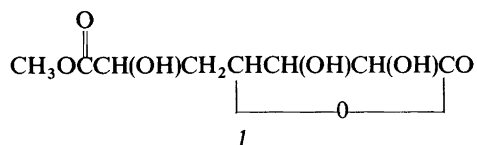


# The Crystal and Molecular Structure of a Lactone-forming Acid, $C_8H_{12}O_7$ , Isolated from *Cereus peruvianus* (L) Mill.

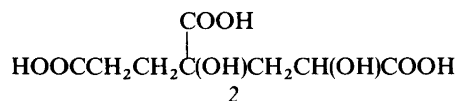
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The title compound (1) was recognized by Nordal *et al.* in 1965<sup>1</sup> but was not isolated until 1976



(Kringstad<sup>2</sup>). The molecule was shown to possess properties similar to phorbic acid (2),<sup>3,4</sup> and spectroscopic and chromatographic evidence indicated a lactone-forming dicarboxylic acid with



several free hydroxyl groups. Since the compound could not be fully identified, it was decided to perform a crystal structure analysis.

The present paper deals with the crystallographic investigation, whereas a detailed report on the

isolation and preliminary identification methods together with essential chemistry will be given elsewhere.<sup>5</sup>

The needle-shaped crystals are orthorhombic with space group  $P2_12_12_1$ , cell dimensions  $a=4.618(2)$ ,  $b=6.684(3)$ ,  $c=31.848(6)$  Å,  $M=220.18$ ,  $Z=4$ ,  $D_m=1.48$  g cm<sup>-3</sup> and  $D_x=1.49$  g cm<sup>-3</sup>.

Three-dimensional intensity data were collected on a SYNTEX P1 diffractometer with graphite crystal monochromated MoK $\alpha$  radiation ( $\lambda=0.71069$  Å). A total of 1103 unique reflections with  $\sin \theta/\lambda \leq 0.60$  were collected; only 487 had a net count larger than  $2.5 \sigma_I$  with e.s.d.'s of the intensities taken as the square root of the total counts with a 2% addition for instrumental instability.

All calculations were done on a CYBER-74 computer utilizing the programs in Ref. 6, except

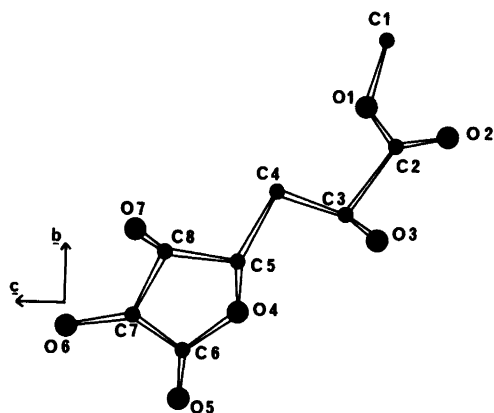


Fig. 1. Asymmetric unit with the atomic numbering.

Table 1. Positional and thermal parameters with e.s.d.'s in parentheses. The anisotropic temperature factors are given by  $\exp(-2\pi^2(U_{11}h^2a^{*2} + \dots + U_{12}hka^*b^* \dots))$ .

