Crystal data

$C_{15}H_{10}O_2$
M_r = 222.24
Monoclinic
$P2_1/n$
a = 20.527 (2) Å
b = 6.144 (2) Å
c = 8.604 (2) Å
β = 90.08 (2)°
V = 1085.0 (4) Å^3
Z = 4
D_x = 1.360 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 13.4–15.0°
μ = 0.084 mm^{-1}
T = 296 K
Clear column
0.35 × 0.19 × 0.19 mm
Yellow

Data collection

AFC-5*S* diffractometer
ω scans
Absorption correction: none
2788 measured reflections
2717 independent reflections
1377 reflections with $I > \sigma(I)$
R_{int} = 0.028
θ_{max} = 27.5°
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 7$
$l = -11 \rightarrow 11$
6 standard reflections
every 150 reflections
intensity variation: ±1.8%
(average maximum relative intensity)

Refinement

Refinement on F
R = 0.054
wR = 0.053
S = 1.56
1377 reflections
195 parameters
All H atoms refined
$w = \sigma_F^{-2}$
$(\Delta/\sigma)_{max}$ = < 0.01
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: 2.7 (3) × 10^{-6}
Scattering factors from Stewart, Davidson & Simpson (1965) for H, Cromer & Waber (1974) for C and O atoms

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

O1—C15	1.315 (3)	C1—C15	1.485 (4)
O2—C15	1.219 (3)		
C2—C1—C15	118.0 (2)	O1—C15—C1	114.4 (3)
C13—C1—C15	122.1 (2)	O2—C15—C1	124.5 (2)
O1—C15—O2	121.1 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O2^i	0.95 (4)	1.69 (4)	2.633 (3)	172 (3)

Symmetry code: (i) $1-x, -1-y, 1-z$.

Scan widths were (1.40 + 0.35tanθ)° in ω with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group $P2_1/n$ (No. 14) and since refinement proceeded well it was adopted. Moreover, axial photos were consistent with monoclinic but not with orthorhombic symmetry. Fourier difference methods were used to locate the initial H-atom positions. The maximum effect of extinction was 9.7% of F_o for $21\bar{2}$. The maximum positive residual peak was located near the midpoint of the C1—C13 bond, while the maximum negative peak was located near the center of the C5–C8, C11, C12 ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1321). Services for accessing these data are described at the back of the journal.

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An Estrone–Glucuronide Conjugate

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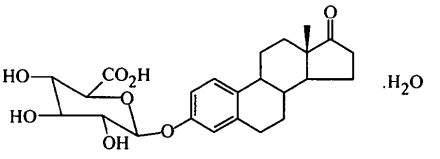
Abstract

The crystal structure of 2-*O*-[17-oxoestra-1,3,5(10)-trien-3-yl]-β-D-glucopyranosiduronic acid hydrate, $C_{24}H_{30}O_8$.-

H_2O, is reported. The angle between the mean plane of the *A* ring of the steroid and the mean plane of the glucuronide is 14.1 (5)°.

Comment

The X-ray structure determination of the title compound, (I), was performed as part of a program to characterize structurally the lysozyme–estrone glucuronide conjugates used in the Ovarian Monitor homogeneous enzyme immunoassay for the delineation of the fertile period (Brown, Blackwell, Holmes & Smyth, 1989). It is necessary to have the structural coordinates of (I) so that an accurate three-dimensional picture of the lysozyme conjugates may be generated by computer modeling based on the known crystal structure of hen egg-white lysozyme. The coordinates of the steroid glucuronide moiety are required so that the computer model correctly represents the possible orientations of the steroid glucuronide with respect to the lysozyme surface. The sites of attachment of the steroid glucuronide in the conjugates have been determined (Smales, 1997); hence the spatial requirements of the antibody–conjugate interaction can now be investigated for the different estrone glucuronide–lysozyme conjugates by computer graphic techniques.



(I)

Although the crystal structures of many steroids have been published (for example see Duax, Weeks, & Rohrer, 1976) and the structure of estrone has been known for some time (Busetta, Courseille & Hospital, 1973), there are very few examples of the crystal structures of steroid glucuronides. Both our recently published estriol 17β-glucuronide structure (Wu, Waters & Blackwell, 1996) and the reported estradiol 17β-glucuronide structure of Hadd *et al.* (1983) contained sugar residues which were acetylated at the sugar hydroxyl groups. Also, in these compounds, the glycosidic linkage between the steroid and the glucuronide ring was *via* the C17 position of the steroid skeleton *D* ring. So far, there are no reported crystal structures of steroid glucuronides where the glycosidic linkage is located at the C3 position of the steroid *A* ring and the hydroxyl groups and the carboxyl group of the carbohydrate moiety are free.

