Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.113$
$S = 1.056$
1955 reflections
221 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2 + 0.1143P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.171$ e Å^{-3}
$\Delta\rho_{min} = -0.166$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O3—C3	1.199 (4)	C5—C51	1.485 (4)
O4—C3	1.349 (4)	C13—C17	1.516 (4)
O4—C5	1.454 (3)	C16—C17	1.513 (5)
O17—C17	1.209 (4)	C51—O51*A*	1.190 (2)
C2—C3	1.501 (5)	C51—O51*B*	1.198 (2)
O3—C3—O4	118.1 (3)	O17—C17—C16	125.2 (3)
O3—C3—C2	122.8 (3)	O17—C17—C13	126.4 (3)
O4—C3—C2	119.0 (3)	C16—C17—C13	108.5 (3)

It should be noted that because none of the atoms are strong enough anomalous scatterers at the Mo $K\alpha$ wavelength, the absolute configuration was not determined by the X-ray data, and the assumed chirality of the molecule is that determined from the synthesis route. The H atoms of the organic moiety were placed at calculated positions and refined as riding using *SHELXL*97 (Sheldrick, 1997) defaults. During the refinement, the C=O bond length refined to an unusually short 1.14 Å, while the electron density at the carbaldehyde H-atom position was found to be higher than expected. Considering the possibility of disorder, the carbaldehyde group was split into two groups with the O- and H-atom positions interchanged. The occupancy of the two alternate fragments were constrained to unity and the C=O and C—H bond lengths restrained to 1.20 and 0.98 Å, respectively. The refinement gave a more satisfactory fit than the original refinement. The refined occupancy of the two groups was 0.842 (7)/0.158 (7). Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice. All calculations were performed on a Pentium 150 MHz PC running LINUX.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

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2-(*N*,*N*-Dimethylamino)-6-hydroxy-1,4-naphthoquinone

ANTÔNIO C. DORIGUETTO, CÁTIA A. SANTOS, DÉLIO S. RASLAN AND NELSON G. FERNANDES

Department of Chemistry, Federal University of Minas Gerais, CP 702, 31270-901 Belo Horizonte, Minas Gerais, Brazil. E-mail: doriguet@dedalus.lcc.ufmg.br

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Abstract

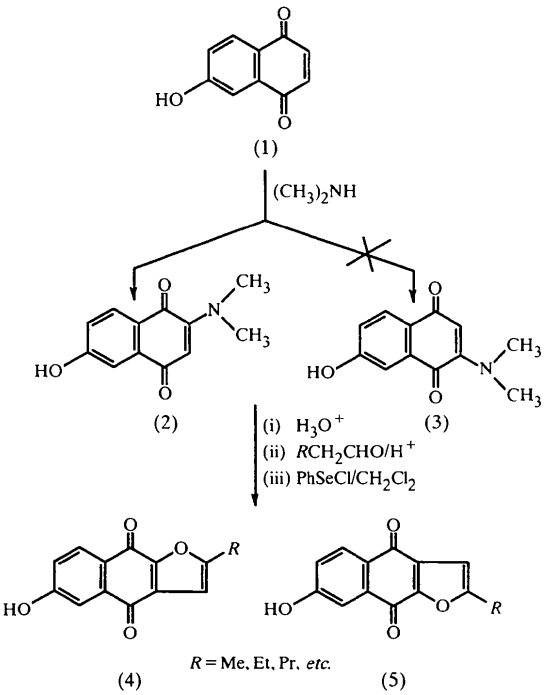
The title compound, $C_{12}H_{11}NO_3$, is an intermediate in the synthesis of furonaphthoquinones. There are two molecules in the asymmetric unit. In one of them all the

non-H atoms form a plane. There are two intermolecular hydrogen bonds.

Comment

Some natural and synthetic furonaphthoquinones have shown themselves to be active against *Trypanosoma cruzy* and *Plasmodium falciparum* (Carvalho *et al.*, 1988; Chiari *et al.*, 1991). These protozoa are known as causative agents of Chagas' disease and malaria.

