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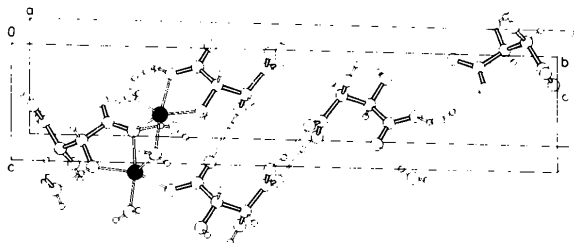

Fig. 2. The unit cell, showing lithium coordination and hydrogen bonding.

$C(2)-O(3) = 7.7$ (1) and $O(6)-C(4)-C(3)-O(4) = -10.4$ (1)°]. 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 $y \simeq \frac{1}{4}$ and $y \simeq \frac{3}{4}$), whereas the neutral carboxyl groups form dimers (at $y \simeq 0$ and $y \simeq \frac{1}{2}$) 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 (4α,8β,13β)-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) Å^3, $Z = 8$, $D_x = 1.174$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.7107$ Å, $\mu(Mo\ K\alpha) = 0.043$ mm^{-1}, $F(000) = 1392$, room temperature. The structure was solved by direct methods and refined by

full-matrix least-squares calculations. The final R was 0·053 for 1157 observed reflections. The two independent molecules are linked by a hydrogen bond. The torsion angles around the bond of the carboxyl group to the diterpenic skeleton differ by practically 180° from one independent molecule to the other.

Introduction. Hydrolysis of stevioside (I), the extremely sweet glucoside extracted from the leaves of the South American shrub *Stevia rebaudiana* (Bert.) Bertoni, yields D-glucose and the agluconic moiety named steviol (kaur-16-en-18-oic acid, II) in enzymatic conditions while in acidic conditions it yields the same sugar and an isomer of steviol, named isosteviol [(4α,8β,-13β)-13-methyl-16-oxo-17-norkauran-18-oic acid, III] (Bridel & Lavieille, 1931). Structural work indicated that these aglucones are tetracyclic diterpenoids of the phyllocladene group (Mosettig & Nes, 1955; Arya, 1962). Further work (Djerassi, Quitt, Mosettig, Cambie, Rutledge & Briggs, 1961; Mosettig, Beglinger, Dolder, Lichti, Quitt & Waters, 1963) led to the absolute configuration depicted in structures (II) and (III).
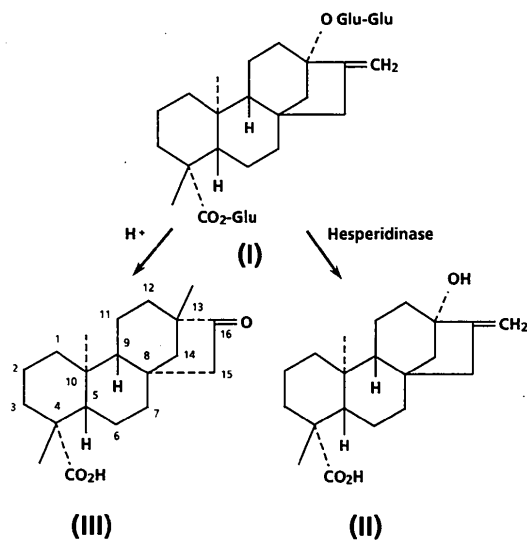
This crystal structure determination is part of a structural study of the constituents of *Stevia rebaudiana* (Bert.) Bertoni and its derivatives and its objectives are to confirm the molecular structure of the title compound and to gather structural information in order to help in solving the crystal structures of related compounds.

Experimental. Colourless hexagonal crystals of the title compound were prepared by Dr Mauro Alvarez (Departamento de Farmácia e Bioquímica, Universidade Estadual de Maringá).

A crystal of dimensions 0·5 × 0·4 × 0·2 mm was used for the data collection. Cell dimensions were refined by a least-squares fit to the setting angles of 25 reflections on a CAD-4 automatic diffractometer, $7 \le \theta \le 16°$. Intensity measurements were carried out up to 25° in θ with graphite-monochromated Mo $K\alpha$ radiation and employing the ω–2θ scan technique. The reflections were collected in the range of 0 to 13 for h, 0 to 20 for k and 0 to 21 for l. Lorentz and polarization corrections were applied but no absorption correction was made. Two standard reflections (400, 186) were measured after every 260 reflections, maximum intensity variation $\pm 5\cdot8\%$. The space group was established by systematic absences. Of the 2758 measured unique reflections, only 1157 were considered observed [$I > 2\cdot5\sigma(I)$, where $\sigma(I)$ was calculated from counting statistics] and were used in the structure determination and refinement. The structure was solved by direct methods using the program *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and weighted Fourier calculations.

