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The Crystal Structure of Reductic Acid (2-Cyclopentene-2,3-diol-1-one)

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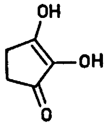
The crystal and molecular structure of reductic acid, $C_5H_6O_3$ (2-cyclopentene-2,3-diol-1-one) has been determined by X-ray methods, using 1919 observed intensities collected by counter methods. The crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions $a = 7.172(1)$, $b = 8.680(1)$, $c = 10.328(2)$ Å, $\beta = 129.37(1)°$. The refinements yielded a conventional R-factor of 0.044; standard deviations in bond lengths and angles are 0.001 Å and 0.1°. The molecular geometry and the hydrogen bond system are discussed.

Reductic acid is a colourless, sublimable compound with a melting point of 214 °C. It is the simplest carbocyclic analogue of triose reductone (2-propen-2,3-diol-1-one), and has the formula (*1*). Being an acireductone the molecule comprises the functional group $-\text{COH}=\text{COH}-\text{CO}-$, also found in ascorbid acid and triose reductone. The title compound is thus an organic acid of strength comparable to the carboxylic acids and possesses the characteristic reducing properties of the acireductones. The compound was first synthesized by the action of mineral acids on certain carbohydrates, as for instance pectins, and alginates.[1] Reductic acid is, however, accessible in high yields (70 %) from 3-bromo-2-hydroxy-2-cyclopentene-1-one by hydrolysis.[2]



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The present X-ray study of reductic acid was undertaken in order to provide a comparison with the previous X-ray investigation of triose reductone[3] and to further examine the hydrogen bonding properties of the conjugated system common to both molecules.

EXPERIMENTAL

An extraordinarily pure sample of the compound, superior to those commercially available, was kindly supplied by prof.dr. G. Hesse. Suitable crystals showing the forms {100}, {010} and {001} were obtained by slow evaporation from formic acid solutions. Preliminary photographic investigations implied the space group to be $P2_1/c$. Unit cell dimensions were determined from measurement of the diffractometer setting angles of 17 reflections, using a manual Picker four-circle diffractometer (Cu$K\beta$ radiation, $\lambda = 1.3894$ Å). Intensity measurements were made on a SYNTEX $P\bar{1}$ computer controlled four-circle diffractometer with graphite monochromated Mo$K\alpha$ ($\lambda = 0.71069$ Å) radiation. With the crystal mounted in an arbitrary orientation, the intensities within one quadrant for $2\theta < 80°$ were measured with the $\omega - 2\theta$ scanning mode and a symmetrical scan range based on 1.8° varied to allow for spectral dispersion. The scan speed for each reflection was calculated from a fast preliminary $\omega - 2\theta$ scan of the reflection and varied between 1.0 and 6.0 °/min, so as to maintain satisfactory counting statistics even for reflections of moderate intensity. A rejection level was specified to avoid measurement of reflections with intensities less than the instrumental threshold value. Background counts were taken at each end of the scan, the ratio of the total background counting time to the scan time was 0.7. A total of 2171 independent reflections were recorded, of which 1919 had intensities greater than twice their standard deviations estimated from counting statistics. These were considered to be observed, the remaining were rejected from the structure

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations. Expression for anisotropic vibration is: $\exp[-2\pi^2(h^2a^{*2}U11+\cdots+2klb^*c^*U23)]$.