The title compound crystallizes along with a single water molecule which appears to form a hydrogen-bonding interaction between the O6 hydroxyl group on one steroid molecule and the O7 hydroxyl group on a second steroid molecule. All bond lengths and angles in the steroid skeleton are in the expected ranges. The H atom associated with the carboxylic acid group and those of the solvent water molecule could not be located and are omitted. The angle between the mean plane of the *A* ring of the steroid (C1–C5, C10) and the mean plane of the glucuronide (C19–C23, O3) is 14.1 (5)°, with a torsion angle (C3, O2, C19, C20) of 158.4 (3)°. The structure also shows that the carbohydrate ring is in a chair conformation and that all of the H-atom substituents of the glucuronide ring occupy axial sites; this results in the adoption of *trans* positions for the H atoms attached to adjacent C atoms with respect to each other. Hence, the orientation of the critical linkage between the carbohydrate moiety and the C3 position of the steroid *A* ring, which determines the orientation of the steroid upon conjugation to lysozyme, is clearly shown.

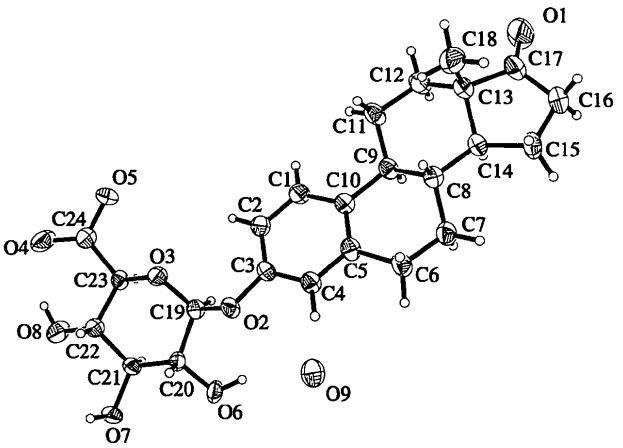


Fig. 1. A *ZORTEP* (Zsolnai, 1994*b*) drawing of (I) with displacement ellipsoids drawn at the 50% probability level.

Experimental

The title compound was synthesized *via* a Koenigs–Knorr (Conrow & Bernstein, 1971) coupling reaction as previously described by Smales, Cooke & Blackwell (1994). The compound was crystallized from a mixture of methanol and Milli-Q water at room temperature.

Crystal data

$C_{24}H_{30}O_8.H_2O$
M_r = 464.50
Orthorhombic
$P2_12_12_1$
a = 7.0337 (2) Å
b = 8.3981 (2) Å
c = 37.9873 (11) Å
V = 2243.90 (11) Å^3
Z = 4
D_x = 1.375 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 6916 reflections
θ = 1–25°
μ = 0.105 mm^{-1}
T = 293 (2) K
Plate
0.500 × 0.120 × 0.035 mm
Colorless

Data collection

Siemens SMART diffractometer	$R_{int} = 0.046$
Absorption correction: none	$\theta_{max} = 23°$
10 397 measured reflections	$h = -8 \rightarrow 8$
3111 independent reflections	$k = -8 \rightarrow 10$
2730 reflections with $I > 2\sigma(I)$	$l = -44 \rightarrow 47$
	Intensity decay: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 1.3262P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.051$	$(\Delta/\sigma)_{max} = -0.066$
$wR(F^2) = 0.133$	$\Delta\rho_{max} = 0.272$ e Å^{-3}
$S = 1.132$	$\Delta\rho_{min} = -0.259$ e Å^{-3}
3110 reflections	Extinction correction: none
337 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
Only coordinates of H atoms refined	

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XPMA* (Zsolnai, 1994*a*) and *ZORTEP* (Zsolnai, 1994*b*). Software used to prepare material for publication: *SHELXL*93.

The authors thank Associate Professor C. E. F. Rickard (University of Auckland) for data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1138). Services for accessing these data are described at the back of the journal.

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endo-3-Trimethylsilyl-2-norbornyl 2-Nitrobenzenesulfinate

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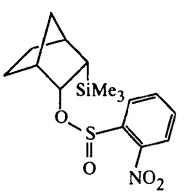
Abstract

The structure of the title compound, $C_{16}H_{23}NO_4SSi$, was solved in order to determine the C(alkyl)—O(ester) bond distance for comparison purposes. There exists a close contact [O3···S 2.766 (2) Å] between one of the nitro O atoms and the sulfinate S atom. The C—O bond distance is 1.464 (3) Å.

Comment

As part of our studies of the effects of silicon substituents on C—O bond lengths at the β position (White & Robertson, 1992; Kuan, Green & White, 1995; Chan *et al.*, 1996), we carried out a structural study on the title compound, (1). The norbornyl framework of (1) which was expected to enforce a synperiplanar relationship between the trimethylsilyl substituent and the 2-nitrobenzenesulfinate substituent would allow us to investigate the effects of the σ(C—Si)–σ^*(C—O) interaction in this geometry. The σ(C—Si)–σ^*(C—O) interaction in the antiperiplanar geometry, as in (2), has been shown to lead to significant lengthening of the C—O bond length (White & Robertson, 1992; Kuan, Green & White, 1995).



(1)

(2)

Compound (1) was prepared from *endo*-3-trimethylsilyl-*endo*-2-norborneol, (3) (Lambert & Chelius, 1990),