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CRYSTAL AND MOLECULAR STRUCTURE OF MELEZITOSE MONOHYDRATE

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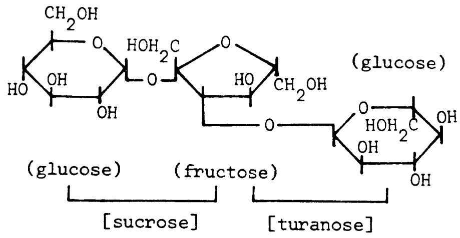
The crystal structure of melezitose monohydrate has been solved by a non-centrosymmetric direct method and refined to an R index of 0.068. The relative orientation of the glucose and fructose units in sucrose moiety is very similar to that found in sucrose itself. There are no intramolecular hydrogen bonds. Two bifurcated hydrogen bonds were found.

Melezitose, O-α-D-glucopyranosyl-(1→3)-O-β-D-fructofuranosyl-(2→1)-α-D-glucopyranoside, is a nonreducing trisaccharide which consists of sucrose and turanose moieties as shown in (I). The crystal structure of sucrose itself was determined by Brown & Levy in 1963[1]. Recently three structures of trisaccharides which have sucrose portion have been accurately determined; raffinose pentahydrate (Berman, 1970)[2], 1-kestose (Jeffrey and Park, 1972)[3] and planteose dihydrate (Rohrer, 1972)[4]. It was the main purpose of this investigation to compare the conformation of sucrose moiety in four compounds mentioned above and in the present one, which have different environments. The conformation of turanose unit and hydrogen bonding scheme in crystal would be of another interest.



(I)

The crystals, $C_{18}H_{32}O_{16}\cdot H_2O$, are orthorhombic, space group $P2_12_12_1$; a= 7.65(1), b=15.37(1), c=19.17(1) Å; Dx=1.55 $g\cdot cm^{-3}$(Z=4). Weissenberg intensity data were collected by means of Cu Kα radiation for seven layers on the a axis and two layers on the b axis. The independent 2661 reflections were observed. No corrections were made for absorption and extinction.

The crystal structure of melezitose monohydrate was solved by direct method, using the general principles described by Karle & Karle[5]. Three phases were assigned to define the origin and the fourth phase was assigned to specify the enantiomorph: 0 11 13 (90°), 0 7 16 (90°), 1 0 3 (90°), 1 7 0 (90°). The phase of 2 0 16 was found to be 0° from Σ_1 relationships. Phases for two additional reflections were designated by symbols: 1 1 16 (A), 0 16 6 (C). About 60 phases were determined with the sum-of-angles formula[5]. In the course of the phase determination, no definitive information was obtained for the symbols A and C.

In order to apply the tangent formula, numerical phases 30° to 345° in steps of 45° were assigned to the symbol A, and 0° and 180° to the symbol C. Each of the sixteen combinations of initial phases was used as input into the tangent formula$^{6)}$. An E map was calculated by use of 421 reflections with the phases in the most consistent set (R=0.31, Z=7087$^{7)}$). The positions of 28 non-hydrogen atoms were located and further confirmed by a least-squares refinement. All of the hydrogen atoms were found by a difference Fourier synthesis. When the non-hydrogen atoms were assigned the anisotropic temperature factors and the hydrogen atoms the isotropic ones, the conventional R factor was reduced to 0.068.

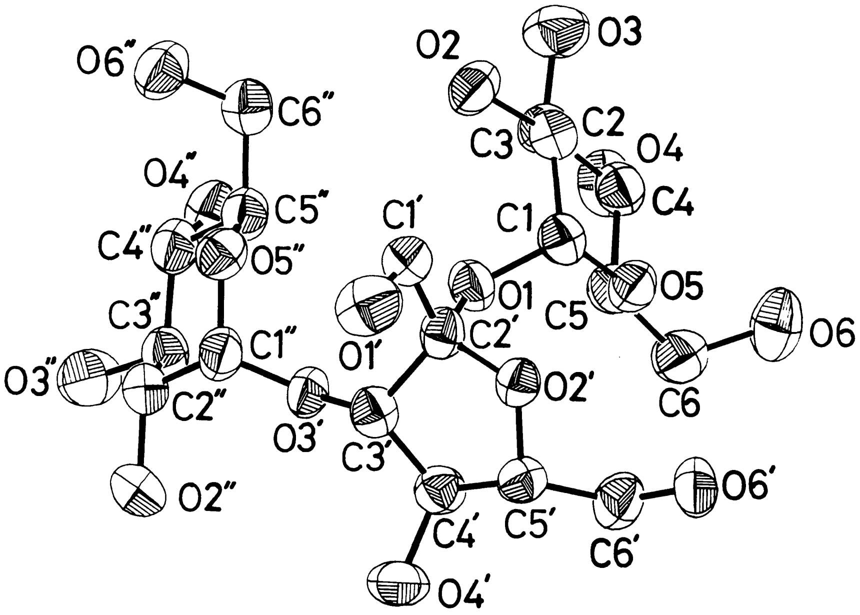


Figure 1. The molecular structure of melezitose.

