Interestingly, de Kok & Romers (1978) observed no forbidden H···H interactions in the totally disordered structure of *trans*-tetrachlorostilbene, in which the two molecules are present in a 1:1 ratio. Tentatively, we conclude that the mentioned packing rules are totally fulfilled in this compound and nearly so in AHCA and DMPC.

The authors thank Dr G. I. Birnbaum for his willingness to put at our disposal the diffraction data of dimethyl 1-hydroxy-1-cycloheptanephosphonate.

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The Structure of Chenodeoxycholic Acid, $C_{24}H_{40}O_4$

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(*Received* 23 *July* 1979; *accepted* 28 *February* 1980)

Abstract

Crystals of the high-melting polymorph (m.p. 438–439 K) of chenodeoxycholic acid are monoclinic, space group $P2_1$, with $a = 18{\cdot}785\ (14)$, $b = 8{\cdot}120\ (6)$, $c = 14{\cdot}889\ (11)$ Å, $\beta = 99{\cdot}10\ (2)°$ and $Z = 4$. The structure has been refined to a residual of 0·069 for 3266 independent significant reflections measured on an automated four-circle diffractometer. The two molecules in the asymmetric unit are typical of the bile acids with *cis A/B* ring junctions, but are different from each other with respect to the conformations of the 17β side chains. In the crystal all the hydroxyl and carboxyl groups are involved in a hydrogen-bonding network.

Introduction

In recent years there has been a resurgence of interest in the bile acid field. This is related to the introduction of chenodeoxycholic acid (CDCA) as a chemotherapeutic alternative to surgery in the treatment of gallstones (Dowling & Bell, 1973; Danziger, Hofmann, Thistle & Schoenfield, 1973).

Its ingestion in suitable quantity alters the composition of bile so that it becomes the dominant bile

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0567-7408/80/081893-05$01.00

acid moiety. This change increases the capacity of bile to accept and retain cholesterol in solution and hence provides the possibility of solubilizing radiolucent (cholesterol-rich) gallstones.

The interest in the clinical possibilities of CDCA has raised the need for more information about the chemistry, pharmacology and toxicology of the free acid, as opposed to the physiologically occurring bile salts. CDCA rapidly enters the enterohepatic circulation and a large proportion is converted to bile salt on its first pass through the liver.

The bile acids are derived from cholesterol and are related to the steroids. They exist in nature as amides of the amino acids glycine and taurine. The sodium/potassium salts of these substituted amides constitute the naturally occurring bile salts. The water-insoluble bile acids are obtained by acidification of alkaline hydrolysates of bile. The alkali-metal salts of the acids are soluble in water but are not to be confused with the bile salts.

Bile salts occur in the bile of all animals, although the bile acid portions vary from species to species. The primary bile acids of man are cholic acid and chenodeoxycholic acid, respectively the 3α,7α,12α-trihydroxy and 3α,7α-dihydroxy derivatives of 5β-cholanic acid. The secondary bile acids, deoxycholic (DCA) and lithocholic acids, are formed by bacterial degradation of the primary acids involving loss of the 7α-hydroxyl group.

The function of bile salts is the emulsification of fats and other lipids in the intestine to promote their passage through the lumen of the gut. The primary requirement for this is detergent power and all di- and trihydroxy bile acids have this property. DCA is strongly detergent and also has the characteristic of forming clathrate complexes to a remarkable degree. X-ray crystal studies have shown that the molecules are aligned to form channels in which the foreign molecules are held. True polymorphic forms of DCA have not been reported.

The structures of lithocholic acid (Arora, Germain & Declercq, 1976), cholic acid (Johnson & Schaefer, 1972) and several isomeric 3,12-dihydroxy acids are already known. Polymorphism of CDCA has been reported (Giuseppetti & Paciotti, 1978) but no crystallographic structure work has been done. The low-melting polymorph of CDCA is known to retain solvent very tenaciously and it would be of interest to know whether structural similarities exist between this crystal form and that of DCA. However, although small crystals of this polymorph have been obtained, none were suitable for an X-ray analysis since the diffraction patterns indicating hexagonal symmetry showed signs of disorder and faded out at a θ value of around 20°.

