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The 2-methoxyphenylhydrazone derivative of dehydroascorbic acid

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.013 Å
R factor = 0.073
wR factor = 0.221
Data-to-parameter ratio = 8.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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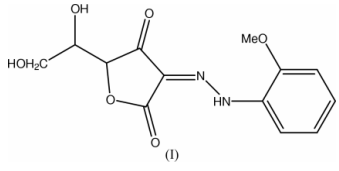
The title compound, (3*Z*)-5-(1,2-dihydroxyethyl)furan-2,3,4-(3*H*,5*H*)-trione 3-[(2-methoxyphenyl)hydrazone], $C_{13}H_{14}N_2O_6$, is produced when dehydro-L-ascorbic acid reacts with 2-methoxyphenylhydrazine. A two-dimensional structure is generated by extensive hydrogen-bonding interactions.

Comment

Vegetables and fruit may turn red–brown when they are kept under aerobic conditions for a long time. A mechanism proposed to account for this indicated that reactions of dehydroascorbic acid with amino acids play an important role in the process of oxidation of L-ascorbic acid to 2,2′-nitrilo-di-2(2′)-deoxy-L-ascorbic acid monoammonium salt, which is red–brown (Kurata *et al.*, 1973*a*,*b*).

In the course of structural studies of the red–brown pigment, hydrazones were prepared by reaction of dehydroascorbic acid with hydrazines. The crystal structure of one of the eight hydrazones synthesized, 2-methoxyphenylhydrazone dehydroascorbic acid, (I), has been determined by single-crystal X-ray diffraction methods (Fig. 1 and Table 1).



(I)

The molecular structure of (I) comprises an ethylene glycol open chain, linked to the hydrazone group *via* a lactone ring. The 15 non-H atoms of the phenylhydrazone and lactone ring are effectively coplanar, the maximum deviation from the least-squares plane through these atoms being 0.066 (9) Å for C8. The bond lengths and angles in (I) are quite similar to those reported for the closely related structure of *p*-bromophenylhydrazone derivative of dehydroascorbic acid (Hvoslef & Nordenson, 1976).

The hydrogen-bonding distances and angles are listed in Table 2. An intramolecular N2—H···O2 hydrogen bond is observed. Both the OH groups of the ethylene glycol residue participate in hydrogen bonds. The terminal OH group (O5) is connected to the carbonyl atom O3. These interactions link the molecules into ribbons that are aligned along the *a* axis, as shown in Fig. 2. The ribbons are stacked along [011], and are connected by hydrogen bonds formed between two OH groups (O3—H···O5). The stacking distance between ribbons is approximately 3.4 Å. The intermolecular hydrogen bonds described above combine to generate a two-dimensional layer structure.

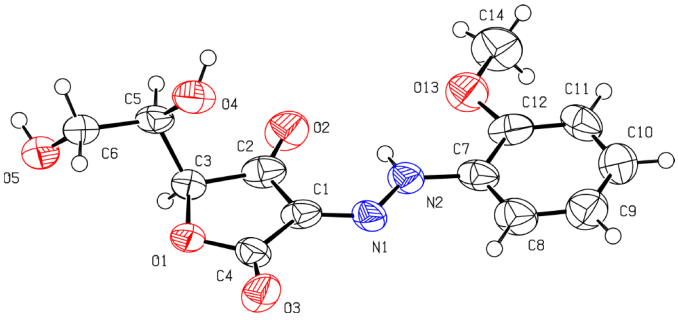


Figure 1
Displacement ellipsoid drawing (50% probability level), showing the atom-labelling scheme.

