of the bonded C atom. Highly disordered solvent molecules located in the vicinity of a $\bar{4}$ center were found distributed over symmetry-related positions. The proportion and identity of the solvent, $CHCl_3$, were confirmed using the *SQUEEZE* routine of the *PLATON* program (Spek, 1995) (V_s = 492.5 Å^3 and 114.5 electrons per cell). Final refinements were carried out using a disordered description of the solvent and no *SQUEEZE* correction was applied to the data for the solvent contribution. Solvent was refined using a constraint (*DFIX*) and restraints (*SAME*/*SADI*) in order to improve the solvent model. All C atoms have the same isotropic displacement parameters and all Cl atoms have the same isotropic displacement parameters. A small hole remained in this structure accounting for zero electrons and 36.2 Å^3 of the volume of the cell. The absolute structure was determined by way of the *SHELXL*96 (Sheldrick, 1996) instructions *TWIN*, with a matrix ($\bar{1}00$, $0\bar{1}0$, $00\bar{1}$), and one *BASF* parameter to give a value of the Flack (1983) parameter of 0.48 (2). The crystal is thus an equicomponent inversion twin.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *NRCVAX* (Gabe *et al.*, 1989) and *SHELXL*96. Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

The financial support of the Natural Sciences and Engineering Research Council of Canada is hereby acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1412). Services for accessing these data are described at the back of the journal.

References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Computer Programs for the IBM/360*. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fukuda, M., Sawada, M. & Yoshino, K. (1989). *Jpn J. Appl. Phys.* **28**, L1433–L1437.

Fukuda, M., Sawada, K. & Yoshino, K. (1993). *J. Polym. Sci.* A**31**, 2465–2471.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Grell, M., Bradley, D. D. C., Insasekaran, M. & Woo, E. P. (1997). *Adv. Mater.* **9**, 798–802.

Jen, K. Y., Miller, G. G. & Elsenbaumer, R. L. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1346–1348.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kaeriyama, K., Tsukahara, Y., Negoro, S., Tamigaki, N. & Masuda, M. (1997). *Synth. Met.* **84**, 263–266.

Miller, R. D., Scott, J. C., Kreyenschmidt, M., Kwak, J., Lee, V., Fuhrer, T. & Karg, S. (1997). *Polym. Preprints*, **38**, 421–422.

Pei, Q. & Yang, Y. (1996). *J. Am. Chem. Soc.* **118**, 7146–7148.

Ranger, M., Rondeau, D. & Leclerc, M. (1997). *Macromolecules*, **30**, 7686–7691.

Sato, M., Tanaka, S. & Kaeriyama, K. (1986). *J. Chem. Soc. Chem. Commun.* pp. 873–875.

Schlüter, A. D., Rehahn, M., Wegner, G. & Feast, W. J. (1989). *Polymer*, **30**, 1054–1059.

Sheldrick, G. M. (1990). *SHELXS*96. Beta test version 03. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1996). *SHELXL*96. Beta test version 03. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1995). *PLATON. Molecular Geometry Program*. Version of July 1995. University of Utrecht, The Netherlands.

Acta Cryst. (1998). C**54**, 801–803

Methyl 7α,12α-Dihydroxy-3α-methacryloyloxy-5β-cholan-24-oate

Huiyou Liu, Francine Bélanger-Gariépy, Mehdi Akram, Mariana Moskova and Xiao-Xia Zhu

Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: zhuj@ere.umontreal.ca

(*Received 28 October 1997; accepted 22 December 1997*)

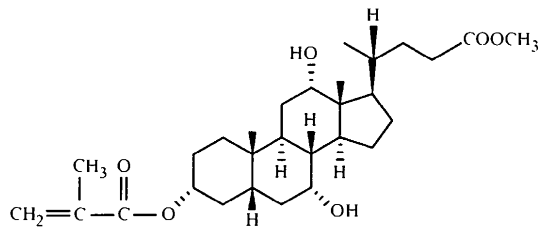
Abstract

The structure determination of the title compound, $C_{29}H_{46}O_6$, establishes the selective esterification of the hydroxyl group on position 3 of the steroid skeleton of the cholic acid methyl ester. The asymmetric unit contains one molecule and the crystal structure is stabilized by intermolecular hydrogen bonds. The two side chains on the steroid skeleton are quite flexible and each has two orientations; a disorder model was introduced and two sets of atoms were refined for the side chains.

Comment

The biological importance, the amphiphilic properties and the acid–base properties of bile acids make them interesting starting materials in the preparation of new polymers with potential biomedical and pharmaceutical applications.

