H(4)—C(4)—C(5)—H(5) = −55·7, H(5)—C(5)—C(6)—H(6*A*) = 57·9 and H(5)—C(5)—C(6)—H(6*B*) = −63·9° have constants $J_{4,5} = 3{\cdot}5$, $J_{5,6A} = 1{\cdot}6$ and $J_{5,6B} = 2{\cdot}0$ Hz. Restricted rotation around the C(1)—C(2) bond, investigated by ^{1}H NMR measurements, gives evidence for the intramolecular hydrogen bond O(1)—H(O1)···O. The F atom does not take part in any hydrogen bonds.

The molecular conformations of β-D-frutopyranose and the 4-fluoro analogue then only differ in the change O(4)—H(O4) for F. It may be concluded that the hydrogen bond O(4)—H(O4)···O(2$^{\rm i}$) in β-D-fructopyranose is not of crucial importance to the structural packing.

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(*R*,*S*)-2,3-Dihydroxy-2,3-dimethylbutanedioic Acid Monohydrate (*meso*-Dimethyltartaric Acid), $C_6H_{10}O_6.H_2O$

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Abstract. $M_r = 196{\cdot}2$, $C2/c$, $a = 12{\cdot}199\,(3)$, $b = 9{\cdot}177\,(2)$, $c = 7{\cdot}589\,(2)$ Å, $\beta = 98{\cdot}57\,(2)$°, $V = 840{\cdot}2\,(4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}55$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}16$ mm^{-1}, $F(000) = 416$, $T = 293\,(2)$ K, $R = 0{\cdot}041$ for 1013 observed, unique reflections. The molecule has a centrosymmetric antiperiplanar conformation and exhibits C—C bond lengths [C(1)—C(2) 1·543 (2), C(2)—C(2′) 1·572 (2) Å] significantly longer than those found for the non-methyl-substituted parent compound (tartaric acid). The organic molecules pack into sheets parallel to the *ac* plane with the sheets separated by water molecules.

Introduction. Probably no compounds have played so great a role in the founding of organic stereochemistry as tartaric acid, which can exist as a *meso* or *R,S* isomer and as the *R,R* and *S,S* enantiomers. In view of this, it is not surprising that in excess of sixty crystal structures of tartaric acid isomers and their salts and complexes have been reported (Tapscott, 1982). However, it is surprising that to date only three structures of alkyl-substituted tartrates have been published and that all of these have been for coordination compounds (Marcovich, Duesler, Tapscott & Them, 1982; Hahs, Ortega, Tapscott, Campana & Morosin, 1982; Ortega, Tapscott & Campana, 1982). Here we report the structure of $HOOCC(CH_3)(OH)C(CH_3)(OH)COOH$ as the monohydrate. This is the first structure reported for a *meso*-dimethyltartrate in any form and the first reported for any alkyl-substituted tartrate as the free acid.

Experimental. Dimethyltartaric acid was prepared and its isomers were separated by literature methods (Leermakers & Vesley, 1963; Tatsumi, Izumi, Imaida, Fukuda & Akabori, 1966). Crystal obtained by evaporation of ethyl acetate solution, 0·21 × 0·35 × 0·41 mm. D_m not determined. Syntex *P*3/*F* diffractometer, graphite monochromator. Lattice parameters from 25 reflections ($10 < 2\theta < 42$°). Empirical absorption correction based on ψ scans; min. and max. transmission coefficients 0·830 and 0·881. θ–2θ scan, $(\sin\theta)/\lambda = 0{\cdot}01$ to $0{\cdot}70$ Å^{-1} ($1 \le 2\theta \le 60$°, $\pm h$, $\pm k$,

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

Coordinates in fractions of the unit-cell edge. Equivalent isotropic thermal parameters in Å^2 are calculated as $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$ with the U_{ii}'s in an orthogonal coordinate system (Willis & Pryor, 1975) and the original anisotropic thermal parameters defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	x	y	z	U_{eq}
O(1)	0·5366 (1)	0·1719 (1)	0·0602 (2)	0·0363 (3)
O(2)	0·6178 (1)	0·0253 (1)	−0·1112 (2)	0·0517 (5)
O(3)	0·6548 (1)	0·4007 (1)	−0·0065 (1)	0·0318 (3)
O(4)	0·5000	0·5464 (2)	−0·2500	0·0371 (5)
C(1)	0·6091 (1)	0·1475 (1)	−0·0305 (2)	0·0228 (3)
C(2)	0·6938 (1)	0·2658 (1)	−0·0623 (2)	0·0227 (3)
C(3)	0·7073 (1)	0·2679 (2)	−0·2586 (2)	0·0333 (4)
H(2)	0·564 (2)	−0·030 (2)	−0·095 (3)	
H(3)	0·611 (1)	0·437 (2)	−0·091 (3)	
H(4)	0·534 (2)	0·596 (2)	−0·306 (3)	
H(3*A*)	0·740 (1)	0·180 (2)	−0·290 (3)	
H(3*B*)	0·633 (1)	0·284 (2)	−0·337 (2)	
H(3*C*)	0·750 (1)	0·347 (2)	−0·278 (3)	

