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Hysterin

BY J. P. DECLERCQ, G. GERMAIN AND M. VAN MEERSSCHE

Laboratoire de Chimie Physique et de Cristallographie de l'Université de Louvain, 1 place L. Pasteur, B-1348 Louvain-la-Neuve, Belgium

AND M. DEMUYNCK, P. DE CLERCQ AND M. VANDEWALLE

State University of Gent, Department of Organic Chemistry, Laboratory of Organic Synthesis, Krijgslaan 271 (S.4), B-9000 Gent, Belgium

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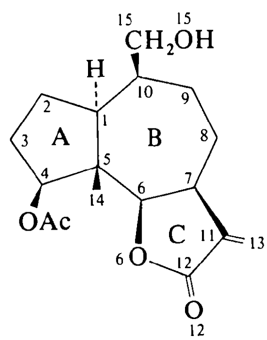
Abstract. $C_{17}H_{24}O_5$, orthorhombic, $P2_12_12_1$, a = 7·938 (3), b = 6·465 (3), c = 31·703 (17) Å, V = 1627 (1) Å^3, $Z = 4$, $M_r = 308{\cdot}37$, $D_x = 1{\cdot}26$ Mg m^{-3}. The structure has been solved by direct methods and refined to a final R value of 0·044 for 1034 observed reflections. The configurations at the asymmetric centers are C(1)(S), C(4)(S), C(5)(S), C(6)(R), C(7)(S) and C(10)(R), in contrast to the previously assigned structure for hysterin which showed the epimeric configuration at C(4). The cyclopentane ring is envelope shaped with C(5) at the flap, while the seven-membered and the lactone rings both possess pseudo-diad axes passing through C(7) and C(12) respectively. The molecules are linked by hydrogen bonds.



OAc = O(4)–C(16)–C(17)
‖
O(16)

Introduction. During work directed towards a stereoselective synthesis of the title compound evidence was found that the originally assigned structure for hysterin (Romo de Vivar, Bratoeff & Rios, 1966) was incorrect at C(4). In order to establish its structure unequivocally a single-crystal X-ray analysis was undertaken. Hysterin was crystallized from isooctane–ethyl acetate.

Intensities of 1443 independent reflections were collected on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·7107 Å) and the ω-scan technique up to $2\theta = 47°$. Only 1034 reflections were considered as observed [$I > 2{\cdot}5\sigma(I)$] and included in the refinement.

The structure was solved by direct methods using the *MULTAN* 78 computer system (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). An E map clearly showed all non-hydrogen atomic positions of the molecule.

The refinement was carried out by the program *SHELX* 76 (Sheldrick, 1976) with anisotropic thermal parameters for the non-hydrogen atoms. 20 out of 24 H atoms were located from a difference Fourier synthesis and refined with one overall isotropic temperature factor.

The final conventional R index is 0·044.* Table 1 gives the atomic positional parameters.

Discussion. Fig. 1 is a stereoscopic drawing of hysterin. Bond distances, bond angles and torsion angles are given in Tables 2, 3 and 4.

The Newman projections of Fig. 2 show how the three rings A, B and C are fused along the C(5)–C(1) and C(6)–C(7) bonds.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34833 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

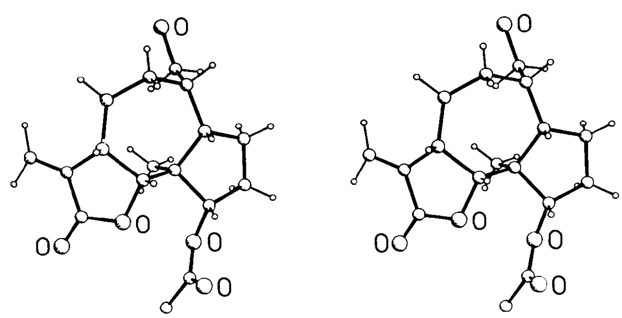


Fig. 1. Stereoscopic view of the molecule.

