

Fig. 2. View of crystal packing along *b*.

oxygen atoms O2 and O3 respectively (Table 2*d*). This is in contrast to the structure of arginyl-glutamic acid which shows specific H-bonding interactions between the guanidyl group and carboxyl oxygen atoms of the

glutamic acid side chain (Pandit, Seshadri & Viswamitra, 1983). Fig. 2 and Table 2(*d*) show that the two water molecules in the asymmetric unit form independent water chains along *b*. These chains are also H-bonded to the L-arginyl-L-aspartic acid residues.

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Conformational Aspects of *meso*-Tartaric Acid. XI.* Structure of Lithium Hydrogen *meso*-Tartrate Monohydrate

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Abstract. $\text{Li}^+\cdot\text{C}_4\text{H}_5\text{O}_6^-\cdot\text{H}_2\text{O}$, $M_r = 174.04$, monoclinic, $P2_1/c$, $a = 4.8848$ (2), $b = 25.366$ (2), $c = 5.3107$ (4) Å, $\beta = 95.768$ (5)°, $V = 654.71$ (7) Å³, $Z = 4$, $D_x = 1.766$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.6$ cm⁻¹, $F(000) = 360$, $T = 294$ K, $R = 0.042$, $wR = 0.048$ for 2326 observed reflections with $I \geq 2.5\sigma(I)$. The crystal structure is a racemate of two conformational antipodes of the *meso*-tartrate anion, which has adopted its usual *gauche* conformation with respect to the carbon chain. The glycolic acid parts are almost planar. The Li⁺ ion is irregularly coordinated to five O atoms at a mean distance of 2.05 (6) Å.

Introduction. The crystal structure determination of the title compound is part of the research program which is being carried out on the molecular conformational aspects of neutral *meso*-tartaric acid and its ionized forms. A second point of interest is the nature of hydrogen-bond schemes in acid salts in general.

Experimental. Suitable crystals were obtained from an aqueous solution. An Enraf-Nonius CAD-4 diffractometer (Mo $K\alpha$ radiation, $\omega/2\theta$ scan) was used for intensity measurements. A colorless crystal 1.0 × 0.7 × 0.2 mm was glued on top of a glass fiber. Accurate cell parameters were calculated from setting angles of 20 reflections (Cu $K\alpha$, 30 < θ < 44°) in four alternative settings. 3023 reflections were measured ($h: -7 \rightarrow 7$, $k: 0 \rightarrow 40$, $l: 0 \rightarrow 8$) of which 2328 with $I \geq 2.5\sigma(I)$, 0.8 < θ < 35°. Three reflections (200, 0, 10, 0, 002) were measured every 2 h and showed no systematic decrease during the experiment. A ψ -scan for the reflection 013 showed an intensity variation up to 7.0% about the mean. Intensities were corrected for Lorentz and polarization effects, not for absorption. Variance $\sigma^2(I)$ was calculated based on counting statistics plus a term $(PI)^2$ where $P(=0.013)$ is the instability constant (McCandlish, Stout & Andrews, 1975). The structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on

* Part X: Blankensteyn & Kroon (1986).

Table 1. Positional and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses
$$U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta.$$

	x	y	z	U_{eq}
Li	-0.0009 (4)	0.2277 (1)	1.0830 (4)	0.0274 (4)
C(1)	0.3909 (2)	0.0475	0.7551 (2)	0.0183 (3)
C(2)	0.2755 (2)	0.0809	0.9552 (2)	0.0165 (2)
C(3)	0.1007 (2)	0.1267	0.8422 (2)	0.0164 (3)
C(4)	0.2776 (2)	0.1680	0.7261 (2)	0.0155 (2)
O(1)	0.2083 (2)	0.0333	0.5761 (2)	0.0325 (3)
O(2)	0.6357 (2)	0.0339	0.7716 (2)	0.0255 (2)
O(3)	0.4937 (2)	0.0982	1.1313 (2)	0.0214 (2)
O(4)	-0.0349 (2)	0.1510	1.0358 (2)	0.0232 (3)
O(5)	0.4432 (2)	0.1511	0.5797 (2)	0.0234 (2)
O(6)	0.2464 (2)	0.2157	0.7858 (2)	0.0199 (2)
H(1)	0.150 (3)	0.0597 (6)	1.030 (3)	0.021 (3)
H(2)	-0.038 (3)	0.1147 (6)	0.709 (3)	0.021 (3)
H(3)	0.263 (4)	0.0091 (9)	0.483 (4)	0.063 (3)
H(4)	0.423 (5)	0.1129 (8)	1.257 (4)	0.063 (3)
H(5)	-0.172 (5)	0.1348 (8)	1.067 (4)	0.063 (3)
O(7)	-0.2622 (2)	0.2269	1.3628 (2)	0.0204 (2)
H(6)	-0.391 (4)	0.2468 (9)	1.319 (4)	0.063 (3)
H(7)	-0.326 (5)	0.2031 (8)	1.425 (4)	0.063 (3)