The molecular conformation and atomic numbering on the carbon and oxygen atoms in melezitose are illustrated in Fig. 1. The glucose in sucrose moiety and the fructose and glucose in turanose moiety are denoted by unprimed, single-primed and double-primed atom designators respectively. The molecule is folded with two glucopyranosyl rings extending away from the central fructofuranosyl ring. The two α-D-glucose units have the normal C1 chair conformation as expected with the ring torsional angles ranging from 48° to 67° in the pyranosyl ring of sucrose moiety and from 51° to 62° in the pyranosyl ring of turanose moiety. The fructofuranosyl ring has an 'envelope' $\underline{E}_3$ conformation with C3' displaced by 0.59 Å out of the plane which contains the other atoms within 0.007 Å. The conformation of the (1→2) linkage in four determined structures and the present one is given in Fig. 2$^{4)}$. The pseudo torsional angles O5-C1---C2'-O2' are 15.2°, 52.0°, 55.9°, 70.6° and 82.1° in 1-kestose, sucrose, melezitose, planteose and raffinose respectively. The differences in these angles are within 30.1° except for 1-kestose which has a steric strain on the central fructofuranosyl ring.

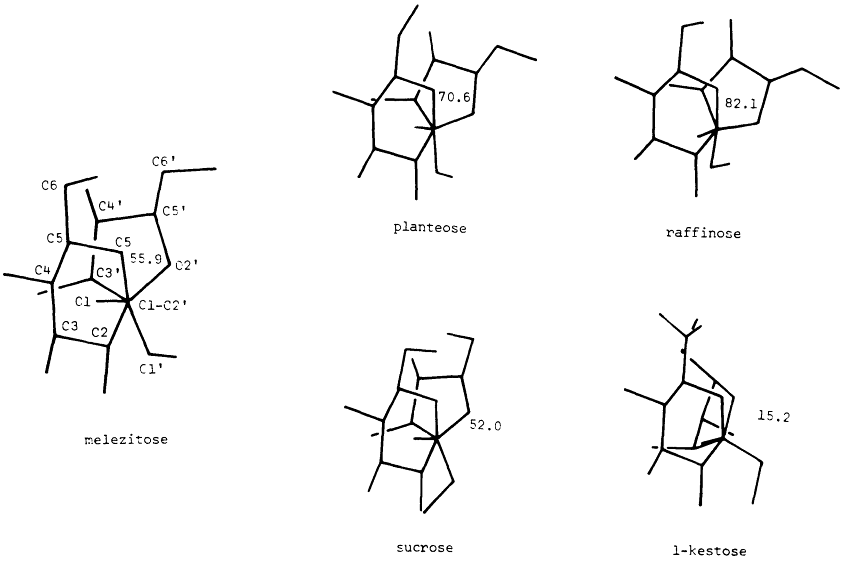


Figure 2. Conformation of the (1→2) linkage in melezitose, planteose, raffinose, sucrose and 1-kestose, as viewed down a pseudolinkage between C1 and C2'.

