4β,5β-Epoxycholestan-6-one

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Abstract. $C_{27}O_2H_{44}$, orthorhombic, $P2_12_12_1$, $a = 30.29$ (1), $b = 10.929$ (5), $c = 7.559$ (5) Å, $M_r = 400$, $Z = 4$. The structure was refined to an R of 0.050 for 1196 counter reflections. Ring A is *cis* fused to ring B whilst the remaining rings are *trans* fused, the side chain being in an extended configuration.

Introduction. The compound was prepared from cholest-4-en-6-one by reaction with alkaline hydrogen peroxide in methanol.

A crystal 0.6 × 0.3 × 0.25 mm was used for data collection. The cell parameters were obtained by least

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Table 1. *Fractional atomic coordinates* ($\times 10^4$) *of the heavy atoms*

	x	y	z
C(1)	−106 (3)	3138 (8)	3145 (10)
C(2)	−467 (3)	2238 (8)	3664 (13)
C(3)	−720 (3)	2649 (9)	5289 (16)
C(4)	−455 (3)	3269 (7)	6655 (14)
C(5)	28 (2)	3560 (6)	6323 (11)
C(6)	323 (3)	3593 (7)	7938 (11)
C(7)	616 (3)	2494 (7)	8123 (8)
C(8)	858 (2)	2205 (6)	6397 (9)
C(9)	533 (2)	2111 (6)	4844 (9)
C(10)	249 (2)	3286 (7)	4574 (10)
C(11)	770 (2)	1712 (7)	3178 (9)
C(12)	1060 (2)	565 (7)	3384 (9)
C(13)	1385 (2)	680 (6)	4934 (8)
C(14)	1105 (2)	996 (6)	6529 (8)
C(15)	1411 (2)	831 (7)	8114 (9)
C(16)	1707 (2)	−262 (7)	7548 (9)
C(17)	1599 (2)	−530 (6)	5554 (8)
C(18)	1741 (2)	1652 (7)	4537 (11)
C(19)	528 (3)	4408 (7)	4112 (13)
C(20)	2004 (2)	−1040 (7)	4557 (10)
C(21)	1919 (2)	−1205 (8)	2579 (10)
C(22)	2140 (2)	−2260 (6)	5384 (10)
C(23)	2592 (2)	−2724 (7)	4853 (11)
C(24)	2734 (2)	−3872 (7)	5808 (11)
C(25)	3216 (3)	−4242 (9)	5478 (13)
C(26)	3348 (3)	−5214 (10)	6808 (16)
C(27)	3295 (3)	−4651 (10)	3600 (15)
O(4)	−302 (2)	4503 (5)	6274 (9)
O(6)	320 (2)	4427 (6)	8995 (9)

squares from the settings of 25 reflections measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, graphite monochromated), $\omega-2\theta$ scan mode (scan width 0.4° θ, scan speed 0.01° θ s^{-1}). 1400 reflections were collected in the range 3° < θ < 20° of which 1196 unique reflections had $I_{(\text{rel})} > 2\sigma I_{(\text{rel})}$ and were considered observed. The intensities of three standard reflections measured every hour remained constant to within 0.71% of their mean values. Lorentz–polarization corrections were applied, but none for absorption. The structure was solved by a multisolution tangent refinement with *SHELX*. A starting set of eight reflections generated 128 permutations. The calculated E maps were ranked by R_A (Sheldrick, 1977) and an E map ($R_A = 0.099$) yielded the positions of all the non-hydrogen atoms. Subsequent refinement with all these atoms isotropic yielded the positions of 36 of the H atoms on a difference map.

The structure was finally refined with anisotropic temperature factors for all the non-hydrogen atoms, the methyl H as rigid groups and the remaining H atoms constrained at 1.08 Å from their respective C atoms, their orientations being dictated by the geometry of the molecule. The isotropic temperature factor for the methyl H refined to 0.146 and for the remaining H

Table 2. *Bond lengths* (Å)

