2,3:4,6-Di-*O*-isopropylidene-2-keto-L-gulonic Acid Monohydrate*

By Shozo Takagi and G. A. Jeffrey

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, USA and Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, USA

Abstract. $C_{12}H_{18}O_7 \cdot H_2O$, $M_r = 292 \cdot 28$, m.p. 100–101 °C, orthorhombic, $P2_12_12_1$, $a = 9 \cdot 214$ (1), $b = 10 \cdot 108$ (1), $c = 15 \cdot 806$ (1) Å [$\lambda(\text{Cu}\,K\alpha_1) = 1 \cdot 54051$ Å], $V = 1472 \cdot 09$ Å^3, $D_x = 1 \cdot 319$ g cm^{-3}, $Z = 4$. The structure was solved by *MULTAN* and refined to $R(F) = 0 \cdot 028$ for 1789 reflections measured with graphite-monochromated Cu $K\alpha$ radiation on a CAD-4 diffractometer. The gulofuranose ring has a twist conformation, the dioxolane ring is an envelope, and the dioxane ring is a distorted chair. The molecule contains sequences of six and four C—O bonds with bond lengths ranging from $1 \cdot 406$ (2) to $1 \cdot 445$ (2) Å. The water molecule accepts a hydrogen bond from the carboxylic acid hydroxyl groups and donates two hydrogen bonds: one to the carboxylic acid keto O atom and the other to one of the dioxane ether O atoms.

Introduction. 2,3:4,6-Di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate, DAG (I), a derivative of L-ascorbic acid, has been used to resolve amines (Brossi & Teitel, 1970; Teitel, O'Brien & Brossi, 1972).

(I)
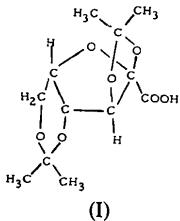
The compound was obtained from Roche Chemical Company and recrystallized from 95% ethanol–water solution at room temperature. A crystal with dimensions $0 \cdot 34 \times 0 \cdot 34 \times 0 \cdot 40$ mm was used to measure 3757 hkl and $\bar{h}kl$ reflections by θ–2θ scans to $\theta = 78°$, using a scan width of $3 \cdot 0° + 0 \cdot 42° \tan \theta$. Absorption corrections were applied with *ABSOR* (Templeton & Templeton, 1973) using $\mu(\text{Cu}\,K\alpha) = 9 \cdot 15$ cm^{-1}. The minimum, maximum and mean corrections to F_o^2 were $1 \cdot 229$, $1 \cdot 394$, and $1 \cdot 284$ respectively. The R factor be-

tween symmetry-equivalent reflections was $0 \cdot 013$. These were averaged to give 1789 independent reflections, of which 33 had $F_o^2 \leq \sigma(F_o^2)$.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) using 200 reflections with $E \geq 1 \cdot 52$ for phase generation. The twenty highest peaks on the E map corresponded to all of the non-hydrogen atoms. Refinement was by full-matrix least squares using *FLINUS*, a local version of *ORFLS* (Busing, Martin & Levy, 1962), to minimize $\sum w|F_o - kF_c|^2$, with $w^{-1} = [\sigma_c^2(F_o^2) + (0 \cdot 015 F_o^2)^2]/4F_o^2$, where σ_c is from counting statistics. All the H atoms were located from a difference Fourier synthesis. The non-hydrogen and H atom parameters were refined anisotropically and isotropically respectively, together with a Zachariasen isotropic extinction parameter (Coppens & Hamilton, 1970), which refined to $0 \cdot 26$ (3) $\times 10^4$. The final $R = \sum |F_o - kF_c|/\sum |F_o|$, $R_w = (\sum w|F_o - kF_c|^2/\sum w|F_o|^2)^{1/2}$ for 1789 reflections were $0 \cdot 028$ and $0 \cdot 034$ respectively.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for the non-hydrogen atoms in* 2,3:4,6-*di-O-isopropylidene-2-keto-L-gulonic acid monohydrate*

	x	y	z
C(1)	6132 (2)	4899 (2)	1485 (1)
C(2)	7166 (2)	5310 (1)	779 (1)
C(3)	8789 (2)	5353 (2)	1013 (1)
C(4)	9147 (2)	6819 (2)	978 (1)
C(5)	8079 (2)	7327 (2)	323 (1)
C(6)	7782 (2)	8790 (2)	414 (1)
C(7)	8479 (2)	3811 (2)	−50 (1)
C(8)	8582 (4)	2452 (2)	346 (3)
C(9)	8713 (4)	3824 (3)	−989 (2)
C(10)	8718 (2)	8733 (2)	1832 (1)
C(11)	8212 (3)	9057 (3)	2717 (1)
C(12)	10163 (3)	9388 (2)	1621 (1)
O(1*A*)	6569 (2)	3837 (2)	1869 (1)
O(1*B*)	5038 (2)	5482 (2)	1663 (1)
O(2)	7068 (1)	4369 (1)	125 (1)
O(3)	9480 (1)	4701 (1)	338 (1)
O(4)	8828 (1)	7323 (1)	1798 (1)
O(5)	6773 (1)	6584 (1)	497 (1)
O(6)	7583 (1)	9155 (1)	1280 (1)
*W*O	4803 (2)	8172 (2)	1798 (1)

