Unfortunately, the experimental data are not sufficient to allow a definite comment on the process of the phase transformation from the γ to α forms. Nevertheless, it may be said that the major process might consist of ordering in a chain along **a**′ to produce the molecular arrangement for the α form. Cooperative displacements, however, would not easily occur during this transformation since a high energy barrier to the displacement of molecules may be rapidly built up as the ordering proceeds. The difficulties of the occurrence of cooperative displacements would certainly explain the occurrence of crystal splitting when high rates of temperature change were employed.

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24-Methylenecholest-5-ene-3*β*,7*β*,19-triol. A Case of Pseudotranslation. Calculation of Structure Invariants from Partial Structure Information

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The title compound, the sterol $C_{28}H_{46}O_3$, was isolated from the soft coral *Litophyton viridis*. The structure crystallizes in space group $P2_1$ with $a = 17{\cdot}00$ (1), $b = 12{\cdot}40$ (1), $c = 12{\cdot}67$ (1) Å, $\beta = 98{\cdot}07$ (5)°, $Z = 4$, $D_x = 1{\cdot}074$ and $D_m = 1{\cdot}09$ g cm^{-3}. The two independent molecules are related by a pseudotranslation $(0,\frac{1}{2},\frac{1}{2})$; they differ in the conformation of the side chain and in the hydrogen bonding. The well known convergence procedure has been applied to discriminate between several structure invariants calculated from origin-displaced partial-structure information and to extract those invariants with phases most probably 0°.

Introduction

Chemical and spectroscopic investigations of the title compound (Fig. 1) were carried out by Bortolotto, Daloze, Braekman, Losman & Tursch (1976). The compound is, as far as we know, the first example of a naturally occurring 19-OH sterol.

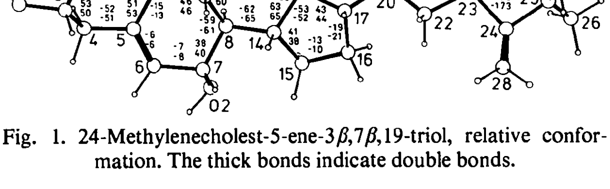

Fig. 1. 24-Methylenecholest-5-ene-3*β*,7*β*,19-triol, relative conformation. The thick bonds indicate double bonds.

The space group, refined cell parameters and structure factors were obtained from data collected on a Philips PW 1100 diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The measurement of half the reciprocal sphere up to a Bragg angle of 79° using an ω–2θ scan technique yielded 5025 unique F's after reduction and correction for the Lp factor.

A characteristic feature of the diffraction record is the relative weakness of all reflexions with $k + l$ odd, a consequence of a $(0,\frac{1}{2},\frac{1}{2})$ pseudotranslation affecting about 75% of the structure as evidenced in the Patterson function. In view of this, the solution of the structure was first attempted in space group $A2$, using the program *MULTAN* (Germain, Main & Woolfson, 1971). The *MULTAN* procedure did not solve the structure, but several recognizable steroid fragments, displaced from the correct origin, appeared in the E maps. The introduction of those *MULTAN* starting phases which gave the best fragment into the *MAGIC*

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procedure (Woolfson, Germain & Declercq, 1975) yielded a three-ring steroid fragment which developed into most of the molecular skeleton by successive Fourier syntheses.

The breaking of the *A*2 symmetry was achieved simply by introduction of the $k + l$ odd reflexions with phases equal to zero in a Fourier synthesis. The *A*2 symmetry appeared to be invalid mainly in the side chain.

Least-squares refinement combined with difference Fourier syntheses, using all data, revealed all C and O atoms. The four C(25)–C(28) atoms had large thermal parameters ($B > 25$ Å^2), however, and their bond angles and distances deviated significantly from normal values. An inspection of a difference Fourier map based on all atoms except C(25)–C(28) showed that very close to the peaks of these four atoms there were several smaller ones. These peaks probably originated from disordered tail ends of both sterol molecules, but the nature of the disorder could not be explained. The peak heights of C(25)—C(28) suggested an occupancy factor of 0·5 rather than 1·0. A final refinement, the results of which are given in Tables 1 and 2, yielded $R = 0{\cdot}12$.* Introduction of H atoms, at positions derived from bonding considerations, into the structure factor calculations did not improve the refinement significantly.

