logie entre ces deux molécules. La noradrénaline adopte une conformation *trans* et c'est également cette conformation privilégiée que l'on observe dans la molécule étudiée, à condition de considérer l'azote N(1). Cette assimilation de l'azote imino N(1) avec l'azote amino de la noradrénaline est confirmée chimiquement, puisque la méthylation (Gozlan, Michelot & Rips, 1974) et la protonation (Mollin & Kasparek, 1961) ont lieu sur l'azote imino N(1) et non pas sur l'azote amino N(2).

La recherche des propriétés pharmacologiques dues à cette analogie est en cours.

Nous remercions M Richard Rips pour son intérêt constant au cours de ce travail et pour une lecture constructive de ce manuscrit.

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# The Structure of an Ascorbate Tautomer: the Methyl Glycoside of 2-*C*-Benzyl-3-keto-L-*lyxo*-hexulosonic Acid Lactone

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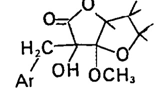
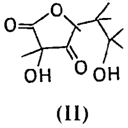
The crystal structure of $C_{14}H_{16}O_6$ has been determined by X-ray diffraction with Mo $K\alpha$ radiation. The space group is $P2_12_12_1$ with $a=6{\cdot}339$ (1), $b=9{\cdot}739$ (2), $c=22{\cdot}484$ (4) Å. The parameters were refined to $R=0{\cdot}047$ and $R_w=0{\cdot}043$ for 1470 reflexions. For the high-angle data $R=0{\cdot}058$ and $R_w=0{\cdot}046$. Standard deviations are 0·004 Å and 0·3° for non-hydrogen atoms. The molecule is a derivative of the ketol tautomer of ascorbic acid and involves a sugar moiety with a fused-ring system analogous to that in dimeric dehydroascorbic acid. A benzyl group is attached to C(2) in ascorbic acid, and the five-membered rings have irregular envelope conformations with the common C(3) atom unique in each case. The C–C distances in the phenyl ring were corrected for $\pi$-electron polarization and thermal motion to give values close to the theoretical ones.

## Introduction

The title compound (I) is interesting as a derivative of the ketol tautomer (II)/(III) of the well known enediol ascorbic acid (IV). It may be synthesized from the ascorbate anion by treatment with benzyl chloride and subsequent reaction with methanol in HCl.



(I)



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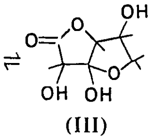

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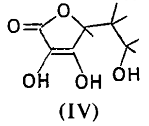

(IV)

During these reactions a nucleophilic internal addition leads to the acetal (I) which is a derivative of (III). This fused-ring system bears great structural resemblance to one-half of the molecule encountered in the crystals of dimeric dehydroascorbic acid (Hvoslef, 1972). The structure of the biologically important monomer has, however, not been determined due to failure in isolating and crystallizing the substance, and also to its instability in many solvents. An open side-chain derivative with *p*-bromophenylhydrazine has recently been reported (Hvoslef & Nordenson, 1976). The title compound proved useful as a model substance in our NMR studies of stable solutions of monomeric dehydroascorbic acid. These were performed in order to decide between the fused ring and the open side-chain alternative for the substance.

## Experimental

The methyl glycoside of 2-*C*-benzyl-3-keto-L-*lyxo*-hexulosonic acid lactone (I) was prepared from L-(+)-ascorbic acid by the procedure given by Jackson & Jones (1965). The compound was recrystallized from water to give soft, needle-shaped crystals with m.p. 137°C. The quality was fair, and a specimen with the dimensions 0·04 × 0·02 × 0·02 cm was used for the collection of X-ray data. Weissenberg photographs identified the space group as $P2_12_12_1$ from systematic absences. The intensities were measured at 18°C using an automatic Syntex $P\bar{1}$ diffractometer operating in the $\omega$–$2\theta$ mode. By restricting $2\theta$ to a maximum of 65°, 1720 reflexions were considered, but only 1470 were stronger than two times the standard deviation in intensity and useful in the final analysis. The radiation was Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) and the scan speed varied between 2° and 8° $\text{min}^{-1}$, whereas the background counts lasted for 0·7 times the scan time on each side of the Bragg peak. The stability of the crystal was checked by three test reflexions whose values were measured with intervals of 47 intensity recordings. No disintegration was observed, but minor corrections had to be made due to re-centring of the crystal.

