

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 $P2_12_12_1$.

References

ASTBURY, W. T. & MARWICK, T. C. (1931). *Nature, Lond.* **127**, 12.

BONNER, W. A., HURD, C. D. & CANTOR, S. M. (1947). *J. Amer. Chem. Soc.* **69**, 1816.

COX, E. G. (1932). *J. Chem. Soc.* p. 138.

FREUDENBERG, K. & BOPEL, H. (1940). *Ber. dtsh. chem. Ges.* **73**, 609.

HENGSTENBERG, J. & MARK, H. (1929). *Z. Kristallogr.* **72**, 301.

LEUCK, G. J. & MARK, H. (1934). *J. Amer. Chem. Soc.* **56**, 1959.

MARK, H. (1940). *Chem. Rev.* **26**, 169.

NOWAKOWSKY, A. (1930). *C. R. Acad. Sci., Paris*, **191**, 411.

RUNDLE, R. E. & EDWARDS, F. C. (1943). *J. Amer. Chem. Soc.* **65**, 2200.

SPONSLER, O. L. & DORE, W. H. (1931). *J. Amer. Chem. Soc.* **53**, 1639.

TISELIUS, A. *et al.* (1944). *The Svedberg 1884–1944*, p.140. Uppsala: Almqvist and Wiksells.

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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

photographs confirmed that the crystals are orthorhombic with,

$$a = 6.290 \pm 0.003, \quad b = 9.318 \pm 0.005, \quad c = 15.39 \pm 0.01 \text{ \AA}.$$

These give 0.674:1:1.652 for the axial ratios. Taking the density to be 1.548 g.cm.⁻³ (the mean of the two values, 1.542 and 1.553 g.cm.⁻³ given by Groth), the unit cell contains 4 molecules of C₆H₅O₇·H₂O per unit cell (density calculated = 1.546 g.cm.⁻³).

The only systematic absences were *h*00 absent when *h* is odd, 0*k*0 when *k* is odd and 00*l* when *l* is odd. The space group is therefore *D*₂^h-*P*2₁2₁2₁. This space group is not consistent with the crystal class quoted by Groth. Quite apart from the absent reflexions, the class *mmm* is unlikely to be correct with a unit cell containing only 4 molecules as it would mean that each molecule of citric acid and the molecule of water would have to possess some element of symmetry.

Potassium citrate monohydrate

Crystals of this substance are monoclinic, with

$$a = 7.06 \pm 0.03, \quad b = 11.72 \pm 0.05, \quad c = 13.69 \pm 0.07 \text{ \AA}; \\ \beta = 112.0^\circ.$$

The density determined by flotation is 2.00 g.cm.⁻³, giving 4 molecules of C₆H₅O₇·K₃·H₂O per unit cell (density calculated = 2.050 g.cm.⁻³). Systematic absences were *h*0*l* when *l* is odd and 0*k*0 when *k* is odd. The space group is therefore *C*₂^h-*P*2₁/*c*.

Sodium citrate dihydrate

Groth gives this substance as monoclinic prismatic (*2/m*), with *a*:*b*:*c* = 0.8923:1:1.3647, $\beta = 115^\circ 55'$. X-ray photographs gave

$$a = 11.23 \pm 0.05, \quad b = 12.501 \pm 0.002, \quad c = 15.82 \pm 0.08 \text{ \AA}; \\ c \sin \beta = 15.262 \pm 0.003 \text{ \AA}, \quad \beta = 104^\circ 22'.$$

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If the same *c* axis is chosen as that of Groth we get *c*' = 16.98 Å and $\beta' = 115^\circ 49'$, giving axial ratios of *a*:*b*:*c*' = 0.898:1:1.358. The density determined by flotation is 1.84 g.cm.⁻³ and there are 8 molecules of C₆H₅O₇·Na₃·2H₂O per unit cell (density calculated = 1.823 g.cm.⁻³). Systematic absences were: *hkl* when (*k*+*l*) is odd, *h*0*l* when *h* or *l* is odd and 0*k*0 when *k* is odd. There are two space groups available *C*₂^h-*Aa* and *C*₂^h-*A2/a*. If the classification given by Groth is correct then the latter space group is the appropriate one.

Sodium citrate pentahydrate

This compound is given by Groth as rhombic bisphenoidal (222) with axial ratios *a*:*b*:*c* = 0.6208:1:0.2431. X-ray photographs confirmed that the crystals are orthorhombic with

$$a = 6.41 \pm 0.03, \quad b = 16.36 \pm 0.08, \quad c = 26.31 \pm 0.10 \text{ \AA}.$$

These give axial ratios *b*:*c*:*a* = 0.6218:1:0.2436. The density determined by flotation is 1.70 g.cm.⁻³, which differs appreciably from the value given by Groth (1.857–1.859 g.cm.⁻³). The calculated density, using the above unit-cell dimensions and assuming 8 molecules of C₆H₅O₇·Na₃·5H₂O per unit cell, is 1.68 g.cm.⁻³. It would appear that the density given by Groth is a misprint and should really refer to the dihydrate, for which he does not give any density. Systematic absences were *h*0*l* when *l* is odd and *hk*0 when (*h*+*k*) is odd. These are characteristic of two space groups, *C*₂^h-*P*2₁*cn* and *D*₂^h-*Pm**cn*. Neither of these space groups is in the class 222 quoted by Groth.

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Reference

GROTH, P. (1906–19). *Chemische Krystallographie*. Leipzig: Engelmann.

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The atomic scattering factors of Au⁺ and Hg⁺⁺. By W. G. HENRY, *Division of Applied Chemistry, National Research Council, Ottawa, Canada*

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Total atomic scattering factors, *f*, for coherent radiation have been calculated for Au⁺ and Hg⁺⁺ by the numerical integration (Scarborough, 1950) of the integral (James & Brindley, 1931)

$$f = \int_0^\infty P^2(r) \frac{\sin \mu r}{\mu r} dr,$$

where $\mu = 4\pi \sin \theta / \lambda$ and *P*²(*r*) is the radial charge density.

The radial charge density *P*²(*r*) has been determined by the method of the self-consistent field, without exchange, for Hg⁺⁺ by Hartree & Hartree (1935) and for Au⁺ by Henry (unpublished work). The effect on the

scattering factor of including exchange is small (Brindley & Ridley, 1938). Results are given in Table 1.

Table 1. *Atomic scattering factors*
(Integration error ±0.02)

$\frac{\sin \theta}{\lambda} \times 10^{-8}$	Au ⁺	Hg ⁺⁺	$\frac{\sin \theta}{\lambda} \times 10^{-8}$	Au ⁺	Hg ⁺⁺
0.0	78.00	78.00	0.7	37.46	37.98
0.1	74.26	74.71	0.8	33.66	34.38
0.2	66.32	67.21	0.9	30.52	31.20
0.3	58.35	59.18	1.0	27.62	28.23
0.4	51.62	52.27	1.1	25.27	25.86
0.5	46.07	46.65	1.2	23.28	23.36
0.6	41.42	41.97			