Table 1. *Atomic coordinates* (×10^4) *for atoms refined anisotropically*

	x	*y*	*z*
Molecule *A*			
C(1)	7042 (8)	4138 (10)	1075 (11)
C(2)	6616 (8)	3008 (10)	1054 (11)
C(3)	6149 (8)	2790 (10)	−37 (10)
C(4)	5530 (8)	3699 (9)	−364 (10)
C(5)	5914 (7)	4821 (9)	−281 (8)
C(6)	5791 (7)	5486 (9)	−1089 (9)
C(7)	6068 (7)	6677 (10)	−1080 (9)
C(8)	6428 (7)	7045 (8)	44 (8)
C(9)	6937 (7)	6129 (10)	664 (9)
C(10)	6424 (7)	5098 (9)	787 (9)
C(11)	7352 (8)	6544 (9)	1760 (9)
C(12)	7898 (8)	7522 (11)	1610 (11)
C(13)	7401 (8)	8461 (10)	1037 (10)
C(14)	7014 (7)	7990 (10)	−55 (9)
C(15)	6645 (8)	9007 (10)	−672 (10)
C(16)	7322 (9)	9872 (11)	−365 (10)
C(17)	7917 (9)	9361 (11)	594 (12)
C(18)	6782 (9)	8920 (12)	1723 (10)
C(19)	5895 (7)	5182 (10)	1677 (8)
C(20)	8247 (10)	10282 (13)	1398 (14)
O(1)	5721 (5)	1782 (6)	−1 (7)
O(2)	5384 (5)	7333 (6)	−1398 (6)
O(3)	5428 (5)	6128 (7)	1672 (6)
Molecule *B*			
C(1)	6989 (7)	9213 (9)	6337 (9)
C(2)	6605 (8)	8059 (10)	6339 (9)
C(3)	6198 (7)	7744 (10)	5250 (10)
C(4)	5588 (7)	8621 (9)	4770 (9)
C(5)	5935 (6)	9747 (9)	4822 (8)
C(6)	5870 (7)	10353 (9)	3959 (9)
C(7)	6126 (7)	11537 (9)	3922 (9)
C(8)	6370 (7)	12011 (8)	5055 (8)
C(9)	6861 (7)	11154 (10)	5794 (8)
C(10)	6356 (6)	10090 (8)	5937 (9)
C(11)	7161 (9)	11678 (9)	6918 (9)
C(12)	7690 (8)	12658 (10)	6792 (10)
C(13)	7213 (8)	13540 (10)	6069 (10)
C(14)	6956 (7)	12955 (9)	4962 (8)
C(15)	6647 (8)	13906 (10)	4217 (10)
C(16)	7243 (8)	14835 (11)	4603 (11)
C(17)	7758 (8)	14447 (10)	5670 (11)
C(18)	6507 (8)	13990 (11)	6600 (10)
C(19)	5760 (7)	10204 (10)	6714 (9)
C(20)	7941 (9)	15421 (11)	6465 (13)
O(1)	5785 (5)	6748 (6)	5357 (7)
O(2)	5422 (5)	12116 (6)	3427 (6)
O(3)	5207 (5)	11065 (7)	6465 (6)

Discussion

The statistical behaviour of the data reflects the presence of the pseudotranslation exactly, as described by Rogers & Wilson (1953). The same can be said of the evolution of the reliability index *R* during the expansion of the correct fragment using the even reflexions: all but four atoms were found with the expected geometry, yet *R* was 0·48.

The examination of a convergence map based on $\alpha_{\mathbf{h}} = \sum_{\mathbf{k}}|E_{\mathbf{h}}E_{\mathbf{k}}E_{-\mathbf{h}-\mathbf{k}}|^2$, as the elimination criterion, which corresponds to an infinite number of atoms in the unit cell,† revealed a 'weak link' in the map: the phase of reflexion 351 ($E = 3{\cdot}67$) was incorrectly determined by the structure invariant $-\varphi(35\bar{1}) + \varphi(837) + \varphi(\bar{5}2\bar{8})$ which has a phase of 97°. Phase errors were thus propagated. How could one avoid such aberrant phase relationships in the most crucial stages of the phase expansion when parts of the structure are known?

Thiessen & Busing (1974) estimate the structure invariants from *n* partial structures with known orientations but with unknown positions relative to each other as described by the formula

$$\mathscr{P}(\mathbf{h},\mathbf{k}) = \sum_j^n T_j(\mathbf{h})\,T_j(\mathbf{k})\,T_j(-\mathbf{h}-\mathbf{k}). \qquad (1)$$

T_j is the structure factor for an equal-atom structural fragment *j* and is defined as

$$T_j(\mathbf{h}) = \sum_m^{N_j} \exp(2\pi i\mathbf{h}\mathbf{r}_m), \qquad (2)$$

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33507 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† See equation (17) of Germain *et al.* (1971). The use of this criterion makes the elimination process independent of the scale of the *E* values.

where N_j is the number of atoms at position $\mathbf{r}_m$ related to an arbitrary origin in the jth partial structure. All symmetry-related fragments are, of course, also included in the sum of (1). It is interesting that $\mathscr{P}$ in (1) can be interpreted as proportional to the average triple product for the infinite number of combinations of relative positions of the n partial structures.