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
O 1	.77041(13)	.10690(8)	.59151(10)	.0254(3)	.0266(3)	.0408(4)	.0007(3)	.0165(4)	.0065(3)
O 2	.26388(13)	.20560(9)	.40128(11)	.0260(3)	.0283(4)	.0589(5)	-.0014(3)	.0268(4)	.0078(3)
O 3	.20701(14)	.48545(9)	.21715(10)	.0238(3)	.0333(4)	.0494(5)	.0028(3)	.0156(3)	.0122(3)
C 1	.68193(16)	.22420(10)	.50091(12)	.0215(3)	.0235(4)	.0283(4)	-.0024(3)	.0140(3)	-.0022(3)
C 2	.43848(15)	.27314(11)	.40484(12)	.0200(3)	.0231(4)	.0304(4)	-.0030(3)	.0161(3)	-.0013(3)
C 3	.40583(16)	.40385(11)	.32060(12)	.0221(4)	.0246(4)	.0283(4)	-.0019(3)	.0134(3)	-.0014(3)
C 4	.63146(19)	.45705(13)	.35634(14)	.0289(5)	.0310(5)	.0366(5)	-.0029(4)	.0212(4)	.0041(4)
C 5	.81733(18)	.33500(13)	.47607(14)	.0235(4)	.0338(5)	.0399(6)	-.0022(4)	.0197(4)	.0037(4)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H 1	.2926(27)	.1103(19)	.4257(18)	4.9(3)	H 2	.0757(31)	.4381(20)	.1884(19)	5.9(4)
H 3	.6693(24)	.5636(15)	.4021(16)	3.5(2)	H 4	.6069(24)	.4642(16)	.2537(17)	4.1(3)
H 5	.9547(26)	.3750(16)	.5833(18)	4.4(3)	H 6	.8908(25)	.2803(16)	.4357(17)	4.0(2)

Table 2. Bond distances, bond angles, and hydrogen bond lengths and angles. Estimated standard deviations in bond lengths between heavy atoms are 0.001 Å, in angles 0.1° (0.01 Å and 1° in bonds and angles involving hydrogen atoms). Distances in parenthesis are corrected for librational thermal motion.

Bond distances (Å)		Bond angles (°)	
C1–O1	1.250 (1.253)	O1–C1–C2	125.6
C2–O2	1.362 (1.366)	O1–C1–C5	125.4
C3–O3	1.321 (1.324)	O2–C2–C3	124.1
C1–C2	1.420 (1.426)	O2–C2–C1	126.3
C2–C3	1.356 (1.360)	O3–C3–C4	118.7
C3–C4	1.487 (1.494)	O3–C3–C2	128.8
C4–C5	1.529 (1.534)	C1–C2–C3	109.5
C1–C5	1.500 (1.505)	C2–C3–C4	112.5
O2–H1	0.85	C3–C4–C5	103.8
O3–H2	0.89	C4–C5–C1	104.8
C4–H3	0.99	C5–C1–C2	109.4
C4–H4	0.96	C4–C5–H5	114.2
C5–H5	0.97	C4–C5–H6	114.9
C5–H6	0.98	C1–C5–H5	109.4
		C1–C5–H6	110.0
		C5–C4–H3	115.1
		C5–C4–H4	113.2
		C3–C4–H3	109.4
		C3–C4–H4	109.9
Hydrogen bond distances (Å)		**Hydrogen bond angles (°)**	
O1···O2	2.729	C2–O2–H1	111.4
O1···O3	2.641	C3–O3–H2	112.9
O1···H1	1.92	C1–O1···H1	139.2
O1···H2	1.78	C1–O1···H2	120.9
		O1···H1–O2	163.5
		O1···H2–O3	160.5

analysis. The intensities of three reference reflections measured at regular intervals showed no significant change. Corrections for Lorentz and polarization effects were applied to the intensities and their standard deviations and a 2 % uncertainty in diffractometer stability was included in the latter.

The structure was determined by the application of symbolic addition procedures and refined by Fourier and fullmatrix least-squares methods. The function minimized was $M = \sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F_o)$. The calculations were performed on CD 6600 using the programs described in Ref. 4. The final residuals were $R_w = 0.048$ and $R = 0.044$. Weight analysis showed that weighting based on standard deviations from counting statistics was satisfactory.

No correction was made for possible sources of systematic error such as absorption, extinction, or multiple diffraction. Atomic scattering factors used during the calculations were those of Doyle and Turner [5] for the carbon and oxygen atoms. For the hydrogen atoms those of Stewart, Davidson and Simpson [6] were used.

The final positional and thermal parameters are given in Table 1, bond lengths and angles in Table 2; estimated standard deviations are calculated from the correlation matrix of the final least-squares refinement cycle.