C(1)–C(10)	1.53 (1)	C(15)–C(14)	1.53 (1)
C(2)–C(1)	1.52 (1)	C(16)–C(15)	1.56 (1)
C(3)–C(2)	1.52 (1)	C(16)–C(17)	1.57 (1)
C(3)–C(4)	1.47 (1)	C(17)–C(13)	1.55 (1)
C(4)–C(5)	1.52 (1)	C(18)–C(13)	1.54 (1)
C(4)–O(4)	1.46 (1)	C(19)–C(10)	1.53 (1)
C(6)–C(5)	1.51 (1)	C(20)–C(17)	1.55 (1)
C(7)–C(6)	1.50 (1)	C(21)–C(20)	1.53 (1)
C(7)–C(8)	1.53 (1)	C(22)–C(20)	1.53 (1)
C(9)–C(8)	1.54 (1)	C(23)–C(22)	1.51 (1)
C(9)–C(10)	1.56 (1)	C(24)–C(23)	1.51 (1)
C(10)–C(5)	1.51 (1)	C(24)–C(25)	1.53 (1)
C(11)–C(9)	1.52 (1)	C(26)–C(25)	1.52 (1)
C(12)–C(11)	1.54 (1)	C(27)–C(25)	1.51 (1)
C(12)–C(13)	1.54 (1)	O(4)–C(5)	1.44 (1)
C(14)–C(8)	1.52 (1)	O(6)–C(6)	1.21 (1)
C(14)–C(13)	1.52 (1)		

Table 3. Bond angles (°)

C(2)–C(1)–C(10)	113·0 (8)	C(19)–C(10)–C(9)	112·8 (6)
C(3)–C(2)–C(1)	112·4 (9)	C(12)–C(11)–C(9)	115·0 (7)
C(2)–C(3)–C(4)	115·5 (8)	C(11)–C(12)–C(13)	112·1 (7)
C(3)–C(4)–C(5)	120 (1)	C(12)–C(13)–C(14)	105·4 (6)
C(3)–C(4)–O(4)	118 (1)	C(12)–C(13)–C(17)	115·5 (7)
O(4)–C(4)–C(5)	57·7 (5)	C(17)–C(13)–C(14)	100·9 (6)
C(4)–C(5)–C(6)	116·2 (9)	C(18)–C(13)–C(12)	110·8 (7)
C(4)–C(5)–C(10)	122·0 (9)	C(18)–C(13)–C(14)	112·9 (7)
C(4)–C(5)–O(4)	59·0 (5)	C(18)–C(13)–C(17)	110·9 (6)
C(10)–C(5)–C(6)	116·6 (7)	C(8)–C(14)–C(13)	114·9 (7)
O(4)–C(5)–C(6)	114·5 (8)	C(15)–C(14)–C(8)	116·9 (7)
O(4)–C(5)–C(10)	115·3 (8)	C(15)–C(14)–C(13)	104·9 (5)
C(7)–C(6)–C(5)	114·0 (8)	C(16)–C(15)–C(14)	103·0 (7)
C(7)–C(6)–O(6)	123 (1)	C(15)–C(16)–C(17)	106·7 (7)
O(6)–C(6)–C(5)	123·0 (9)	C(16)–C(17)–C(13)	102·7 (7)
C(8)–C(7)–C(6)	111·7 (7)	C(16)–C(17)–C(20)	111·7 (7)
C(7)–C(8)–C(9)	110·9 (6)	C(20)–C(17)–C(13)	119·6 (7)
C(7)–C(8)–C(14)	111·0 (7)	C(21)–C(20)–C(17)	112·6 (7)
C(14)–C(8)–C(9)	107·9 (6)	C(21)–C(20)–C(22)	110·1 (9)
C(8)–C(9)–C(10)	113·5 (7)	C(22)–C(20)–C(17)	109·2 (7)
C(11)–C(9)–C(8)	110·5 (6)	C(23)–C(22)–C(20)	115·3 (7)
C(11)–C(9)–C(10)	113·0 (7)	C(24)–C(23)–C(22)	114·2 (7)
C(1)–C(10)–C(5)	109·0 (7)	C(23)–C(24)–C(25)	114·4 (8)
C(1)–C(10)–C(9)	113·1 (8)	C(26)–C(25)–C(24)	109 (1)
C(9)–C(10)–C(5)	107·0 (7)	C(27)–C(25)–C(24)	112·5 (9)
C(19)–C(10)–C(1)	108·1 (8)	C(27)–C(25)–C(26)	112 (1)
C(19)–C(10)–C(5)	106·6 (8)	C(4)–O(4)–C(5)	63·4 (5)

atoms to 0·107 Å². The refinement converged to $R_w = \Sigma w^{1/2}|F_o - F_c|/\Sigma w^{1/2}|F_o| = 0·054$ and $R = 0·055$ with $w = 1/\sigma^2$. Final coordinates for the non-hydrogen atoms are given in Table 1 and bond lengths and angles in Tables 2 and 3 respectively.[*]