The aberrant phase relationship above was calculated, from (1), to have a phase of 165°, using the first 20 C atoms in Table 1. All the 37 invariants or triplets belonging to 10 E values in the convergence map which were eliminated after the $35\bar{1}$ reflexion had absolute phases estimated by (1) which were less than 37°. The calculation of about 2000 invariants shows that the larger $\mathscr{P}$ is, the better is the agreement between the correct phases and those calculated by (1). Moreover, the phases of the largest $\mathscr{P}$ values were clustered around 0°

As a consequence of this observation a new convergence map was calculated using the real part of $\sum_{\mathbf{k}}\mathscr{P}(\mathbf{h},\mathbf{k})$ as the elimination criterion. In this way those invariants with phases most certainly close to 0° will appear at the end of the convergence procedure and thus be used in the beginning of the phase expansion. The new convergence map had five starting phases as before but no 'weak links'. A phase expansion with the ordinary tangent formula, which followed the construction of the convergence map, gave the correct structure.

Description of the structure

Bond distances and angles are given in Tables 3 and 4 where the C(24)–C(28) part has been omitted owing to disorder. The conformations of the two molecules differ mainly about the C(20)–C(22) bond (Fig. 1). All six

Table 2. *Atomic coordinates* (×10³) *and thermal parameters* (×10) *for atoms refined isotropically*

	x	y	z	B(Å²)
Molecule *A*				
C(21)	885 (1)	982 (2)	228 (2)	87 (5)
C(22)	874 (1)	1102 (2)	68 (1)	84 (5)
C(23)	904 (2)	1210 (3)	138 (2)	110 (9)
C(24)	949 (3)	1293 (4)	71 (4)	140 (15)
C(25)	984 (4)	1392 (7)	143 (5)	113 (24)
C(26)	941 (3)	1460 (5)	90 (5)	124 (24)
C(27)	1062 (3)	1359 (5)	153 (4)	107 (21)
C(28)	951 (3)	1277 (5)	−26 (4)	201 (23)
Molecule *B*				
C(21)	847 (1)	1507 (2)	749 (2)	79 (5)
C(22)	837 (1)	1633 (2)	588 (2)	85 (5)
C(23)	912 (1)	1595 (3)	551 (2)	87 (7)
C(24)	964 (3)	1689 (5)	484 (4)	145 (15)
C(25)	1025 (3)	1667 (5)	439 (4)	112 (17)
C(26)	994 (3)	1653 (5)	366 (4)	129 (18)
C(27)	1083 (3)	1666 (6)	525 (5)	136 (25)
C(28)	920 (4)	1785 (5)	492 (5)	171 (19)

Table 4. *Bond angles* (°)

The average e.s.d. is 0·9°.

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
2–1–10	112	111	1–10–19	108	110
1–2–3	111	112	9–10–19	114	115
2–3–4	111	112	9–11–12	111	111
2–3–O(1)	109	108	11–12–13	110	110
4–3–O(1)	108	109	12–13–14	105	105
3–4–5	112	113	12–13–18	112	111
4–5–6	120	120	14–13–18	113	114
4–5–10	116	115	8–14–13	114	112
6–5–10	124	125	8–14–15	115	117
5–6–7	125	125	13–14–15	103	102
6–7–8	112	112	14–15–16	101	103
6–7–O(2)	108	105	15–16–17	106	107
8–7–O(2)	107	108	13–17–16	103	102
7–8–9	112	110	13–17–20	117	114
7–8–14	109	108	16–17–20	109	110
9–8–14	106	105	10–19–O(3)	116	114
8–9–10	111	112	17–20–21	110	111
8–9–11	111	110	17–20–22	103	108
10–9–11	112	110	21–20–22	107	110
1–10–9	106	105	20–22–23	108	113

Table 3. *Bond distances* (Å)

The average e.s.d. is 0·01 Å.

	Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*		Molecule *A*	Molecule *B*
1–2	1·58	1·57	8–9	1·57	1·58	15–16	1·58	1·57
1–10	1·59	1·56	8–14	1·55	1·55	16–17	1·60	1·58
2–3	1·52	1·51	9–10	1·57	1·60	17–20	1·58	1·57
3–4	1·56	1·56	9–11	1·55	1·58	19–O(3)	1·42	1·43
3–O(1)	1·45	1·44	10–19	1·54	1·51	20–21	1·52	1·54
4–5	1·53	1·51	11–12	1·55	1·53	20–22	1·60	1·58
5–6	1·31	1·32	12–13	1·56	1·57	22–23	1·64	1·51
5–10	1·54	1·55	13–14	1·56	1·58			
6–7	1·55	1·53	13–17	1·57	1·58			
7–8	1·54	1·55	13–18	1·56	1·56			
7–O(2)	1·43	1·46	14–15	1·57	1·56			

Table 5. *Hydrogen-bond* (O—H···O′) *distances* (Å)

The hydrogen positions are calculated with H—O 1·08 Å and H—O—C 109°. The average e.s.d. for O—O′ is 0·01 Å.

O	O′	O—O′	H—O′	H—O[a]	*x*	*y*	*z*
O(1)*A*	O(2)*A*	2·84	1·85	1·84	0·53	0·19	0·05
O(2)*A*	O(2)*B*	2·75	1·78	1·93	0·52	0·72	−0·22
O(2)*B*	O(1)*B*	2·77	1·77	1·77	0·50	1·19	0·39
O(1)*B*	O(3)*B*	2·79	1·81	1·96	0·54	0·66	0·46
O(3)*B*	O(3)*A*	2·73	1·75	1·73	0·49	1·12	0·71
O(3)*A*	O(1)*A*	2·79	1·86	1·84	0·51	0·62	0·09

(*a*) Values corresponding to the alternative, less probable, hydrogen-bond system.

OH groups are involved in hydrogen bonding (Table 5). The positions of the six H atoms of the OH groups were not clearly indicated as individual peaks in the difference Fourier map but their expected positions were at positive electron densities. The expected positions for the six H atoms (Table 5) were obtained by rotating the hydroxyls about their C—O bonds and examining neighbouring interactions. One other possibility for the hydrogen-bond system can be created by substituting O′—H···O for O—H···O′ (Table 5). However, this possibility corresponds to lower electron density at the sites of H, and two of the H···O distances are too long compared with their O—O′ distances. It is notable that even if the conformations of the two independent molecules were equal, the space group could not be transformed into *A*2 without assumption of disorder in the hydrogen-bond system.

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Three Crystal Structures of 1*β*-(*p*-Methoxybenzyl)-9*α*,10*β*-dihydroxydecahydroisoquinoline and 1*β*-(*p*-Methoxybenzyl)-9*β*,10*α*-dihydroxydecahydroisoquinoline, $C_{17}H_{25}NO_3$*

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The first isomer (9α,10β) of the title compound has two crystal forms: (I*A*) is orthorhombic, $Pna2_1$, $a = 8{\cdot}571$ (4), $b = 30{\cdot}754$ (2), $c = 5{\cdot}957$ (2) Å, $Z = 4$; and (I*B*) is orthorhombic, $P2_12_12_1$, $a = 8{\cdot}730$ (5), $b = 30{\cdot}094$ (4), $c = 5{\cdot}950$ (2) Å, $Z = 4$. Crystals of the 9β,10α isomer (II) are triclinic, $P\bar{1}$, $a = 9{\cdot}467$ (3), $b = 14{\cdot}132$ (3), $c = 5{\cdot}983$ (3) Å, $\alpha = 101{\cdot}93$ (4), $\beta = 94{\cdot}18$ (4), $\gamma = 85{\cdot}05$ (4)°, $Z = 2$. Their structures have been refined to $R = 0{\cdot}048$, 0·069, 0·041 for the 928, 1259, 2517 observed reflexions of (I*A*), (I*B*), and (II) respectively. In each of the three structures, the isoquinoline consists of two *trans*-fused six-membered rings in the chair form, and the methoxybenzyl is nearly planar. The latter is axial to the isoquinoline in (I*A*) and (I*B*), and equatorial in (II). The terminal methyl group is $\rangle$C—O$^{\diagup CH_3}$ in (I*A*) and $\rangle$C—O$_{\diagdown CH_3}$ in (I*B*), with approximately 180° rotation about the $\rangle$C—O bond and a slight shift of O in the plane of the aromatic ring. Each molecule has an intramolecular O—H···N bond, and the molecules in each structure are interlinked by O—H···O bonds into endless chains parallel to *c*, the shortest axis.

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