The E map based on the set of phases giving the highest combined figure of merit allowed the location of 45 atoms belonging to the two independent molecules; the last atom was located by difference synthesis. The H atoms were placed at their calculated positions. Those positions were recalculated after each refinement cycle. The hydroxyl H atoms were located by difference synthesis, and their coordinates were refined.

Refinement was carried out by a full-matrix least-squares method minimizing $\sum w_i(k|F_o| - |F_c|)^2$ with $w_i^{-1} = \sigma(F)^2 + 0\cdot00196F^2$ for observed and $w_i = 0$ for unobserved reflections until all the atomic parameter shifts were smaller than each standard deviation. The atomic scattering factors used were those of Cromer & Waber (1974).

Anisotropic temperature factors were assigned to all non-hydrogen atoms. The final R and wR, omitting unobserved reflections and refining 435 parameters, were respectively 0·053 and 0·055; $S = 1\cdot62$. The maximum and minimum heights in the final difference Fourier synthesis were 0·168 and $-0\cdot185$ e Å^{-3} respectively. The ratio of maximum least-squares shift to e.s.d. in final refinement cycle was $< 1\cdot0$. The final atomic parameters are given in Table 1.*

Discussion. Fig. 1 gives a representation of the two independent molecules which constitute the asymmetric unit. The molecular structure, as long as relative configuration is considered, is exactly that given by Mosettig *et al.* (1963). Except for C12—C13, bonds are within 3σ in both molecules. The structural parameters of the carboxyl groups are close to those corre-

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959), with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