F by (in the final stages full-matrix) least-squares techniques, using *SHELX76* (Sheldrick, 1976) with anisotropic thermal parameters for all atoms except H and Li^+ . The almost equal lengths of the C—O bonds in the ionized carboxyl group indicated a delocalization of charge. In order to take this into account, both a neutral O atom and an O^- ion with identical coordinates and temperature factors and with a site occupation factor of 0.5 were used instead of one O atom; this also preserves electroneutrality. Two strong reflections (131 and $\bar{1}81$) were omitted, because $|F(\text{calc})| - |F(\text{obs})| > 10\sigma(F)$, which is most likely due to extinction effects. Li^+ and H were located in difference Fourier maps, and included in further refinement with separate overall isotropic temperature factors for hydroxyl H atoms and aliphatic H atoms respectively and an individual isotropic one for the Li^+ ion. Convergence was reached at $R = 0.042$, $wR = 0.048$ where $w = 1/\sigma^2(F)$, $S = 2.84$, with 127 refined parameters. Minimum and maximum residual electron densities in the final difference Fourier map are -0.28 and 0.46 e \AA^{-3} , the three highest maxima being located on bonds. The final values of the refined parameters are given in Table 1.* Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for all others (C and O atoms, O^- and Li^+ ions) from Cromer & Mann (1968). Calculations were carried out on an in-house microVAX II and on the Cyber 180-855 of the Utrecht University Computer Center. The program package *EUCLID* (Spek, 1982) was used for

* Lists of structure factors, anisotropic thermal parameters of all atoms except H and Li and geometrical data involving H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51155 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA), bond angles and torsion angles ($^\circ$) involving non-hydrogen atoms

O(1)—C(1)	1.288 (1)	O(5)—C(4)	1.253 (1)
C(2)—C(3)	1.5284 (9)	O(2)—C(1)	1.239 (1)
O(4)—C(3)	1.419 (1)	C(3)—C(4)	1.527 (1)
C(1)—C(2)	1.512 (1)	O(6)—C(4)	1.2639 (4)
O(3)—C(2)	1.415 (1)		
O(1)—C(1)—O(2)	124.48 (9)	O(6)—C(4)—C(3)	117.91 (9)
O(1)—C(1)—C(2)	113.33 (9)	O(2)—C(1)—C(2)	122.12 (9)
O(3)—C(2)—C(1)	109.21 (8)	O(3)—C(2)—C(3)	112.19 (4)
C(1)—C(2)—C(3)	112.52 (8)	O(4)—C(3)—C(2)	109.20 (8)
O(4)—C(3)—C(4)	108.60 (4)	C(2)—C(3)—C(4)	111.32 (8)
O(5)—C(4)—O(6)	125.80 (8)	O(5)—C(4)—C(3)	116.28 (3)
O(1)—C(1)—C(2)—O(3)	-175.10 (6)	O(1)—C(1)—C(2)—C(3)	-49.83 (8)
O(2)—C(1)—C(2)—O(3)	7.65 (8)	O(2)—C(1)—C(2)—C(3)	132.92 (8)
O(3)—C(2)—C(3)—O(4)	-65.5 (1)	O(3)—C(2)—C(3)—C(4)	54.4 (1)
C(1)—C(2)—C(3)—O(4)	170.85 (6)	C(1)—C(2)—C(3)—C(4)	-69.26 (9)
O(4)—C(3)—C(4)—O(5)	169.3 (1)	O(4)—C(3)—C(4)—O(6)	-10.4 (1)
C(2)—C(3)—C(4)—O(5)	49.0 (1)	C(2)—C(3)—C(4)—O(6)	-130.6 (1)

Table 3. Hydrogen-bond geometries and lithium coordination (distances in \AA , angles in $^\circ$)

	O...O	O—H	H...O	O—H...O
O(1)—H(3)...O(2a)	2.679 (1)	0.85 (2)	1.84 (2)	168 (2)
O(3)—H(4)...O(5b)	2.766 (1)	0.87 (2)	1.96 (2)	154 (2)
O(4)—H(5)...O(3c)	2.755 (1)	0.81 (2)	1.94 (2)	177 (2)
O(7)—H(7)...O(5d)	2.725 (1)	0.77 (2)	1.97 (2)	168 (2)
O(7)—H(6)...O(6e)	2.802 (1)	0.82 (2)	2.00 (2)	164 (2)
			Li...O	
			Li...O(4)	1.967 (3)
			Li...O(7f)	2.006 (2)
			Li...O(7)	2.054 (2)
			Li...O(6g)	2.102 (2)
			Li...O(6)	2.104 (2)
			O...Li...O	O...O
O(4)...Li...O(7f)	116.9 (1)	3.3859 (6)		
O(4)...Li...O(7)	91.8 (1)	2.888 (1)		
O(4)...Li...O(6g)	141.1 (1)	3.8363 (7)		
O(4)...Li...O(6)	78.79 (9)	2.591 (1)		
O(7f)...Li...O(7)	91.27 (9)	2.902 (1)		
O(7f)...Li...O(6g)	101.9 (1)	3.190 (1)		
O(7f)...Li...O(6)	91.46 (9)	2.943 (1)		
O(7)...Li...O(6g)	90.17 (9)	2.943 (1)		
O(7)...Li...O(6)	170.6 (1)	4.144 (1)		
O(6g)...Li...O(6)	98.02 (9)	3.175 (1)		

