Refinement

Refinement on F^2
$R(F) = 0.0438$
$wR(F^2) = 0.1228$
$S = 1.040$
2802 reflections
308 parameters
H-atom coordinates refined, $U_{\rm eq}$(H) constrained to a single free variable and refined
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.3764P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.131$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.141$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N1—C18	1.403 (2)	C15—C20	1.395 (3)
N1—C21	1.423 (3)	C16—C17	1.371 (3)
N1—C27	1.430 (3)	C17—C18	1.391 (3)
C1—C2	1.352 (4)	C18—C19	1.385 (3)
C1—C11	1.422 (3)	C19—C20	1.375 (3)
C2—C3	1.404 (4)	C21—C22	1.380 (3)
C3—C4	1.354 (4)	C21—C26	1.383 (3)
C3—C2	1.404 (4)	C22—C23	1.384 (3)
C4—C12	1.418 (3)	C23—C24	1.354 (4)
C9—C11	1.410 (3)	C24—C25	1.370 (4)
C9—C12	1.413 (3)	C25—C26	1.379 (3)
C9—C13	1.433 (3)	C27—C28	1.375 (3)
C11—C12	1.426 (3)	C27—C32	1.377 (3)
C12—C11	1.426 (3)	C28—C29	1.390 (4)
C13—C14	1.192 (3)	C29—C30	1.374 (4)
C14—C15	1.435 (3)	C30—C31	1.352 (4)
C15—C16	1.386 (3)	C31—C32	1.365 (4)
C18—N1—C21	121.6 (2)	C19—C18—N1	120.9 (2)
C18—N1—C27	119.0 (2)	C17—C18—N1	121.2 (2)
C21—N1—C27	119.3 (2)		

The red transparent prismatic data crystal was mounted using epoxy resin on a thin glass fiber with the $(\bar{1}0\bar{1})$ scattering planes roughly normal to the spindle axis. The data crystal was bound by the $(1\bar{1}\bar{2})$, $(\bar{1}12)$, $(11\bar{2})$, $(\bar{1}\bar{1}2)$, $(\bar{1}01)$ and $(10\bar{1})$ faces.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software* and *PROFILE* (Blessing, Coppens & Becker, 1972). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

The authors thank the School of Chemical Sciences Materials Characterization Laboratory at the University of Illinois for X-ray data collection, and the Office of Naval Research (grant N00014-94-I-0639) and the National Science Foundation (grant CHE-94-23121) for financial assistance. Additional support from 3M Company and the Camille Dreyfus Teacher–Scholar Awards Program is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: BK1186). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Novel Tricyclic Cyclobutanone Ketal

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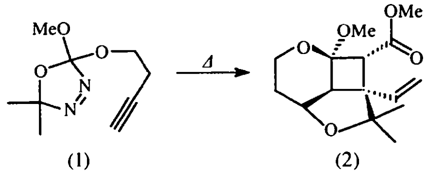
Abstract

Methyl (±)-(1α,1aα,3aα,6aα,6bα)-1a-ethenyl-1,1a,2,3a,-4,5,6a,6b-octahydro-6a-methoxy-2,2-dimethyl-3,6-dioxa-cyclobut[*cd*]indene-1-carboxylate, $C_{15}H_{22}O_5$, adopts a hemispherical conformation with the methoxy, methoxy-carbonyl and vinyl groups pointing outwards from the hemisphere. The tetrahydropyran ring is in a chair conformation and the tetrahydrofuran ring is in an envelope conformation.

Comment

The title compound, (2), is formed in high yield by a complex cascade of reactions resulting from thermolysis of oxadiazoline, (1), in benzene (Kassam & Warkentin, 1994). Its complexity, including a tricyclic framework and five asymmetric centres, left several structural possibilities on the basis of spectroscopic evidence alone and so an X-ray structure determination was necessary.



(1) (2)

The molecule consists of a four-membered carbon ring, a tetrahydrofuran ring and a tetrahydropyran ring, all with a common CH group (C6b). The cavity formed is enclosed by the O3 atom, the C5 methylene group and the H atom on C1. The exocyclic groups all extend away from the centre of the fused-ring system (Fig. 1). The shape of the molecule and the fact that it has no significant hydrogen-bond donors, contributed to the difficulty in crystal growth.

