

Rotation, zero-level Weissenberg photographs about the needle (*b*) axis, and precession photographs indicate the space group $C_{2h}^2-P2_1/c$ with unit cell dimensions*

$$a = 21.35 \pm 0.05, \quad b = 6.05 \pm 0.03, \quad c = 14.96 \pm 0.05 \text{ \AA}; \\ \beta = 111^\circ 15' \pm 15'.$$

Assumption of eight molecules in this unit cell gives a calculated density of 1.673 g.cm.⁻³ in agreement with the observed value of 1.654 g.cm.⁻³.

The Patterson projection on (010) shows a large peak at $u = 0.223$ and $w = 0.362$ in the quarter-cell $0 \leq u \leq \frac{1}{2}$ and $0 < w \leq \frac{1}{2}$. It is possible that the projection of the two molecules in the asymmetric unit on (010) are mutually parallel, so that this large peak is the sum of interatomic vectors between corresponding atoms. This peak lies on the line from $(0, \frac{1}{4})$ to $(\frac{1}{2}, \frac{1}{2})$, which together with the line from $(0, 0)$ to $(\frac{1}{2}, \frac{1}{4})$ determine the pseudo-orthorhombic cell in this projection. Further analysis of this structure is being undertaken.

The orthorhombic form, with some orthorhombic variants, was obtained by dropping an acetone solution of TNT into ether or alcohol held in a dry-ice-acetone bath. From rotation and zero-level Weissenberg photographs about the needle axis of a needle-like lath the unit-cell dimensions

$$a = 20.07 \pm 0.08, \quad b = 6.09 \pm 0.04 \quad \text{and} \quad c = 15.03 \pm 0.07 \text{ \AA}$$

were obtained. Extinction of $\{h0l\}$ with *l* odd and $\{hk0\}$ with *h* odd indicate that $C_{2v}^2-P2_1ca$ or $D_{2h}^{11}-Pmca$ are probable space groups. Assumption of eight molecules in this unit gives a calculated density of 1.642 g.cm.⁻³.

When TNT crystals are grown, either from solution in various solvents or by sublimation, at temperatures between 0° C. and 70° C., the simple monoclinic form is very rarely found and the simple orthorhombic form never has been found in the course of this study. Instead of the simple monoclinic form, several variants of this form appear. These variant forms appear simultaneously and are recognized by the appearance of additional reflections in the pseudo-orthorhombic reciprocal lattice rows for which *l* is odd of the first- and higher-layer-line Weissen-

* A pseudo-orthorhombic cell with these same *b* and *c* values and with $a = 39.81 \pm 0.05 \text{ \AA}$ and $\beta = 90^\circ 30' \pm 5'$ can be chosen. Ito (1950) chose this cell, but concluded that the space group is C_{2h}^2-B2/c . However, his crystals did not consist solely of the monoclinic form.

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Unit-cell data for maltose hydrate and some acyl saccharide derivatives.* By DEXTER FRENCH, *Chemistry Department, Iowa State College, Ames, Iowa, U.S.A.*

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The unit cell data presented in Table 1 were obtained by the author and by previous investigators from oscillation and goniometer patterns of single crystals using Cu K α radiation. The compounds were selected in hopes of obtaining packing information which could be applied to the problem of the starch crystal structure.

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berg photographs. The appearance of these added reflections doubles (42.70 Å) or quadruples (85.40 Å) the length along the *a* axis without changing the lengths along the other two axes. In many cases, a streak appears along the pseudo-orthorhombic reciprocal-lattice rows for which *l* is odd, in the first- or higher-layer-line photographs, with or without additional spots, indicating some form of disorder along the *a* axis. A similar situation occurs in the case of orthorhombic crystals grown at low temperature (-70° C.). Here, along with the simple orthorhombic form, crystals have been obtained which show additional reflections on the first- and higher-layer-line photographs which indicate a doubling of the *a*-axis length (40.14 Å). Other crystals show a streak along the reciprocal lattice rows for which *l* is odd, with or without additional reflections, on the first- and higher-layer-line photographs. Some crystals obtained from acetone solution at 0° C. have given photographs which appear to be identical to those obtained from low-temperature orthorhombic crystals with the doubled *a* axis. Ito (1950), whose studies were based solely on photographs containing the additional reflections, reports a monoclinic variant with a tripling of the *a* axial length. This has not been observed in these studies.

In examining photographs of the variant forms, considerable variation is noted in the shape and intensity of equivalent reflections from crystal to crystal. These variations appear best explained by considering the crystals to be composed of twinned fragments of the simple or variant forms which are nearly aligned with respect to their pseudo-orthorhombic axes.