A rigid-body motion analysis was carried out by the method of Schomaker and Trueblood.[7] There is good agreement between the observed and calculated vibration tensor elements; $\Delta U_{ij} = 0.0007$ Å^2, while the average estimated standard deviation in U_{ij} is 0.0010 Å^2, suggesting that the molecular motion may be regarded as that of an oscillating rigid body. The r.m.s. translational amplitudes are 0.17, 0.15, and 0.13 Å and the r.m.s. librational amplitudes are 5.5, 4.2, and 2.3°. Correction

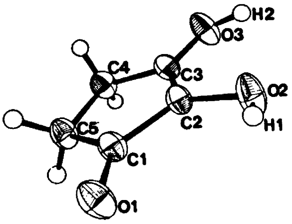

Fig 1. Perspective drawing of the molecule with atom numbering as indicated. Thermal ellipsoids are scaled to include 50 % probability.

Table 3. Bond distances in the conjugated system in reductic acid and some related compounds. Atom numbering as in Fig. 1.

	C1 – O1	C2 – O2	C3 – O3	C1 – C2	C2 – C3	Ref.
L-Ascorbic acid	1.216(2)	1.361(2)	1.326(3)	1.452(3)	1.338(2)	10
D-Isoascorbic acid	1.200(5)	1.340(5)	1.329(5)	1.446(5)	1.331(5)	9
α-Methyltetronic acid	1.219(3)	–	1.326(3)	1.436(3)	1.335(3)	11
Dimedone (5,5-dimethyl-1,3-cyclohexanedione)	1.246(2)	–	1.326(2)	1.418(2)	1.351(2)	8
Triose reductone (2-propene-2,3-diol-1-one)	1.241(2)	1.351(2)	1.322(2)	1.414(2)	1.352(2)	3
Reductic acid (2-cyclopentene-2,3-diol-1-one)	1.250(1)	1.362(1)	1.321(1)	1.420(1)	1.356(1)	–

in bond lengths range from 0.003 Å to 0.006 Å. However, discussion of the structure is based on the uncorrected values.

CRYSTAL DATA

Reductic acid $C_5H_6O_3$, monoclinic; $P2_1/c$, $a = 7.172(1)$ Å, $b = 8.680(1)$ Å, $c = 10.328(2)$ Å, $\beta = 129.37$ $(0.01)°$, $\varrho_{obs} = 1.50$ g/cm^3, $\varrho_{cal} = 1.52$ g/cm^3, $Z = 4$, $V = 497.03$ Å^3, M = 114.10 g/mol, $F(000) = 240$.

DISCUSSION

The molecular structure and atom numbering is shown in Fig. 1. Reductic acid is thus found to have the acireductone structure (*1*) with bond lengths in the alternating bond system which agree well with those previously found in triose reductone [3] and dimedone [8] (see Table 3). The values of these bond lengths are of intermediate character indicating a substantial amount of π-electron delocalization in the conjugated system. The formal single bond C3 – O3 (1.321 Å) has considerably more doublebond character than the C2 – O2 (1.362 Å) bond. It is therefore reasonable to assume that O3 – H2 is the acidic group in the molecule, thereby forming a symmetrically delocalized anion on dissociation, which will account for the acidic properties of reductic acid. Similar differences (0.03 – 0.04 Å) between the central and terminal hydroxyl groups have been found in many other acireductone crystal structures. The only marginal exception known to the author is in the crystal structure D-isoascorbic acid, where the difference is only 0.01 Å and where the central hydroxyl group participates in an unusually strong hydrogen bond (2.585 Å).[9]

It is interesting to compare the bond lengths found in the present investigation with those found in the related 5-membered ring systems of D-isoascorbic-,[9] L-ascorbic-,[10] and α-methyltetronic acids.[11] Table 3 shows the relevant bond lengths observed in the investigation of these compounds together with those from the investigation of reductic acid and also those from the dimedone [8] and triose reductone [3] determinations. It is seen that the conjugation in reductic acid is higher than it is in the 5-membered lactone ring systems. With the exception of the hydroxyl bond length (C3 – O3) the differences in bond lengths are significant, judged by the combined standard deviations from the individual investigations. The reason for the higher double bond fixation in the molecules containing the γ-lactone ring is probably that lone pairs on the ring oxygen

Table 4. Deviations (Å) from least-squares planes through parts of the molecule. For atom numbering see Fig. 1. Deviations of atoms not defining the planes in parenthesis.

