

refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

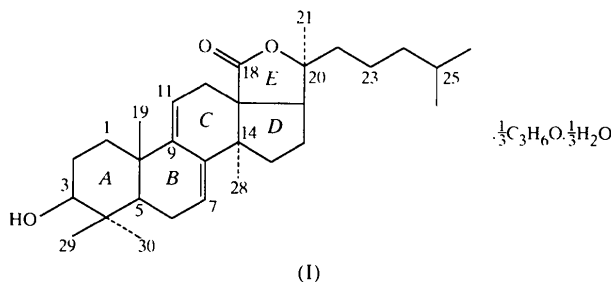
Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1005). Services for accessing these data are described at the back of the journal.

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Comment

Two types of transformation of the pentacyclic holostane skeleton in triterpene glycosides of holothurians resulting from the action of protonic acids are well known (Elyakov & Stonik, 1986). One type is related to a double-bond migration in aglycones with a labile 9β-H-7(8)-ene fragment. The stereochemical details of this migration have been studied carefully (Ilyin *et al.*, 1991). The second transformation is typical for aglycones with a labile 12α-hydroxy-9(11)-ene fragment and forms holosta-7,9-dienes under appropriate conditions (Chanley & Rossi, 1969). We report herein the structure of a product (Fig. 1) of this type of transformation, namely the artificial genin of the holothurian *Bohadschia argus* glycosides (Antonov & Stonik, 1986), as its 1/3-acetone solvate 1/3-hydrate, (I). This holothurinogenin, seychellogenin, has been isolated from the sea cucumber *Bohadschia koellikeri* (Roller *et al.*, 1969).



Acta Cryst. (1998). **C54**, 1156–1158

(20S)-3β-Hydroxyholosta-7,9-diene

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(Received 2 April 1997; accepted 30 January 1998)

Abstract

The crystal and molecular structures of the title triterpenoid have been determined. There are three molecules of this triterpenoid (C₃₀H₄₆O₃), one molecule of acetone (C₃H₆O) and a molecule of water (H₂O) in the asymmetric unit, *i.e.* formula C₃₀H₄₆O₃ · 1/3 C₃H₆O · 1/3 H₂O. The molecules of the triterpenoid have different conformations of both the side chains and the γ-lactone rings.

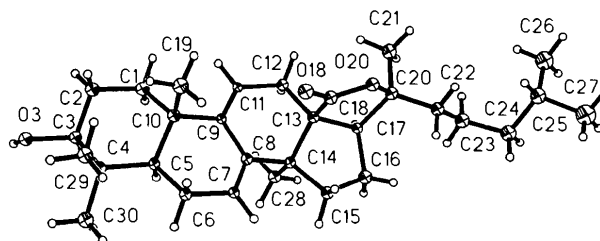


Fig. 1. The molecular structure of molecule *A* of the title compound with 30% probability non-H-atom displacement spheres (H atoms as spheres of arbitrary radii).

All hydroxy groups, water molecules and the O1 atoms of the acetone molecules are involved in a system of hydrogen bonds with distances O1...O1W 2.928 (5), O1...O3B 2.903 (5), O1W...O3C 2.722 (5) and O1W...O3A(x + 1, y + 1, z) 2.785 (5) Å.

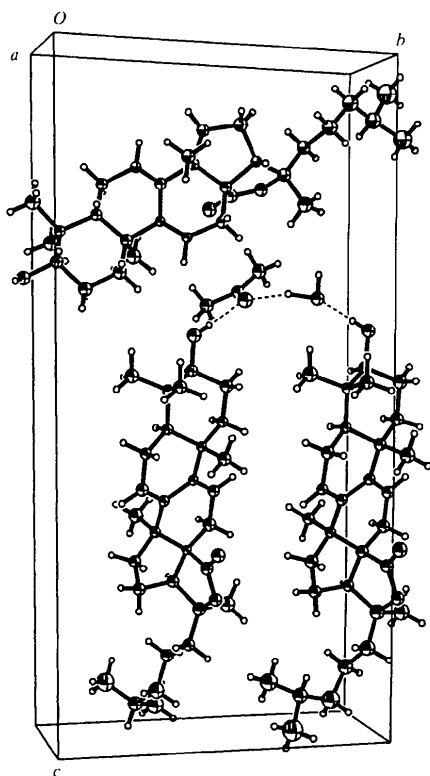
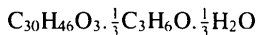


Fig. 2. Unit-cell contents (molecule A top; molecule C right).

Experimental

The title compound was obtained by hydrolysis of glycosides isolated from the holothurian *Bohadschia argus* (Antonov & Stonik, 1986). Crystallization of the compound was performed by dissolving the powdered material in acetone and adding water.