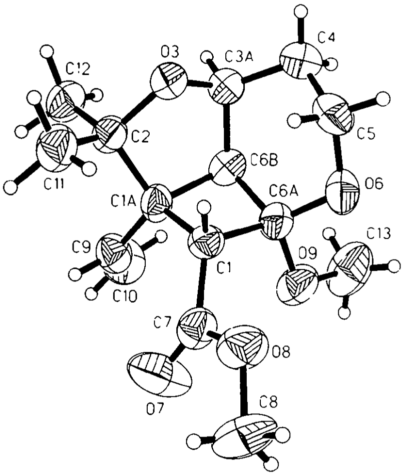
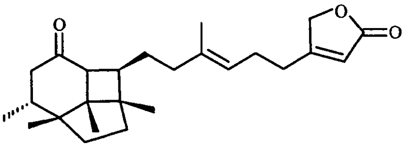


Fig. 1. A view of compound (2) showing the labelling and 50% probability displacement ellipsoids for the non-H atoms.

Although many polycyclic organic compounds have hemispherical shapes, no examples of analogues of (2) having ring O atoms arbitrarily placed, with or without substituents, were found in the literature. A similar all-carbon analogue, characterized by NMR, is the recently reported novel sesterterpene lintenone, (3), from Caribbean sponge (Fattorusso, Lanzotti, Magno, Mayol & Pansini, 1992).



(3)

Experimental

The preparation and spectroscopic characterization of compound (2) have been detailed by Kassam & Warkentin (1994).

Crystal data

$C_{15}H_{22}O_5$
$M_r = 282.33$
Monoclinic
$P2_1/c$
$a = 14.438\,(5)$ Å
$b = 8.697\,(5)$ Å
$c = 11.964\,(7)$ Å
$\beta = 98.44\,(4)°$
$V = 1486.0\,(13)$ Å^3
$Z = 4$
$D_x = 1.262$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 20 reflections
$\theta = 9.90–17.75°$
$\mu = 0.776$ mm^{-1}
$T = 296\,(2)$ K
Fragment from a multiple crystal
0.26 × 0.11 × 0.06 mm
Colourless

Data collection

AFC-6*R* diffractometer
2θ-ω scans
Absorption correction: none
2578 measured reflections
1865 independent reflections
857 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0521$

$\theta_{\rm max} = 54.99°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -0 \rightarrow 13$
3 standard reflections every 150 reflections intensity decay: −0.54%

Refinement

Refinement on F^2
$R(F) = 0.0456$
$wR(F^2) = 0.1077$
$S = 1.189$
1806 reflections
268 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.4258P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.015$
$\Delta\rho_{\rm max} = 0.174$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.214$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.0016 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O3—C3a	1.442 (6)	C1a—C2	1.552 (6)
O3—C2	1.450 (5)	C1a—C1	1.568 (6)
O6—C6a	1.412 (5)	C1—C7	1.511 (7)
O6—C5	1.447 (6)	C1—C6a	1.546 (6)
O7—C7	1.180 (6)	C2—C11	1.512 (8)
O8—C7	1.332 (6)	C2—C12	1.527 (7)
O8—C8	1.469 (8)	C3a—C4	1.501 (8)
O9—C6a	1.389 (5)	C3a—C6b	1.526 (7)
O9—C13	1.459 (8)	C4—C5	1.505 (9)
C1a—C9	1.504 (7)	C6a—C6b	1.540 (7)
C1a—C6b	1.552 (7)	C9—C10	1.290 (7)
C3a—O3—C2	107.7 (4)	O3—C3a—C4	109.1 (5)
C6a—O6—C5	114.5 (4)	O3—C3a—C6b	105.3 (4)
C7—O8—C8	117.0 (5)	C4—C3a—C6b	112.4 (5)
C6a—O9—C13	114.2 (6)	C3a—C4—C5	111.5 (5)
C9—C1a—C6b	119.5 (4)	O6—C5—C4	111.9 (6)
C9—C1a—C2	113.1 (4)	O9—C6a—O6	106.9 (4)
C6b—C1a—C2	103.9 (4)	O9—C6a—C6b	115.0 (4)
C9—C1a—C1	117.3 (4)	O6—C6a—C6b	118.3 (4)
C6b—C1a—C1	88.2 (3)	O9—C6a—C1	108.8 (4)
C2—C1A—C1	112.0 (4)	O6—C6a—C1	117.8 (4)
C7—C1—C6a	116.6 (4)	C6b—C6a—C1	89.4 (4)
C7—C1—C1a	122.4 (4)	C3a—C6b—C6a	114.9 (4)
C6a—C1—C1a	88.9 (3)	C3a—C6b—C1a	104.9 (4)
O3—C2—C11	106.5 (5)	C6a—C6b—C1a	89.7 (4)
O3—C2—C12	110.1 (5)	O7—C7—O8	122.7 (5)
C11—C2—C12	110.6 (5)	O7—C7—C1	128.3 (5)
O3—C2—C1a	101.8 (3)	O8—C7—C1	109.0 (5)
C11—C2—C1a	115.5 (5)	C10—C9—C1a	127.6 (6)
C12—C2—C1a	111.8 (5)		