The title compound, (I), was synthesized from one of the most commonly occurring bile acids, cholic acid, and was one of the monomers synthesized for the preparation of the new polymers. It can be readily polymerized by a free-radical polymerization in solution (Ahlheim & Hallensleben, 1992; Zhu *et al.*, 1996) and co-polymerized with methacrylic monomers such as methacrylic acid and 2-hydroxyethyl methacrylate (Zhu *et al.*, 1996).



(I)

Most of the bond distances and angles in the title compound are in the normal range for steroidal compounds. The set of atomic coordinates for (I) can be regarded as the absolute structure based on the known stereochemistry of cholic acid and its derivatives. The rings have a geometry similar to the structures of the other cholic acid derivatives reported to date (Miki *et al.*, 1990, 1992), while the two side chains attached to the steroid skeleton are more flexible and each has two orientations.

The two side chains cannot be described without the introduction of a disorder model. Firstly, the carbonyl group of the methacryloyloxy group on C3 was found in two positions which affected the whole methacryloyloxy group. Secondly, the carbonyl group of the side chain on C17 was also found to adopt two orientations which affected the whole side chain. Two sets of atoms (orientations *A* and *B*) were defined and refined using the *SADI* restraint technique in *SHELXL*96 (Sheldrick, 1996). The occupancy for each side chain in both orientations (*A* and *B*) was initially refined, but as these did not differ significantly, the occupancy factor for each was then fixed at 0.50 in the final cycles of the refinement (Fig. 1).

The conformation of the methacryloyloxy group on C3 and that of the side chain on C17 are different from those found in the crystal structure of methyl 3α-methacryloylamino-7α,12α-dihydroxy-5β-cholan-24-oate (Akram *et al.*, 1996). The O3—C26—C27—C28 torsion angles in the methacryloyl group are −14 (5)° for orientation *A* and −13 (6)° for orientation *B*, while the N3—C26—C27—C28 torsion angles in the methacrylamino group are −28.8 (4)° for molecule 1, and 28 (3) and −171.8 (19)° for molecules 2*A* and 2*B*, respectively. On the other hand, the C17—C20—C22—C23 torsion angle in methyl 3α-methacryloylamino-7α,12α-dihydroxy-5β-cholan-24-oate (Akram *et al.*, 1996) ranges from 58.3 (2) to 62.3 (2)°, while in the title compound, this angle ranges from −168.1 (13) to −164.0 (15)°. The molecular dimensions are normal and are included with the supplementary material.

The two axial hydroxyl groups link the molecules which are translated along the *a* axis in a helical arrangement. Two hydrogen bonds (O—H···O) are formed intermolecularly between the hydroxyl group on position 7 of one molecule (orientation *A* or *B*) and the hydroxyl group on position 12 of the other molecule (orientation *B* or *A*) (Table 1). A disorder of the hydrogen bonding was observed with the hydroxyl H atoms disordered equally over the two sites. Therefore, alternative positions are required for H7, as well as for H12. In the first pattern, H7*A* is directed towards O12 and H12*B* is not involved in hydrogen bonding. In the second pattern, H12*A* is directed towards O7 and H7*B* is not involved in hydrogen bonding.

In conclusion, the selective esterification of the hydroxyl group at position 3 of the steroid skeleton and the α configuration of the methacryloyl group have been confirmed unambiguously by this X-ray analysis.

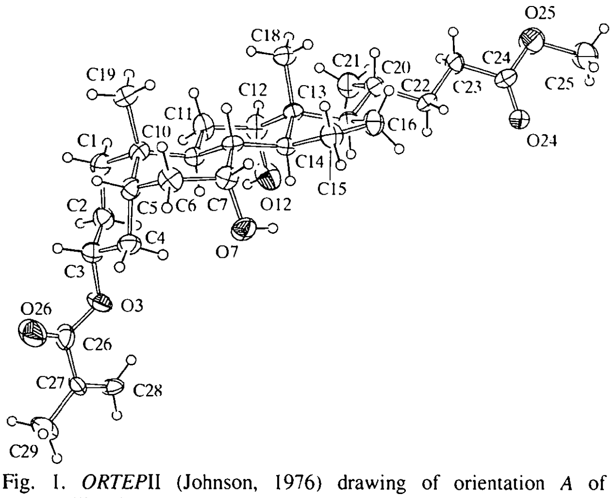


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of orientation *A* of (I). Ellipsoids correspond to 40% probability. The site-occupancy factors of the methacryloyloxy group on C3 and the side chain attached to C20 are both 0.50. H atoms are represented by spheres of arbitrary size.

Experimental

The title compound was prepared according to the method described by Zhu *et al.* (1996). Single crystals were grown from an ethanol solution.