|	x	y	z	$B_{eq}(\text{Å}^2)$
Molecule *A*				
C1	0·879 (1)	0·2828 (7)	0·9274 (6)	4·4 (5)
C2	0·866 (1)	0·3226 (7)	0·8543 (8)	4·5 (5)
C3	0·905 (1)	0·2693 (8)	0·7951 (7)	5·0 (6)
C4	0·831 (1)	0·1941 (7)	0·7900 (7)	4·3 (6)
C5	0·8353 (9)	0·1562 (7)	0·8682 (6)	3·6 (5)
C6	0·773 (1)	0·0794 (7)	0·8744 (7)	6·5 (7)
C7	0·819 (1)	0·0412 (6)	0·9438 (7)	5·1 (6)
C8	0·808 (1)	0·0825 (7)	1·0152 (6)	3·6 (5)
C9	0·8459 (9)	0·1660 (6)	1·0061 (6)	3·1 (5)
C10	0·805 (1)	0·2077 (7)	0·9342 (6)	3·5 (5)
C11	0·828 (1)	0·2098 (6)	1·0759 (6)	3·8 (5)
C12	0·875 (1)	0·1676 (8)	1·1427 (7)	5·2 (6)
C13	0·841 (1)	0·0839 (7)	1·1438 (6)	3·9 (6)
C14	0·886 (1)	0·0479 (6)	1·0754 (7)	4·5 (5)
C15	0·680 (1)	0·0752 (7)	1·0495 (7)	5·1 (6)
C16	0·704 (1)	0·0785 (7)	1·131 (1)	5·6 (7)
C18	0·889 (1)	0·1420 (8)	0·7326 (7)	6·1 (6)
C19	0·709 (1)	0·2108 (8)	0·7638 (7)	4·2 (6)
C20	0·6706 (9)	0·2300 (6)	0·9373 (6)	3·9 (5)
C21	0·881 (1)	0·0455 (8)	1·2136 (7)	5·6 (6)
O17	0·6288 (9)	0·0791 (6)	1·1788 (5)	8·2 (5)
O22	0·6306 (8)	0·1548 (5)	0·7590 (5)	6·3 (4)
O23	0·6791 (7)	0·2731 (5)	0·7355 (5)	5·7 (4)
Molecule *B*				
C1	0·317 (1)	0·2488 (7)	0·4574 (7)	5·1 (5)
C2	0·362 (1)	0·3163 (6)	0·5029 (7)	5·0 (6)
C3	0·291 (1)	0·3266 (6)	0·5711 (8)	4·7 (5)
C4	0·283 (1)	0·2546 (7)	0·6203 (7)	3·8 (5)
C5	0·239 (1)	0·1878 (6)	0·5726 (7)	3·8 (5)
C6	0·222 (1)	0·1133 (7)	0·6139 (6)	4·6 (5)
C7	0·142 (1)	0·0611 (6)	0·5679 (7)	4·4 (5)
C8	0·197 (1)	0·0418 (6)	0·4942 (6)	3·6 (5)
C9	0·243 (1)	0·1139 (7)	0·4549 (7)	4·0 (5)
C10	0·314 (1)	0·1740 (6)	0·5019 (6)	3·6 (5)
C11	0·303 (1)	0·0921 (7)	0·3810 (6)	4·9 (5)
C12	0·235 (1)	0·0372 (7)	0·3373 (7)	5·4 (6)
C13	0·183 (1)	−0·0315 (7)	0·3850 (7)	5·2 (6)
C14	0·107 (1)	0·0037 (6)	0·4441 (7)	4·6 (5)
C15	0·295 (1)	−0·0198 (7)	0·4978 (8)	4·8 (5)
C16	0·289 (1)	−0·0618 (8)	0·4258 (8)	5·0 (6)
C18	0·192 (1)	0·2708 (8)	0·6824 (7)	5·9 (6)
C19	0·402 (1)	0·2430 (9)	0·6596 (7)	4·4 (6)
C20	0·444 (1)	0·1499 (7)	0·5182 (7)	4·8 (5)
C21	0·121 (1)	−0·0875 (8)	0·3327 (7)	6·7 (6)
O17	0·3549 (9)	−0·1129 (5)	0·4066 (6)	7·7 (5)
O22	0·4796 (8)	0·2977 (5)	0·6585 (4)	5·6 (4)
O23	0·4252 (8)	0·1838 (6)	0·6924 (5)	7·0 (4)
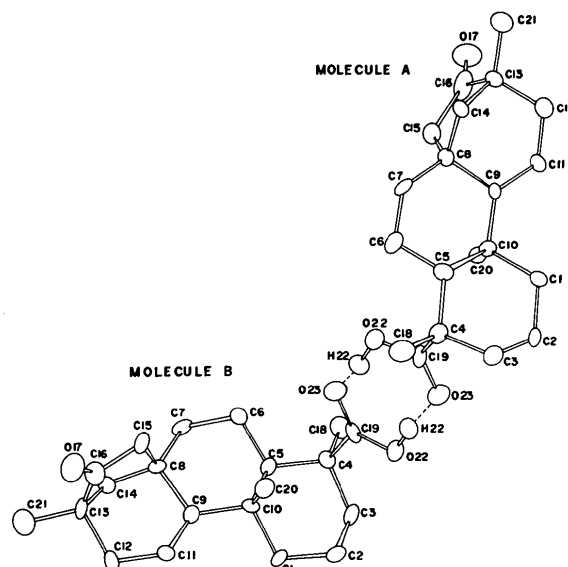
Fig. 1. Representation of the independent molecules of isosteviol, giving atomic numbering and hydrogen-bonding scheme.

the hydroxyl O22 for molecule *A* and carbonyl O23 for molecule *B* is 2·64 (1) Å and the distance for the corresponding oxygen pair completing the hydrogen-bonding scheme of the dimer is 2·67 (1) Å.

All calculations, unless otherwise mentioned in the text, were performed in this Institute on a VAX 11/780 computer using the *SHELX* crystallographic program (Sheldrick, 1976).

sponding to the typical geometry of the —COOH group (Borthwick, 1980).

The molecules are associated in pairs *via* hydrogen bonding involving the carboxyl groups, to form the cyclic hydrogen-bonded dimer which is the most common motif observed in the solid state (Leiserowitz, 1976). The angle between the planes through the carboxyl groups is 6 (1)°. The hydrogen-bonding scheme may be considered responsible for the conformational differences observed in the independent molecules. The torsion angle around the C4—C19 bond differs by practically 180° from one molecule to the other, relevant angles being τ(C18—C4—C19—O23) equal to −104 (1) and 76 (3)° for molecule *A* and *B* respectively.

The strength of the hydrogen bond may be classified as intermediate (Novak, 1974). The distance between

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