We report here the X-ray single-crystal structure analysis of the high-melting polymorph, m.p. 438–439 K.

Experimental

The high-melting polymorph of CDCA crystallizes from acetonitrile in the form of prismatic crystals. Preliminary unit-cell and space-group information was obtained from precession photographs. Accurate cell dimensions were obtained by least-squares refinement of the θ values of the Cu $K\alpha_1$ components ($\lambda = 1{\cdot}5405$ Å) of 20 reflections on a Hilger & Watts Y290 automated four-circle diffractometer. Intensity data were also collected on this instrument with Ni-filtered Cu radiation. The ω–2θ step scanning technique was used with steps of 0·01° in ω at 1 s step^{-1} and a step width of 0·70° plus a dispersion correction; stationary background counts were measured at both ends of each scan for one tenth of the scan time. Gradual variations in the experimental conditions during data collection were monitored by measuring three reference reflections every 50 reflections and the intensity sums of the reference reflections were used to scale the observed intensities by interpolation between groups of references; the overall variation in the reference sum was 1·5%.

A total of 5825 reflections were measured over the range $1° \le \theta \le 70°$. Averaging of the symmetry-related reflections (563 reflections with an agreement residual of 0·027) yielded 4751 reflections of which 3266 had $I/\sigma(I) \ge 3$ and were thereby classified as significant. The data were corrected for Lorentz and polarization effects but not for absorption; μ(Cu $K\alpha$) = 0·61 mm^{-1}.

Crystal data

$C_{24}H_{40}O_4$, $M_r = 392{\cdot}3$, monoclinic, $a = 18{\cdot}785$ (14), $b = 8{\cdot}120$ (6), $c = 14{\cdot}889$ (11) Å, $\beta = 99{\cdot}10$ (2)°, $D_c = 1{\cdot}162$ Mg m^{-3}, $Z = 4$, $F(000) = 864$; space group $P2_1$ (C_2^2, No. 4).

Structure solution and refinement

The structure was solved by a Patterson space vector verification technique (Braun, Hornstra & Leenhouts, 1969) after numerous attempts using weighted multi-solution tangent-formula refinements had proved unsuccessful. The input model for the vector verification method consisted of 19 atoms and was taken from the steroid nucleus of 5β-androstane-3α,17β-diol (Weeks, Cooper, Norton, Hauptman & Fisher, 1971); it comprised rings *A*, *B*, *C*, *D*, C(18) and C(19). The best solution enabled molecule (I) in the asymmetric unit to be located but no solution was found corresponding to molecule (II). The remaining non-hydrogen atom positions in molecule (I) and the whole of molecule (II) were obtained by the iterative Fourier synthesis technique using weighted coefficients (Sim, 1959).

Full-matrix least-squares refinement with all atoms treated isotropically and using only the significant reflections gave an R value of 0·141. A difference Fourier synthesis revealed diffuse electron density maxima, 0·2–0·5 e Å^{-3}, corresponding to the H atoms, except for those in the hydroxyl and carboxyl groups. In subsequent calculations the H atoms were placed in calculated positions with a C–H bond length of 1·0 Å and no attempt was made to refine their positional or thermal parameters (arbitrarily assessed as $U = 0{\cdot}10$ Å^2).

Further refinement with the non-hydrogen atoms treated anisotropically proceeded by a partial full-matrix refinement technique. Molecules (I) and (II) were refined in alternate cycles to give final values of $R = 0{\cdot}069$ and $R' = 0{\cdot}093$. Weights were assigned to the observed structure factors according to the function $w = [1 - \exp(-20 \sin^2 \theta/\lambda^2)]/(10 + |F_o| + 0{\cdot}005|F_o|^2)$ during refinement and a final weighting analysis showed uniform average values of $\sum w\Delta^2$ when analysed in batches of increasing $|F_o|$ and $\sin\theta/\lambda$. A final difference map confirmed the correctness of the refinement and a satisfactory tensor analysis of the anisotropic thermal-vibration parameters was obtained in all cases. Throughout the structure factor calculations the atomic scattering factors listed by Hanson, Herman, Lea & Skillman (1964) were used and all computations were performed on the CDC 6600 computer at the University of London Computing Centre. The final atomic coordinates for the non-hydrogen atoms are shown in Table 1.*

