}}$ = 6 Hz; 7·94 s, 3H; 8·83 s, 6H; and 9·00 s, 3H). On reduction by the method of Huang-Minlon VII gave a monoalcohol which was identical in all respects with trachinol (TLC, mixed m.p., IR and

NMR spectra).

To conclude, trachinodiol (Ia) is 7β,18-dihydroxy-trachilobane, and trachinol (IXa) 7β-hydroxy-trachilobane.

From the same plant have been isolated the hydrocarbon trachilobane for the first time in nature, and the known compounds (-)-kaurene, dehydroabietane, 12β,18-dihydroxy-(-)-kaurene [6], as well as a not yet characterized cyclopentanone belonging to the labdane series. From the biogenetical standpoint the broad variety of diterpene skeletons found in this species is of great interest.

The NMR spectra were performed in $CDCl_3$ with TMS as internal reference.

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