

Sheldrick, G. M. (1997b). *SHELXL97. Program for Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON*. Version of January 1998. *Program for the Automatic Analysis of Molecular Geometry*. University of Utrecht, The Netherlands.

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Cholest-5-ene-3 β ,4 β -diyl diacetate

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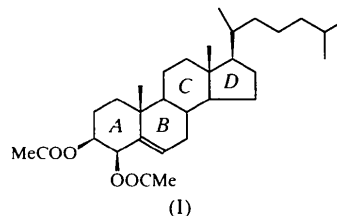
Abstract

The title steroid, C₃₁H₅₀O₄, is shown to pack in a highly anisotropic manner. Only α -face-to- β -face contacts are found in the stacks formed along the *b* direction, there are only head-to-tail contacts in the *c* direction and the acetate groups lie in layers normal to *c*.

Comment

Although the basic biological functions of cholesterol have been known for many years, little is known in detail of its molecular interactions with enzymes, cholesterol-binding proteins and related effectors of gene transcription. As part of our continuing programme studying fluoro-cholesterols for this purpose, we attempted to generate oxygenated steroids for subsequent fluorination. A rearrangement of 4,5-epoxycholestanyl-

3 β -acetate was attempted using acetic and sulfuric acids. 5 α -Hydroxycholestan-3 β ,4 β -diacetate was formed and subsequently treated with diethylaminosulfur trifluoride. The expected fluorination did not occur, with the dehydrated steroid cholest-5-ene-3 β ,4 β -diyl diacetate, (I), being the only isolated product. The crystal structure of (I) was determined, both to confirm its composition and to determine its stereochemistry.



The molecular structure of (I) (Fig. 1) shows that the acetate groups are positioned at the 3- and 4-sites and that both are substituents of the β -face of the steroid. Their methyl groups project out from the β -face and the CO groups are *syn* to the C_{ring}—O bonds [C5—O2—C2—O1 –7.8 (4), C10—O4—C4—O3 0.9 (4)^o]. A similar arrangement is found for the monoacetate cholest-5-en-3 β -yl acetate (II; Sawzik & Craven, 1979; Weber *et al.*, 1991). No previous structures of 3,4-substituted cholest-5-en species were found in the Cambridge Structural Database (Allen & Kennard, 1993) and only the β -ketone cholest-5-en-4-one (Wawrzak *et al.*, 1991) had a substituent at the 4-position. However, the C9=C15 bond length of 1.330 (4) Å is in good agreement with the average distance of 1.324 (3) Å found for the 123 cholest-5-en-based fragments with substituents at the 3-position.

The aliphatic chain adopts a fully extended geometry with *-gauche, trans* conformation as defined by Duax *et al.* (1980). The C18—C21—C24—C25 torsion angle of 158.7 (3)^o is, however, twisted further from 180^o than any of the 69 examples given therein (the closest is 166^o; see Gilliland *et al.*, 1977). As in (II), the steroid rings A and C adopt chair conformations, with ring A being the more distorted. Ring B is a half-chair, with

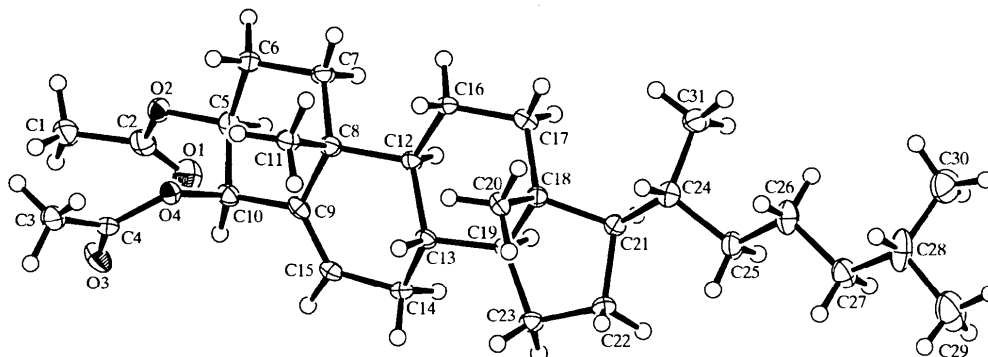


Fig. 1. The molecular structure of (I) showing the atom-numbering scheme. Non-H atoms are drawn as 40% probability displacement ellipsoids and H atoms as spheres of an arbitrary size.

C13 displaced towards the β -face and C12 displaced towards the α -face.

The crystal structure of (I) consists of discrete molecules separated by at least van der Waals distances. The structure is highly anisotropic, with head-to-tail ordering along the a direction [in contrast to the tail-to-tail packing of (II)] and with all the steroid β -faces orientated in the same direction. Thus, stacks form in the b direction where the β -faces are in contact with α -faces (Fig. 2). It can also be seen that the action of the screw axis generates an interdigitated structure, with steroid tails lying between ring systems and the acetate groups forming layers perpendicular to the c axis.