No correction for absorption was necessary for the compound, and the data were converted to structure amplitudes by a program adapted to CDC 3300 by Dahl, Gram, Groth, Klewe & Rømming (1970).

*Crystal data*

$a = 6{\cdot}339\ (1)$ Å
$b = 9{\cdot}739\ (2)$
$c = 22{\cdot}484\ (4)$
Space group: $P2_12_12_1$
$Z = 4$

$C_{14}H_{16}O_6$
$M = 280{\cdot}280$
$V = 1388{\cdot}1\ (5)$ Å$^3$
$d_{\text{obs}} = 1{\cdot}35$ g cm$^{-3}$
$d_{\text{calc}} = 1{\cdot}341$
$\mu(\text{Mo } K\alpha) = 1{\cdot}1$ cm$^{-1}$.

## Structure determination and refinement

The structure was solved by direct methods using the *MULTAN* programs designed by Germain, Main & Woolfson (1971). The calculations were performed with the 250 largest $E$ values ($E_{\text{max}} = 3{\cdot}48$, $E_{\text{min}} = 1{\cdot}39$) and the 1200 strongest $\sum_2$ relations between these. 6 reflexions were chosen as an adequate starting set, and of the 32 possible combinations, one was singled out by the 'figure of merit' criteria. In the corresponding $E$-map, however, only 8 maxima could definitely be associated with the molecule. During tangent refinements, which were based upon the first and subsequent partial structures, all the atoms except those in the phenyl group were found ($R = 0{\cdot}38$ for 250 reflexions). The latter were localized from weighted Fourier syntheses (Sim, 1959, 1960). A cautious least-squares refinement using isotropic thermal parameters improved $R$ from 0·36 to 0·13 for 1470 reflexions. Introduction of anisotropic thermal parameters for the heavy atoms significantly improved the parameters, and 11 hydrogen atoms were located from difference Fourier maps. Those attached to C(6) and C(7) were uncertain due to the large thermal parameters of the latter, and were given estimated coordinates and thermal amplitudes

Table 1. *Fractional coordinates for the atoms in the methyl glycoside of* 2-*C*-*benzyl*-3-*keto*-L-*lyxo*-*hexulosonic acid lactone*

Standard deviations are in parentheses. The values are multiplied by $10^4$ for the heavy atoms and by $10^3$ for the hydrogen atoms. The latter are identified by the atoms to which they are attached. (√) refers to fixed values.

