The Unit Cell and Space-Group of β-Octamethylcellobiose and β-Hendecamethylcellotriose.

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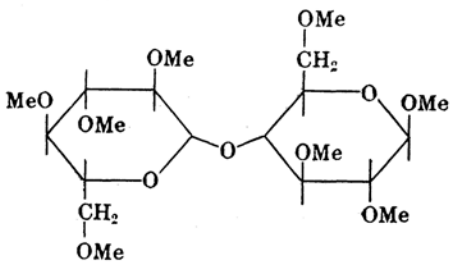
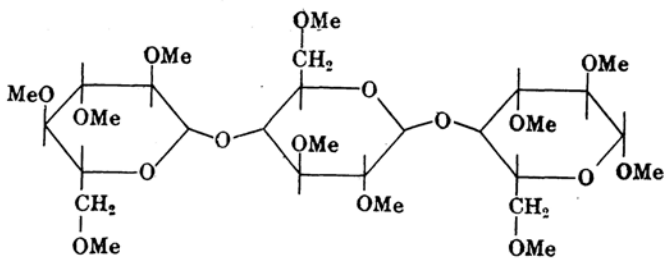
By means of X-rays the dimensions of the rhombic unit cell have been determined to be $a = 12.0$ Å, $b = 43.7$ Å, $c = 4.50$ Å for β-octamethylcellobiose and $a = 21.3$ Å, $b = 34.5$ Å, $c = 4.50$ Å for β-hendecamethylcellotriose. These substances possess the same corresponding space group $D_2^4 - P2_12_12_1$, the number of molecules in the unit being four. The results are completely different from that reported by Trogus and Hess.

Introduction. An X-ray investigation on the crystals of β-octamethylcellobiose and β-hendecamethylcellotriose had already been made by Trogus[1] in 1932 and by Trogus and Hess[2] in 1935, who determined the identity period along the needle axis of the former crystal to be 4.3Å



β-Octamethylcellobiose



β-Hendecamethylcellotriose

and the unit cell of the latter to be monoclinic having the dimensions $a = 20.4$Å, $b = 4.8$Å (along the needle axis), $c = 21.0$Å, with $\beta = 75°$. From these constants and the density $\rho = 1.25$, the number of the methylcellotriose molecules in the unit was calculated to be 2–3, and, according to their choice, the two molecule unit is more probable. The substances

(1) C. Trogus, *Naturwissenschaften*, **20** (1932), 317.
(2) C. Trogus and K. Hess, *Ber.*, **68** (1935), 1605.

used in these investigations were bundles of fine long crystals paralleled along the needle axis and so the photographs taken corresponded to the complete rotation or fiber diagrams. Thus not quite free from doubt is the correctness in indexing the reflexions from these photographs and it seems also strange that the number of molecules in the unit calculated by us to be 2.3 is so much deviated from the whole number 2.

Accordingly, it seems very desirable to make re-examination more precisely by the single crystal methods. Fortunately comparatively large single crystals of β-methylcellobiose and β-methylcellotriose were obtained from aqueous solutions in our laboratory and the present investigation has been carried out with these substances.[3]

The Unit Cell and Space-Group. The crystals used were long thin rhombic prisms, the diameters being about 0.3 mm. for octamethylcellobiose and about 0.1 mm. for hendecamethylcellotriose.

In each case, the needle axis was taken as the c-axis which corresponds to the b-axis chosen by Trogus and Hess. There is a perfect cleavage parallel to a plane along the needle axis, and the axis perpendicular to this cleavage plane was chosen as the a-axis.

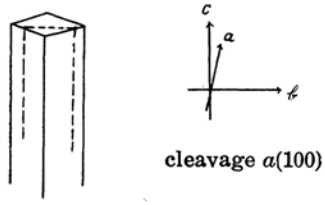


Fig. 1.

The apparent densities, which were measured by the floatation method in aqeous solution of K_2CO_3, are about 1.23 and 1.26 respectively. The true values should perhaps be somewhat larger than the above, because of the adsorbed air on the surface of the crystals which could not be removed completely.

The symmetry of Laue photographs taken with X-ray beams normal to the a-plane (100) and b-plane (010) was D_{2h}. Oscillation photographs about the c-axis and Weissenberg photographs of $(hk0)$, (hkl) with $l = 1$ to 3, and $(0kl)$ were taken with Cu K_α-radiation. The results of the analyses of these photographs are as follows:

	a	b	c	Number of mols. in the unit.
Octamethylcellobiose	12.0 Å	43.7	4.50	$3.88 \approx 4$
Hendecamethylcellotriose . . .	21.3 Å	34.5	4.50	$3.87 \approx 4$

Assuming the number of molecules in the unit to be four, the densities are calculated to be 1.27 and 1.30 respectively. Taking the accuracy of the measurements into account, these values seem very reasonable.