Discussion

The intramolecular bond lengths and angles and other details of the molecular geometry for both molecules in the asymmetric unit are given in Tables 2 and 3. In both molecules, (I) and (II), the geometry of the steroid nucleus is that expected for a cholane derivative. Rings *A*, *B* and *C* adopt chair conformations characterized by the following asymmetry parameters (Duax & Norton,

* Lists of structure factors, anisotropic thermal parameters and calculated H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35240 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters: fractional coordinates of non-hydrogen atoms with estimated standard deviations in parentheses*

	x	y	z	$\bar{U}$ (×10^3)†		x	y	z	U_{ii} (Å^2 ×10^3)
Molecule (I)					Molecule (II)				
C(1)	−0·0066 (3)	0·2144*	0·1520 (5)	61	C(1)	0·3996 (3)	0·3398 (9)	0·4532 (4)	49
C(2)	0·0581 (5)	0·2317 (10)	0·1033 (5)	66	C(2)	0·3760 (3)	0·5120 (9)	0·4205 (4)	49
C(3)	0·0649 (5)	0·0826 (12)	0·0439 (4)	75	C(3)	0·2961 (3)	0·5125 (9)	0·3844 (4)	45
C(4)	0·0688 (4)	−0·0733 (10)	0·0998 (4)	57	C(4)	0·2783 (3)	0·3827 (8)	0·3111 (4)	39
C(5)	0·0049 (3)	−0·0923 (10)	0·1522 (4)	51	C(5)	0·3040 (3)	0·2113 (8)	0·3401 (4)	45
C(6)	0·0092 (3)	−0·2523 (9)	0·2068 (4)	51	C(6)	0·2845 (3)	0·0858 (9)	0·2628 (5)	50
C(7)	0·0665 (3)	−0·2528 (7)	0·2913 (3)	38	C(7)	0·3310 (3)	0·0982 (9)	0·1869 (4)	46
C(8)	0·0621 (3)	−0·0980 (7)	0·3486 (3)	34	C(8)	0·4113 (3)	0·0986 (8)	0·2273 (4)	39
C(9)	0·0570 (3)	0·0633 (8)	0·2929 (3)	35	C(9)	0·4305 (3)	0·2252 (8)	0·3033 (4)	37
C(10)	−0·0061 (3)	0·0587 (10)	0·2107 (4)	47	C(10)	0·3853 (3)	0·2035 (8)	0·3812 (4)	41
C(11)	0·0552 (4)	0·2118 (9)	0·3534 (4)	50	C(11)	0·5121 (3)	0·2304 (10)	0·3376 (4)	52
C(12)	0·1172 (3)	0·2182 (8)	0·4342 (4)	41	C(12)	0·5578 (3)	0·2447 (10)	0·2607 (4)	52
C(13)	0·1210 (2)	0·0635 (7)	0·4907 (3)	29	C(13)	0·5400 (3)	0·1089 (8)	0·1903 (4)	39
C(14)	0·1251 (3)	−0·0847 (7)	0·4271 (3)	32	C(14)	0·4594 (3)	0·1254 (8)	0·1537 (4)	37
C(15)	0·1426 (3)	−0·2312 (8)	0·4914 (4)	41	C(15)	0·4474 (3)	0·0177 (10)	0·0701 (4)	57
C(16)	0·1913 (3)	−0·1544 (9)	0·5738 (4)	45	C(16)	0·5171 (3)	0·0411 (10)	0·0281 (4)	55
C(17)	0·1921 (3)	0·0327 (7)	0·5587 (3)	35	C(17)	0·5714 (3)	0·1328 (8)	0·0997 (4)	39
C(18)	0·0562 (3)	0·0533 (9)	0·5423 (4)	48	C(18)	0·5596 (4)	−0·0620 (10)	0·2296 (5)	63
C(19)	−0·0793 (3)	0·0528 (14)	0·2424 (5)	74	C(19)	0·4021 (4)	0·0403 (10)	0·4308 (5)	68
C(20)	0·2058 (3)	0·1318 (9)	0·6483 (4)	49	C(20)	0·6497 (3)	0·0826 (8)	0·0948 (3)	43
C(21)	0·2125 (5)	0·3181 (11)	0·6307 (5)	73	C(21)	0·7041 (3)	0·1583 (12)	0·1712 (4)	66
C(22)	0·2723 (3)	0·0671 (11)	0·7087 (4)	57	C(22)	0·6688 (3)	0·1289 (9)	0·0016 (4)	47
C(23)	0·2921 (4)	0·1416 (12)	0·8029 (5)	72	C(23)	0·7451 (3)	0·0854 (9)	−0·0115 (4)	47
C(24)	0·2436 (6)	0·1196 (12)	0·8695 (4)	82	C(24)	0·7622 (3)	0·1279 (8)	−0·1037 (4)	40
O(3)	0·1262 (5)	0·0940 (12)	−0·0013 (4)	129	O(3)	0·2720 (2)	0·6718 (6)	0·3517 (3)	46
O(7)	0·1353 (2)	−0·2686 (6)	0·2636 (2)	45	O(7)	0·3114 (2)	0·2430 (7)	0·1339 (3)	49
O(24-1)	0·1849 (4)	0·0424 (19)	0·8475 (5)	156	O(24-1)	0·8279 (2)	0·0872 (7)	−0·1137 (3)	59
O(24-2)	0·2628 (8)	0·1585 (17)	0·9469 (5)	206	O(24-2)	0·7200 (3)	0·1964 (6)	−0·1626 (3)	53