| | *x* | *y* | *z* |
|---|---|---|---|
| O(1) | 5350 (4) | 4656 (3) | 2191 (1) |
| O(2) | 4563 (3) | 6294 (2) | 1125 (1) |
| O(3) | 9327 (3) | 7273 (2) | 801 (1) |
| O(4) | 8616 (3) | 5451 (2) | 2141 (1) |
| O(5) | 12564 (4) | 8023 (3) | 1887 (1) |
| O(6) | 7388 (3) | 8040 (2) | 1619 (1) |
| C(1) | 6660 (5) | 5249 (3) | 1910 (1) |
| C(2) | 6561 (4) | 5807 (3) | 1280 (1) |
| C(3) | 8301 (4) | 6910 (3) | 1319 (1) |
| C(4) | 9882 (4) | 6333 (3) | 1757 (1) |
| C(5) | 10616 (5) | 7561 (4) | 2123 (2) |
| C(6) | 8864 (6) | 8606 (4) | 2031 (2) |
| C(7) | 8100 (7) | 8119 (5) | 402 (2) |
| C(8) | 7137 (5) | 4651 (3) | 845 (2) |
| C(9) | 5693 (5) | 3427 (3) | 878 (1) |
| C(10) | 3698 (6) | 3450 (4) | 620 (2) |
| C(11) | 2381 (7) | 2329 (4) | 648 (2) |
| C(12) | 3006 (7) | 1163 (4) | 939 (2) |
| C(13) | 4962 (8) | 1123 (4) | 1199 (2) |
| C(14) | 6292 (7) | 2255 (4) | 1163 (2) |
| O(2)H | 413 (6) | 692 (4) | 138 (2) |
| O(5)H | 1310 (6) | 847 (4) | 211 (2) |
| C(4)H | 1100 (4) | 580 (3) | 159 (1) |
| C(5)H | 1085 (5) | 727 (3) | 254 (1) |
| C(6)H1 | 820 (√) | 884 (√) | 240 (√) |
| C(6)H2 | 944 (√) | 945 (√) | 187 (√) |
| C(7)H1 | 863 (√) | 801 (√) | 3 (√) |
| C(7)H2 | 815 (√) | 906 (√) | 52 (√) |
| C(7)H3 | 665 (√) | 785 (√) | 40 (√) |
| C(8)H1 | 704 (5) | 504 (3) | 45 (1) |
| C(8)H2 | 863 (5) | 443 (3) | 92 (1) |
| C(10)H | 335 (5) | 420 (3) | 42 (1) |
| C(11)H | 98 (5) | 233 (3) | 47 (1) |
| C(12)H | 201 (6) | 34 (4) | 94 (2) |
| C(13)H | 551 (6) | 32 (4) | 140 (2) |
| C(14)H | 759 (6) | 219 (4) | 134 (2) |

in the further refinement, which was terminated at $R=0{\cdot}047$ and $R_w=0{\cdot}043$.

Additional analyses were also made with data where $\sin\theta/\lambda>0{\cdot}4$, and for 1025 reflexions, $R=0{\cdot}058$ and $R_w=0{\cdot}046$. The intention was to reduce the contribution from the valence electrons and to see what happened to the interatomic distances.

The atomic form factors for carbon and oxygen atoms were from Hanson, Herman, Lea & Skillman (1964), and those for hydrogen from Stewart, Davidson & Simpson (1965). No indication of secondary extinction was observed, and the final residual electron density was nowhere above 0·3 e Å$^{-3}$. The atomic fractional coordinates are in Table 1, the thermal parameters in Table 2.*

Table 2. *Thermal parameters for the title compound*

Standard deviations are in parentheses, except where (*) represents a fixed value. Temperature factors are in the form $T=\exp(-\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)$, and the values are multiplied by $10^4$. For the hydrogen atoms the isotropic $B$ values are given.