This work reports the structure of an aminoquinone, (2), an intermediate used to obtain a novel furonaphthoquinone. Compound (1) is the starting material for



the aminoquinones (2) and (3) (Grinev *et al.*, 1960) which are precursors of the furonaphthoquinones (4) and (5), respectively (MacLeod & Thomson, 1960; Hooker, 1936; Oliveira *et al.*, 1990). However, from spectroscopic data analysis, including ^1H and ^{13}C NMR, UV, IR and MS, it is not possible to identify which compound, (2) or (3), is obtained. On the other hand, using theoretical considerations on regioselectivity, Rozeboom *et al.* (1981) have demonstrated that the reaction yields a single aminoquinone, (2). Therefore, a crystal structure analysis was required to answer this question. The X-ray data ratify Rozeboom *et al.*'s ideas on the formation of compound (2). The structure is shown in Fig. 1.

Both molecules show equivalent C—C distances in the benzenoid ring [mean distance 1.39 (1) Å]. However, the C—C bonds in the quinonoid ring have different lengths due to resonance involving an N electron pair and an adjacent carbonyl group as can be seen in Fig. 1 and Table 1. In spite of different bond lengths, the bond angles in all rings for both molecules are constant [mean angle 120 (1)°]. Table 2 shows two moderate intermolecular hydrogen bonds.

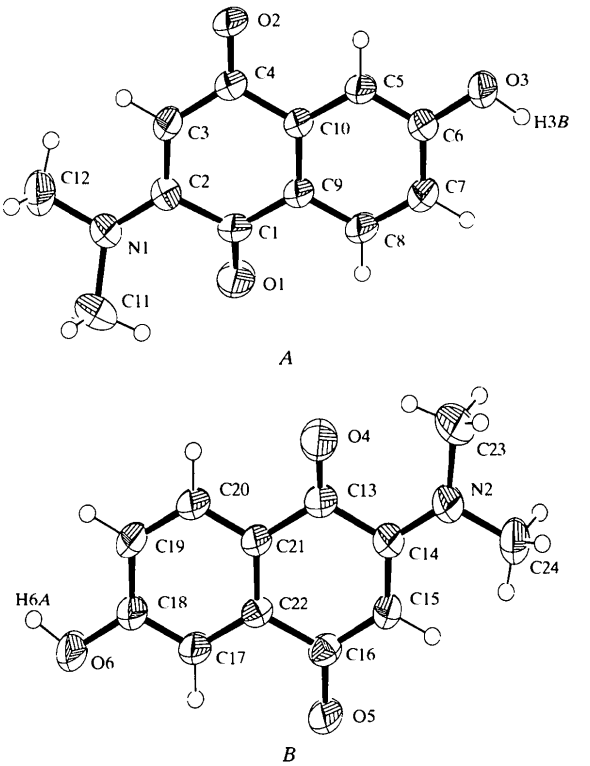


Fig. 1. Views of the independent molecules (*A* and *B*) with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

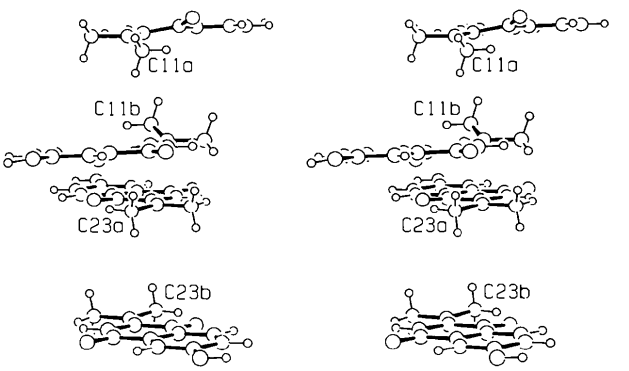


Fig. 2. Stereoscopic crystal-packing illustration of the title compound. The molecules stack parallel to the (101) plane. The label modifiers denote symmetry equivalent positions: C11*a*(x, y, z); C11*b*$(-x-1, 1-y, 1-z)$; C23*a*$(-x-1, \frac{1}{2}+y, \frac{1}{2}-z)$; C23*b*$(x-1, \frac{1}{2}-y, -\frac{1}{2}+z)$.

