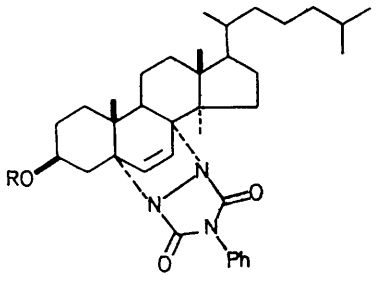
A Novel Route to Anthrasteroids: *X*-Ray Crystal Structure of 1(10→6)*abeo*-Cholesta-5,7,9-trien-3-yl *p*-Bromobenzoate

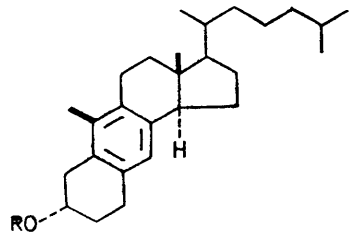
By NIGEL BOSWORTH, JOHN M. MIDGLEY, CHRISTOPHER J. MOORE, and W. BASIL WHALLEY*
(*The School of Pharmacy, The University, London* WC1N 1AX, *England*)
and GEORGE FERGUSON and WAYNE C. MARSH
(*Department of Chemistry, The University, Guelph, Ontario, Canada*)

Summary Treatment of the adduct from a steroidal 5,7-diene, and 4-phenyl-1,2,4-triazoline-3,5-dione, with boron trifluoride–diethyl ether gives the corresponding anthrasteroid whose structure was determined by *X*-ray crystallography.

ANTHRASTEROIDS, frequently of ill defined stereochemistry, have previously been prepared, in unsatisfactory yield, by the vigorous action of acidic reagents upon unsaturated steroids.[1] We now report a superior route commencing from steroidal 5,7-dienes.



(1)



(2)

Thus, the adduct, type (**1**; R = H, Ac, or PhCO), of a steroidal 5,7-diene, and 4-phenyl-1,2,4-triazoline-3,5-dione, is treated at room temperature in solution in benzene with BF_3Et_2O, when oxidative rearrangement occurs smoothly to give the corresponding anthrasteroid, type (**2**; R = Ac, PhCO), in which the original stereochemistry of the appropriate centres is preserved. For example, the adduct (**1**; R = H), m.p. 141—143°, from 7-dehydrocholesterol yields (**2**; R = H), having appropriate spectral and analytical properties.

The structure of (**2**) was established *via* a single crystal *X*-ray analysis of the *p*-bromobenzoate (**2**; R = *p*-Br-C_6H_4CO). The crystals are monoclinic, space group *C*2, $a = 25{\cdot}853(3)$, $b = 12{\cdot}102(1)$, $c = 10{\cdot}049(1)$ Å, $\beta = 104{\cdot}38(2)°$. Three-dimensional data were obtained using Mo-K_α radiation and a Hilger & Watts four-circle diffractometer fitted with a graphite monochromator. The structure was solved by the heavy-atom method, and refined by least-squares methods to a final *R* of 7·6% for 1684 observed reflections. The aromatic nature of ring B in the molecule (Figure 1) is determined by the planarity of the ring (see Figure 2) the equivalence of its bond lengths (mean value 1·390 Å) and the location of the hydrogen atom on C(7).

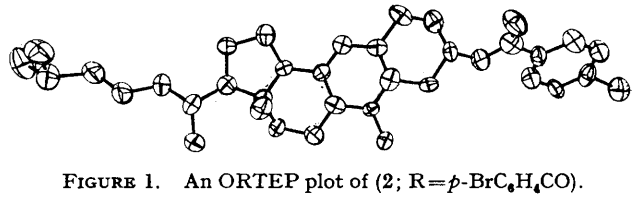


FIGURE 1. An ORTEP plot of (2; R=*p*-BrC_6H_4CO).

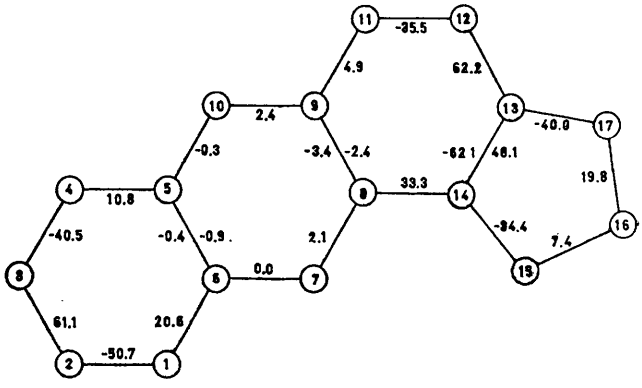


FIGURE 2. Torsion angles within the ring system in one anthrasteroid (2; R=*p*-BrC_6H_4CO).

The α-orientation of the hydroxy-group in the anthrasteroid (**2**;R = H) adumbrates the mechanism of this rearrangement; this will be discussed in our full paper.

This route to anthrasteroids appears to be of general applicability, and has been applied to ergosterol, and to the 5,7-dienes derived from, *e.g.*, stigmasterol, pregnenolone, dehydro-isoandrosterone, *etc*; the yield in the two-step process from the diene is generally greater than 90%.

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[1] See for example N. L. Wendler, 'Molecular Rearrangements', vol. 2, ed. P. de Mayo, Interscience, New York, 1964, pp. 1019, 1063 and references cited therein.