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| O(1) | 266 (6) | 149 (3) | 20 (1) | −119 (9) | 31 (3) | 21 (2) |
| O(2) | 155 (5) | 99 (3) | 19 (1) | 30 (7) | −7 (3) | −16 (2) |
| O(3) | 242 (6) | 123 (3) | 17 (0) | −35 (8) | 37 (3) | 16 (2) |
| O(4) | 206 (6) | 128 (3) | 20 (1) | −36 (8) | −17 (3) | 37 (2) |
| O(5) | 176 (6) | 131 (3) | 31 (1) | −58 (8) | 28 (4) | −56 (3) |
| O(6) | 173 (5) | 82 (2) | 20 (0) | 13 (7) | −10 (3) | −15 (2) |
| C(1) | 186 (8) | 91 (4) | 17 (1) | 0 (10) | 12 (4) | 1 (3) |
| C(2) | 129 (7) | 81 (3) | 14 (1) | −11 (9) | 14 (4) | −6 (2) |
| C(3) | 153 (7) | 74 (3) | 15 (1) | −6 (9) | 15 (4) | 1 (2) |
| C(4) | 127 (7) | 88 (4) | 20 (1) | 11 (10) | 14 (4) | 6 (3) |
| C(5) | 161 (8) | 125 (4) | 19 (1) | −15 (11) | 7 (4) | −13 (3) |
| C(6) | 188 (9) | 170 (6) | 34 (1) | 72 (13) | −18 (5) | −66 (4) |
| C(7) | 444 (16) | 193 (6) | 27 (1) | −19 (20) | 30 (7) | 53 (4) |
| C(8) | 188 (9) | 96 (4) | 19 (1) | 6 (10) | 23 (4) | −7 (3) |
| C(9) | 219 (8) | 83 (4) | 17 (1) | 22 (10) | 13 (4) | −18 (3) |
| C(10) | 269 (11) | 97 (4) | 20 (1) | 0 (12) | −18 (5) | −6 (3) |
| C(11) | 270 (12) | 147 (6) | 27 (1) | −69 (15) | −8 (6) | −36 (4) |
| C(12) | 379 (16) | 109 (5) | 41 (1) | −158 (16) | 38 (8) | −24 (4) |
| C(13) | 452 (18) | 86 (5) | 47 (2) | 25 (17) | −2 (9) | 28 (5) |
| C(14) | 304 (12) | 101 (5) | 31 (1) | 62 (14) | −25 (6) | 3 (4) |

| | $B$ | | $B$ |
|---|---|---|---|
| O(2)H | 6·0 (1·1) | C(7)H3 | 7·0 (*) |
| O(5)H | 5·7 (1·2) | C(8)H1 | 3·0 (0·7) |
| C(4)H | 2·3 (0·6) | C(8)H2 | 2·7 (0·6) |
| C(5)H | 4·5 (0·8) | C(10)H | 3·0 (0·7) |
| C(6)H1 | 5·0 (*) | C(11)H | 4·0 (0·8) |
| C(6)H2 | 5·0 (*) | C(12)H | 6·1 (0·9) |
| C(7)H1 | 7·0 (*) | C(13)H | 6·8 (1·0) |
| C(7)H2 | 7·0 (*) | C(14)H | 4·9 (0·9) |

## Discussion

### *The crystal structure and hydrogen bonding*

Simplified views of the crystal structure and hydrogen bonding as seen along the negative *a* and *c* axes are shown in the stereo pairs (Johnson, 1965) in Fig. 1. Strata of molecules parallel to the (00*l*) planes are interwoven by hydrogen bonds of two categories. The first links translationally equivalent molecules together along the *a* axis, whereas the second generates helical interactions along *b*. Between the strata van der Waals forces only are operating, and we have listed some short non-bonded contacts among the hydrogen bonds in Table 3. None of the interactions mentioned are strong, and the observed physical properties of the crystals are thus readily explained.

### *Molecular geometry*

This molecule, as shown in Fig. 2, comprises two fused, non-planar five-membered rings with a benzyl group attached to C(2) and a methoxy group attached to C(3). Relative to ascorbic acid, new asymmetric centres are created at these two carbon atoms, and the configurations are *S* and *R* for C(2) and C(3), respectively. The entirely planar benzyl group is almost coplanar with the methoxy group and roughly parallel to the $\gamma$-lactone ring. The five-membered rings have irregular envelope conformations with the common C(3) atom deviating from the best planes through the four other atoms in the rings (Table 4). The unique role of C(3) is presumably caused by repulsion between the benzyl and the methoxy groups, whereby an eclipsed conformation for O(3) and C(8) is avoided by a 38·8° twist about the C(2)–C(3) bond. Details of the conformation are shown in Newman projections (Fig. 3) and in Table 4. Although the geometry of the sugar moiety bears great resemblance to that of the asymmetric unit in the crystalline dimeric dehydroascorbic acid and in

