par deux molécules homologues par un axe binaire. Dans notre exemple, les associations se font par deux molécules non équivalentes par symétrie.

Références

BALLY, R. & SURCOUF, E. (1976). Communication privée.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, E.-U.

International Tables for X-ray Crystallography (1968). Tome III. Birmingham: Kynoch Press. (Distributeur actuel D. Reidel, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEPII*. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, E.-U.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. de York, Angleterre, et Louvain, Belgique.

MORNON, J. P., DELETTRÉ, J. & LEPICARD, G. (1979). Communication privée.

MURAKAMI, T., TANAKA, N., IIDA, H. & IITAKA, Y. (1981). *Chem. Pharm. Bull.* **29**(3), 773–778.

SURCOUF, E. (1982). Thèse Doctorat Es Sciences Physiques, Univ. de Paris VI.

WOLLENWEBER, E., MARX, D., FAVRE-BONVIN, J. & BRASSY, C. (1983). *Z. Naturforsch. Teil C*, **38**, 146–47.

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Structure of 3α,12α-Diacetoxycholan-24-oic Acid Methyl Ester

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Abstract. $C_{29}H_{46}O_6$, $M_r = 490{\cdot}68$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}702\,(1)$, $b = 15{\cdot}257\,(3)$, $c = 27{\cdot}893\,(3)$ Å, $V = 2852\,(1)$ Å^3, $Z = 4$, D_m(flotation) $= 1{\cdot}137$, $D_x = 1{\cdot}143$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\bar{\alpha}) = 1{\cdot}54184$ Å, $\mu = 0{\cdot}63$ mm^{-1}, $F(000) = 1072$, $T = 293\,(1)$ K, $R = 0{\cdot}089$ for 2176 unique observed reflections. The six-membered *A*, *B* and *C* rings are in chair conformations and the five-membered *D* ring exhibits a transition form between envelope and half-chair conformations. The long side chain at C(17) is in a β-equatorial position and exhibits a zigzag structure.

Introduction. During the acetylation of deoxycholic acid under strongly acidic conditions, besides the expected 3α,12α-diacetoxycholanic acid (obtained in *ca* 80% yield), the formation of a less-polar component (in *ca* 20% yield) lacking the free carboxyl group was also observed. Chemical reasoning and spectral data could not identify the unknown by-product unambiguously. This prompted us to determine its structure by X-ray diffraction. It turned out that the unexpected by-product was deoxycholic acid methyl ester. The mechanism of formation of this compound in an acid-catalyzed acetylation reaction is not yet clear and its further careful investigation is in progress. In this work the detailed X-ray determination of the molecular structure of the title compound is described.

Experimental. A crystal $0{\cdot}15 \times 0{\cdot}32 \times 0{\cdot}45$ mm was mounted on an Enraf–Nonius CAD-4 diffractometer. Cell constants were determined by least squares from the setting angles of 25 reflections with $35 \le \theta \le 45°$. Systematic absences $h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, $00l$: $l = 2n + 1$. Intensities were measured with graphite-monochromated Cu $K\alpha$ radiation. Scan range $0{\cdot}017 \le \sin\theta/\lambda \le 0{\cdot}631$ Å^{-1}, ω–2θ scan, h 0 to 8, k 0 to 19, l 0 to 35. Three standard reflections ($\bar{1}1\bar{4}$, $\bar{1}06$, $\bar{1}1\bar{6}$) were measured every hour and remained constant throughout the measurement. Of 3420 independent reflections, 2176 with $I > 2{\cdot}5\sigma(I)$ were considered as observed and used for calculation. Data were corrected for Lorentz and polarization effects but not for absorption.

The phase problem was solved with the *MULTAN* (Germain, Main & Woolfson, 1971) program. However, the straightforward application of the program for 248 $E \ge 1{\cdot}9$ values failed to give a solution. An increased number of carefully selected *E* values

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(360) resulted in a phase combination which gave the positions of 26 non-H atoms ($R = 0·48$).