Discussion. The title compound (Figs. 1 and 2) differs conformationally from its parent cholest-4-en-6-one

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[*] Lists of hydrogen atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32847 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
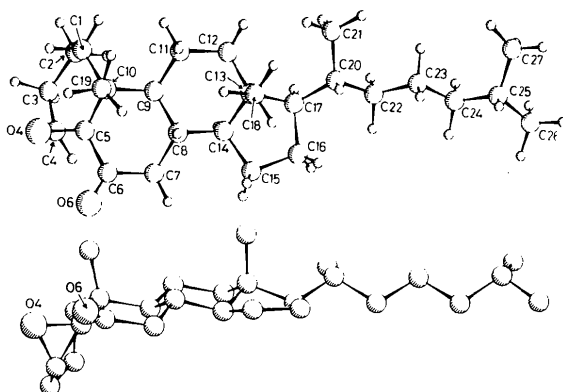
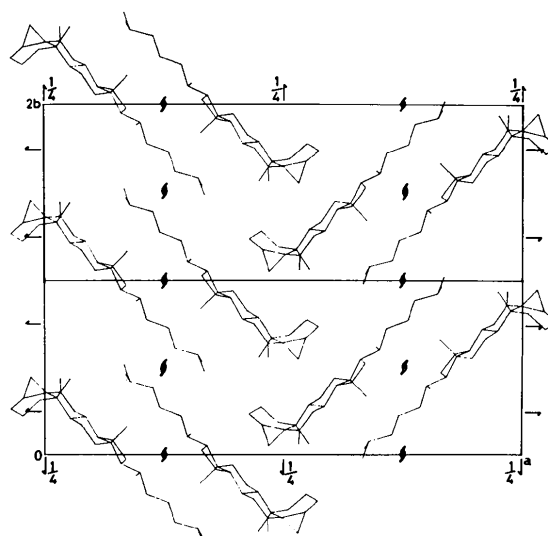Fig. 1. Perspective views of the molecule with atomic nomenclature.

Fig. 2. |001| projection of the structure.

Table 4. Least-squares plane calculation for ring A

The equation of the plane is expressed in orthogonalized space as $lX + mY + nZ = P$. d is the perpendicular distance (Å) from the plane. Atoms marked with an asterisk are those included in the least-squares plane calculation.

$$-0·2810X + 0·8665Y - 0·4126Z = 1·4241$$

	d		d
C(1)	0·657	C(4)	−0·017
C(2)*	−0·049	C(5)*	−0·048
C(3)*	0·048	C(10)*	0·049

(Nassimbeni, Russell & Cragg, 1977) in the A ring and at the A/B ring juncture. The quasi-trans fused A ring of the parent compound becomes a cis fused ring on epoxidation. The conformation of the A ring of the title compound approximates to a 1β-sofa, mirror symmetry about C(1)–C(4) dominating, asymmetry parameter: $\Delta C_s^1 = 12·5°$ (Duax & Norton, 1975). Mean-plane calculations for ring A are shown in Table 4. Ring B has a highly symmetrical chair conformation with all asymmetry parameters below 7°. Ring C also has a symmetrical chair conformation, mirror symmetry about C(11)–C(14) predominating, $\Delta C_s^{11} = 1·1°$. Ring D has the common intermediate conformation lying between a 13β,14α-half chair and a 13β-envelope with pseudorotation parameters (Altona, Geise & Romers, 1968): $\Delta = 13·5°$ and $\varphi_{max} = 47·7°$. The extended side chain lies approximately in the same plane as rings B, C and D.

All calculations were performed on a Univac 1106 computer system at the University of Cape Town. We thank the University for research grants and the CSIR (Pretoria) for the use of the diffractometer.

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Silber(I)-disilicat

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Abstract. $Ag_6Si_2O_7$, monoclinic, $P2/n$ (No. 13), $a = 10 \cdot 264$ (4), $b = 5 \cdot 259$ (3), $c = 8 \cdot 052$ (4) Å, $\beta = 110 \cdot 5$ (1)°, $Z = 2$, $D_o = 6 \cdot 58$, $D_c = 6 \cdot 655$ g cm^{-3}. The structure was solved by direct methods (Ag positions) and Fourier syntheses; the final R value was $6 \cdot 2\%$. Bond lengths and angles of $Si_2O_7^{6-}$ are in agreement with those in earlier investigated disilicates; the relevant Ag—O distances range from $2 \cdot 18$ to $2 \cdot 76$ Å.

