

## Revised Structure of the Triterpenoid Baccharis Oxide

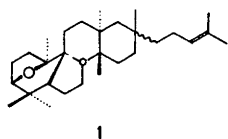
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Recently the constitution and partial stereochemistry of baccharis oxide was suggested as in 1.<sup>1</sup> The experimental data at that time did not allow assignment of the stereochemistry at C-17. This point recently has been settled.<sup>2</sup>

An X-ray study has been undertaken in order to establish the structure of baccharis oxide. The problem of determining the structure by X-ray methods appeared to be a suitable case for testing various versions of a programme being written for the direct determination of phase in non-centrosymmetric space groups.<sup>3</sup>



1

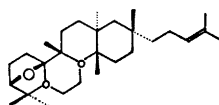
Single crystals were obtained from a petroleum ether solution. Crystal data are:

baccharis oxide  $C_{30}H_{50}O$ , orthorhombic, space group  $P2_12_12_1$ , cell parameters (with e.s.d.'s in parentheses)  $a = 7.413(1)$  Å,  $b = 11.866(2)$  Å,  $c = 29.057(2)$  Å, calculated density  $1.108 \text{ g cm}^{-3}$ ,  $Z = 4$ .

Intensity data were measured on an automatic Picker FACS-1 diffractometer using  $\text{CuK}\alpha$  radiation. A data set comprising 2453 reflexions with  $2\theta \leq 129^\circ$  (space-group extinctions not included) were recorded using the  $\omega/2\theta$  scanning mode.

The structure was solved by a multisolution tangent refinement procedure and refined by Fourier and least-squares techniques. All hydrogen atoms could be localized in a difference map and were included in a refinement where all atoms have been assigned isotropic temperature factors. The conventional  $R$ -factor is 0.097 at the present stage and is based on the full data set, including zero observations, using unit weights for all reflexions. Further refinement is in progress.

Fig. 1 gives a view of the structure as seen down the  $a$  axis. A more conventional representation is shown in 2. The ring skeleton consists of four 6-membered rings labelled from A to D and two 5-membered rings  $a$  and  $b$ . Rings A,  $a$  and



2

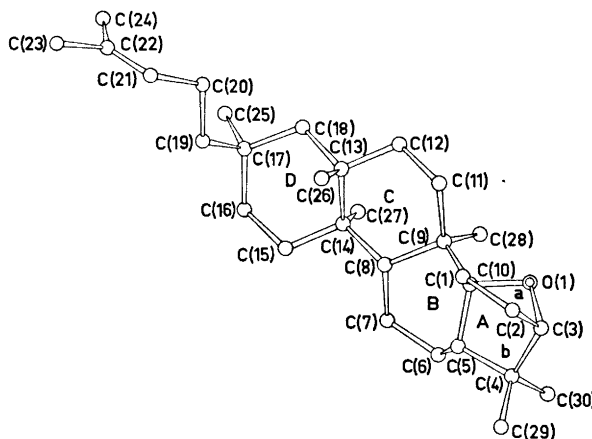
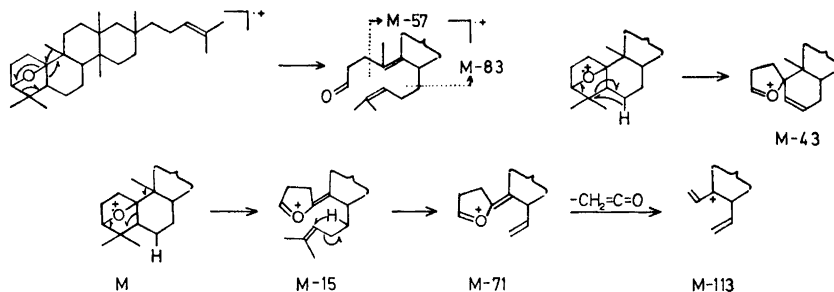


Fig. 1. Structure of baccharis oxide as seen along the  $a$  axis.



Scheme 1.

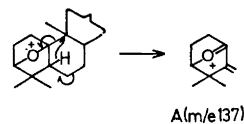
*b* form a tricyclic system where *a* and *b* share atoms C(3), O(1) and C(10) in the oxide bridge. C(5) is bonded to C(10), not to C(9) as proposed earlier,<sup>1</sup> and the methyl group is attached to C(9). This arrangement permits a conformation of the 6-membered ring system which can be described briefly as follows: *A* boat, *B* twist boat, *C* and *D* chairs in *trans* junction.

The methyl group at C(9) is axial and *gauche* to the oxide bridge the torsion angle O(1)–C(10)–C(9)–C(28) being *ca.* 32°. There is an angle of about 114.5° between the planes defined approximately by atoms C(3)–C(2)–C(1)–C(10) in ring *a* and by C(3)–C(4)–C(5)–C(10) in ring *b*. The side chain at C(17) is axial which confirms previous results.<sup>2</sup>

Lengths of bonds between formally *sp*<sup>3</sup>-hybridized ring carbon atoms range from 1.50 to 1.58 Å, the two C–O bonds are 1.47 Å. Internal C–C–C angles in rings *a* and *b* are in the range 99.8–102.7°, whereas a larger variation of *ca.* 7.0° around a mean value of 111.4° is found for the other C–C–C angles in the ring system. The C–O–C angle is calculated as 96.5°.

In our original proposal we were guided by the assumption that the rearrangements leading to baccharis oxide would proceed so rapidly that they simulate a series of S<sub>N</sub>2-like reactions. The present result suggests that the penultimate step, closure of the (protonated) heterocyclic ring, is sufficiently slow to allow the carbonium ion at C-10 to attain trigonal structure. Furthermore, the close proximity of the methyl group at C-9 to the ether oxygen

must be the reason for its rather low shift value ( $\tau$  8.80) in the NMR spectrum, and not that it is connected to an oxygen carrying carbon atom.



Scheme 2.

A revised proposal for the cleavages leading to the most prominent peaks in the mass spectrum of baccharis oxide is presented in Schemes 1 and 2.

The result presented here makes it necessary to delete halimane as a generic name.

A more detailed account of structure and programmes will be published elsewhere when refinement has been completed.

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1. Anthonsen, T., Bruun, T., Hemmer, E., Holme, D., Lamvik, A., Sunde, E. and Sørensen, N. A. *Acta Chem. Scand.* **24** (1970) 2479.
2. Suokas, E. and Hase, T. *Acta Chem. Scand.* **25** (1971) 2359.
3. Mo, F. *To be published.*

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