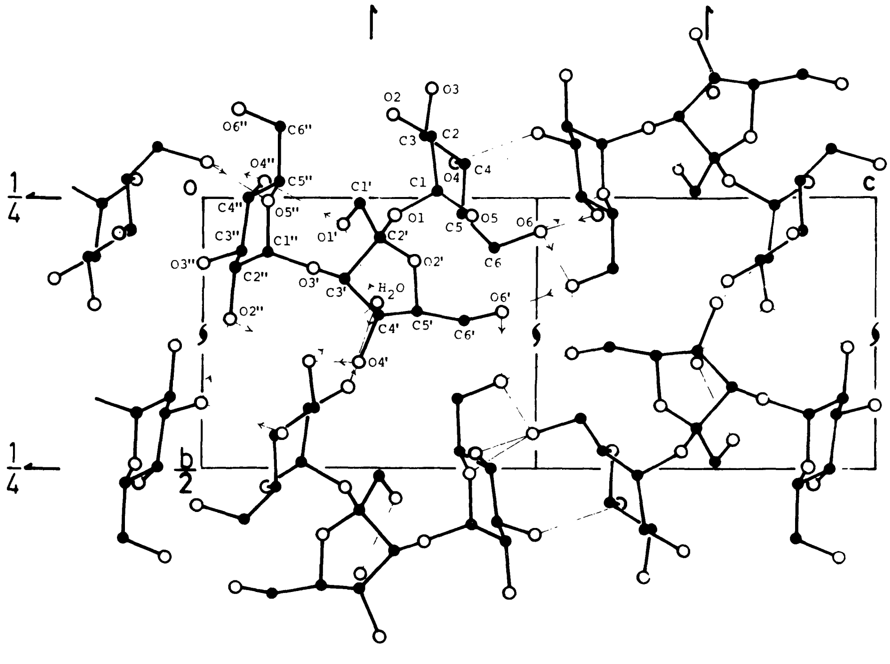


Figure 3. Hydrogen bonding and molecular packing as viewed down the a axis.

The relative orientation of the glucose and the fructose units of sucrose moiety in melezitose is very similar to that found in sucrose itself. This shows that two intramolecular hydrogen bonds found in sucrose itself may not play an important role in the determination of the conformation of (1→2) linkage, in view of no intramolecular hydrogen bonds in melezitose. The (1→3) linkage of turanose moiety has a pseudo torsional angle, C2''-C1''---C3'-C4' of 7.3°.

The estimated errors in C-C and C-O bond distances are 0.008 and 0.007 Å respectively. The C-C bond distances range from 1.501 to 1.555 Å with the average value of 1.523 Å. The C-O distances vary between 1.407 and 1.454 Å with the mean value of 1.425 Å. The C1-O5 and C1''-O5'' bond lengths in the two glucopyranosyl rings show the same type of bond length shortening as found in raffinose, 1-kestose, planteose, sucrose and other related compounds. The C5-O5 and C5''-O5'' distances are longer than C1-O5 and C1''-O5'' distances by 0.025 and 0.015 Å respectively. The difference between the corresponding C-O distances in fructofuranosyl ring is more distinct. Thus, the C2'-O2' and C5'-O2' bond distances are 1.413 and 1.454 Å respectively.

The molecular packing and hydrogen bonding in melezitose monohydrate are shown in Fig. 3. The molecules are linked by the intricate three-dimensional hydrogen bond network. All of the hydroxyl groups participate in hydrogen bonds as donors and acceptors. The water molecule serves as two donors and one acceptor. In the ring oxygen atoms, only O5'' in glucopyranosyl ring of turanose moiety takes part in the hydrogen bond as acceptor. There are no intramolecular hydrogen bonds. It is interesting that the intramolecular hydrogen bonds have been often found in many crystal structures of disaccharides, but there have been no intramolecular ones in those of trisaccharides. O6 and O4' atoms seem to be included in the bifurcated hydrogen bonds as shown in Fig. 4, although O6---O6'' and O4---O4' may be weak hydrogen bonds.

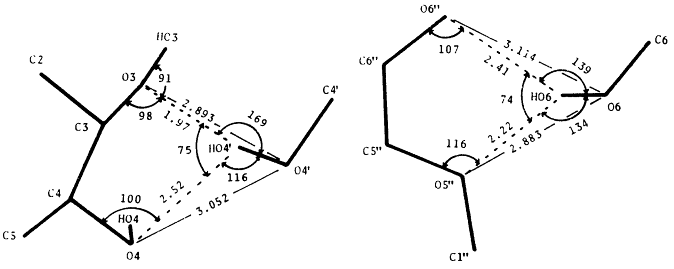


Figure 4. Illustration showing weak hydrogen bonds in melezitose monohydrate.

Footnote and References

1. G. M. Brown and H. A. Levy, Science, 141, 920(1963).
2. H. M. Berman, Acta Cryst., B26, 290(1970).
3. G. A. Jeffrey and Y. J. Park, Acta Cryst., B28, 257(1972).
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5. J. Karle and I. L. Karle, Acta Cryst., 21, 849(1966).
6. J. Karle and H. Hauptman, Acta Cryst., 9, 635(1956).
7. $Z=2\sigma_3\sigma_2^{-3/2}\sum_h|E_h|\{(\sum_k|E_kE_{h-k}|\sin(\phi_k+\phi_{h-k}))^2+(\sum_k|E_kE_{h-k}|\cos(\phi_k+\phi_{h-k}))^2\}^{1/2}$

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