Subsequent structure-factor and Fourier calculations revealed the positions of the missing nine non-H atoms ($R = 0·39$). Full-matrix least-squares refinement, $\sum w(\Delta F^2)$ minimized, 317 parameters refined. As indicated by profile analysis of the reflections, the quality of the crystal was rather poor. Accordingly, the refinement was terminated at $R = 0·089$, $wR = 0·106$, $R_{\rm tot} = 0·104$, $S = 8·29$, $w = [\sigma^2(F_o) + 0·25(pF_o)^2]^{-1}$, where $p = 0·01$. Max. and min. peak heights in final $\Delta\rho$ map $\pm 0·32\,(5)$ e Å^{-3}. Data were not corrected for extinction. $(\Delta/\sigma)_{\rm max} = 0·66$. The H-atom positions were generated from assumed geometries and were taken into account without refinement in structure-factor calculations with isotropic temperature factors ($B_{i\rm H} = B_{i\rm C} + 1$ Å^2). Scattering factors were taken from *International Tables for X-ray Crystallography* (1962). Program system used: Enraf–Nonius (1981) *SDP* adapted on a PDP 11/34 minicomputer (Budapest).

Discussion. Atomic coordinates for non-H atoms are given with their e.s.d.'s in Table 1.* The molecular

Table 1. *Final fractional coordinates* (×10^4) *and equivalent isotropic thermal parameters for non*-H *atoms*

Estimated standard deviations are in parentheses and are 1 Å^2 for $B_{\rm eq}$ values. $B_{\rm eq} = \frac{4}{3}\,{\rm trace}(B\mathbf{G})$ where **G** is the direct metric tensor.

	x	y	z	$B_{\rm eq}$(Å^2)
C(1)	6497 (10)	1392 (5)	−604 (2)	8·4
C(2)	4553 (11)	1609 (4)	−330 (2)	8·6
C(3)	3989 (10)	788 (5)	−13 (2)	8·2
C(4)	3751 (9)	7 (4)	−315 (2)	7·1
C(5)	5624 (9)	−182 (4)	−606 (2)	7·8
C(6)	5328 (11)	−1005 (4)	−906 (2)	9·1
C(7)	3887 (10)	−866 (4)	−1349 (2)	8·3
C(8)	4573 (9)	−97 (4)	−1637 (2)	6·8
C(9)	4924 (8)	716 (3)	−1335 (2)	5·9
C(10)	6377 (9)	605 (4)	−920 (2)	7·6
C(11)	5561 (8)	1488 (4)	−1672 (2)	6·8
C(12)	4110 (8)	1711 (3)	−2082 (2)	6·0
C(13)	3595 (8)	874 (4)	−2375 (2)	5·8
C(14)	3020 (8)	129 (3)	−2042 (2)	5·7
C(15)	2304 (10)	−582 (4)	−2376 (2)	7·5
C(16)	1331 (9)	−89 (4)	−2788 (2)	7·8
C(17)	1773 (8)	905 (3)	−2696 (2)	5·3
C(18)	5517 (9)	650 (4)	−2669 (2)	8·2
C(19)	8514 (10)	430 (6)	−1087 (2)	10·7
C(20)	1787 (10)	1459 (4)	−3185 (2)	7·6
C(20′)	2349 (14)	2407 (4)	−3105 (2)	11·1
C(21)	−181 (10)	1344 (4)	−3454 (2)	7·8
C(22)	−176 (12)	1686 (4)	−3941 (2)	8·3
C(23)	−2207 (14)	1631 (5)	−4163 (2)	10·5
O(23)	−3728 (12)	1459 (7)	−3957 (2)	18·5
O(24)	−2312 (9)	1755 (4)	−4604 (1)	12·8
C(25)	4185 (13)	1727 (5)	−4853 (2)	11·9
O(26)	2241 (6)	1995 (2)	−1859 (1)	5·7
C(27)	2120 (10)	2862 (3)	−1776 (2)	6·2
O(28)	3273 (8)	3386 (2)	−1899 (1)	9·8
C(29)	195 (13)	3046 (4)	−1532 (2)	9·1
O(30)	2096 (7)	1024 (3)	213 (1)	9·5
C(31)	1789 (12)	706 (4)	632 (2)	9·3
O(32)	2900 (10)	210 (4)	831 (2)	13·9
C(33)	−369 (16)	909 (5)	802 (2)	13·2

