Short Communications

The Configuration of the α-Phloroglucitol Molecule

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The configurations of the two stereo-isomeric phloroglucitols $^1,^2$ have not been determined and it has therefore not been known which of them corresponds to the $1 \alpha, 3 \alpha, 5 \times \text{compound}$ and which to the $1 \alpha, 3 \varepsilon, 5 \times \text{compound}$. Wislicenus $^1$ observed, however, that the phloroglucitol dihydrate crystallizes in rhombic dodecahedrons and we have carried out an X-ray analysis in order to ascertain whether the molecule itself has trigonal symmetry in these crystals or not.

The α-phloroglucitol examined was prepared from phloroglucinol using Wislicenus’ original method $^1$. The crystals (from aqueous solution) were indeed trigonal, and X-ray examinations based on Laue, rotation and Weissenberg photographs show that the unit cell is rhombohedral with $r = 8.71 \text{Å}$, $a = 56^\circ 10'$, The density of the crystals is 1.31 and the number of $C_6H_8(OH)_3 \cdot 2H_2O$ in the unit cell therefore 2. The Laue symmetry is $D_{3d} - \bar{3}m$. Besides the extinctions characteristic of a rhombohedral cell the only systematic extinction is the absence of $hhl$ (rhomb.) where 1 is odd. Possible space groups are therefore $C_{3v}^6 - R3c$ and $D_{3d}^3 - R3c$. Now according to observations by Mr. Erik Blomgren in Uppsala, the crystals exhibit strong piezoelectricity, and the correct space group is therefore $C_{3v}^6 - R3c$. In this space group the coordinates of the centers of the phloroglucitol molecules may be chosen as $000$ and $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, and the molecules have trigonal symmetry. The coordinates of the four water molecules are: $uuu; u + \frac{1}{2} \cdot u + \frac{1}{2}, u + \frac{1}{2}$ and $vvv; v + \frac{1}{2}, v + \frac{1}{2}$. It is obvious therefore, that the α-phloroglucitol is the $\alpha, \beta, \varepsilon = \varepsilon, \varepsilon, \varepsilon$ compound. The β-phloroglucitol must therefore be the $\alpha, \varepsilon, \varepsilon = \varepsilon, \varepsilon, \varepsilon$ compound.

We now assume the $\alpha, \varepsilon, \varepsilon$ form to be present in the crystal, tetrahedral valency angles, and the C—C and C—O distances to be 1.54 and 1.42 Å respectively. Remembering that all the water molecules are situated on the trigonal axes, one parameter only has to be determined as far as the projection of the structure into the (111) plane is concerned. We choose as a parameter the angle $\varphi$ between the line joining neighbouring molecular centers situated in the same (111) plane and the projection into that plane of the carbon-oxygen bond. Using the trial and error method it was found that this angle can only differ very little from zero.

This is far from surprising when we consider the positions of the water molecules. Throughout the structure two sets of equilateral triangles of alcoholic oxygen atoms will occur. The oxygen atoms of each triangle belong to three different phloroglucitol molecules, but they are all lying in the same (111) plane. If the angle $\varphi$ is equal to zero the dimensions of the two sets of triangles are identical with a O—O distance of 4.67 Å.

On the (111) axis joining the centers of two neighbouring $O_2$-tringles two water molecules will have to be placed. The
length of this axis is $\frac{21.96}{6} \text{ Å} = 3.66\text{ Å}$.

The resulting $0-O$ distances will then be shorter than should be expected in the absence of hydrogen bonds. The angle $\varphi$ being zero or very nearly so, four hydrogen bonds from each water oxygen will be formed, one to the oxygen atom of the other water molecule and one to each of the three nearest alcoholic oxygens. The fact that the two $O_3$ triangles are identical or nearly identical in size suggests that the vertical distances between their planes and the nearest water oxygens will be nearly identical. The best agreement between calculated and estimated intensities was

indeed reached if the $O_3-O-O_3$ group was assumed to be symmetrical and the distance between the two water oxygens equal to 2.76 Å. The distance from each of these oxygen atoms to the three alcoholic oxygen neighbours will then be 2.74 Å. These distances are in good agreement with hydrogen bond distances found in similar cases. It should be pointed out, however, that the oxygen tetrahedrons surrounding each of the water oxygens are not regular tetrahedrons. The shape of the $O_3-O-O_3$ groups linking the organic molecules together is illustrated in Fig. 1. In Fig. 2 a projection into the (111) plane of part of the structure is reproduced. As an illustration of the agreement between estimated intensities (chiefly from Weissenberg photographs) and calculated intensities Fig. 3 has been drawn. The figure contains calculated (joined by fully drawn lines) and estimated intensities (dotted lines) of 36 of the more important reflexions.

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1. Wislicenus, W. *Ber.* 27 (1894) 357.

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