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Table 1. *Atomic coordinates* (× 10⁴; *for* H × 10³)

For H atoms $B = 4.9$ Å^2.

	x	y	z	B_{eq} (Å^2)
C(1)	−10907 (7)	−7327 (8)	−3591 (2)	3·5
C(2)	−11702 (10)	−7201 (11)	−3144 (2)	5·1
C(3)	−10575 (9)	−5815 (12)	−2880 (2)	5·3
C(4)	−9046 (7)	−5366 (10)	−3173 (2)	3·8
C(5)	−9789 (6)	−5348 (7)	−3623 (2)	2·9
C(6)	−8369 (6)	−5650 (8)	−3940 (2)	3·3
C(7)	−8725 (6)	−5699 (9)	−4425 (1)	3·2
C(8)	−10481 (7)	−6405 (9)	−4579 (2)	3·7
C(9)	−11168 (8)	−8325 (9)	−4366 (2)	4·1
C(10)	−12080 (7)	−7977 (8)	−3953 (2)	3·7
C(11)	−8240 (7)	−3566 (9)	−4562 (2)	3·8
C(12)	−7188 (8)	−2696 (11)	−4226 (2)	4·8
C(13)	−8673 (9)	−2515 (13)	−4904 (2)	5·3
C(14)	−10754 (8)	−3352 (9)	−3697 (2)	3·5
C(15)	−13651 (7)	−6599 (10)	−4003 (2)	4·2
C(16)	−6620 (9)	−3361 (14)	−3003 (2)	5·6
C(17)	−5997 (10)	−1163 (14)	−2973 (2)	7·4
O(4)	−8274 (5)	−3407 (6)	−3059 (1)	4·3
O(6)	−7179 (4)	−3933 (6)	−3891 (1)	4·2
O(12)	−6397 (7)	−1084 (9)	−4230 (1)	7·8
O(15)	−14723 (5)	−7326 (7)	−4334 (1)	5·1
O(16)	−5752 (7)	−4888 (10)	−2987 (2)	7·7
H(C1)	−1012 (7)	−816 (9)	−358 (2)	
H(C2)	−1197 (7)	−857 (9)	−302 (2)	
H′(C2)	−1271 (8)	−651 (9)	−316 (2)	
H(C3)	−1028 (7)	−645 (9)	−260 (2)	
H′(C3)	−1104 (7)	−446 (9)	−287 (2)	
H(C4)	−798 (7)	−646 (9)	−319 (2)	
H(C6)	−776 (8)	−676 (9)	−391 (2)	
H(C7)	−784 (7)	−665 (9)	−453 (2)	
H(C8)	−1147 (7)	−508 (9)	−454 (2)	
H′(C8)	−1044 (7)	−681 (8)	−491 (2)	
H(C9)	−1195 (8)	−888 (9)	−451 (2)	
H′(C9)	−1023 (8)	−926 (9)	−434 (2)	
H(C10)	−1253 (7)	−944 (9)	−387 (2)	
H(C13)	−805 (7)	−91 (9)	−489 (2)	
H′(C13)	−952 (7)	−320 (9)	−510 (2)	
H(C14)	−1007 (8)	−215 (9)	−366 (2)	
H′(C14)	−1109 (7)	−317 (9)	−397 (2)	
H″(C14)	−1171 (8)	−312 (9)	−350 (2)	
H(C15)	−1427 (7)	−657 (9)	−373 (2)	
H′(C15)	−1316 (8)	−509 (9)	−408 (2)	

Table 2. *Bond lengths* (Å)

C(1)–C(2)	1·551 (8)	C(7)–C(11)	1·496 (8)
C(1)–C(5)	1·561 (7)	C(8)–C(9)	1·515 (8)
C(1)–C(10)	1·536 (7)	C(9)–C(10)	1·512 (7)
C(2)–C(3)	1·518 (10)	C(10)–C(15)	1·542 (8)
C(3)–C(4)	1·555 (8)	C(11)–C(12)	1·466 (8)
C(4)–C(5)	1·544 (7)	C(11)–C(13)	1·324 (8)
C(4)–O(4)	1·452 (7)	C(12)–O(6)	1·330 (7)
C(5)–C(6)	1·523 (7)	C(12)–O(12)	1·217 (7)
C(5)–C(14)	1·519 (7)	C(15)–O(15)	1·430 (6)
C(6)–C(7)	1·565 (7)	C(16)–C(17)	1·508 (11)
C(6)–O(6)	1·466 (6)	C(16)–O(4)	1·325 (8)
C(7)–C(8)	1·545 (7)	C(16)–O(16)	1·205 (9)
⟨C–H⟩	0·99 (6)		