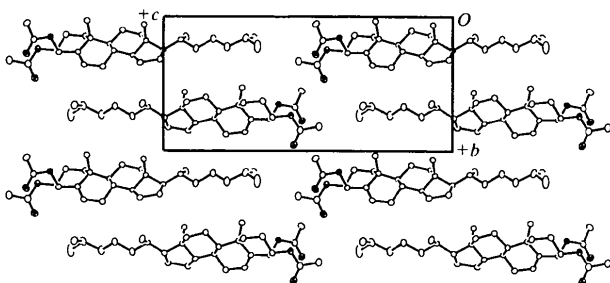


Fig. 2. The packing diagram of (I) viewed along the a axis.

Experimental

Diethylaminosulfur trifluoride (1 ml, 7.5 mmol) and one drop of fuming sulfuric acid were added under a nitrogen atmosphere to 5 α -hydroxycholestan-3 β ,4 β -diacetate (350 mg, 0.69 mmol) in 7 ml of glyme. The solution was stirred for 3 h and then poured into aqueous sodium bicarbonate solution (5%, 10 ml). This was extracted with dichloromethane (3 \times 10 ml) and the combined organic fractions were dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure. Flash chromatography (20% ether in hexane) gave a white solid. Recrystallization from methanol gave (I) as clear needles (210 mg, 0.43 mmol; yield 62%; m.p. 442–443 K). IR: ν_{\max} (KBr, cm^{-1}) 2950–2868 s (aliphatic CH), 1731 s (C=O), 1373 m , 1256 s ; $^1\text{H NMR}$: δ_{H} (250 MHz, CDCl_3 , p.p.m.) 5.81 (m , 1H, HC=C), 5.50 (m , 1H, HCOAc C4), 4.72 (m , 1H, HCOAc C3), 2.09, 2.01 (2 s , 6H, 2H₃CCOO), 1.13 (s , 3H, CH₃ C19), 0.92–0.88 (m , 9H, CH₃ C21/C26/C27), 0.67 (s , 3H, CH₃ C18); FAB MS m/z : 487 [$M + \text{H}^+$], 35%, 427 (100%), 366 (60%).

Crystal data

$\text{C}_{31}\text{H}_{50}\text{O}_4$
 $M_r = 486.71$
 Monoclinic
 $P2_1$
 $a = 6.293$ (3) \AA
 $b = 10.255$ (2) \AA
 $c = 22.172$ (5) \AA
 $\beta = 96.17$ (3) $^\circ$
 $V = 1422.5$ (8) \AA^3
 $Z = 2$
 $D_x = 1.136$ Mg m^{-3}
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ \AA
 Cell parameters from 25 reflections
 $\theta = 10.1$ – 13.3 $^\circ$
 $\mu = 0.073$ mm^{-1}
 $T = 123$ K
 Needle
 $0.40 \times 0.10 \times 0.02$ mm
 Colourless

Data collection

Rigaku AFC-7S diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 5834 measured reflections
 5018 independent reflections
 3933 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 25$ $^\circ$
 $h = -7 \rightarrow 7$
 $k = -12 \rightarrow 12$
 $l = -26 \rightarrow 26$
 3 standard reflections
 every 150 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.147$
 $S = 1.052$
 5018 reflections
 323 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.2168P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.201$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.228$ e \AA^{-3}
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C2	1.203 (4)	O4—C4	1.360 (4)
O2—C2	1.356 (4)	O4—C10	1.463 (4)
O2—C5	1.447 (4)	C9—C15	1.330 (4)
O3—C4	1.199 (4)		
C2—O2—C5	116.9 (3)	O2—C2—C1	111.3 (3)
C4—O4—C10	117.0 (2)	O3—C4—O4	123.5 (3)
O1—C2—O2	122.7 (3)	O3—C4—C3	125.7 (3)
O1—C2—C1	126.0 (3)	O4—C4—C3	110.9 (3)
C5—O2—C2—O1	−7.8 (4)	C21—C24—C25—C26	179.5 (3)
C5—O2—C2—C1	172.0 (3)	C24—C25—C26—C27	173.1 (3)
C10—O4—C4—O3	0.9 (4)	C25—C26—C27—C28	−179.6 (3)
C10—O4—C4—C3	−178.9 (3)	C26—C27—C28—C30	−60.7 (5)
C18—C21—C24—C25	158.7 (3)	C26—C27—C28—C29	175.7 (3)

The absolute structure could not be determined by diffraction methods and was thus assigned to be that found in natural steroids. Methyl-H atoms were modelled in a riding mode and their orientations were found by refining rotation about the C—Me bonds. All other H atoms were placed in calculated positions and in riding modes.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GDI035). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
 Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
 Duax, W. L., Griffin, J. F., Rohrer, D. C. & Weeks, C. M. (1980). *Lipids*, **15**, 783–792.