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
C1	.0521(22)	.7444(12)	.3042( 2)	.0862(86)	.0370(57)	.0651(59)	.0221(68)	-.0108(61)	.0107(52)
C2	.3531(20)	.4614(13)	.3031( 3)	.0515(69)	.0367(59)	.0316(52)	-.0067(62)	-.0166(54)	-.0027(48)
C3	.4629(17)	.2759(12)	.3266( 2)	.0407(59)	.0304(56)	.0309(45)	.0013(55)	-.0060(51)	.0062(46)
C4	.5276(18)	.3185(10)	.3722( 2)	.0441(56)	.0245(48)	.0311(47)	.0020(50)	.0102(48)	-.0025(41)
C5	.6257(18)	.1327(12)	.3950( 2)	.0310(62)	.0383(51)	.0247(49)	.0005(54)	.0063(45)	.0043(40)
C6	.3786(19)	-.1307(12)	.4256( 3)	.0402(70)	.0366(56)	.0501(61)	.0137(57)	.0297(56)	-.0012(52)
C7	.5939(19)	-.0528(12)	.4579( 3)	.0383(59)	.0458(59)	.0387(50)	.0184(59)	.0017(48)	.0174(48)
C8	.6611(21)	.1595(11)	.4423( 2)	.0443(62)	.0365(56)	.0267(52)	.0078(58)	-.0036(47)	.0062(43)
O1	.1807(14)	.5751( 8)	.3253( 1)	.0722(48)	.0374(39)	.0353(32)	.0154(38)	.0040(40)	.0031(32)
O2	.4143(13)	.4893( 8)	.2564( 1)	.0896(56)	.0487(40)	.0335(33)	.0046(46)	-.0025(37)	.0171(31)
O3	.7146(14)	.1992( 8)	.3079( 1)	.0629(44)	.0509(40)	.0313(29)	.0163(42)	-.0034(34)	-.0132(29)
O4	.4080(12)	-.0239( 8)	.3902( 1)	.0531(46)	.0347(33)	.0294(30)	-.0026(38)	-.0004(33)	.0110(29)
O5	.2026(12)	-.2506( 8)	.4298( 2)	.0573(42)	.0402(36)	.0555(34)	-.0160(40)	.0304(41)	.0044(33)
O6	.4815(14)	-.0598( 8)	.4993( 1)	.0620(43)	.0806(41)	.0233(25)	.0028(41)	.0031(30)	.0042(32)
O7	.9445(12)	.2159( 9)	.4531( 1)	.0411(39)	.0678(45)	.0407(35)	-.0008(43)	-.0150(31)	-.0013(31)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1C1	-.081	.823	.325	5.0	H2C1	-.073	.694	.279	5.0
H3C1	.216	.840	.293	5.0	H1C4	.339	.373	.387	2.0
H2C4	.692	.427	.374	2.0	H3C3	.295	.170	.325	3.0
H4C5	.827	.097	.387	2.0	H4C7	.787	-.135	.460	3.0
H5C8	.530	.272	.455	2.5	H03	.673	.132	.284	3.5
H06	.555	-.126	.523	4.0	H07	.956	.329	.468	3.5

Table 2. Bond lengths (Å), bond angles (°) and torsional angles (°).

Distance (Å)	Angle (°)
C1—O1	1.446(8)
C2—O1	1.308(8)
C2—O2	1.218(8)
C2—C3	1.534(9)
C3—O3	1.403(9)
C3—C4	1.511(9)
C4—C5	1.508(8)
C5—O4	1.460(8)
C5—C8	1.526(9)
C6—O4	1.343(8)
C6—O5	1.192(8)
C6—C7	1.528(10)
C7—O6	1.422(8)
C7—C8	1.535(10)
C8—O7	1.404(9)
C1—O1—C2	117.1(6)
O1—C2—O2	124.8(8)
O1—C2—C3	114.1(7)
O2—C2—C3	121.0(8)
C2—C3—C4	112.4(6)
C2—C3—O3	111.2(7)
O3—C3—C4	108.3(6)
C3—C4—C5	111.5(6)
C4—C5—O4	109.4(6)
C4—C5—C8	114.2(6)
C5—O4—C6	111.5(6)
O4—C6—O5	123.6(9)
O4—C6—C7	108.4(7)
O5—C6—C7	128.0(9)
C6—C7—C8	103.3(7)
C6—C7—O6	111.0(7)
O6—C7—C8	116.6(7)
C7—C8—C5	100.9(7)
C7—C8—O7	110.9(7)
O7—C8—C5	111.9(7)
C8—C5—O4	105.2(6)