The atomic scattering factors for O and C were those tabulated by Doyle & Turner (1968) and those for H were given by Stewart, Davidson & Simpson (1965). The final positional parameters are given in Tables 1 and 2.*

Discussion. The atomic notation, bond lengths and principal torsion angles are given in Figs. 1 and 2. A

---

* Lists of structure factors, anisotropic thermal parameters, and valence bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33613 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

table of bond angles has been deposited;* the values of note are as follows: in the furanose ring, the valence angle at O(5) is 109° and at the C atoms it is between 102 and 107°. In the dioxolane and dioxane rings, the oxygen valence angles are 110, 109°, and 114, 115° respectively. The carbon valence angles between the vicinal methyl groups are C(8)–C(7)–C(9) 114°, and C(11)–C(10)–C(12) 112°. The dihedral angles between the three ring systems are defined by the following torsion angles: O(3)–C(3)–C(2)–O(5) −104°, O(4)–C(4)–C(5)–O(5) −74°. The carboxylic acid group is inclined so that the O(1*B*)–C(1)–C(2)–O(5) torsion angle is +11°.

One of the interesting structural features of the molecule is the bond-length variation in the sequence of

---

* See previous footnote.

Table 2. *Fractional atomic coordinates* (×10³), *isotropic thermal parameters* (Å²) *and bond distances* (Å) *for the hydrogen atoms in 2,3:4,6-di-O-isopropylidene-2-keto-L-gulonic acid monohydrate*

	x	y	z	B(iso)	C, O–H
H(C3)	903 (2)	494 (2)	159 (1)	3·9 (4)	1·03 (2)
H(C4)	1012 (2)	697 (2)	80 (1)	3·6 (4)	0·95 (2)
H(C5)	843 (2)	714 (2)	−25 (1)	3·0 (4)	0·98 (2)
H(C61)	696 (2)	904 (2)	10 (1)	4·3 (5)	0·94 (2)
H(C62)	865 (2)	927 (2)	15 (1)	4·0 (4)	1·02 (2)
H(C81)	950 (4)	207 (3)	29 (2)	8·0 (8)	0·93 (3)
H(C82)	845 (3)	251 (3)	100 (2)	8·3 (8)	1·04 (3)
H(C83)	783 (3)	197 (3)	9 (2)	6·3 (7)	0·94 (3)
H(C91)	864 (3)	476 (3)	−117 (2)	7·3 (7)	0·99 (3)
H(C92)	793 (4)	322 (4)	−128 (2)	9·1 (8)	1·05 (3)
H(C93)	959 (4)	346 (3)	−109 (2)	8·4 (9)	0·90 (3)
H(C111)	900 (3)	877 (3)	313 (2)	6·4 (6)	1·02 (3)
H(C112)	737 (3)	858 (3)	281 (2)	6·3 (6)	0·93 (3)
H(C113)	830 (3)	999 (3)	277 (2)	7·4 (7)	0·95 (3)
H(C121)	1042 (2)	924 (2)	107 (1)	4·4 (5)	0·91 (2)
H(C122)	1003 (3)	1028 (3)	179 (2)	6·6 (6)	0·95 (3)
H(C123)	1089 (3)	895 (3)	200 (2)	6·1 (6)	1·00 (3)
H(O1*A*)	603 (3)	361 (3)	232 (2)	6·1 (6)	0·90 (3)
H(*W*O1)	483 (4)	736 (4)	169 (2)	9·2 (9)	0·84 (4)
H(*W*O2)	557 (4)	860 (3)	165 (2)	9·3 (10)	0·86 (4)

Fig. 2. Molecular dimensions of 2,3:4,6-di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate. The signed values are ring torsion angles. The standard deviations are 0·002 to 0·004 Å in the bond lengths, 0·2 to 0·4° in the angles.