Crystal data



$M_r = 480.113$

Triclinic

$P1$

$a = 6.235 (9) \text{ \AA}$

$b = 13.137 (10) \text{ \AA}$

$c = 25.73 (3) \text{ \AA}$

$\alpha = 88.05 (9)^\circ$

$\beta = 86.38 (10)^\circ$

$\gamma = 84.50 (9)^\circ$

$V = 2093 (4) \text{ \AA}^3$

$Z = 3$

$D_x = 1.1427 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 24 reflections

$\theta = 8-9^\circ$

$\mu = 0.073 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism

$0.50 \times 0.16 \times 0.08 \text{ mm}$

Colourless

Data collection

Syntex $P2_1$ diffractometer

$\theta/2\theta$ scans

Absorption correction: none

4501 measured reflections

4501 independent reflections

2457 reflections with

$I > 2\sigma(I)$

$\theta_{\text{max}} = 25.04^\circ$

$h = 0 \rightarrow 6$

$k = -15 \rightarrow 15$

$l = -30 \rightarrow 30$

2 standard reflections

every 100 reflections

intensity decay: 5.0%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.084$

$wR(F^2) = 0.126$

$S = 1.829$

4501 reflections

414 parameters

H atoms not refined

$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 0.001P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.019$

$\Delta\rho_{\text{max}} = 0.297 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.375 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute configuration:

assigned to agree with the known chirality at C10 and C13 arising from the synthesis precursor lanosterine

Table 1. Selected torsion angles ($^\circ$)

C13A—C18A—O20A—C20A	−1.8 (4)
C22A—C23A—C24A—C25A	−66.8 (5)
C23A—C24A—C25A—C26A	−68.2 (5)
C23A—C24A—C25A—C27A	168.4 (3)
C13B—C18B—O20B—C20B	−6.2 (4)
C22B—C23B—C24B—C25B	179.6 (3)
C23B—C24B—C25B—C26B	66.7 (5)
C23B—C24B—C25B—C27B	−55.4 (5)
C13C—C18C—O20C—C20C	−9.6 (4)
C22C—C23C—C24C—C25C	76.3 (5)
C23C—C24C—C25C—C26C	68.1 (5)
C23C—C24C—C25C—C27C	−166.7 (4)

In the structure solution, three fragments containing 15–20 non-H atoms were found in the best E map. Successive Fourier syntheses defined the remaining C- and O-atom positions. H atoms were located on the basis of geometrical considerations and ΔF map suggestions (for methyl and hydroxy groups). C and O atoms were refined with isotropic displacement parameters. Several attempts at anisotropic refinement reduced R to 0.06. However, these attempts were not successful as there were some 'non-positive' definitions of principle mean-square atomic displacements.

Data collection: $P2_1$ Diffractometer Program (Syntex, 1975). Cell refinement: $P2_1$ Diffractometer Program. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

The authors are grateful to Drs T. N. Makarieva and S. V. Lindeman for their help in the work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1012). Services for accessing these data are described at the back of the journal.

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some D-seco estrone derivatives (Baran, 1967; Miljković *et al.*, 1978).

In our recent work concerning structure–activity relationships in 16- and 17-substituted estrane derivatives, a D-oxa derivative, (2), was obtained unexpectedly (Petrović *et al.*, 1992) under demethylation reaction conditions from 3-methoxy-17-*p*-toluenesulfonyloxy-16,17-secoestra-1,3,5(10)-triene-16-carbonitrile, (1) (Stanković *et al.*, 1992). The formation of (2) could be explained by a two-step mechanism: demethylation of the 3-methoxy function and hydrolysis of the CN group, followed by a neopentyl rearrangement and a five-membered lactone ring formation. However, the structure of lactone (2) could not be determined unambiguously on the basis of spectroscopic data. Therefore, an X-ray structural analysis has been undertaken.

Acta Cryst. (1998). **C54**, 1158–1160

D-Secoestrone Derivatives. IV. 3-Hydroxy-18-methyl-17-oxaestra-1,3,5(10)-triene-16-one

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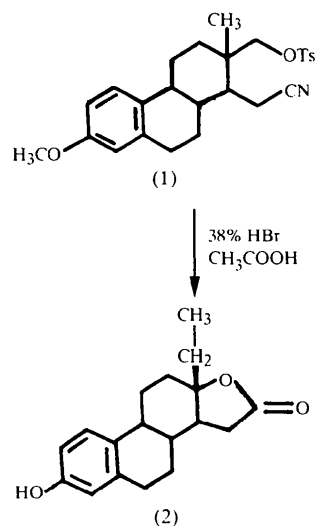
(Received 5 December 1996; accepted 11 December 1997)

Abstract

X-ray structure analysis of the title compound, $C_{18}H_{22}O_3$, obtained under demethylation reaction conditions from 3-methoxy-17-*p*-toluenesulfonyloxy-16,17-secoestra-1,3,5(10)-triene-16-carbonitrile, revealed an unusual C/D ring junction. The molecules are connected in a head-to-tail manner by bifurcated hydrogen bonds, forming twisted chains along the *a* axis.

Comment

It has been shown that some estrone derivatives with an O atom in ring *D* show significant effects on blood lipids and low estrogenic activity at screening levels (Baran, 1967). These compounds have been prepared either by Baeyer–Villiger oxidation of estrone (Bollinger & Courtney, 1964), or by chemical transformations of



The title molecule is shown in Fig. 1. The bond lengths and valence angles are within the range of mean values for steroid structures (Duax *et al.*, 1976).

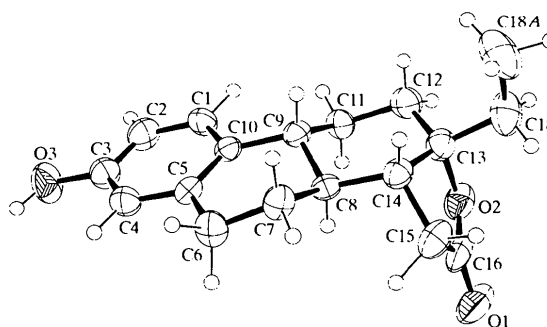


Fig. 1. A perspective view of the title molecule with the atomic labelling. Displacement ellipsoids are shown at the 30% probability level; H atoms (not labelled) are drawn as spheres of arbitrary radii.