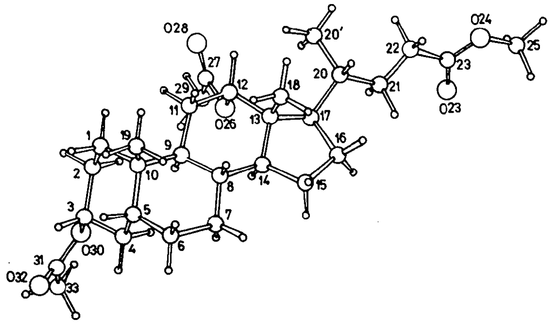

Fig. 1. A perspective view of the molecule showing atomic and ring labelling. Numbers represent C atoms unless otherwise indicated.

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with their e.s.d.'s in parentheses*

C(1)–C(2)	1·546 (9)	C(14)–C(15)	1·508 (8)
C(1)–C(10)	1·492 (9)	C(15)–C(16)	1·520 (8)
C(2)–C(3)	1·579 (9)	C(16)–C(17)	1·566 (8)
C(3)–C(4)	1·468 (9)	C(17)–C(20)	1·605 (8)
C(4)–C(5)	1·522 (8)	C(20)–C(20′)	1·511 (9)
C(5)–C(6)	1·522 (8)	C(20)–C(21)	1·528 (9)
C(5)–C(10)	1·570 (8)	C(21)–C(22)	1·455 (8)
C(6)–C(7)	1·583 (9)	C(22)–C(23)	1·498 (12)
C(7)–C(8)	1·494 (8)	C(23)–O(23)	1·199 (12)
C(8)–C(9)	1·518 (8)	C(23)–O(24)	1·247 (6)
C(8)–C(14)	1·574 (8)	O(24)–C(25)	1·435 (10)
C(9)–C(10)	1·522 (8)	C(12)–O(26)	1·464 (7)
C(10)–C(19)	1·530 (9)	O(26)–C(27)	1·345 (6)
C(9)–C(11)	1·566 (8)	C(27)–O(28)	1·164 (7)
C(11)–C(12)	1·539 (8)	C(27)–C(29)	1·485 (10)
C(12)–C(13)	1·555 (8)	C(3)–O(30)	1·462 (8)
C(13)–C(14)	1·518 (8)	O(30)–C(31)	1·282 (7)
C(13)–C(17)	1·515 (8)	C(31)–O(32)	1·198 (9)
C(13)–C(18)	1·565 (8)	C(31)–C(33)	1·553 (13)