Experimental

The method of preparation of aminoquinones has been described by Grinev *et al.* (1960).

Crystal data

$C_{12}H_{11}NO_3$
M_r = 217.22
Monoclinic
$P2_1/c$
a = 13.657 (1) Å
b = 14.464 (1) Å
c = 11.014 (1) Å
β = 112.104 (3)°
V = 2015.8 (3) Å^3
Z = 8
D_x = 1.431 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 12.15–12.45°
μ = 0.104 mm^{-1}
T = 293 (2) K
Prismatic
0.40 × 0.35 × 0.30 mm
Dark red

Data collection

Siemens $P4$ diffractometer
θ–2θ scans
Absorption correction: none
4496 measured reflections
3548 independent reflections
2234 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

θ_{max} = 25°
$h = -16 \rightarrow 15$
$k = -17 \rightarrow 1$
$l = -1 \rightarrow 13$
3 standard reflections
every 397 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R(F)$ = 0.054
$wR(F^2)$ = 0.096
S = 1.02
3112 reflections
305 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 3.40P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0066 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.222 (4)	O4—C13	1.205 (4)
O2—C4	1.245 (4)	O5—C16	1.254 (4)
O3—C6	1.357 (4)	O6—C18	1.358 (4)
N1—C2	1.349 (4)	N2—C14	1.348 (4)
C1—C2	1.514 (4)	C13—C14	1.504 (4)
C1—C9	1.465 (4)	C13—C21	1.469 (4)
C2—C3	1.371 (4)	C14—C15	1.378 (4)
C3—C4	1.427 (4)	C15—C16	1.416 (4)
C4—C10	1.490 (4)	C16—C22	1.491 (4)
C9—C10	1.397 (4)	C21—C22	1.388 (4)
C11—N1—C12	114.2 (3)	C23—N2—C24	114.5 (3)
C2—N1—C11	124.0 (3)	C14—N2—C23	126.6 (3)
N1—C2—C1	117.8 (3)	N2—C14—C15	123.3 (3)
O2—C4—C3	121.7 (3)	O5—C16—C22	118.9 (3)
O3—C6—C5	117.9 (3)	O6—C18—C19	121.9 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3B···O2^{i}	0.95 (4)	1.76 (4)	2.706 (3)	179 (4)
O6—H6A···O5^{ii}	0.94 (4)	1.75 (4)	2.693 (4)	175 (3)

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $-1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

There are two independent molecules in the asymmetric unit. The approximate symmetry relationships are (x, y, z) and ($\frac{1}{2} - x$, 0.565 − y, 1 − z). This pseudosymmetry was examined carefully using the *PLATON* symmetry-checking program (Spek, 1990). It was concluded that $P2_1/c$ is an acceptable space group. The absence of additional symmetry may be explained by all the atoms in B, except H atoms from methyl groups, forming a plane. On the other hand, for A, the atoms O1 and C11 are displaced by 0.398 (4) and −0.824 (5) Å, respectively, from the best plane for the aromatic rings. The packing distortion may arise from steric effects between C11 and C23 as can be seen in Fig. 2. This means the actual distances C11a···C11b, C11b···C23a and C23a···C23b are 3.658 (5), 3.883 (5) and 4.405 (5) Å, respectively (Fig. 2). If all atoms in molecule A formed a plane, the distance C11b···C23a would become very short, 3.059 (5) Å. The methyl group has a van der Waals radius approximately equal to 2.0 Å (Pauling, 1960).

Positional and anisotropic displacement parameters were refined for all non-H atoms. The coordinates for H atoms were calculated and the X—H distances were restrained. Three different isotropic displacements were refined for H atoms: (i) aromatic rings, (ii) methyl groups and (iii) hydroxyl groups. *SHELXL*93 (Sheldrick, 1993) was used to refine the structure and generate the H atoms in idealized positions.

