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X RAY STUDY OF SESQUITERPENE CONSTITUENTS OF THE ALGA *L OBTUSA* LEADS TO STRUCTURE REVISION [1]

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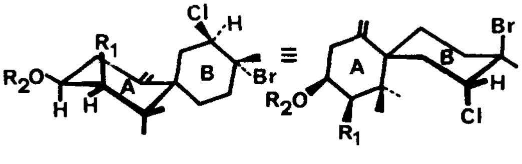
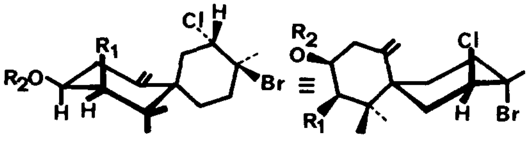
SUMMARY *L obtusa* sesquiterpenes were subjected to an x ray analysis in order to determine definitively the position of the Br and Cl atoms. As a result some previously-published structures [2] had to be revised.

In an earlier paper the structure and absolute configuration of a number of new polyhalogenated chamigrene-skeleton compounds (1, 2, 5 and 6) isolated from *Laurencia obtusa* were reported [2]. The placement of the Br and Cl atoms on Ring B in these substances was decided by applying a general rule based on observation of Laurencia sesquiterpenes whereby, whenever a vicinal *trans*-bromochloro substitution occurs, either the Cl or the Br will be in the tert position according to whether the system is *trans*-diequatorial or *trans*-diaxial [2]. Chemical techniques are not exact enough to determine the positions of the Br and Cl atoms in systems such as these as they change places with apparent ease[3,4] The compounds 1 (*iso*-obtusol, mp 118-120°, $\{\alpha\}_D$+33°) and 5 (obtusol, mp 145-146°, $\{\alpha\}_D$+10°) were therefore subjected to x ray analysis.

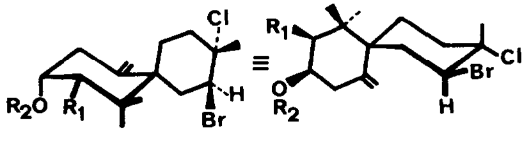
Our findings indicate that the structures 1 (and 2) and 5 (and 6) should be revised to 3 (and 4) and 7 (and 8), respectively, and hence that no general rule about the location of Cl and Br atoms in relation to the *trans*-diaxial or *trans*-diequatorial nature of the Br-Cl system can be devised.



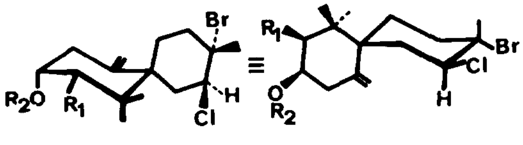
1, R_1=Br, R_2=H
2, R_1=H, R_2=H



3, R_1=Br, R_2=H
4, R_1=H, R_2=H



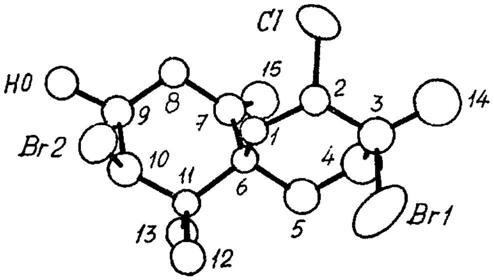
5, R_1=Br, R_2=H
6 R_1=H, R_2=H



7, R_1=Br, R_2=H
8, R_1=H, R_2=H

Iso-obtusol: monoclinic space group $P2_1$ with four molecules in a cell, *a*=15•821(3), *b*=7•157(1), *c*= 15•569(4)Å, β=104•64(1)°. 1146 observed Bijvoet pairs in the range 2<θ<25° were recorded on an automatic four-circle diffractometer with monochromatic MoKα radiation. The crystal structure was solved by the heavy atom method and refined by weighted least-squares analysis using the Bijvoet pairs. The lowest agreement factors for the absolute configuration in the Figure were R=•066 and Rw=•074 as opposed to R=•075 and Rw=•086 for the wrong enantiomorph which also showed, upon comparison of the 133 more relevant Bijvoet pairs, an averaged Bijvoet difference and Bijvoet ratio of 8•85 and •38, respectively, compared with the figures 1•57 and •09 for the right enantiomorph. No significant discrepancies were noted between the two crystallographically-independent molecules which were linked through hydrogen bonds O-H•••O. Both rings in the molecule have a chair conformation.

The crystalline structure of obtusol will be discussed elsewhere.



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