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THE COMPLETE STRUCTURE OF THE TRITERPENE ARBORINOL[1]

Olga Kennard* and L. Riva di Sanseverino
University Chemical Laboratory, Cambridge, England
H. Vorbrüggen** and Carl Djerassi
Department of Chemistry, Stanford University, California

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Partial structure I has recently been assigned[2] on the basis of various physical measurements and chemical reactions to the triterpene arborinol isolated from the leaves of Glycosmis arborea (fam. Rutaceae). Particularly noteworthy from a biogenetic standpoint was the unusual C/D stereochemistry, which had not been encountered hitherto among pentacyclic triterpenes. Insufficient material was available to settle the nature of rings D and E, although II and III were considered to be likely candidates.

The structure of arborinol has now been determined, through a three-dimensional X-ray diffraction study of 2α-bromo-arborinone. The particular derivative chosen afforded an analysis of the structure, without recourse to chemical assumptions other than the existence of discrete atoms in the molecule. The results indicate unequivocally the structure of 2α-bromo-arborinone as (IV). Previous chemical studies[2] relating to rings A, B, C and the trans configuration of the methyl

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* External Staff, Medical Research Council.

** Present address: Woodward Research Institute, Basel 7, Switzerland.

groups at the C/D ring junctions are confirmed. The ring systems D and E found in arborinol (VII) are similar to the structure recently proposed[3] for arundoin (V) which occurs[4] together with the methyl ether of isoarborinol[2] (3β-isomer of VII) in Imperata cylindrica (fam. Gramineae). Biogenetically, the structure of arborinol may be considered as being derived from a squalene-cyclization precursor (VI) followed by a concerted rearrangement to arborinol (VII).

The presence of the bromine atom in 2α-bromo-arborinone allows the direct application of the heavy atom method. This method commonly involves a series of electron density and structure factor calculations with gradual recognition of the molecule from the electron density maps.

In the present study this process was greatly speeded up and made more objective, by the use of a computer program "FATAL", developed by Dr. J. Rollett of Oxford University, to whom we are greatly indebted for his personal help with the calculations. "FATAL" lists, at each stage of the analysis, the position of all electron density peaks above a predetermined level and also the distances between the peaks. It is possible to select from such a list the peaks to be included in the next cycle of calculations, using, as criteria, the electron density levels and normal limits for interatomic distances. At each stage of the calculation the percentage disagreement factor R between observed and calculated structure factors is also printed out as an indication of the progress of the analysis.

"FATAL" was applied directly to the observed data and after 5 cycles the disagreement factor R dropped from 57% with Br alone to 26.5% with

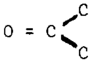
32 peaks, which accounted for all atoms (excluding hydrogens) of the empirical formula. The set of 32 peaks defined a chemically reasonable molecule with inter peak distances ranging from 1.33 to 1.58 Å: the oxygen atom could be recognised from the planarity of the  $O = C{<}^{C}_{C}$ and the short O = C distance. The double bond in ring C was also clearly recognizable. At this stage the chemical structure was essentially solved as (IV). Atomic positions were adjusted by a series of least squares calculations, first with isotropic and later with anisotropic temperature factors assigned to all atoms. (Diagonal matrix program by R. Diamand, Atlas Computer, University of London.)

Fig. (1) shows the configuration of the molecule and the interatomic distances at the present stage of the calculations. The R factor is 13.8% for observed terms only and the average standard deviation in interatomic distances between light atoms is 0.05 Å. Refinement is being continued and a full account of the analysis will be published elsewhere.