Table 2. *Bond lengths* (Å) *and angles* (°) *involving non-hydrogen atoms with e.s.d.'s in parentheses*

C(1)–C(2)	1·543 (2)	C(1)–O(1)	1·219 (2)
C(2)–C(2′)	1·572 (2)	C(1)–O(2)	1·290 (2)
C(2)–C(3)	1·522 (2)	C(2)–O(3)	1·413 (2)
C(1)–C(2)–C(2′)	108·7 (1)	O(3)–C(2)–C(1)	107·8 (1)
C(1)–C(2)–C(3)	109·5 (1)	O(3)–C(2)–C(2′)	106·4 (1)
C(3)–C(2)–C(2′)	112·3 (1)	O(3)–C(2)–C(3)	111·9 (1)
O(1)–C(1)–C(2)	121·2 (1)	O(1)–C(1)–O(2)	123·1 (1)
O(2)–C(1)–C(2)	115·7 (1)		

$\pm l$). Three standard reflections (400, 020, 004) every 93 reflections (5% variation). 2688 reflections measured, 1233 unique, $R_{int} = 0{\cdot}012$, 220 unobserved [$I < 4{\cdot}0\,\sigma(I)$]. No secondary-extinction correction. The space group from systematic absences (hkl, $h+k = 2n+l$ and $h0l$, $l = 2n+l$) could have been either $C2/c$ or Cc; however, E statistics indicated a centrosymmetric space group and successful refinement showed that the choice of $C2/c$ was correct. All computer programs taken from the *SHELXTL* package (Sheldrick, 1981) and scattering-factor data from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods. H atoms were located from difference maps and their positions were allowed to vary but their isotropic thermal parameters were fixed at 1·2 times the last value of U_{eq} for the atom to which they are attached. Anisotropic refinement on F of all nonhydrogen atoms with isotropic refinement of H atoms (fixed U_{iso}) converged to $R = 0{\cdot}041$, $wR = 0{\cdot}044$ [$w^{-1} = \sigma(F)^2 + |g|F_o^2$ with $g = 0{\cdot}00027$] and $S = 1{\cdot}76$ for 1013 observations and 78 refined variables. Max. and min. peak heights in final difference map 0·40 and −0·19 e Å^{-3}. Max. and mean Δ/σ during the final cycle of refinement 0·003 and 0·001.

Discussion. The final fractional coordinates for all atoms and the U_{eq} values for the non-hydrogen atoms are given in Table 1.*

Despite the use of nonaqueous solvent in crystal preparation, water molecules of crystallization, lying on twofold axes, are found in the structure. Apparently water was present in the ethyl acetate solvent, which had not been dried. The organic molecules in the structure sit on inversion centers. Thus the conformation of the *meso* molecule (Fig. 1) is antiperiplanar† in contrast to the (±)-synclinal conformations found for the *meso* isomer of the unsubstituted compound in structures of the free acid and its simple salts (Tapscott, 1982). NMR studies earlier indicated a significant antiperiplanar conformer population for *meso*-dimethyltartrate(2−) ion in aqueous solution (Marcovich & Tapscott, 1980); however, the stabilization of this conformation through methyl substitution is still a little surprising since *meso*-dimethyltartrate(4−) is known to give binuclear complexes with As^{III} while *meso*-tartrate(4−) does not, despite the fact that such complexes require a ligand conformation intermediate between synperiplanar and synclinal (Marcovich & Tapscott, 1980). We note that Tatsumi (1966) assumes a synclinal conformation to explain the IR spectra of calcium and barium *meso*-dimethyltartrate(2−).