- Gilliland, G. L., Newcomer, M. E., Parish, E. J., Schroepfer, G. J. & Quioco, F. A. (1977). *Acta Cryst.* B33, 3117–3121.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Sawzik, P. & Craven, B. M. (1979). *Acta Cryst.* B35, 895–901.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Wawrzak, Z., Grochulski, P. & Galdecki, Z. (1991). *Acta Cryst.* C47, 687–689.
- Weber, H.-P., Craven, B. M., Sawzik, P. & McMullan, R. K. (1991). *Acta Cryst.* B47, 116–127.

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Triphenylselenonium iodide

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Abstract

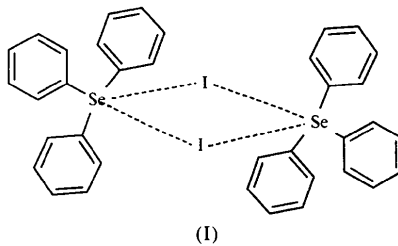
The title compound, Ph₃SeI or C₁₈H₁₅Se⁺·I⁻, forms an ionic solid comprised of centrosymmetric dimers, in which two Ph₃Se⁺ ions are bridged by two I⁻ ions. The coordination about the Se^{IV} centers can be described as either a twofold capped trigonal pyramid or a distorted pseudo-octahedron, with the selenium lone pair occupying the sixth position. Selected structural parameters are: Se—C 1.926 (4), 1.929 (4) and 1.944 (4) Å, Se···I 3.722 (1) and 4.153 (1) Å, C—Se—C 100.21 (15), 102.51 (15) and 98.62 (16)°, and C—Se···I 84.4 (1), 166.5 (1), 92.7 (1), 94.3 (1), 86.2 (1) and 161.4 (1)°.

Comment

In our study of ligand-exchange reactions of group 16 elements, we attempted the synthesis of triorganoselenonium iodides from triorganoselenonium chlorides by the exchange of Cl for I *via* NaI. In contrast to NaI, NaCl does not dissolve in acetonitrile, and its precipitation is the driving force of the reaction. The ⁷⁷Se NMR shifts of Ph₃SeCl and Ph₃SeI in CD₃CN

do not differ substantially (504.8 and 499.4 p.p.m., respectively), which suggests dissociation into Ph₃Se⁺ and X⁻. We were thus curious to see whether Ph₃SeI is also a more or less ionic solid.

The molecular structure of the triphenylselenonium iodide centrosymmetric dimer in the solid state is shown in Fig. 1 and selected structural parameters are given in Table 1. The dimer, (I), consists of two Ph₃Se⁺ ions bridged by two I⁻ ions. One Se···I distance is slightly shorter and the other longer than the sum of the van der Waals radii (3.88 Å; Bondi, 1964); Ph₃SeI is thus predominantly ionic in the solid state.



This view is confirmed by the angles at selenium. The three C—Se—C angles are of similar size and are thus more like those in a trigonal pyramid than in a pseudo-trigonal bipyramid. Furthermore, four out of six C—Se···I angles and the I—Se···I angle are close to 90°, the remaining two C—Se···I angles being close to 180°. The trigonal pyramid is thus capped by two I⁻ ions to give a distorted pseudo-octahedral geometry about the Se atom, with the lone pair of the Se atom occupying the sixth position. The sum of the C—Se—C angles in Ph₃SeI is 301.34° and is thus similar to those in other Ar₃SeX compounds, *e.g.* 302.4° in Ph₃SeNCS (Ash *et al.*, 1977), 300.2° in (*p*-Tol)₃SeCl·H₂O, 302.6° in (*p*-Tol)₃SeBr·H₂O (Bel'skii *et al.*, 1982) and 301.2° in Ph₃SeCl·2H₂O (Lee & Titus, 1976), and 15–20° larger than in the corresponding

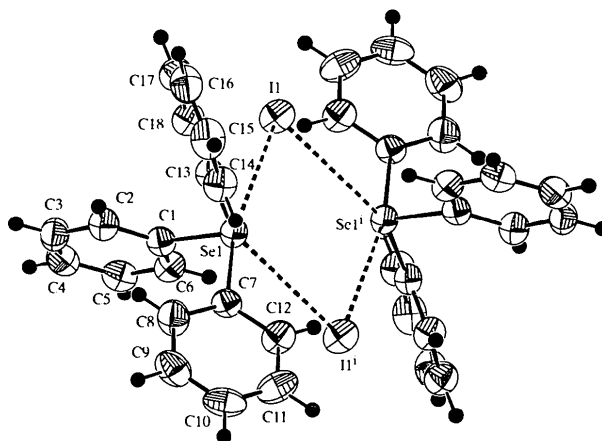


Fig. 1. *ORTEPII* plot (Johnson, 1976) of Ph₃SeI with 50% probability displacement ellipsoids. The radius of the H atoms is arbitrary. [Symmetry code: (i) 1 - x, 1 - y, 1 - z.]