C(2)–C(1)–C(10)	114·8 (9)	C(12)–C(13)–C(18)	105·8 (8)
C(1)–C(2)–C(3)	108·0 (9)	C(14)–C(13)–C(18)	111·5 (8)
C(2)–C(3)–C(4)	110·4 (9)	C(14)–C(13)–C(17)	100·4 (7)
C(2)–C(3)–O(30)	104·7 (8)	C(17)–C(13)–C(18)	111·1 (8)
C(4)–C(3)–O(30)	110·7 (9)	C(8)–C(14)–C(13)	115·8 (8)
C(3)–C(4)–C(5)	111·7 (9)	C(8)–C(14)–C(15)	119·7 (8)
C(4)–C(5)–C(6)	110·0 (8)	C(13)–C(14)–C(15)	104·0 (8)
C(4)–C(5)–C(10)	114·7 (8)	C(14)–C(15)–C(16)	104·3 (8)
C(6)–C(5)–C(10)	111·5 (8)	C(15)–C(16)–C(17)	105·9 (8)
C(5)–C(6)–C(7)	113·5 (9)	C(13)–C(17)–C(16)	102·7 (7)
C(6)–C(7)–C(8)	109·7 (9)	C(13)–C(17)–C(20)	120·9 (8)
C(7)–C(8)–C(9)	113·0 (8)	C(16)–C(17)–C(20)	111·8 (8)
C(7)–C(8)–C(14)	110·8 (8)	C(17)–C(20)–C(20′)	112·3 (9)
C(9)–C(8)–C(14)	108·8 (8)	C(17)–C(20)–C(21)	110·6 (8)
C(8)–C(9)–C(10)	115·5 (8)	C(20′)–C(20)–C(21)	113·4 (9)
C(8)–C(9)–C(11)	108·9 (8)	C(20)–C(21)–C(22)	114·5 (9)
C(10)–C(9)–C(11)	111·5 (8)	C(21)–C(22)–C(23)	111·3 (10)
C(1)–C(10)–C(5)	107·7 (8)	C(22)–C(23)–O(23)	125·9 (13)
C(1)–C(10)–C(9)	113·2 (9)	C(22)–C(23)–O(24)	116·8 (11)
C(1)–C(10)–C(19)	105·7 (9)	O(23)–C(23)–O(24)	117·3 (13)
C(5)–C(10)–C(9)	107·7 (8)	C(23)–O(24)–C(25)	121·5 (10)
C(5)–C(10)–C(19)	109·7 (9)	C(12)–O(26)–C(27)	114·6 (7)
C(9)–C(10)–C(19)	112·8 (9)	O(26)–C(27)–O(28)	125·8 (9)
C(9)–C(11)–C(12)	116·1 (8)	O(26)–C(27)–C(29)	108·5 (8)
C(11)–C(12)–C(13)	110·4 (8)	O(28)–C(27)–C(29)	125·6 (10)
C(11)–C(12)–O(26)	106·9 (7)	C(3)–O(30)–C(31)	116·1 (9)
C(13)–C(12)–O(26)	106·0 (7)	O(30)–C(31)–C(32)	124·2 (11)
C(12)–C(13)–C(14)	110·5 (8)	O(30)–C(31)–C(33)	110·6 (10)
C(12)–C(13)–C(17)	117·6 (8)	O(32)–C(31)–C(33)	124·3 (11)

C(2)–C(3)–O(30)–C(31)	−148·1 (10)	C(13)–C(17)–C(20)–C(20′)	−55·1 (9)
C(3)–O(30)–C(31)–O(32)	−3·4 (11)	C(13)–C(17)–C(20)–C(21)	177·0 (10)
C(9)–C(11)–C(12)–O(26)	62·8 (7)	C(17)–C(20)–C(21)–C(22)	−169·1 (11)
C(11)–C(12)–O(26)–C(27)	90·5 (8)	C(20)–C(21)–C(22)–C(23)	−174·3 (12)
C(12)–O(26)–C(27)–O(28)	6·4 (9)	C(21)–C(22)–C(23)–O(24)	−167·4 (14)
C(14)–C(13)–C(17)–C(20)	−167·4 (10)	O(23)–C(23)–O(24)–C(25)	2·4 (13)

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* Lists of structure factors, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44495 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