* Held constant.

† $\bar{U}$ is the spherical average of U_{ii} (Å^2).

1975): ring *A*, molecule (I), $\Delta C_2^{2-3} = 1{\cdot}43$, $\Delta C_s^2 = 2{\cdot}40$, $\Delta C_s^1 = 4{\cdot}55°$, molecule (II), $\Delta C_s^2 = 2{\cdot}62$, $\Delta C_2^{2-3} = 3{\cdot}13$, $\Delta C_2^{3-4} = 6{\cdot}71°$; ring *B*, molecule (I), $\Delta C_s^7 = 1{\cdot}14$, $\Delta C_2^{7-8} = 3{\cdot}26$, $\Delta C_2^{5-6} = 7{\cdot}90°$, molecule (II), $\Delta C_s^7 = 1{\cdot}28$, $\Delta C_2^{6-7} = 2{\cdot}33$, $\Delta C_2^{5-8} = 4{\cdot}58°$; ring *C*, molecule (I), $\Delta C_s^9 = 2{\cdot}50$, $\Delta C_2^{9-11} = 2{\cdot}70$, $\Delta C_2^{11-12} = 4{\cdot}27°$, molecule (II), $\Delta C_2^{9-11} = 2{\cdot}93$, $\Delta C_s^9 = 3{\cdot}81$, $\Delta C_s^8 = 9{\cdot}50°$. The *A*/*B* ring junction is *cis* in both molecules with the sums of the absolute values of the endocyclic torsion angles being $C_1 = 106{\cdot}4°$ for (I) and $C_1 = 103{\cdot}9°$ for (II). The *B*/*C* ring junctions are *trans* with $T_2 = 101{\cdot}0°$ for (I) and $T_2 = 100{\cdot}4°$ for (II).

The *C*/*D* ring junction is again *trans* with $T_3 = 105{\cdot}6°$ for (I) and $T_3 = 109{\cdot}4°$ for (II), but the *D* ring adopts a slightly different conformation in the two molecules. In molecule (I) the pseudorotational phase parameters (Altona, Geise & Romers, 1968) are $\Delta = 18{\cdot}3°$ and $\varphi_m = 48{\cdot}3°$, indicating a conformation midway between a 13β,14α half-chair ($\Delta = 0°$) and a 13β envelope ($\Delta = 36°$). For molecule (II) the half-chair conformation predominates with $\Delta = 7{\cdot}0°$ and $\varphi_m = 46{\cdot}9°$.

Arora, Germain & Declercq (1976) have noted that the C—O bond length of a hydroxyl group attached to a steroid nucleus tends to be slightly shorter, 1·425 Å, if the hydroxyl group is involved in hydrogen bonding than otherwise, 1·450 Å. The C(3)—O(3) and C(7)—O(7) bond lengths, average value 1·428 Å, and all of which are involved in intermolecular hydrogen bonding in CDCA, are consistent with this observation.