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Astbury & Marwick (1931) have pointed out that the spatial requirements of a glucopyranose unit are c. 4.5 Å (thickness), 5.5 Å (length along a line joining C₁ and C₄) and 7.5 Å (breadth). From space-filling models it appears that 4.5 Å is practically an irreducible packing thickness and that any other overall packing dimension is considerably larger than this. It is likely then that the 5 Å dimensions of glucose, cellobiose and maltose are closely related to the thickness of the glucopyranose unit.

Table 1. *Unit-cell data for carbohydrates and derivatives*

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	Space group
α -Glucose (<i>a</i>), (<i>b</i>)	10.40	14.89	4.99	—	$P2_12_12_1$
α -Glucose hydrate (<i>b</i>)	8.72	5.03	9.59	98	$P2_1$
β -Cellobiose (<i>a</i>)	11.1	13.2	5.00	90	$P2_1$
β -Maltose hydrate	10.7	15.2	4.9	97.5	$P2_1$
Sucrose (<i>c</i>)	11.0	8.7	7.65	103.5	$P2_1$
Levoglucofan	6.7	13.4	7.5	—	$P2_12_12_1$
Raffinose.5H ₂ O	9.0	12.2	23.4	—	$P2_12_12_1$
α -Glucose pentaacetate	5.54	23.9	14.8	—	$P2_12_12_1$
β -Glucose pentaacetate (<i>d</i>)	5.68	25.0	14.0	—	$P2_12_12_1$
α -Cellobiose octaacetate	5.5	27.6	23.1	—	$P2_12_12_1$
β -Cellobiose octaacetate (<i>d</i>)	5.6	19.2	31.6	—	$P2_12_12_1$
β -Maltose octaacetate	5.75	25.8	24.2	—	$P2_12_12_1$
Glucose tetrapropionate (<i>e</i>)	5.7	16.0	23.5	—	$P2_12_12_1$
β -Cellobiose octapropionate	5.5*	—	—	—	—
β -Cellobiose octabutyrate	5.5	18.5	52.0	—	$P2_12_12_1$
β -Maltose octapropionate	10.2	17.2	23.6	—	$P2_12_12_1$
β -Maltose octabutyrate	10.3	17.2	28.6	—	$P2_12_12_1$
Dimethylamino heptaacetyl maltose	23.8	—	10.6	—	(Hex.)
Sucrose octaacetate	22.1	18.2	8.4	—	$P2_12_12_1$
Mannitol hexaacetate	12.2	9.0	20.0	—	$P2_12_12_1$
Sorbitol hexaacetate	8.4	10.3	12.6	96	$P2_1$
Levoglucofan triacetate	8.3	15.8	11.3	—	$P2_12_12_1$
β -Phenyl tetraacetyl glucose	5.9	18.8	39.3	—	$C222_1$

(a) Data from Hengstenberg & Mark (1929).

(b) Data from Sponsler & Dore (1931).

(c) See Astbury & Marwick (1931).

(d) Previous data from multiple crystals or fibers were reported by Leuck & Mark (1934). Later Mark (1940) revised some of the values for cellobiose acetate. Except for the needle-axis spacing, the values reported by Mark are not in agreement with the present single-crystal data.

(e) Bonner, Hurd & Cantor (1947).

* Needle-axis spacing; monoclinic

Further, it appears unlikely that maltose and cellobiose are significantly bent or folded, as the maltose residues must be in the Schardinger dextrans (Freudenberg & Boppel, 1940) or helical amylose (Rundle & Edwards 1943).

Acetates of glucose, cellobiose and maltose, as well as glucose and cellobiose propionates and cellobiose butyrate, exhibit a very characteristic needle-axis spacing of c. 5.6 Å (Nowakowsky, 1930). These derivatives appear to align themselves in regular stacks without appreciable overlap of adjacent molecules such as would be allowed by the screw axes present. Again, the glucose residues in maltose and cellobiose appear nearly co-planar.

In agreement with observations by Cox (1932) and Hägg (Tiselius *et al.*, 1944), the space groups preferred by these optically active substances are $P2_1$ and especially $P2_12_12_1$.

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Unit cells and space groups of citric acid and some potassium and sodium citrates. By D. M. BURNS* and J. IBALL, *University of St. Andrews, Physics Department, University College, Dundee, Scotland*

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Citric acid monohydrate

Groth (1906–19) reports this substance as rhombic bipyramidal (*mmm*) with axial ratios 0.6740:1:1.6621, but no X-ray data have apparently been published

previously. The crystals used in the present investigation were obtained by recrystallization of 'Analar' grade from cold water. They were deliquescent and small crystals were coated with collodion to preserve them. The X-ray