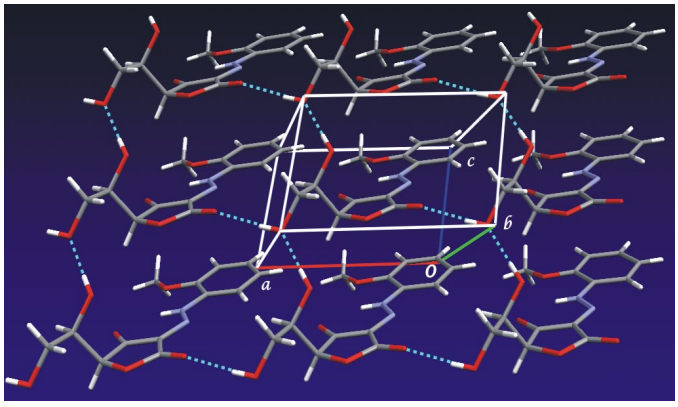


Figure 2
A perspective packing diagram. Dotted lines indicate the intermolecular hydrogen-bonding interactions.

Experimental

The title compound was prepared according to a literature procedure (Hvoslef & Nordenson, 1976). Plate-like yellow crystals were obtained by recrystallization from an ethanol solution of the compound.

Crystal data

$C_{13}H_{14}N_2O_6$
M_r = 294.26
Triclinic, $P\overline{1}$
a = 8.194 (2) Å
b = 8.308 (2) Å
c = 5.463 (3) Å
α = 106.12 (3)°
β = 101.98 (3)°
γ = 95.69 (2)°
V = 344.6 (2) Å^3
Z = 1
D_x = 1.418 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 28.0–30.0°
μ = 0.11 mm^{-1}
T = 295 (2) K
Plate, clear pale yellow
0.30 × 0.15 × 0.05 mm

Data collection

Rigaku AFC-7*S* diffractometer
θ-2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.960, T_{max} = 0.998
1680 measured reflections
1575 independent reflections
961 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 27.5°
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -7 \rightarrow 6$
3 standard reflections
every 150 reflections
intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.073
$wR(F^2)$ = 0.221
S = 1.05
1575 reflections
193 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0983P)^2 + 0.4777P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.334 (11)	O1—C4	1.363 (10)
C1—C2	1.431 (12)	O1—C3	1.458 (10)
C1—C4	1.443 (10)	N1—N2	1.298 (8)
C2—O2	1.232 (9)	N2—C7	1.404 (11)
C2—C3	1.501 (12)		
N1—C1—C2	128.3 (7)	O1—C3—C5	109.7 (6)
N1—C1—C4	122.4 (7)	C2—C3—C5	110.3 (6)
C2—C1—C4	109.0 (8)	O3—C4—O1	119.1 (7)
O2—C2—C1	128.2 (9)	O3—C4—C1	132.2 (8)
O2—C2—C3	125.4 (8)	O1—C4—C1	108.6 (7)
C1—C2—C3	106.4 (7)	N2—N1—C1	115.3 (7)
C4—O1—C3	110.9 (6)	N1—N2—C7	122.8 (7)
O1—C3—C2	104.9 (6)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2	0.86	2.04	2.743 (10)	139
O4—H4···O5^{i}	0.82	1.86	2.680 (8)	178
O5—H5*A*···O3^{ii}	0.82	1.91	2.721 (8)	172

Symmetry codes: (i) $x, y, 1+z$; (ii) $1+x, y, z$.

All H atoms were included in the riding-model approximation, with U_{iso}(methyl and hydroxy H) = 1.5U_{eq}(parent atom) and U_{iso}(other H) = 1.2U_{eq}(parent atom). H atoms on C, O and N atoms were fixed at 0.98, 0.97, 0.96, 0.93, 0.82, and 0.86 Å for methine, methylene, methyl, phenyl, hydroxy and NH H atoms, respectively. Friedel pairs were merged and the $\Delta f''$ term was set to zero. The calculated absolute structure parameter (Flack, 1983) of 0 (10) is thus meaningless in this analysis, and the absolute configuration was assumed from that of the starting material.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *MERCURY* (CCDC, 2003); software used to prepare material for publication: *SHELXL*97.

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