Table 3. *Bond angles* (°)

C(2)–C(1)–C(5)	104·3 (4)	C(8)–C(7)–C(11)	114·4 (5)
C(2)–C(1)–C(10)	116·7 (5)	C(7)–C(8)–C(9)	115·3 (5)
C(5)–C(1)–C(10)	121·4 (4)	C(8)–C(9)–C(10)	115·9 (5)
C(1)–C(2)–C(3)	107·2 (5)	C(1)–C(10)–C(9)	113·4 (4)
C(2)–C(3)–C(4)	103·9 (5)	C(1)–C(10)–C(15)	114·1 (4)
C(3)–C(4)–C(5)	104·8 (5)	C(9)–C(10)–C(15)	112·6 (5)
C(3)–C(4)–O(4)	110·2 (5)	C(7)–C(11)–C(12)	106·8 (5)
C(5)–C(4)–O(4)	112·5 (4)	C(7)–C(11)–C(13)	130·1 (6)
C(1)–C(5)–C(4)	98·7 (4)	C(12)–C(11)–C(13)	123·1 (6)
C(1)–C(5)–C(6)	111·0 (4)	C(11)–C(12)–O(6)	110·7 (5)
C(4)–C(5)–C(6)	109·1 (4)	C(11)–C(12)–O(12)	128·0 (6)
C(1)–C(5)–C(14)	114·8 (4)	O(6)–C(12)–O(12)	121·3 (6)
C(4)–C(5)–C(14)	110·0 (4)	C(10)–C(15)–O(15)	111·5 (5)
C(6)–C(5)–C(14)	112·3 (4)	C(17)–C(16)–O(4)	110·8 (8)
C(5)–C(6)–C(7)	121·2 (4)	C(17)–C(16)–O(16)	125·6 (7)
C(5)–C(6)–O(6)	108·0 (4)	O(4)–C(16)–O(16)	123·7 (7)
C(7)–C(6)–O(6)	103·7 (4)	C(4)–O(4)–C(16)	118·1 (6)
C(6)–C(7)–C(8)	118·6 (4)	C(6)–O(6)–C(12)	111·5 (4)
C(6)–C(7)–C(11)	102·7 (4)		

Table 4. *Torsion angles* (°) (⟨σ⟩ = 0·5°)

Endocyclic	
Ring *A* (cyclopentane)	
C(5)–C(1)–C(2)–C(3)	−22·4
C(1)–C(2)–C(3)–C(4)	−5·8
C(2)–C(3)–C(4)–C(5)	32·5
C(3)–C(4)–C(5)–C(1)	−45·1
C(4)–C(5)–C(1)–C(2)	40·8
Ring *B* (seven-membered)	
C(10)–C(1)–C(5)–C(6)	−70·4
C(1)–C(5)–C(6)–C(7)	72·4
C(5)–C(6)–C(7)–C(8)	−26·9
C(6)–C(7)–C(8)–C(9)	−45·1
C(7)–C(8)–C(9)–C(10)	85·0
C(8)–C(9)–C(10)–C(1)	−70·0
C(9)–C(10)–C(1)–C(5)	58·1
Ring *C* (lactone)	
C(6)–C(7)–C(11)–C(12)	17·7
C(7)–C(11)–C(12)–O(6)	−8·0
C(11)–C(12)–O(6)–C(6)	−6·6
C(12)–O(6)–C(6)–C(7)	17·7
Side groups	
C(1)–C(10)–C(15)–O(15)	−177·8
C(5)–C(4)–O(4)–C(16)	−113·2
C(4)–O(4)–C(16)–O(16)	−9·9