Table 3. *Hydrogen bonds and short non-bonded contacts*

Average standard deviations are 0·04 Å and 3° for bonds involving hydrogen atoms and 0·004 Å for $A\cdots B$ distances.

| $A$–(H)$\cdots B$ | Symmetry code for $B$ | $A$–H | H$\cdots B$ | $A\cdots B$ | $A$–H$\cdots B$ | C–$A$–H |
|---|---|---|---|---|---|---|
| O(2)–H$\cdots$O(5) | $x+1,\ y,\ z$ | 0·74 Å | 2·19 Å | 2·929 Å | 175° | 110° |
| O(5)–H$\cdots$O(1) | $\frac{1}{2}-x,\ \frac{1}{2}+y,\ -z$ | 0·88 | 1·85 | 2·715 | 165 | 111 |
| C(7)$\cdots\cdot$O(2) | $\frac{1}{2}+x,\ \frac{3}{2}-y,\ 1-z$ | | | 3·60 | | |
| C(7)$\cdots\cdot$O(3) | $x-\frac{1}{2},\ \frac{3}{2}-y,\ 1-z$ | | | 3·63 | | |
| C(7)$\cdots\cdot$C(7) | $x-\frac{1}{2},\ \frac{3}{2}-y,\ 1-z$ | | | 3·84 | | |
| C(11)$\cdots$C(8) | $x-\frac{1}{2},\ \frac{1}{2}-y,\ -z$ | | | 3·87 | | |
| C(11)$\cdots$C(9) | $x-\frac{1}{2},\ \frac{1}{2}-y,\ -z$ | | | 3·67 | | |
| C(11)$\cdots$C(10) | $x-\frac{1}{2},\ \frac{1}{2}-y,\ -z$ | | | 3·76 | | |

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* A list of structure factors and a table of bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31521 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

glucurono-γ-lactone (Kim *et al.*, 1967), the different substituents cause conformational changes in the furanose ring. This feature is emphasized by the relatively large thermal amplitude of C(6) normal to the ring, indicating that the conformation has no well-defined energy minimum. Also O(5) and C(7) are influenced by this and have large thermal amplitudes ($u$ r.m.s.$_{\max}$ =0·31 and 0·34 Å).

### *Interatomic distances and angles*

The carbon–carbon distances in the phenyl ring have been examined with respect to high-angle scattering

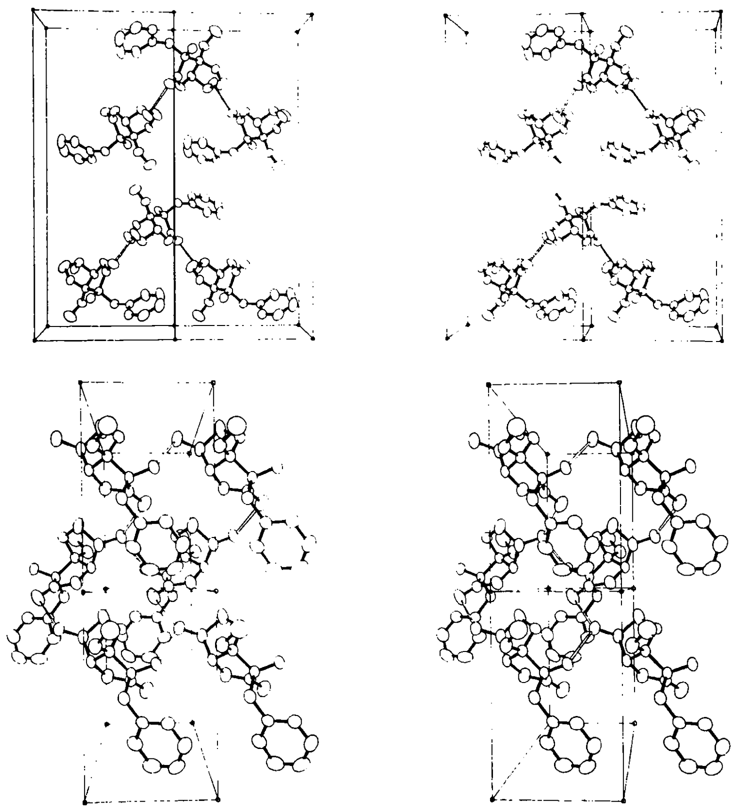

Fig. 1. Simplified stereo views of the title compound as seen along the negative $a$ (upper part) and $c$ axes and with $b$ horizontal in each case. The hydrogen bonds are indicated by open lines.