From a consideration of the torsion angles in the 17β side chains of other cholane compounds the above authors have also suggested that intermolecular hydrogen bonding *via* the carboxyl group is associated with the conformation about the C(20)—C(22) bond; a synclinal conformation is favourable but antiperiplanarity indicates a lack of such bonding. Thus in lithocholic acid (Arora, Germain & Declercq, 1976) and 3α,12α-dihydroxy-5β-cholan-24-oic acid (Candeloro De Sanctis, Giglio, Pavel & Quagliata, 1972) where the torsion angles C(17)—C(20)—C(22)—C(23) are 64 and 62° respectively the carboxyl groups are involved in hydrogen bonding, but not in 3α,6α-dihydroxy-5β-cholan-24-oic acid (Hall, Maslen & Cooper, 1974), 4′-bromo-3α,12α-dihydroxy-5β-cholan-24-anilide (Schaefer & Reed, 1972) and cholic acid (Johnson & Schaefer, 1972) where the conformation is antiperiplanar [the mean C(17)—C(20)—C(22)—C(23) torsion angle is −175°]. Both molecules of CDCA are anomalous in this respect since they have complete intermolecular hydrogen bonding and yet the torsion angles C(17)—C(20)—C(22)—C(23) are −176 and 180° for molecules (I) and (II) respectively.

In the 17β side chain of CDCA the H atoms at C(17) and C(20) are in an antiperiplanar conformation. C(22) is antiperiplanar with respect to the

Table 2. *Intramolecular bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)
C(1)–C(2)	1·517 (11)	1·524 (10)	C(8)–C(14)	1·531 (7)	1·541 (7)	C(14)–C(15)	1·529 (8)	1·509 (8)
C(2)–C(3)	1·517 (12)	1·513 (8)	C(9)–C(10)	1·565 (7)	1·552 (7)	C(15)–C(16)	1·542 (8)	1·549 (9)
C(3)–O(3)	1·425 (10)	1·430 (8)	C(9)–C(11)	1·508 (9)	1·538 (7)	C(16)–C(17)	1·537 (9)	1·545 (8)
C(3)–C(4)	1·511 (11)	1·516 (9)	C(10)–C(1)	1·537 (8)	1·535 (10)	C(17)–C(20)	1·545 (7)	1·540 (7)
C(4)–C(5)	1·539 (10)	1·514 (9)	C(10)–C(19)	1·523 (8)	1·526 (9)	C(20)–C(21)	1·545 (12)	1·533 (9)
C(5)–C(10)	1·537 (10)	1·554 (8)	C(11)–C(12)	1·537 (8)	1·539 (8)	C(20)–C(22)	1·513 (9)	1·533 (7)
C(5)–C(6)	1·529 (10)	1·538 (9)	C(12)–C(13)	1·508 (8)	1·522 (9)	C(22)–C(23)	1·520 (9)	1·519 (8)
C(6)–C(7)	1·521 (8)	1·537 (8)	C(13)–C(14)	1·542 (7)	1·532 (7)	C(23)–C(24)	1·459 (12)	1·499 (7)
C(7)–O(7)	1·423 (6)	1·432 (8)	C(13)–C(17)	1·564 (7)	1·567 (7)	C(24)–O(24·1)	1·265 (13)	1·310 (7)
C(7)–C(8)	1·529 (8)	1·534 (7)	C(13)–C(18)	1·539 (6)	1·529 (10)	C(24)–O(24·2)	1·194 (10)	1·219 (7)
C(8)–C(9)	1·546 (8)	1·530 (8)						

	Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)		Molecule (I)	Molecule (II)
C(10)–C(1)–C(2)	114·5 (5)	115·4 (5)	C(8)–C(9)–C(11)	111·3 (4)	111·7 (5)	C(8)–C(14)–C(13)	114·6 (4)	113·0 (4)
C(1)–C(2)–C(3)	110·6 (6)	109·8 (5)	C(10)–C(9)–C(11)	113·6 (5)	112·9 (4)	C(8)–C(14)–C(15)	119·1 (5)	118·5 (5)
C(2)–C(3)–O(3)	111·8 (8)	111·5 (5)	C(1)–C(10)–C(5)	108·9 (4)	107·4 (5)	C(13)–C(14)–C(15)	104·5 (4)	104·7 (4)
C(2)–C(3)–C(4)	110·4 (5)	110·3 (5)	C(1)–C(10)–C(9)	111·2 (5)	112·6 (5)	C(14)–C(15)–C(16)	103·0 (5)	103·7 (5)
O(3)–C(3)–C(4)	110·0 (7)	111·3 (5)	C(1)–C(10)–C(19)	106·1 (6)	106·8 (5)	C(15)–C(16)–C(17)	107·6 (5)	106·7 (4)
C(3)–C(4)–C(5)	112·9 (6)	114·2 (5)	C(5)–C(10)–C(9)	108·0 (5)	108·6 (4)	C(13)–C(17)–C(16)	103·0 (4)	103·7 (4)
C(4)–C(5)–C(6)	112·1 (6)	111·6 (5)	C(5)–C(10)–C(19)	111·1 (6)	110·0 (5)	C(13)–C(17)–C(20)	119·0 (4)	120·0 (4)
C(4)–C(5)–C(10)	113·2 (6)	113·5 (5)	C(9)–C(10)–C(19)	111·5 (4)	111·4 (5)	C(16)–C(17)–C(20)	113·2 (5)	111·8 (5)
C(6)–C(5)–C(10)	112·2 (5)	111·8 (5)	C(9)–C(11)–C(12)	114·1 (5)	113·5 (5)	C(17)–C(20)–C(21)	111·8 (5)	112·9 (5)
C(5)–C(6)–C(7)	114·4 (5)	114·3 (5)	C(11)–C(12)–C(13)	111·8 (5)	111·7 (5)	C(17)–C(20)–C(22)	109·9 (5)	109·8 (4)
C(6)–C(7)–O(7)	108·5 (4)	109·4 (5)	C(12)–C(13)–C(14)	108·1 (4)	106·2 (4)	C(21)–C(20)–C(22)	111·1 (6)	110·5 (5)
C(6)–C(7)–C(8)	111·4 (5)	110·5 (5)	C(12)–C(13)–C(17)	117·1 (4)	115·6 (5)	C(20)–C(22)–C(23)	117·9 (7)	114·8 (5)
O(7)–C(7)–C(8)	111·6 (4)	111·5 (5)	C(12)–C(13)–C(18)	110·6 (5)	112·4 (5)	C(22)–C(23)–C(24)	119·4 (7)	114·0 (5)
C(7)–C(8)–C(9)	113·7 (4)	113·1 (4)	C(14)–C(13)–C(17)	98·7 (4)	99·7 (4)	C(23)–C(24)–O(24·1)	119·7 (6)	112·8 (5)
C(7)–C(8)–C(14)	112·4 (4)	111·8 (4)	C(14)–C(13)–C(18)	112·7 (4)	112·4 (5)	C(23)–C(24)–O(24·2)	119·8 (12)	123·7 (5)
C(9)–C(8)–C(14)	108·9 (4)	109·6 (4)	C(17)–C(13)–C(18)	109·3 (4)	110·0 (5)	O(24·1)–C(24)–O(24·2)	120·0 (11)	123·5 (5)
C(8)–C(9)–C(10)	111·9 (5)	112·6 (5)						