The stereochemistry of the molecule is as follows: C(1)–αH is *trans* to C(5)–βCH_3; C(6)–αH is *cis* to C(7)–αH; C(4)–αO(4) is *cis* to C(5)–βCH_3; C(10)–βCH_2OH is *trans* to C(1)–αH. Thus the *AB* and *BC* ring junctions are *trans* and *cis* respectively. No attempt was made to determine the absolute configuration of hysterin by diffraction techniques given the weak anomalous scattering of the O atoms when Cu radiation is employed, but correlation with ambrosin (Romo de Vivar, Bratoeff & Rios, 1966) establishes the absolute stereochemistry of the molecule to be that shown in Fig. 1.

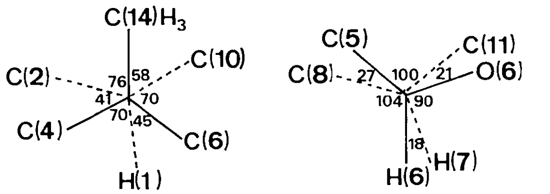

Fig. 2. Newman projections around C(5)–C(1) and C(6)–C(7).

Table 5. *Ring conformations*

	Ring *A* (cyclopentane)	Ring *B* (seven-membered)	Ring *C* (lactone)
Description	Deformed envelope	Deformed twist–chair	Half-chair
Approximate symmetry	C_s	C_2	C_2
Pseudo-symmetry element	*m*	2	2
from atom	C(5)	C(7)	C(12)
to the midpoint of bond	C(2)–C(3)	C(1)–C(10)	C(6)–C(7)
Average torsion angle (magnitude)	29·2°	61·0°	14·4°
Asymmetry parameter (Duax, Weeks & Rohrer, 1976)	7·8°	12·8°	0·7°

The conformations of the three fused rings given by the torsion angles in Table 4 are described in another way with some further comments in Table 5. The torsion angles of the cyclopentane ring indicate a somewhat deformed, highly puckered envelope conformation.

In the seven-membered ring the C_2 symmetrized values of the torsion angles, *i.e.* 58, −70, 79, −36°, are quite similar to those (54, −72, 88, −39) proposed by Hendrickson (1967) for a cycloheptane molecule with equal bond lengths and in a perfect twist–chair conformation.

The lactone ring shows a relatively flat half-chair conformation which induces only a small torsion angle [C(5)–C(6)–C(7)–C(8) = −27°] in the seven-membered ring; as a consequence, perfect C_2 symmetry in that ring conformation in the four bonds between C(5) and C(9) is destroyed.

The hysterin molecules are linked together by hydrogen bonds between the O(15)–H hydroxyl group and O(12) of the lactone carbonyl group; O(15)···O(12) is 2·79 Å. These bonds form infinite chains parallel to [100].

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Structure of Cholesteryl Undecanoate

By Patricia Sawzik and B. M. Craven

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *USA*

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Abstract. $C_{38}H_{66}O_2$, monoclinic, $P2_1$, $a = 13{\cdot}008$ (6), $b = 9{\cdot}006$ (7), $c = 31{\cdot}063$ (9) Å, $\beta = 90{\cdot}60$ (4)°, $Z = 4$ (2 molecules/asymmetric unit), $d_{meas} = 1{\cdot}009$ (flotation in aqueous sucrose), $d_{calc} = 1{\cdot}013$ Mg m^{-3}. The final R factor for 1888 observed reflections is 0·127. The molecular packing in the crystal structure of cholesteryl undecanoate is isostructural with the cholesteryl *n*-alkanoate series C_9-C_{12}.

Introduction. The structure of cholesteryl undecanoate is one of a series of cholesteryl ester structure determinations we have undertaken. These structures are of interest as they may provide models for molecular associations in less ordered lipid systems. The liquid-crystalline phases of cholesteryl undecanoate are monotropic. For samples recrystallized from *n*-pentanol, the solid–isotropic transition occurs at 364·5

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