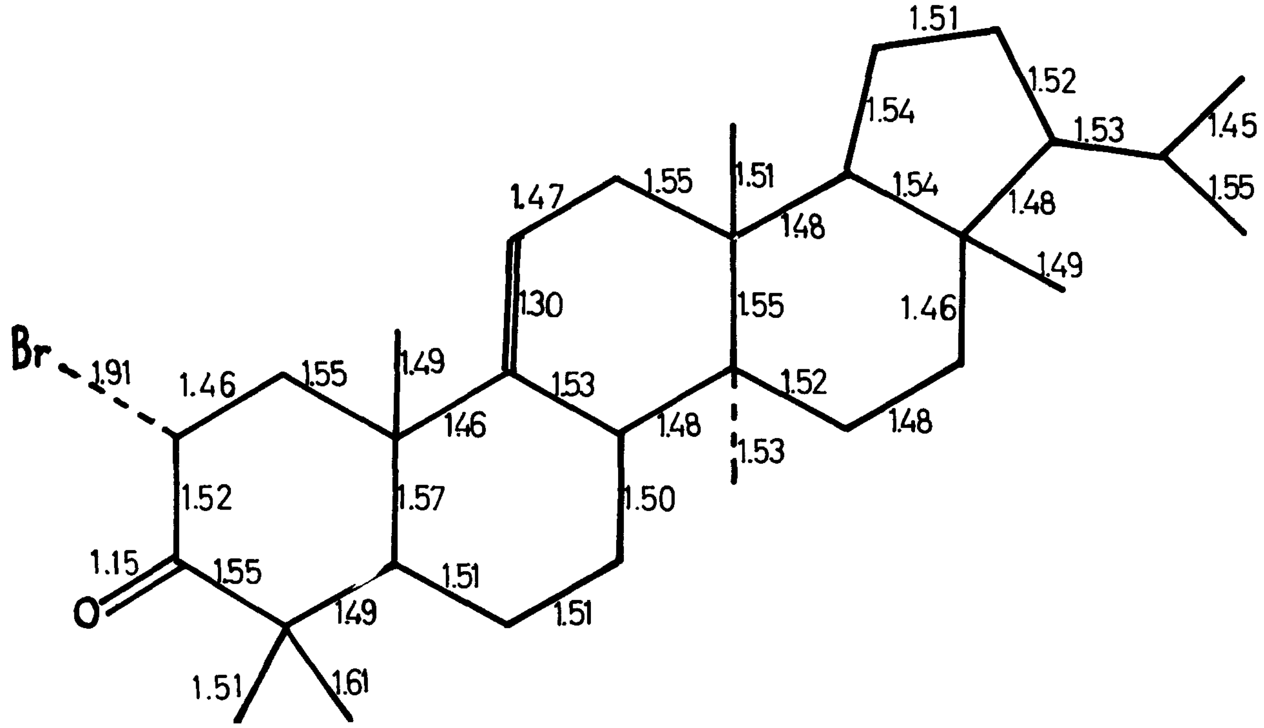
Crystal Data

2α-bromo-arborinone, $C_{30}H_{47}OBr$. Molecular Weight 503.3. M.P. = 219-220°. Provenance: see ref. (2). Orthorhombic, thick dipyramidal. Twinning common. a = 12.8398±120, b = 8.6786±111, c = 22.4576±436 Å; V = 2435.04 Å^3. Density measured by flotation = 1.39 gm. cm^{-3}. CuKα radiation ($\lambda K\alpha_1$ = 1.5403 Å, $\lambda K\alpha_2$ = 1.5443 Å). Cell dimensions by Woolfson's method[5] from the separation of $\alpha_1\alpha_2$ reflexions. Space group $P2_12_12_1$ (from absences).

Experimental

The intensities of 1800 reflexions were measured by eye from a series of Weissenberg photographs taken about the b axis. 76% of the Cu sphere was explored. The intensities were corrected for the usual factors other than absorption and the square root of these values used in the structure factor calculations.

Figure 1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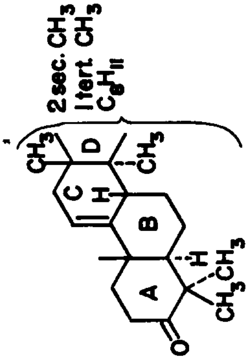

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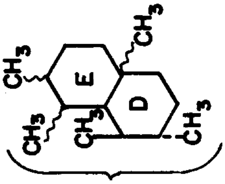

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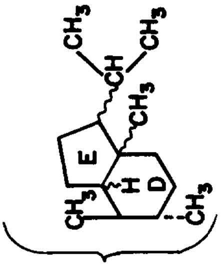

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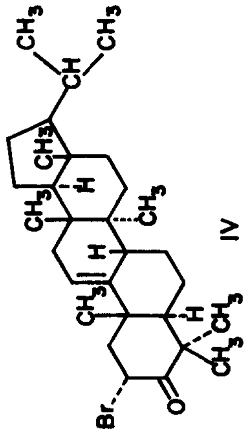

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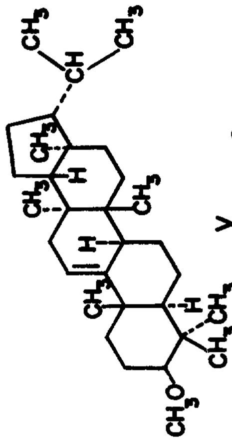

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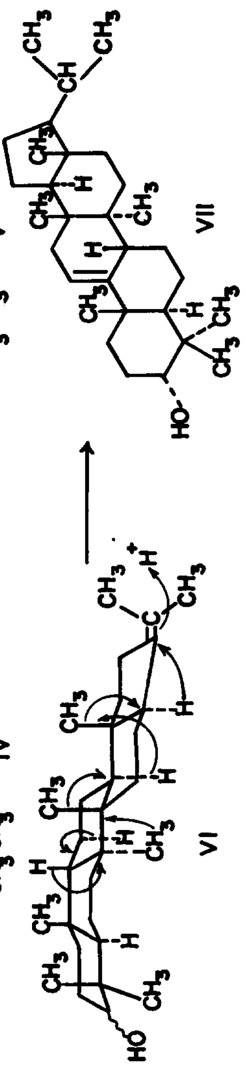

VI

VII

Acknowledgement

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