Table 3. *Torsion angles* (°) *for CDCA*

Estimated standard deviations are all less than 1·0°

	Molecule (I)	Molecule (II)
Ring *A*		
C(1)–C(2)–C(3)–C(4)	−56	−55
C(2)–C(3)–C(4)–C(5)	55	54
C(3)–C(4)–C(5)–C(10)	−53	−52
C(4)–C(5)–C(10)–C(1)	50	49
C(5)–C(10)–C(1)–C(2)	−53	−54
C(10)–C(1)–C(2)–C(3)	57	58
Ring *B*		
C(5)–C(6)–C(7)–C(8)	49	51
C(6)–C(7)–C(8)–C(9)	−48	−51
C(7)–C(8)–C(9)–C(10)	54	56
C(8)–C(9)–C(10)–C(5)	−56	−56
C(9)–C(10)–C(5)–C(6)	57	55
C(10)–C(5)–C(6)–C(7)	−55	−54
Ring *C*		
C(8)–C(9)–C(11)–C(12)	53	50
C(9)–C(11)–C(12)–C(13)	−55	−55
C(11)–C(12)–C(13)–C(14)	54	58
C(12)–C(13)–C(14)–C(8)	−58	−63
C(13)–C(14)–C(8)–C(9)	57	60
C(14)–C(8)–C(9)–C(11)	−52	−51
Ring *D*		
φ_4 C(13)–C(14)–C(15)–C(16)	−34	−36
φ_3 C(14)–C(15)–C(16)–C(17)	7	11
φ_2 C(15)–C(16)–C(17)–C(13)	23	17
φ_1 C(16)–C(17)–C(13)–C(14)	−42	−39
φ_0 C(17)–C(13)–C(14)–C(15)	48	47
17β Side-chain		
C(13)–C(17)–C(20)–C(21)	−64	−52
C(16)–C(17)–C(20)–C(21)	175	−176
C(13)–C(17)–C(20)–C(22)	173	−176
C(17)–C(20)–C(22)–C(23)	−176	180
C(20)–C(22)–C(23)–C(24)	65	179
C(22)–C(23)–C(24)–O(24-1)	170	−179
C(22)–C(23)–C(24)–O(24-2)	−2	2

C(13)–C(17) bond in both molecules whereas C(21) is synclinal; the relevant torsion angles are given in Table 3. The orientation of the C(24) carboxyl group is different in the two molecules; in (II) this group adopts the more usual antiperiplanar conformation with respect to the C(20)–C(22) bond whereas in (I) it is synclinal. The carboxyl group in (I) is less precisely defined than in (II), the magnitudes of the thermal-vibration parameters giving indications of librational motion.

The molecules are held together in the crystal by a complex hydrogen-bonding network. Fig. 1 is a stereodrawing showing the molecular packing. Hydrogen bonds occur between molecules of type (I), between molecules of type (II) and between molecules of types (I) and (II). The molecule (I)–molecule (I) interactions are bifurcated and involve the C(3) hydroxyl group of one molecule and the carboxyl group of an adjacent molecule; O(3)···O(24-1) = 2·74, O(3)···O(24-2) = 2·90 Å. The molecule (II)–molecule (II) bonds are single hydrogen bonds between the hydroxyl group at C(3′) and the carboxyl O atom O(24-1′), O(3′)··· O(24-1′) = 2·86 Å, resulting in a head-to-tail helix parallel to the *b* axis with the general plane of the type (II) molecules nearly perpendicular to this axis. Molecules (I) and (II) are approximately perpendicular to one another. The chains formed by the type (I) molecules on either side of the helical arrangement of type (II) molecules are linked to it *via* bifurcated hydrogen bonds from O(7) to pairs of molecules lying above each other in the helix. One of the pairs of type (II) molecules presents its head and is linked *via* O(3′) and the other presents its tail and is linked by O(24-2′), the distances being 2·74 and 2·71 Å respectively. At the opposite side of the helix these linkages are reversed, the chains of type (I) molecules being displaced vertically along the *b* axis by one link of helix. An additional hydrogen bond exists between a second type (I) molecule in the chain and a type (II) molecule in the helix such that O(24-2)···O(7′) = 2·87 Å. Helices of type (II) molecules are not directly linked but only indirectly through the chains of type (I) molecules.

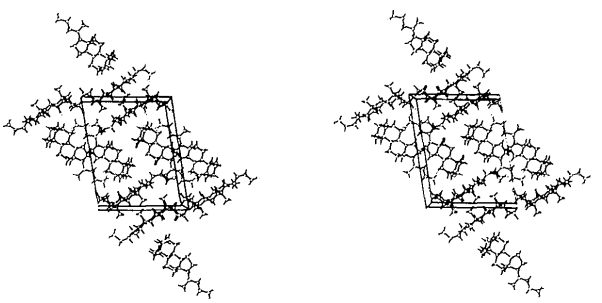

Fig. 1. Stereoscopic packing diagram of chenodeoxycholic acid viewed down the *y* axis.

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