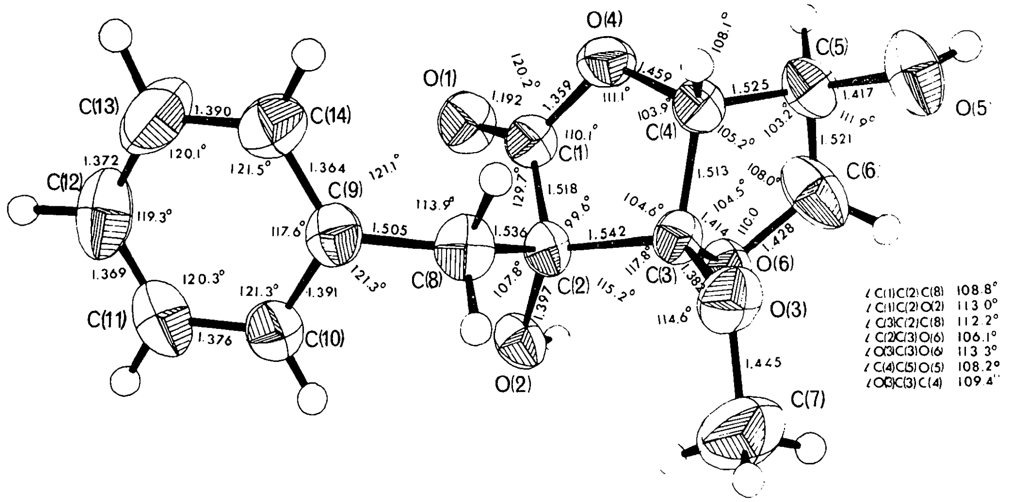

Fig. 2. *ORTEP* plot of the methyl glycoside of the 2-*C*-benzyl-3-keto-L-*lyxo*-hexulosonic acid lactone molecule with thermal ellipsoids scaled to 50% probability. The drawing conforms to the absolute configuration of the molecule. Distances (Å) and angles (°) for the heavy atoms are included in the drawing, and average standard deviations are 0·004 Å and 0·3°.

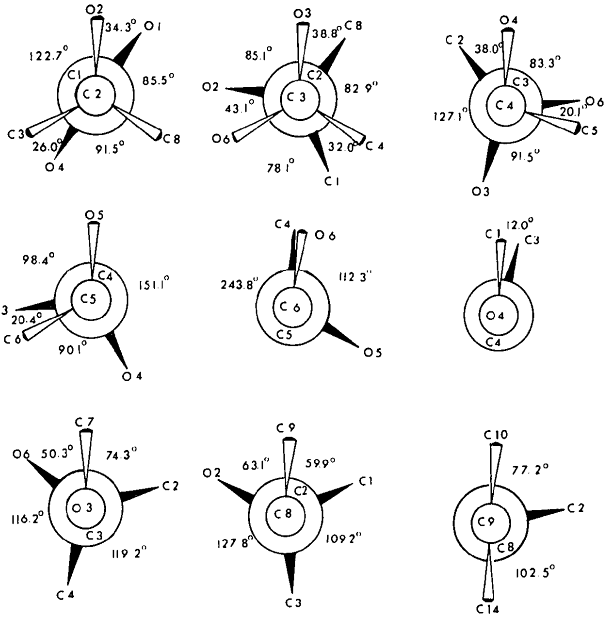

Fig. 3. Newman projections showing conformational angles (°) in the methyl glycoside of 2-*C*-benzyl-3-keto-L-*lyxo*-hexulosonic acid lactone.