Examination of the recrystallized solid under cross-polarized light indicated that the crystals were not single, so a small clear fragment was removed for X-ray analysis. The sample did not diffract very well, but the data obtained were suitable for routine structure solution and refinement and for verification of the stereochemistry.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *XL* in *SHELXTL/PC* (Sheldrick, 1995). Molecular graphics: *XP* in *SHELXTL/PC*.

Software used to prepare material for publication: *XL* in *SHELXTL/PC*.

The authors gratefully acknowledge financial support from NSERC and for the name of compound (2) we acknowledge the Manager and staff of the Authority Database Operations Department at Chemical Abstracts Service.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: CR1168). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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3-Acetamido-5-*O*-acetyl-1,2-*O*-isopropylidene-D-ribofuranose

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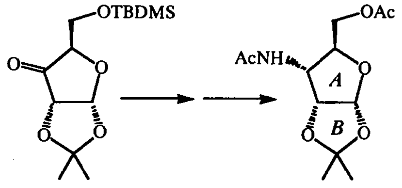
Abstract

The crystal structure of the title compound, $C_{12}H_{19}NO_6$, was determined in order to ascertain its relative configuration. It was synthesized by the stereospecific reduction of the novel oxime derived from 5-*O*-acetyl-1,2-isopropylidene-3-oxo-α-D-ribofuranose and comprises two *cis*-fused heterocyclic five-membered rings, furanose and dioxolane, which adopt envelope conformations.

Comment

In the course of synthetic studies towards *trans,trans-N*-(1-carboxyethyl)-3,5-dihydroxy-4-acetamidopiperidine, a key step was the stereospecific incorporation of the *N*-acetyl moiety. We devised a synthetic route to the diacetate (2) (see scheme below).



(1) (2)

While ^{1}H NMR and mass spectroscopic data indicated (2) to be a single diastereomer, assignment of the absolute stereochemistry by ^{1}H NMR methods was not possible. This was due to the uncertainty of relating scalar coupling constants to torsion angles in the furanosyl rings. Furthermore, because of the similar chemical shifts of the relevant proton signals, irradiation of a single signal alone, required for NOE difference experiments, was not possible. The crystal structure was, therefore, determined in order to ascertain the stereochemistry of the title compound, (2).

The displacement ellipsoid drawing of (2) with the atom-labeling scheme is given in Fig. 1. The absolute configuration of (2) was assigned from knowledge of the stereochemistry of its synthetic precursor. Molecules of (2) comprise two heterocyclic five-membered rings [*A* (furanose) and *B* (dioxolane)] *cis*-fused along the C1—C2 bond. Both rings adopt envelope conformations

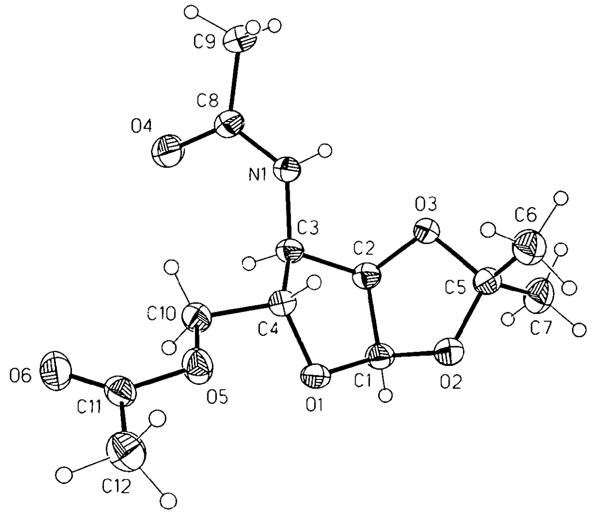


Fig. 1. The molecular structure of (2), with 50% probability ellipsoids, showing the atom-numbering scheme. The carbonyl O atom is disordered over two positions, O4 and O4′, with occupancies of 0.63 (5) and 0.37 (5), respectively. H atoms are shown as small circles of arbitrary radii.