Crystallographic Data of Two Pinoresinol Derivatives

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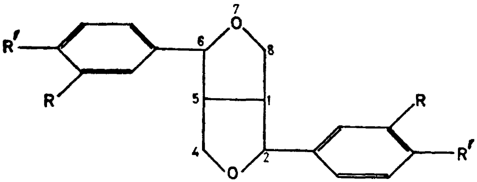
Pinoresinol belongs to that class of naturally occurring lignans which contains the 2,6-diaryl-3,7-dioxabi*cyclo*[3.3.0]octane nucleus:



In pinoresinol R = OCH_3, R' = OH. In the same class of lignans is found a number of compounds, some of which are optical isomers or diastereoisomers.

Conclusive evidence for a *cis*-configuration of the central bi*cyclo*-octane nucleus is given by the presence of optical activity in the dilactone formed by oxydative degradation [1] and in the diol formed by opening of the tetrahydrofuran rings by mild hydrogenolysis[2]. Another argument against a *trans* configuration is that this would be a sterically highly strained structure. It has further been shown by Erdtman [3] and by Gripenberg [4] that pinoresinol is symmetrical in the respect that the substituted phenyl groups are either both in *cis* or both in *trans* position to the bridge hydrogen atoms at 1 and 5.

In order to decide which of the two possibilities is present in pinoresinol, an X-ray crystallographic investigation has been started. Compounds chosen for this study are dibromo- and diiodopinoresinol-dimethylether (R = R' = OCH_3, halogen in *para* position to R). Crystals of these two compounds have been prepared by Professor H. Erdtman and placed at the author's disposal for an X-ray study.

Both halogen derivatives crystallize in very fine needles. The crystals of the bromo-compound show monoclinic symmetry with unit cell dimensions: a = 8.25 Å, b = 26.7 Å, c = 4.83 Å, β = 103.3°. With two molecules in the unit cell the calculated density is 1.75 gcm^{-3}. Very fine thread-like crystals have been observed to float in an aqueous solution of zinc iodide of density 1.70 gcm^{-3}.

Extinctions of the reflexions $0k0$ with $k = 2n + 1$ indicate one of the space groups $P2_1/m$ or $P2_1$. With two molecules in the unit cell only the latter is possible, because a point or plane of symmetry is not compatible with what is known about the molecule.

The crystals of the iodo-compound are tetragonal with unit cell dimensions a = 21.3 Å, c = 4.86 Å. Calculated density on the basis of four molecules in the unit cell is 1.93 gcm^{-3}. The observed density of very fine, thread-like needles, determined in the same way as for the bromo-compound, is 1.96 gcm^{-3}.

Extinctions of the reflexions 001 and 003 indicate one of the space groups $P4_2/m$ or $P4_2$. The former of these requires the molecule to possess a plane of symmetry. Therefore the space group $P4_2$ is considered to be the most probable.

An important detail of the unit cell of both halogen derivatives is the short c-axis of about 4.8 Å. This fact in itself may decide between the two possibilities for the geometry of the pinoresinol molecule, because it has to be confined to a rather low-ceilinged unit cell.

From what is known about the structure of furanose compounds certain details of the five-membered rings in the nucleus can be inferred. Each ring may be characterized by a plane of reference containing the bridge C—C bond and the oxygen atom. It is highly probable that the two remaining carbon atoms of one ring are situated on each side of such a plane. With a *cis* configuration of the central nucleus the planes of the two condensed five-membered rings make an angle of about 120° with one another.

As a plane of reference of the whole molecule may be chosen one going through the two oxygen atoms and being parallel to the bridge C—C bond. Taking reasonable bond angles and interatomic distances into account, the following features of the molecular structure may be inferred with a high degree of probability. Of the two bonds at each of the carbon atoms 2 and 6, not engaged in the ring, one must be pointing nearly perpendicular to the plane of reference, being in *trans* position to the bridge hydrogen atoms at 1 and 5. The other bond at 2 and 6 is closer to being parallel to the plane mentioned, making probably an angle near the tetrahedral with the first bond mentioned. For the molecule to be accommodated in the unit cell, the last mentioned bond must be the one occupied by the substituted phenyl group. A conclusion of these considerations is thus that the phenyl groups must be in *cis* position to the hydrogen atoms at the bridge carbons. The same conclusion is reached by Beroza[5], taking stability and intramolecular steric factors into consideration.

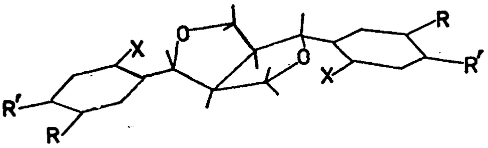


Fig. 1. A probable model of halogen derivatives of pinoresinoldimethylether. X = Br or I.

Fig. 1 shows a drawing in perspective of a probable model based on the arguments given.

A detailed structure determination of diiodopinoresinoldimethylether is in progress.

The author wishes to thank Professor H. Erdtman for placing crystals of the halogen derivatives of pinoresinoldimethylether at his disposal.

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The Structure and Conformation of 1,2,3-Tribromo*cyclohexane* (m.p. 51° C) in the Gas Phase

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Bornubert, Rio and Senechal[1] synthesized a 1,2,3-tribromo*cyclo*hexane (m.p. 51°C) to which they assigned the *eee* conformation on grounds of the compounds reaction used. A sample of their compound was investigated by gas phase electron diffraction in Oslo in order to test the validity of the asigned conformation. The diagrams were taken using distances of 48 cm and 19 cm between the diffraction point and the photographic plate. The data was treated in our usual manner[2], using a damping factor of 0.0036. The $\sigma(r)/r$ radial distribution curve obtained is shown in Fig. 1 (a).

The peak at $r = 5.72$ Å can only be due to a Br (1*e*)—Br (3*e*) distance. Of the six conformations of 1,2,3-tribromo*cyclo*hexane that can be distinguished with electron diffraction, only those corresponding to *eee* and *eae* contain this distance. Theoretical radial distribution curves were therefore calculated for each of these conformations. It was found that the theoretical *eee* curve gave better agreement with the experimental curve than did the theoretical *eae* curve. However, the agreement was still not particularly good. The peaks at $r = 5.72$ Å and 4.27 Å in the theoretical *eee* curve were too high, and that at $r = 4.63$ Å too low. Since the substance is a well defined isomer, these anomalies could only be explained by assuming that in the gas phase it contains either a mixture of the *eee* and *aaa* forms, or else a mixture of the *eae* and *aea* forms. Only the *aaa* conformation would give rise to a substantial peak in the neighbourhood of $r = 4.63$ Å (due to the Br (1*a*)—Br (2*a*) and Br (2*a*)—Br (3*a*) distances), so it was concluded that the substance must be a mixture of the *eee* and *aaa* forms in the gas phase.

Further theoretical calculations were made using structural models based on the latest parameters for the *cyclo*-hexane ring obtained in our department: C—H=1.103 Å,