X-Ray Crystal and Molecular Structure of the Acid-catalysed Rearrangement Product of a Beyer-15(16)-en-12-one System

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Summary A double 1,2-rearrangement of a 12-oxo-beyer-15(16)-ene system across the 12,13-single bond, reversible after reduction of the double bond, is confirmed by *X*-ray crystal structural analysis.

The isolation and identification of a new naturally occurring compound of the beyerane class[1] was recently reported.[2] Dissolution of *ent*-3β-hydroxybeyer-15(16)-en-2,12-dione (Ia)† in acetic acid–acetic anhydride resulted in its ready acetylation to (Ib): λ_{max} (EtOH throughout) 296 nm (ϵ 233), τ 9·26 (3H, s, 20-H). Addition of either conc. H_2SO_4, 70% $HClO_4$, or BF_3–Et_2O to the ice cold solution of either (Ia) or (Ib) induced rearrangement in high yield to the $\alpha\beta$-unsaturated ketone (IIa), m.p. 221—222°, λ_{max} 236, 305, and 324 nm (ϵ 7750, 82, and 92), ν_{max} (KBr throughout) 1742, 1716, 1665, 1235, and 820 cm^{-1}, τ 3·17 (1H, q, 15-H, $J_{15,16}$ 10 and J 2 Hz), 4·17 (1H, d, 16-H, $J_{16,15}$ 10 Hz), 9·38 (3H, s, 20-H). Compound (IIa) was

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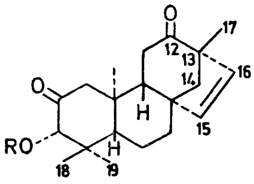
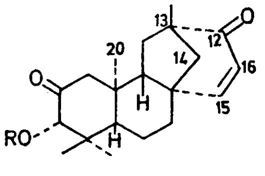
† The composition of all numbered compounds is based on high resolution mass spectrometry. Assignment of all structures is supported by spectroscopic evidence.

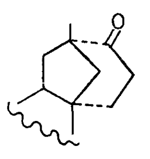
readily hydrogenated (Pd) at room temperature and atmospheric pressure to give (III), m.p. 213—214°, λ_{max} 287 nm (ϵ 62), ν_{max} 1750, 1725, 1705, and 1240 cm^{-1}, τ 9·00 (3H, s, 20-H). Addition of conc. H_2SO_4 to an ice-cold acetic acid–acetic anhydride solution of the dihydro-compound (III) afforded an isomer (IV), m.p. 215—216° (subl.), λ_{max} 288 nm (ϵ 59), τ 9·06 (3H, s, 20-H), identical in all respects to the 15,16-dihydro-derivative of (Ib).



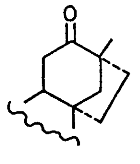
(I) a; R = H
b; R = Ac
c; $R = p\text{-}BrC_6H_4CO$



(II) a; R = Ac
b; $R = p\text{-}BrC_6H_4CO$

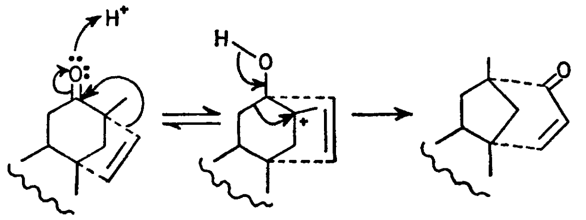


(III)



(IV)

The easy rearrangement of the beyer-15(16)-en-12-one system probably proceeds as indicated in the Scheme, the final product being stabilised by the conjugation of the two unsaturated functions.



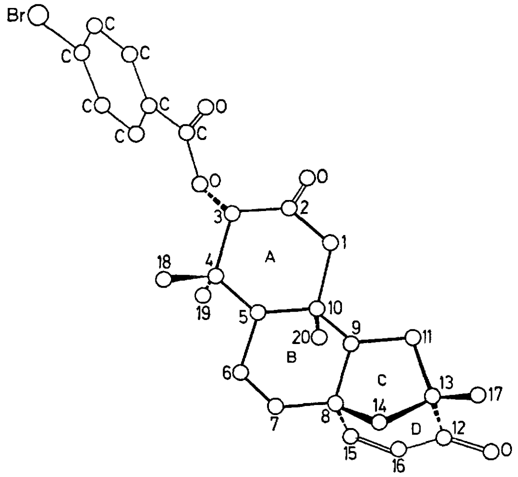
Scheme

Suitable crystals of the *p*-bromobenzoate (IIb), $C_{27}H_{31}BrO_4$, m.p. 297—299°, proved to be triclinic: space group $P1$, $a = 6{\cdot}35$, $b = 8{\cdot}71$, $c = 11{\cdot}93$ ($\pm 0{\cdot}01$ Å), $\alpha = 108{\cdot}3°$, $\beta = 97{\cdot}6°$, $\gamma = 102{\cdot}2°$ ($\pm 0{\cdot}1°$), $U = 598$ Å^3, $D_m = 1{\cdot}37$ g cm^{-3}, $Z = 1$, $M = 499$.

Integrated intensity data were collected by the multiple film Weissenberg method with Ni-filtered Cu-K_α radiation and measured with a densitometer. The structure was solved by the usual heavy atom and Fourier methods, and has been refined isotropically by block-diagonal least-squares to $R = 0{\cdot}17$ for 2430 observed data. (All calculations were done with the local set of programs;[3] further refinement is continuing.)

The basic stereochemistry of the skeleton is essentially similar to that of *ent*-beyerol,[4] (Figure: a projection down *a*) with all bond lengths within 0·03 Å of the usual values. The geometry of the C and D rings confirms that the rearrangement took place as suggested. The reason for the large chemical shift of the methyl group C(20) is now quite evident.[5] The distance between the two angular methyl groups C(20) and C(19) is 3·21 Å, while the distance between C(20) and C(15) of the double bond is 3·04 Å. This latter separation is distinctly shorter than the normal value of *ca.* 3·2 Å.[6] The close proximity of the π-cloud on C(15) to the hydrogen atoms on C(20) causes the marked shielding effect observed in the n.m.r. spectrum. The additional splitting of the n.m.r. signal of the C(15) proton may be due to either long-range coupling with the α axial hydrogen atom on C(6), or possibly coupling with the β proton on C(14), with which it forms an M system,[7] albeit not coplanar. As expected, the atoms O, C(12), C(16), and C(15) of the conjugated unsaturated ketone system are coplanar within 0·015 Å.

The large strain experienced by C(20) is reflected in the bond angles: C(9)–C(10)–C(20) 113°, C(5)–C(10)–C(20) 116°, C(1)–C(10)–C(20) 104°, showing that the C(20)–C(10) bond is bent outwards and away from both C(19) and C(15).



Figure

The angles in the C and D rings show quite large deviations from the usual tetrahedral value. The values of 104° for C(8)–C(9)–C(11) and 99° for C(9)–C(8)–C(14) are not unusual; similar small values have been observed in many other molecules for angles involving atoms in environments analogous to that of C(8).[8] In each case, where one carbon atom at the fusion of the rings of the perhydroindane system carries an angular (axial) carbon atom, the angle at this atom lies between 97 and 100° while that for the other carbon is between 104 and 105°. Distortions caused by variations in the torsion angle at the fusion of the trans fused perhydroindane system have been discussed in detail,[9] but distortions specifically due to one angular methyl group have not.

The ease with which the reverse rearrangement takes place in the dihydro-compound appears to be due to the increased compression at C(20) and C(15) caused by the additional hydrogen on C(15).[10]

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