Crystal data

$C_{29}H_{46}O_6$
$M_r = 490.66$
Orthorhombic
$P2_12_12_1$
$a = 7.6630\,(10)$ Å
$b = 11.833\,(3)$ Å
$c = 29.452\,(7)$ Å
$V = 2670.6\,(10)$ Å^3
$Z = 4$
$D_x = 1.220$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 19–22°$
$\mu = 0.668$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.42 × 0.22 × 0.10 mm
Colourless

Data collection

Nonius CAD-4 diffractometer

2244 reflections with $I > 2\sigma(I)$

$\omega/2\theta$ scans
Absorption correction:
by integration (*ABSORP* in *NRCVAX*; Gabe *et al.*, 1989)
$T_{\min} = 0.831$, $T_{\max} = 0.939$
19 833 measured reflections
5062 independent reflections (including Friedel pairs)
$R_{\rm int} = 0.045$
$\theta_{\max} = 69.81°$
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -35 \rightarrow 35$
4 standard reflections
frequency: 30 min
intensity variation: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.068$
$S = 0.888$
5062 reflections
434 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.046$
$\Delta\rho_{\max} = 0.138$ e Å^{-3}
$\Delta\rho_{\min} = -0.134$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996)
Extinction coefficient: 0.00065 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.1 (3)

Table 1. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O12$^{\rm i}$	0.82	2.45	3.204 (3)	152.9
O12—H12*A*···O7$^{\rm ii}$	0.82	2.46	3.204 (3)	150.6

Symmetry codes: (i) $\frac{1}{2} + x, \frac{3}{2} - y, 2 - z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$.

H atoms were constrained to their parent sites using a riding model [*SHELXL*96 (Sheldrick, 1996) defaults; C—H 0.93 to 0.98 and O—H 0.82 Å]. The H-atom isotropic displacement parameters, $U_{\rm iso}$, were adjusted to be 50% greater than the displacement parameters of the parent site for the methyl and hydroxyl H atoms, and 20% greater for the remaining H atoms. A final verification of possible voids was performed using the *VOID* routine of the *PLATON* program (Spek, 1995).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRC*-2 and *NRC*-2*A* (Ahmed *et al.*, 1973). Program(s) used to solve structure: *SHELXS*96 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*96. Molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX* (Gabe *et al.*, 1989). Software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

The financial support from the Natural Sciences and Engineering Research Council of Canada and from the Fonds FCAR du Ministère de l'Éducation du Québec is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1407). Services for accessing these data are described at the back of the journal.

References

Ahlheim, M. & Hallensleben, M. L. (1992). *Macromol. Chem.* **193**, 779–797.

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Computer Programs for the IBM/360.* Accession Nos. 133–147; *J. Appl. Cryst.* **6**, 309–346.

Akram, M., Denike, J. K., Bélanger-Gariépy, F. & Zhu, X. X. (1996). *Acta Cryst.* C**52**, 2905–2907.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Miki, K., Kasai, N., Shibakami, M., Chirachanchai, S., Takemoto, K. & Miyata, M. (1990). *Acta Cryst.* C**46**, 2442–2445.

Miki, K., Masui, A., Kasai, N., Goonewardena, W., Shibakami, M., Takemoto, K. & Miyata, M. (1992). *Acta Cryst.* C**48**, 503–507.

Sheldrick, G. M. (1990). *SHELXS*96. Beta test version 03. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1996). *SHELXL*96. Beta test version 03. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Spek, A. L. (1995). *PLATON. Molecular Geometry Program*. Version of July 1995. University of Utrecht, The Netherlands.

Zhu, X. X., Moskova, M. & Denike, J. K. (1996). *Polymer*, **37**, 493–498.

Acta Cryst. (1998). C**54**, 803–805

Methyl 2-(2-Methoxyphenyl)-2,3,3a,4,6,6a-hexahydro-1*H*-thieno[3,4-*b*]pyrrole-6a-carboxylate

A. MATOS BEJA,[a] J. A. PAIXÃO,[a]* M. RAMOS SILVA,[a] L. ALTE DA VEIGA,[a] A. M. D'A. ROCHA GONSALVES,[b] T. M. V. D. PINHO E MELO[b] AND A. M. T. D. P. V. CABRAL[b]

[a]*Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3000 Coimbra, Portugal, and* [b]*Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, P-3000 Coimbra, Portugal. E-mail: jap@pollux.fis.uc.pt*

(*Received 13 October 1997; accepted 6 January 1998*)

Abstract

The title compound, $C_{15}H_{19}NO_3S$, has *cis* stereochemistry at the ring junction, resulting from an *exo* intramolecular 1,3-dipolar cycloaddition. It crystallizes as a racemate. The tetrahydrothieno ring has an S-envelope form and the pyrrole ring adopts a half-chair conformation. The amino H atom is shared in a bifurcated intramolecular hydrogen bond between the bare O atoms of the carboxylate and methoxy groups. Cohesion of the structure is achieved through weak intermolecular interactions only.