geometry with atomic numbering is shown in Fig. 1. The bond lengths, angles and relevant torsion angles are listed in Table 2. Atom C(12) is substituted by an acetoxy moiety which assumes an α-axial position as is evidenced by the torsion angle C(14)—C(13)—C(12)—O(26) = −67·0 (7)°. The long side chain, *i.e.* the 1′-methyl-3′-methoxycarbonyl-*n*-propyl moiety at C(17), is in a β-equatorial position relative to the C(13)—C(17) bond [C(20)—C(17)—C(13)—C(14) = −167·4 (10)°]. Its zigzag structure can be characterized by the sequence of rotations about the bonds C(13)—C(17), C(17)—C(20), C(20)—C(21), C(21)—C(22), C(22)—C(23) and C(23)—C(24), which is *−ap, ap, −ap, −ap, −ap* and *−ap* (*ap* = antiperiplanar). The lowest torsion angle value of −167·4 (10)°, *i.e.* the greatest deviation (12·6°) from 180°, is found about C(22)—C(23) and C(13)—C(17). The position of the side chain relative to the five-membered ring is presumably influenced by the repulsion between the neighbouring C(18) and C(20′) methyl groups which assume an anticlinal position as shown by the non-bonded torsion angle C(20′)—C(20)···C(13)—C(18) = −94·7 (5)°. Otherwise, the vicinal C(18) and O(26) atoms are in *trans* positions. The β-axial C(18) methyl group is almost perfectly eclipsed with the C(19) methyl moiety; C(18)—O(13)···C(10)—C(19) is 3·8 (6)°. As a result of the *cis* junction [C(5)—C(10)] between rings *A* and *B*, C(19) is β-equatorial relative to ring *A*. The second acetoxy group linked to C(3) of ring *A* assumes an α-equatorial position.

Rings *A*, *B* and *C* condensed with *cis* (*A*:*B*) and *trans* (*B*:*C*) junctions are invariably in an almost perfect chair conformation. The five-membered ring *D* exhibits a transition form between the envelope and half-chair conformations; the puckering parmeters (Cremer & Pople, 1975) are $Q = 0{\cdot}462\ (6)$ Å, $\varphi = 187{\cdot}6\ (8)°$.

References

CREMER, D. & POPLE, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Enraf–Nonius (1981). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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Structure of 4-Dimethylaminopyridine *N*-Oxide Dihydrate

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Abstract. $C_7H_{10}N_2O.2H_2O$, $M_r = 174{\cdot}2$, monoclinic, $P2_1/c$, $a = 8{\cdot}391\ (6)$, $b = 16{\cdot}320\ (4)$, $c = 6{\cdot}847\ (6)$ Å, $\beta = 103{\cdot}10\ (7)°$, $V = 913{\cdot}0\ (10)$ Å^3, $Z = 4$, $D_x = 1{\cdot}267$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}11$ mm^{-1}, $F(000) = 376$, $T = 295$ K, $R = 0{\cdot}052$ for 1898 observed reflections [$F_o > \sigma(F_o)$]. The dimethylamino group is planar, and the C—N bond length is shorter than that in 4-dimethylaminopyridine. These findings indicate the presence of strong conjugation between the dimethylamino group and the pyridine ring. The two water molecules interact with the O atom in the N—O bond through hydrogen bonds, by which the N—O bond is lengthened to 1·344 (1) Å.

Introduction. Chao & Schempp (1977) have studied the crystal structures of six-membered *N*-heteroaromatics which contain an amino group by X-ray analysis, and found that the planarity of the amino groups was linearly correlated with the bond lengths of C(*ipso*)—N(amino). The bond lengths are a measure of the degree of conjugation between the amino group and the aromatic ring. Therefore, the planarity also indicates the degree of conjugation. X-ray crystal analyses of 4-dimethylaminopyridine (Ohms & Guth, 1984) and its hydrochloride dihydrate (Chao, Schempp & Rosenstein, 1977) reflect this situation; the conformation of the dimethylamino group is slightly pyramidal in the former but planar in the latter, and the bond length between the dimethylamino nitrogen and the *ipso* carbon is 0·027 Å longer in the former than in the latter.

We were interested in the effect on the molecular structure of coordination of the O atom to the N atom in pyridine. As crystals of the anhydride of 4-dimethylaminopyridine *N*-oxide could not be obtained, the structure of its dihydrate was determined by X-ray crystal analysis.

Experimental. Prismatic colorless crystals grown from acetonitrile solution. Crystal of dimensions 0·5 ×

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