X-Ray Crystal and Molecular Structure of a New Diterpenoid of the *ent*-Atisane Class

By Isabel Carrascal, Benjamín Rodríguez, and Serafín Valverde*
(*Instituto de Química Orgánica, Juan de la Cierva, 3, Madrid 6, Spain*)

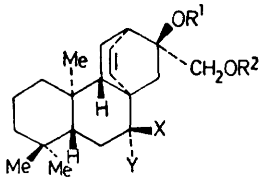
and José Fayos
(*Departamento de Rayos X, Instituto Rocasolano, Serrano 119, Madrid 6*)

Summary Chemical and crystallographic data are presented for a new diterpenoid, *ent*-atis-13-en-7α,16α,17-triol (**1**).

Recently, the first example of an oxygenated nitrogen-free diterpenoid of the *ent*-atisane class has been described.[1] This diterpenoid, sideritol (*ent*-atis-13-en-1β,16α,17-triol), isolated from *Sideritis angustifolia*, was assigned its structure on spectroscopic grounds and by correlation with *ent*-17-*nor*-atisane, previously prepared from atisine.[2] Mass spectral data of a minor component (**1**) isolated from the same source indicated it to be isomeric with sideritol. The i.r. and n.m.r. spectra of a diacetyl derivative of (**1**) showed them to be remarkably similar to those of sideritol diacetate.[1] In addition, a biogenetic relationship postulated[1] for these diterpenoids and others with the *ent*-15-beyerene skeleton[3] have been chemically achieved in the case of sideritol.[4]

All these considerations made structure (**1**) highly probable for this new compound. The half-width of the signal due to the proton geminal to the secondary alcohol ($W_{\frac{1}{2}}$ 5 Hz) indicates an axial configuration.

Since lack of material precluded a direct chemical correlation between both substances we attempted the preparation of a derivative suitable for a single-crystal *X*-ray diffraction analysis.



(1), $R^1 = R^2 = H$; $X = OH$, $Y = H$
(2), $R^1,R^2 = -CMe_2-$; $X = OH$, $Y = H$
(3), $R^1,R^2 = -CMe_2-$; $X,Y = O$

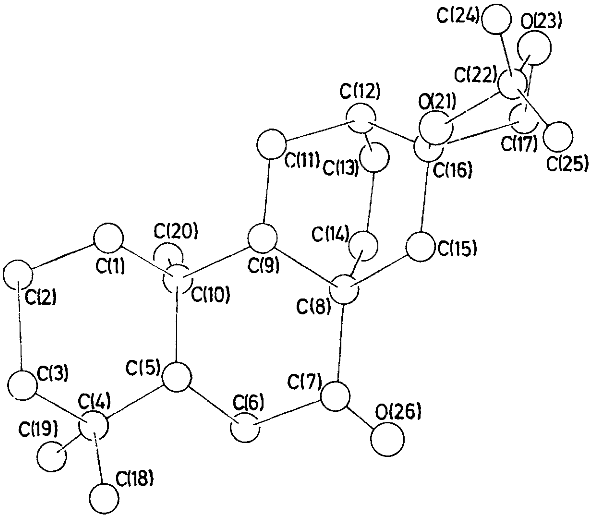


Figure. A perspective drawing of the *X*-ray model of the isosideritol derivative (**3**).

Compound (**1**) (isosideritol) affords readily the acetonide derivative (**2**) (m.p. 167—168 °C) and by oxidation of (**2**) with Py–CrO_3 a ketoacetonide (**3**) is obtained. The c.d. curve of (**3**) ($\Delta\epsilon_{290} = + 2{\cdot}2$) supports the proposed structure assuming ring B is in a chair-like conformation.[5]

Crystal data: Compound (**3**), transparent needles, orthorhombic, space group $P2_12_12_1$, with four molecules of $C_{23}H_{34}O_3$ in a unit cell of dimensions $a = 18{\cdot}500(5)$, $b = 16{\cdot}393(3)$ and $c = 6{\cdot}627(1)$ Å. A total of 3318 unique diffraction maxima with $\theta < 30°$ were recorded using monochromated Mo-K_α radiation (0·71069 Å) on a fully automated four-circle diffractometer and the structure was solved using the Multan program. Positional and anisotropic thermal parameters were corrected by least squares; the procedure converged to a standard crystallographic discrepancy index of 6·3%.[6] The Figure shows the final three dimensional *X*-ray model with the absolute configuration of the analogous molecule of sideritol.[1]

This molecular model confirms the proposed structure of (**3**). No bond distances and angles deviate from accepted values[7] for the given bond types. Double bond distances for the carbonyl O(26) and olefinic bridge C(13)–C(14) are 1·208(6) and 1·336(8) Å respectively. No intermolecular contacts between non-hydrogen atoms less than 3·38 Å were found. Information concerning molecular deformation and five-membered ring conformation is shown in this *X*-ray study. Electronic repulsion between all α-substituents: C(19), C(20), C(14) = C(13) and C(17) causes a bending effect on the main plane of the molecule (Figure). Distances between the α-substituents are C(19)–C(20) = 3·333(9), C(20)–C(14) = 3·122(8) and C(13)–C(17) = 3·101-(8) Å. Another deformation on the B ring is due to the presence of the carbonyl O(26) which flattens this side of the chair-ring B half way (40%) between the chair and half chair conformations. The bicyclo-octene system has, however, no torsion on the C(9)–C(11), C(14)–C(13) or C(15)–C(16) bonds. The five-membered ring has a C_2 half chair conformation with the pseudobinary axis going from C(16) to the C(22)–O(23) bond. Calculated values for Δ and Φ_m[8] are 497° and 36°, assuming the torsion Φ_0 on the C(16) C(17) bond.

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