Short Communications

The Configuration of the α-Phloroglucitol Molecule

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The configurations of the two stereo-iso-meric phloroglucitols [1,2] have not been determined and it has therefore not been known which of them corresponds to the 1 ϰ, 3 ϰ, 5 ϰ compound and which to the 1 ϰ, 3 ε, 5 ϰ compound. Wislicenus [1] observed, however, that the phloroglucitol dihyrate crystallizes in rhombohedrons 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 $r = 8.71$ Å, $a = 56° 10'$. The density of the crystals is 1.31 and the number of $C_6H_9(OH)_3 \cdot 2H_2O$ 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 l is odd. Possible space groups are therefore C_{3v}^6—$R3c$ and D_{3d}^6—$R\bar{3}c$. 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: $u\,u\,u$; $u + \frac{1}{2} \cdot u + \frac{1}{2}$, $u + \frac{1}{2}$ and $v\,v\,v$; $v + \frac{1}{2}$, $v + \frac{1}{2}$, $v + \frac{1}{2}$. It is obvious therefore, that the α-phloroglucitol is the ϰ, ϰ, ϰ ⇌ ε, ε, ε compound. The β-phloroglucitol must therefore be the ϰ, ε, ϰ ⇌ ε, ϰ, ε compound.

We now assume the ϰ ϰ ϰ 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 φ 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 φ 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_3-triangles *two* water molecules will have to be placed. The
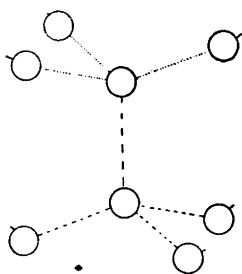
Fig. 1. The O_3—O—O—O_3 arrangement.

length of this axis is $\dfrac{21.96}{6}$ Å = 3.66 Å.
The resulting O—O distances will then be
shorter than should be expected in the
absence of hydrogen bonds. The angle φ
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
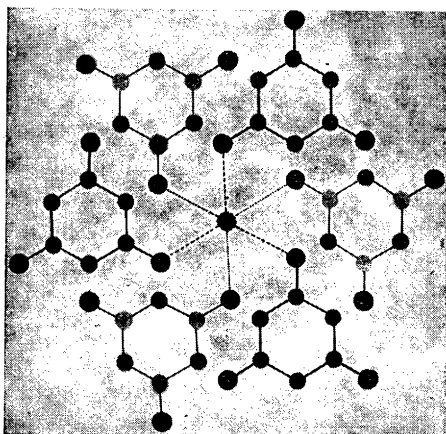calculated and estimated intensities was
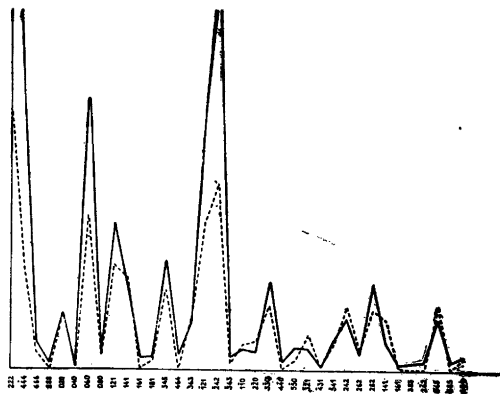

*Fig. 2. Part of the structure projected along
[111].*

*Fig. 3. Calculated (—) and estimated (- - -)
intensities.*

indeed reached if the O_3—O—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 alcoho-
lic 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 regu-
lar tetrahedrons. The shape of the
O_3—O—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 Weis-
senberg photographs) and calculated inten-
sities 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 re-
flexions.

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1. Wislicenus, W. *Ber.* **27** (1894) 357.
2. Lindemann, H., and Baumann, H. *Ann.*
   477 (1929) 78.