Einleitung. Wegen der thermischen Zersetzlichkeit von Ag_2O waren Silbersilicate bisher nur über topochemische Reaktionen von geschmolzenem $AgNO_3$ mit Alkalisilicaten zugänglich (Thilo & Wodtke, 1958; Wodtke & Jost, 1962; Liebau, 1961). Die Anwendung hoher Sauerstoffdrucke ermöglicht es, Silbersilicate auf direktem Wege durch Umsetzung von Ag_2O mit SiO_2 zu synthetisieren; durch Vergleich der so erhaltenen Silicate mit den durch Ionenaustausch dargestellten soll festgestellt werden, inwieweit Zusammensetzung und Aufbau der bis jetzt bekannten Silbersilicate durch das ursprüngliche Alkalisilicat bestimmt sind. Bei diesen Untersuchungen wurde das vorher unbekannte $Ag_6Si_2O_7$ in Form leuchtend roter, unregelmässig gewachsener Einkristalle erhalten. Zur Darstellung wurden Gemenge von Silber(I)-oxid und Tiefquarz im molaren Verhältnis von 3:1 intensiv vermahlen (Achatkugelmühle) und anschliessend in einem gegen Sauerstoff resistenten Stahlautoklaven erhitzt ($t = 580°C$, $P_{O_2} = 2000$ atm, Reaktionsdauer $= 6$ d, Aufheizrate $= 5°$ min^{-1}, Abkühlrate $= 1°$ min^{-1}). Für die röntgenographischen Untersuchungen wurde ein Einkristall mit einem Durchmesser von ungefähr 0,07 mm ausgewählt: Metrik und Symmetrie wurden aus einem vollständigen Satz von Filmaufnahmen bestimmt, während die Intensitätsmessung mit einem automatischen Vierkreisdiffraktometer vorgenommen wurde (PW 1100, Mo $K\alpha$, $\omega/2\theta$-Abtastung, $0,04°$

s^{-1}, Graphitmonochromator, $4° < \theta < 35°$, 1761 unabhängige Reflexe). Es wurde eine Lorentz- und Polarisationsfaktor-Korrektur, jedoch keine Absorptionskorrektur durchgeführt ($\mu R \simeq 0,47$). Die Schweratomlagen wurden mittels direkter Methoden (Sheldrick, 1976) ermittelt, Si- und O-Positionen entnahm man anschliessenden ($F_o - F_c$)- und F_o-Fouriersynthesen. Die Orts- und anisotropen Temperaturparameter wurden nach der Methode der kleinsten Quadrate mit vollständiger Matrix verfeinert. 351 Reflexe mit $I < \sigma(I)$ wurden hierbei nicht berücksichtigt, gewichtet wurde mit $w = k/[\sigma^2(F_o) + gF_o^2]$, σ aus der Zählstatistik, k und g wurden gegen Ende der Verfeinerung (Änderung der Orts- und Temperaturparameter $< 1/10$ der Standardabweichungen) freigegeben und konvergierten gegen 1,32 bzw. 0,00053 (Sheldrick, 1976). Atomformfaktoren sowie Korrekturen bezüglich der anomalen Dispersion wurden den Arbeiten von Cromer & Mann (1968) sowie Cromer & Liberman (1970) entnommen. Die endgültigen R-Werte betragen $R_w = \Sigma w^{1/2}|F_o - F_c|/\Sigma w^{1/2}|F_o| = 0,060$, $R = \Sigma |F_o - F_c|/\Sigma |F_o| =$

Tabelle 1. *Atomkoordinaten* ($\times 10^4$) *und isotrope Temperaturfaktoren*, $\exp(-8\pi^2 U \sin^2 \theta/\lambda^2)$, *mit Standardabweichungen in Klammern*

	x	y	z	U (Å$^2 \times 10^3$)
Ag(1)	1323 (1)	2276 (2)	5800 (1)	244
Ag(2)	6000 (1)	3018 (2)	2871 (1)	208
Ag(3)	3851 (1)	2425 (2)	4495 (1)	227
Si	−1380 (2)	2816 (5)	6628 (3)	115
O(1)	6338 (7)	5915 (14)	−1801 (9)	182
O(2)	5142 (7)	8395 (15)	2694 (9)	192
O(3)	6882 (7)	1986 (15)	435 (9)	193
O(4)	2500	8313 (16)	2500	206