O1	– 0.019	(– 0.002)	– 0.006
O2	0.031	(0.069)	(– 0.065)
O3	– 0.022	(– 0.019)	– 0.005
C1	– 0.006	0.001	0.004
C2	– 0.013	0.004	0.007
C3	– 0.009	– 0.007	0.003
C4	0.028	0.007	(0.024)
C5	0.012	– 0.005	(0.006)
H1	(– 0.29)	(– 0.27)	(– 0.25)
H2	(– 0.19)	(– 0.17)	(– 0.16)

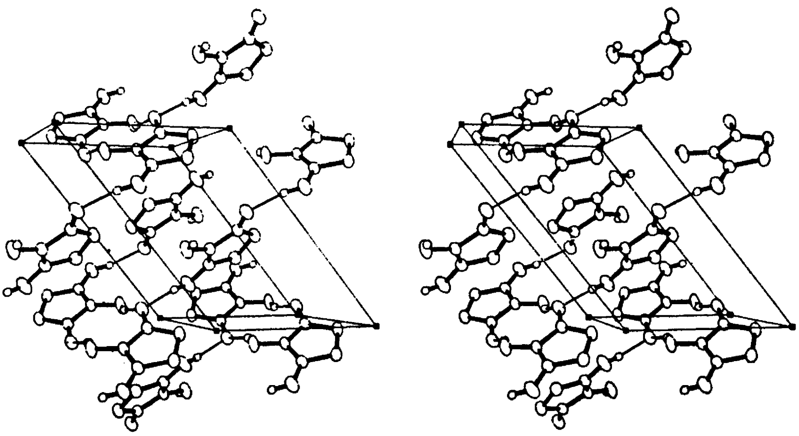

Fig. 2. Stereoscopic illustration of the crystal structure as viewed along the *b* axis. Thermal ellipsoids are scaled to include 50 % probability.

atom may to a certain extent also supply electron density to the neighbouring carbonyl group. In reductic acid, on the other hand, charge will essentially be transmitted through the conjugated system. The interior angles in the 5-membered ring vary from 103.8 to 112.5°. The average value is 108.0°, in good agreement with the angle in a regular pentagon. The larger deviations occur in the angles about the double bond. The external O – C – C angles vary from 118.7° to 128.8°, the larger angles being *cis* to the hydroxyl hydrogen atoms which are situated approximately in the molecular plane. This feature is also observed in many phenol crystal structures,[12,13] and in the crystal structure of squaric acid.[14]

Deviations from least-squares planes through various parts of the molecule are given in Table 4. Although the molecule as a whole is essentially planar, there are significant deviations from a least-squares plane through all heavy atoms. However, the atoms which make up the 5-membered ring and those which make up the conjugated system are separately planar. The deviations of O2 from these planes cause the enediol group in reductic acid to be slightly but significantly non-planar. The deviations from planarity mentioned above are not considered to be of chemical origin, but rather due to deformations from packing and hydrogen bonding forces.

The hydrogen bonding scheme deduced from the approach distances and hydrogen atom positions is shown in Fig. 2. The carbonyl group accepts two intermolecular hydrogen bonds, the shorter of which at 2.641 Å involves the terminal hydroxyl group, and is of a similar order of strength as the hydrogen bonds found in carboxylic acid crystal structures. The other hydrogen bond is somewhat weaker, 2.729 Å and comes from the central hydroxyl group. This is in keeping with the above conclusion that H2 is the acidic proton in the molecule.

The hydrogen bonding scheme is formally very similar to that found in the crystal structure of triose reductone, which contains the same number of donors and acceptors for hydrogen bonding per molecule as reductic acid. The hydrogen bond lengths (2.641, 2.729 Å) also correspond closely to those previously found in triose reductone structure (2.635, 2.744 Å). Although none of the hydrogen bonds in reductic acid lie exactly in the plane of the conjugated system, the stronger hydrogen bond deviates somewhat less from this plane. The crystal structure is built up from hydrogen-bonded dimers around the center of inversion through the longer hydrogen bonds. These dimers are tied together into pairs of chains *via* the shorter hydrogen bond (2.641 Å), running along [201].

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