Difference Fourier electron-density maps for the refined structure without the H3B and H6A signs were performed using the *FORDUP* program (Lundgren, 1982). However, no alternative sites for H atoms were found.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *SHELXTL/PC*. Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1411). Services for accessing these data are described at the back of the journal.

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A fused furanoside-1,4-lactone at 173 K

ANTHONY LINDEN,[a] C. KUAN LEE[b] AND XIAOFENG LI[b]

[a]*Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland, and* [b]*Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 119260. E-mail: alinden@oci.unizh.ch*

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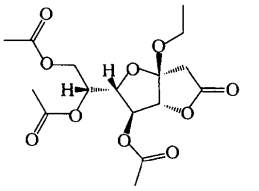
Abstract

The asymmetric unit of the title compound, (ethyl 5,7,8-tri-*O*-acetyl-2-deoxy-α-D-*erythro*-L-*arabino*-3-octulofuranosid)ono-1,4-lactone, $C_{16}H_{22}O_{10}$, contains two symmetry-independent molecules which have very similar molecular dimensions and no significant conformational differences, except for slight twists in some of the substituents. The furanoid sugar ring in both molecules has the envelope conformation, in which the anomeric C atom is out of the plane of the ring. The lactone ring is not planar and also adopts the envelope conformation, but the lactone group itself shows only a very small deviation from planarity.

Comment

Recent growth in the study of the chemistry of *C*-glycosides has been tremendous. These compounds have been widely used as chiral templates for complex synthetic target molecules and many have shown interesting and useful biological activities. One group of *C*-glycoside derivatives that has not been studied widely for synthetic behaviour (Bandzouzi & Chapleur, 1987*a*,*b*; Csuk & Glänzer, 1990, 1991) and enzyme inhibitory activity (Brockhaus & Lehmann, 1977, 1978; Lehmann & Schwesinger, 1982*a*,*b*) consists of those compounds that contain an exocyclic double bond at the anomeric centre. Such compounds are potential inhibitors, in that they interact with the enzyme to form intermediates which are covalently bound to the enzyme. In this paper, we describe the crystal structure of a fused furanoside-1,4-lactone derivative, (I), which was obtained in the course of our search for convenient and efficient approaches to the synthesis of exoalkylenic sugar compounds.



(I)

The structure of compound (I) is composed of two symmetry-independent molecules, one of which (molecule *A*) is shown in Fig. 1. Molecule *B* has essentially the same appearance, and its atom-numbering scheme can be derived from that for molecule *A* by adding 20. Fig. 1 depicts the correct absolute configuration of molecule *A*, which was assigned to agree with the known chirality of D-galactose, from which compound (I) was synthesized. The two molecules, *A* and *B*, have very similar molecular dimensions and no significant conformational differences, except for slight twists in some of the substituents. The bond lengths and angles (Table 1) agree well with those reported for other compounds with a lactone ring (Jeffrey *et al.*, 1967; Kim *et al.*, 1967; Usher & English, 1978; Conde *et al.*, 1980). However, the difference between the lactone ring C—O distances is rather small [0.080 (5) and 0.076 (5) Å in molecules *A* and *B*, respectively] compared with that

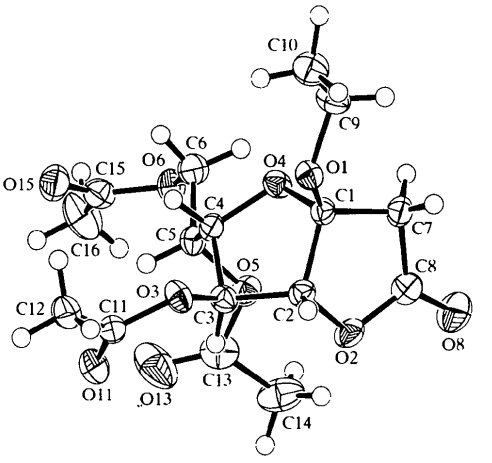


Fig. 1. A view of molecule *A* of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. Molecule *B* has essentially the same appearance.