Table 4. *Distances* (Å) *from planes through parts of the title compound*

Atoms used to define the planes are indicated by an asterisk. C(8) is included to show the direction of the deviation.

| Benzyl group | | Lactone group | |
|---|---|---|---|
| C(8)* | 0·001 | C(1)* | 0·016 |
| C(9)* | −0·001 | C(2)* | −0·005 |
| C(10)* | 0·004 | O(1)* | −0·005 |
| C(11)* | −0·004 | O(4)* | −0·003 |
| C(12)* | 0·000 | C(3) | 0·632 |
| C(13)* | 0·004 | C(4) | 0·188 |
| C(14)* | −0·004 | C(8) | −1·463 |
| Lactone ring | | Furanose ring | |
| C(1)* | 0·054 | C(4)* | −0·014 |
| C(2)* | −0·030 | C(5)* | 0·022 |
| C(4)* | 0·031 | C(6)* | −0·023 |
| O(4)* | −0·042 | O(6)* | 0·012 |
| C(3) | 0·489 | C(3) | 0·434 |
| C(8) | −1·498 | | |

Table 5. *Conformational angles* (°)

The furanose moiety of the title compound is compared with glucuronolactone (GL) and dehydroascorbic acid dimer (DHA).

| | GL | DHA | Present work |
|---|---|---|---|
| C(3)–C(4)–C(5)–C(6) | 26·2 | −12·4 | +20·4 |
| C(4)–C(5)–C(6)–O(6) | −35·8 | 32·1 | −3·9 |
| C(5)–C(6)–O(6)–C(3) | 32·1 | −42·2 | +15·8 |
| C(6)–O(6)–C(3)–C(4) | −14·7 | 33·8 | +28·7 |
| O(6)–C(3)–C(4)–C(5) | −8·7 | −12·1 | −20·1 |

Conformational angle $A(1)$–$A(2)$–$A(3)$–$A(4)$ is viewed down the $A(2)$–$A(3)$ bond with a clockwise angle of $A(1)$ to $A(2)$ taken to be positive.

and to rigid-body vibrations in addition to the normal analysis. We observed an increase in the average bond length from 1·378 to 1·390 Å when the reflexions with $\sin \theta/\lambda < 0{\cdot}4$ were excluded from the least-squares refinements. This trend may be interpreted as due to the removal of the contribution from the $\pi$ electrons in the valence shell. The additional corrections provided by the rigid-body analysis (Schomaker & Trueblood, 1968) were +0·008 Å in both cases, so that the fully corrected value for the aromatic C–C bond amounts to 1·398 Å with no individual bond significantly different from this.

For the sugar moiety no satisfactory rigid-body model could be established. The removal of low-angle reflexions generally increased the C–C bond lengths, whereas the C–O bonds were either unchanged or shortened. It is not unlikely that this effect is caused by the lone-pair electrons at the oxygen atoms which tend to lengthen the C–O bond relative to the nuclear position.

The interatomic distances and angles in Fig. 2 are those found when all reflexions were included in the refinements. Most of them compare well with the values observed in related substances, *e.g.* glucuronolactone and dimeric dehydroascorbic acid. Particular interest is associated with the C(2)–C(3) bond because of its significant role in the function of the vitamin. The bond is long (1·542 Å), as should be expected from the significant deviation from staggered conformation of the substituents (Fig. 3). Moreover, the adjacent C–O bonds are short (1·382, 1·397 and 1·414 Å). No significant deviation in the C–H average of 0·96 Å was observed, but O–H bonds are apparently significantly shorter (0·81 and 0·74 Å) for the weak hydrogen bonds present in this crystal.

We are indebted to P. Groth, B. Klewe and C. Rømming for their kind assistance and valuable discussions.

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