Symmetry codes: (a) $1-x, -y, 1-z$; (b) $x, y, 1+z$; (c) $-1+x, y, z$; (d) $-1+x, y, 1+z$; (e) $-1+x, 0.5-y, 0.5+z$; (f) $x, 0.5-y, -0.5+z$; (g) $x, 0.5-y, 0.5+z$.

the calculation of geometric data and preparation of illustrations.

Discussion. Geometrical data are given in Tables 2 and 3. Fig. 1 shows the conformation of the *meso*-tartrate anion together with the atom numbering. The hydrogen-*meso*-tartrate (HMT) ion has adopted a conformation which is observed in most crystal structures of α -hydroxy carboxylic acid derivatives (Kroon, 1982): the carboxyl groups are in a *gauche* position (the C—C—C torsion angle being -69°), and both carboxyl groups are almost coplanar with their respective adjacent (α) C—O groups [O(2)—C(1)—

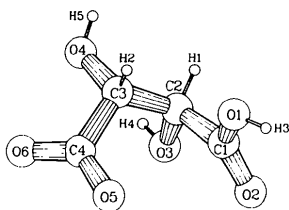


Fig. 1. Perspective view of the hydrogen-*meso*-tartrate anion, showing the atom labelling.

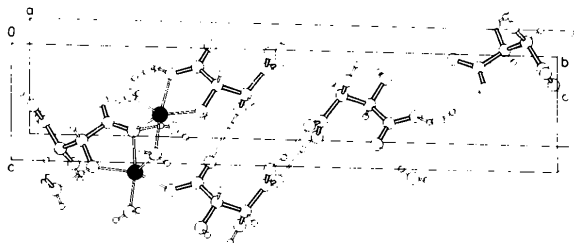


Fig. 2. The unit cell, showing lithium coordination and hydrogen bonding.

$C(2)-O(3) = 7.7(1)$ and $O(6)-C(4)-C(3)-O(4) = -10.4(1)^\circ$. The Li^+ ion is coordinated to five O atoms (Table 3) that form an irregular polyhedron, whose shape is approximately halfway between a trigonal bipyramid [threefold axis from O(6) to O(7)] and a square pyramid [pivot atom O(7f)].

The Li^+ ion, the water molecule and the charged carboxyl group form infinite layers perpendicular to the b axis (at $y \approx \frac{1}{4}$ and $y \approx \frac{3}{4}$), whereas the neutral carboxyl groups form dimers (at $y \approx 0$ and $y \approx \frac{1}{2}$) that are not interconnected. This is noteworthy since acid salts of dicarboxylic acids show the tendency to have two carboxyl groups coupled by one proton, where the proton either distinctly belongs to one carboxyl group (*B*-type) or is shared equally by the two carboxyl groups (*A*-type) (Speakman, 1972; Stouten, Blankensteyn & Kroon, 1984). This distinction between an essentially charged and an essentially neutral carboxyl

group coupling has also been observed in the crystal structure of lithium hydrogen malate (van Havere & Lenstra, 1980) which suggests that this phenomenon is caused by the presence of the small Li^+ ion.

In addition to the carboxyl group coupling, two hydrogen bonds, originating from the hydroxyl groups, interconnect the HMT anions in the x direction [$O(4)-H(5)\cdots O(3c)$] and the z direction [$O(3)-H(4)\cdots O(5b)$]. It is evident that the packing (shown in Fig. 2) is determined by a combination of complex formation and hydrogen bonding.

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Structure of (4 α ,8 β ,13 β)-13-Methyl-16-oxo-17-norkauran-18-oic Acid (Isosteviol)

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Abstract. $C_{20}H_{30}O_3$, $M_r = 318.46$, orthorhombic, $P2_12_12_1$, $a = 11.134(4)$, $b = 17.678(3)$, $c = 18.314(5)$ Å, $V = 3605(3)$ Å³, $Z = 8$, $D_x =$

1.174 Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu(\text{Mo } K\alpha) = 0.043$ mm⁻¹, $F(000) = 1392$, room temperature. The structure was solved by direct methods and refined by

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