There are some interesting differences between the bond parameters determined for *meso*-dimethyltartaric acid (Table 2) and those which have been reported for both the (+) and *meso* isomers of the unsubstituted acid

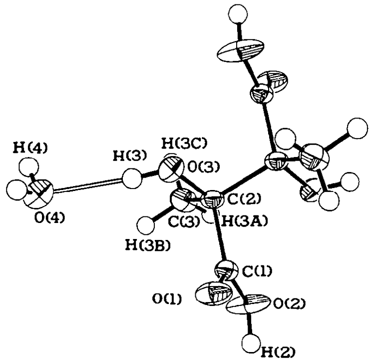

Fig. 1. View of the *meso*-dimethyltartaric acid molecule and accompanying water molecule with the associated hydrogen bond. The thermal ellipsoids (except for the H atoms, which are depicted as arbitrarily sized spheres) are shown at the 50% probability level.

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* Tables of structure factors, anisotropic thermal parameters, fixed H-atom thermal parameters and bond parameters involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39359 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† See Klyne & Prelog (1960) for definitions of the conformation designations.

(Okaya, Stemple & Kay, 1966; Bootsma & Schoone, 1967, three crystal forms). For *meso*-dimethyltartaric acid, the C(1)—C(2) distance is 1·543 (2) Å compared to a range of 1·511 to 1·527 Å for the C(carbinol)—C(carboxyl) distances in the four structures cited for the unsubstituted compound. Similarly the C(2)—C(2′) distance is 1·572 (2) Å for the present structure compared to the range of 1·523 to 1·542 Å found for the corresponding bond length in the tartaric acids. Thus the C—C bonds are distinctly lengthened by methyl substitution. The same trend is seen in crystal structures of the vanadyl(IV) complexes of tartrate(4—) and dimethyltartrate(4—) (Hahs *et al.*, 1982; Ortega, Campana & Tapscott, 1980).

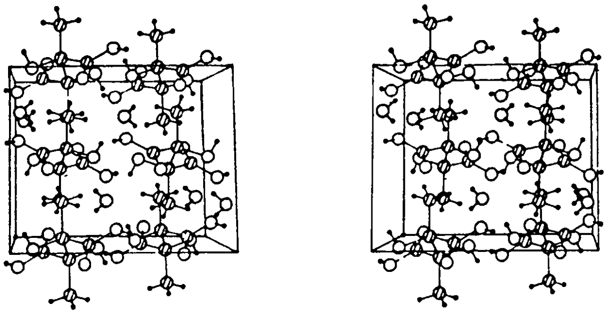

Fig. 2. Stereoview of the crystal packing as viewed down the *a* axis. The origin lies at the back of the bottom left corner with the *b* axis pointing to the right, the *c* axis pointing up, and the *a* axis projecting toward the viewer. The atoms are shown as spheres of arbitrary size (C atoms, cross hatched; O atoms, open; H atoms, black).

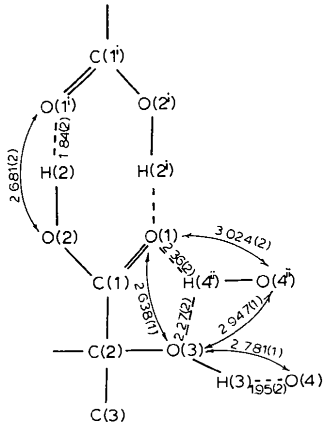

Fig. 3. Hydrogen bonds (- - -) with associated nonbonded contact distances (Å) (curved arrows). The symmetry operations generating the atoms are: (i) $1-x, \bar{y}, \bar{z}$; (ii) $x, 1-y, \frac{1}{2}+z$.

The α-hydroxycarboxylate group is almost planar with an O(1)—C(1)—C(2)—O(3) torsion angle of −13·0 (2)° [for C(2) with an *S* absolute configuration]. The α-hydroxycarboxylate groups of most α-hydroxycarboxylic acids are nearly planar with the small deviations which are observed usually toward a (−)-synperiplanar conformation (negative O—C—C—O dihedral angle) for groups containing a carbinol of *S* absolute configuration (though unsubstituted tartaric acids seem to be an exception!) (Tapscott, 1982).

The molecular packing of this structure is of some interest in view of the widely studied tartaric acids. The organic molecules pack into sheets parallel to the *ac* plane with the sheets separated by water molecules (Fig. 2). The sheets are joined by hydrogen bonds between carboxyl groups related by a center of symmetry and between water molecules and dimethyltartrate O atoms (Fig. 3). Each water molecule acts as a donor of H atoms to two α-hydroxycarboxylate groups (both involving bifurcated hydrogen bonds) within one sheet and as an acceptor of H atoms from two hydroxyl groups within a second sheet.

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