As mentioned above Laue photographs show D_{2h} symmetry. Weissenberg photographs show that the angles α, β and γ between three axes are all 90° and, moreover, the intensities of the reflexions of $(hk1)$, $(\bar{h}k1)$, $(h\bar{k}1)$ and $(\bar{h}\bar{k}1)$ are all completely equal to each other and those of $(hk2)$, and $(\bar{h}k2)$, and $(h\bar{k}2)$, and $(\bar{h}\bar{k}2)$ are all equal, and so on. Thus there is

(3) These substances were prepared by means of acetolysis followed by methylation of cellulose.

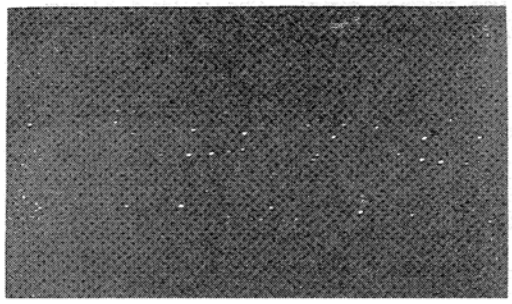


Plate 1. (*hk*0) Weissenberg photograph of β-octametylcellobiose.

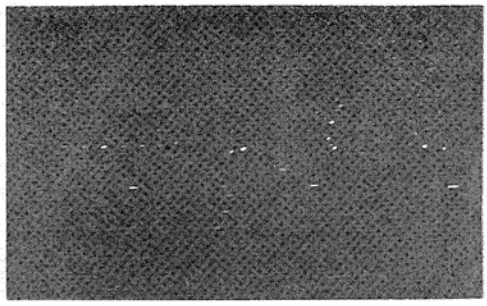


Plate. 2. (*hk*1) Weissenberg photograph of β-octamethylcellobiose.

no doubt that the crystals belong to the rhombic system instead of monoclinic. Powder photographs of these substances agree with those of Trogus and Hess completely, so that the substances used by them and by the present author must be identical, possibility of polymorphism being thus eliminated. Perhaps the results of Trogus and Hess would be incorrect.

It is characteristic that reflections (*h*00), (0*k*0) and (00*l*) are not present when $h = 2n + 1$, $k = 2n + 1$ and $l = 2n + 1$. Accordingly, the space groups of these substances are D_2^4–$P2_12_12_1$.

Some Discussion about Molecular Arrangement in the Crystals. The value 4.50A of the identity periods along the *c*-axis for both substances and the present chemical view of the pyranose unit lead to the arrangement that the molecular plane containing the pyranose rings, or at least the longest axis of these molecules, lies perpendicular, or almost perpendicular, to the needle axis. Although this was suggested by Trogus and Hess, the present equality of the value 4.50Å for both crystals seems to account for the analogous structure in a more natural manner.

The acetyl derivatives of these substances were investigated in 1934 by Leuck and Mark,[4] and they also concluded that the molecular chains lie perpendicular to the needle axis from the fact that their identity periods of these acetyl-compounds are always 5.7Å corresponding to the above value 4.50Å.

In this respect, molecular arrangement in crystals of acetylderivatives suggested by Leuck and Mark is quite analogous to that of methylderivatives given by Trogus and Hess and by the present author.

Furthermore, Leuck and Mark speculated that the identity period 15Å along the *b*-axis is common to all these substances and that along the *a*-axis increases steadily with the number of glucose residues in the molecule: viz. $\frac{1}{2} \times 24.3$Å, 21Å and 29–30Å for acetyl derivatives of glucose, cellobiose, and cellotriose. According to this view, the molecular chains of these substances are to be parallel, or almost parallel, to the *a*-axis in the crystals.

In the present investigation of the methyl derivatives, however, such a relation is not found between the dimensions of the two unit cells. There

(4) G. J. Leuck and H. Mark, *J. Am. Chem. Soc.*, **56** (1934), 1959.

are no common values except along the needle axis. The period along the a-axis of methylcellobiose (12.0Å) is smaller than that of methylcellotriose (21.3Å), and the b-axis of the former (43.7Å) is larger than that of the latter (34.5Å). These facts suggests that the molecular chains are not parallel but have some inclination to each other, accordingly to the a-axis, and have such a tendency that the angle of this inclination decreases with the increasing number of glucose residues in the molecule, in other words the molecular chains of methylcellotriose are more parallel to each other (or to the a-axis) than methylcellobiose.

In such a way the molecules of β-octamethylcellobiose or β-hendecamethylcellotriose are presumably arranged in the rhombic crystal lattice, fulfilling at the same time the condition of the space group symmetry D_2^4.

In conclusion, the author wishes to express his best thanks to Professor I. Nitta, Professor Y. Go, and Dr. T. Watanabe for their kind interest during the work, and also to Mr. H. Tani for supplying the crystals which were used in this investigation.

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