Fig. 1. 2,3:4,6-Di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate. The atomic notation and thermal ellipsoids at 50% probability (Johnson, 1976) are shown.
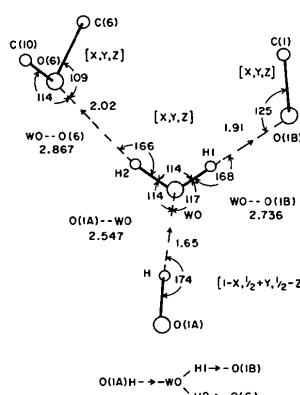
Fig. 3. The hydrogen-bond structure in 2,3:4,6-di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate. The standard deviations are 0·003 Å in the O···O distances, 0·04 Å in the O–H and H···O distances, and 3° in the O–H···O angles.
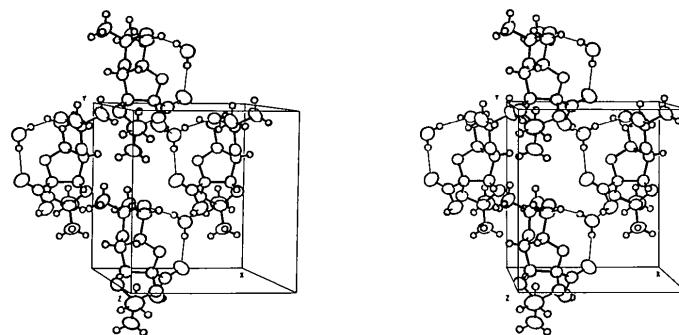
Fig. 4. The unit-cell contents of 2,3:4,6-di-*O*-isopropylidene-2-keto-L-gulonic acid monohydrate, viewed down the *b* axis. The thin lines are hydrogen bonds.

C—O bonds which originate at C(3) and terminate at C(5). These are
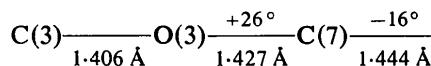
A stereoview of the contents of the unit cell is shown in Fig. 4.

$$C(3) \underset{1\cdot406\ \text{Å}}{\rule{1.5cm}{0.4pt}} O(3) \overset{+26°}{\underset{1\cdot427\ \text{Å}}{\rule{1.5cm}{0.4pt}}} C(7) \overset{-16°}{\underset{1\cdot444\ \text{Å}}{\rule{1.5cm}{0.4pt}}} O(2) \overset{+117°}{\underset{1\cdot408\ \text{Å}}{\rule{1.5cm}{0.4pt}}} C(2) \overset{-100°}{\underset{1\cdot410\ \text{Å}}{\rule{1.5cm}{0.4pt}}} O(5) \underset{1\cdot445\ \text{Å}}{\rule{1.5cm}{0.4pt}} C(5),$$
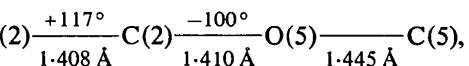
where the angles refer to the bond torsion angles. The four-bond sequence C(7)—C(5) resembles that occurring in methyl pyranosides, where both experiment and theory agree that the inner bonds are shorter than the outer bonds by about 0·03 Å (Jeffrey, Pople, Binkley & Vishveshwara, 1978). There is, however, another four C—O bond sequence where these differences are not observed, *i.e.*

$$C(6) \underset{1\cdot429\ \text{Å}}{\rule{1.5cm}{0.4pt}} O(6) \overset{-59°}{\underset{1\cdot427\ \text{Å}}{\rule{1.5cm}{0.4pt}}} C(10) \overset{+60°}{\underset{1\cdot430\ \text{Å}}{\rule{1.5cm}{0.4pt}}} O(4) \underset{1\cdot423\ \text{Å}}{\rule{1.5cm}{0.4pt}} C(4).$$
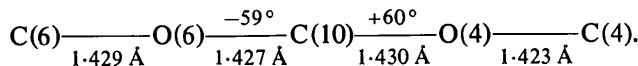
Further experimental and theoretical study is necessary to understand these differences. The C—C distances in this molecule lie in the normal range of 1·500 to 1·541 Å.

The hydrogen bonding consists of short finite chains, shown in Fig. 3, which link the water molecules to the carboxylic acid groups. The closest intermolecular methyl—methyl contacts are C(9)···C(12) 3·868 Å, C(8)···C(12) 3·972 Å, and C(9)···C(11) 3·976 Å.

References

BROSSI, A. & TEITEL, S. (1970). *J. Org. Chem.* **35**, 3559–3561.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.

DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

JEFFREY, G. A., POPLE, J. A., BINKLEY, S. & VISHVESHWARA, S. (1978). *J. Am. Chem. Soc.* **100**, 373–379.

JOHNSON, C. K. (1976). *ORTEP* II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TEITEL, S., O'BRIEN, J. & BROSSI, A. (1972). *J. Med. Chem.* **15**, 845–846.

TEMPLETON, L. K. & TEMPLETON, D. H. (1973). Abstract E10. Am. Crystallogr. Assoc. Meet., Storrs, Connecticut.