Dihedral angle (°)	
C1—O1—C2—O2	.7(12)
C1—O1—C2—C3	-175.6(8)
O1—C2—C3—O3	-159.7(6)
O1—C2—C3—C4	-38.1(10)
O2—C2—C3—C4	145.4(8)
O2—C2—C3—O3	23.8(11)
C2—C3—C4—C5	178.1(8)
C3—C4—C5—O4	-55.6(8)
C3—C4—C5—C8	-173.3(7)
O3—C3—C4—C5	-58.6(8)
C4—C5—O4—C6	-141.6(6)
C4—C5—C8—O7	-91.6(9)
C4—C5—C8—C7	150.4(7)
C5—O4—C6—O5	176.5(7)
C5—O4—C6—C7	-2.3(8)
O4—C6—C7—C8	21.9(8)
O4—C6—C7—O6	147.6(6)
C6—C7—C8—O7	-149.8(6)
C6—C7—C8—C5	-31.1(9)
O5—C6—C7—O6	-31.1(11)
O5—C6—C7—C8	-156.8(8)
O6—C7—C8—O7	88.3(9)
O6—C7—C8—C5	-153.0(7)
O7—C8—C5—O4	148.3(6)

for the phase determination.<sup>7</sup> Atomic form factors were those in Ref. 8 (O,C) and Ref. 9 (H).

MULTAN<sup>7</sup> was used for the phase determination, and successive Fourier syntheses, isotropic

and anisotropic full-matrix least-squares refinements gave an *R*-factor of 0.09. Positional coordinates for all the hydrogen atoms were calculated, but these atoms were not refined. The refinement converged at *R*=0.047 (*R*<sub>w</sub>=0.032) and final parameters are given in Table 1. A list of the structure factors may be obtained from the author upon request.

*Discussion.* A schematic view of the molecular structure is given in Fig. 1. The present study shows that the compound is a  $\gamma$ -monolactone with one methyl ester group. Furthermore, this natural product has several free hydroxyl groups, in full agreement with all the chemical evidence,<sup>2</sup> and the molecule is indeed closely related to phorbic acid (2). The lack of a hydroxyl group at C4 and any relationship with naturally occurring heptoses will be described elsewhere.<sup>5</sup>

Bond lengths, angles and torsional angles are listed in Table 2. All the observed quantities have normal and expected values and will not be discussed in detail. The lactone group displays the usual C—O bonds of 1.460 and 1.343 Å,<sup>10</sup> respectively, and the five-membered lactone-ring exhibits the envelope conformation, C8 being displaced by 0.57 Å from the planar part. The molecule is nearly fully extended with torsional angles C2—C3—C4—C5 and C3—C4—C5—O4 of 178 and -56°, respectively. The planar ester group forms an angle of 144° with the atomic sequence C2—C3—C4, whereas the torsional angle O2—C2—C3—O3 is 24°. This latter value deviates considerably from those normally encountered for  $\alpha$ -hydroxy acids. Recently Newton *et al.*<sup>11</sup> reported the results of some *ab initio* calculations on the planarity of  $\alpha$ -hydroxycarboxylic acids and related molecules, which confirmed the situation most frequently observed for similar crystalline compounds, namely

a planar configuration of the  $>C(OH)-\overset{O}{\parallel}C-O$  moiety. Such a nearly synclinal conformation about C(*sp*<sup>3</sup>)-C(*sp*<sup>2</sup>) bonds thus seems to be a general feature.<sup>12</sup>

Table 3. Distances of the hydrogen bonds. The hydrogen atoms are excluded as their positions have been calculated and not refined. (Mean e.s.d.: 0.008 Å).

Atoms	Distance (Å)	Symmetry code
O3...O2 (i)	2.814	(i) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$
O6...O5 (ii)	2.724	(ii) $\frac{1}{2}+x, -y-\frac{1}{2}, 1-z$
O7...O6 (iii)	2.814	(iii) $x+\frac{1}{2}, -y+\frac{1}{2}, 1-z$
		Reference atom: <i>x, y, z</i>

The network of hydrogen bonds connects molecules in all three directions. Each lactone molecule is linked to six different entities, thus all the hydroxyl hydrogen atoms are engaged in moderately strong hydrogen bonds (*cf.* Table 3). There are no particularly short intermolecular contacts, and an explanation of the non-planarity mentioned above is not easily accessible from crystal packing considerations.

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