

C3—C2—C1	111.4 (2)	C18—C10—C1	109.8 (2)
C2—C3—C4	114.2 (3)	C18—C10—C5	114.4 (2)
C3—C4—C19	110.7 (3)	C1—C10—C5	107.6 (2)
C3—C4—C20	107.0 (3)	C18—C10—C9	108.8 (2)
C19—C4—C20	106.9 (3)	C1—C10—C9	109.2 (2)
C3—C4—C5	108.2 (2)	C5—C10—C9	107.0 (2)
C19—C4—C5	114.3 (3)	C12—C11—C9	112.3 (2)
C20—C4—C5	109.5 (2)	C13—C12—C11	117.8 (3)
C6—C5—C10	111.6 (2)	C14—C13—C16	124.7 (3)
C6—C5—C4	113.5 (2)	C14—C13—C12	121.6 (3)
C10—C5—C4	116.7 (2)	C16—C13—C12	113.6 (3)
C7—C6—C5	110.8 (2)	C13—C14—C15	126.7 (3)
C8—C7—C6	110.6 (3)	O1—C15—O2	122.0 (3)
C17—C8—C7	121.2 (3)	O1—C15—C14	120.7 (3)
C17—C8—C9	125.8 (3)	O2—C15—C14	117.2 (3)
C7—C8—C9	112.9 (3)		

Intensity data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction (North, Phillips & Mathews, 1968) based on azimuthal scans of several reflections was applied. The intensities of three reflections were measured after every 150 reflections; no variation was observed. The crystal structure was solved by using direct methods followed by conventional Fourier techniques and subsequent least-squares refinement. All non-H atoms were refined anisotropically. The H atoms were included in their found positions, except for those of the C3, C7 (C—H = 0.97 Å) and C5 (C—H = 0.98 Å) atoms, and those of the methyl group (C—H = 0.96 Å), which were included in calculated positions. All these H atoms were refined riding on their C atoms with a common isotropic displacement parameter. The two H atoms of the symmetrically hydrogen-bonded carboxylic dimer occupy two positions on a twofold axis. Thus, both positions were included in the last cycles and their y coordinates and isotropic displacement parameters were successfully refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) and *PARST95* (Nardelli, 1995). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL93*.

The authors thank Dr F. R. Fronczek for his helpful assistance with the final version of the manuscript. We also thank CONICIT (project No. RP-I-C-128) for providing the funds for the acquisition of the Rigaku X-ray diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1024). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
- Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- De Santis, V. & Medina, J. D. (1981). *J. Nat. Prod.* **44**, 370–372.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gaitán, R. (1996). PhD thesis, Faculty of Pharmacy, Universidad Central de Venezuela, Venezuela.
- Grant, P. K., Hanton, L. R. & Wong, G. (1995). *Acta Cryst.* **C51**, 743–744.
- Molecular Structure Corporation (1992). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1995). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Singh, S., Gray, A. I., Skelton, B. W., Waterman, P. G. & White, A. H. (1991). *Aust. J. Chem.* **44**, 1789–1793.
- Acta Cryst.* (1997). **C53**, 1070–1073

Hydrogen-Bonding Networks Involving Water in Amphiphilic *N*-Dodecanoyl-L-serine Monohydrate

BORIS SCHADE,^a JÜRGEN-HINRICH FUHRHOP,^a VERA HUBERT,^b MANUELA WEBER^b AND PETER LUGER^b

^aInstitut für Organische Chemie, Freie Universität Berlin, Takustrasse 3, D-14195 Berlin, Germany, and ^bInstitut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14195 Berlin, Germany. E-mail: fuhrhop@chemie.fu-berlin.de

(Received 25 November 1996; accepted 27 March 1997)

Abstract

The amphiphilic title compound, C₁₅H₂₉NO₄·H₂O, forms a head-to-tail bilayer packing arrangement in the crystal. The crystal structure shows an entangled network of hydrogen bonds in which the water molecule has a central position. A rarely observed methine donor hydrogen bridge was found.

Comment

Many crystal structure investigations aim to examine the intra- and intermolecular interactions of biologically relevant compounds. Among these, amino acids, peptides and their derivatives are of special interest. To overcome the unfavourable ionic interactions due to the zwitterionic appearance of most of the amino acid compounds in the crystal, we linked L-serine with lauric acid to give *N*-dodecanoyl-L-serine (Fig. 1). Thus, the amino acid retains its normal properties in peptides without any ammonium-to-carboxylate attractions. We present here the crystal structure of this amino acid derivative, (I), which contains a network of hydrogen bonds. Spe-

cial attention was paid to the face-to-face interactions within the polar head-group region which determine the bilayer arrangements in supramolecular assemblies.

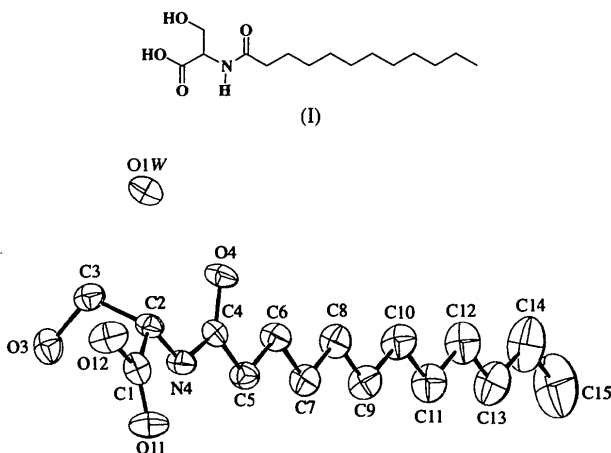


Fig. 1. A view (ORTEP; Johnson, 1977) of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

The conformation of the serine moiety (Table 1) can be explained in terms of the dihedral angles ψ , φ and χ , which are used in studies of amino acid and peptide structures. The values are $\psi = 178.4(2)$, $\varphi = -157.8(2)$ and $\chi_1 = 60.9(2)^\circ$ ($N4-C2-C3-O3$); the amino group is nearly planar [$170.2(3)^\circ$]. This is in good agreement with the values of 5° (ψ) and 60° (χ_1) given by Cody (1985) for free serine, based on the X-ray data of 15 different crystal structures of serine. [Note that Cody (1985) refers to ψ as the dihedral angle from the N atom to the *cis* O atom.] On the other hand, the ψ value, together with the φ value, agree with the value of 180° for a completely extended chain conformation for a peptide. The dodecanoyl chain is, as expected, in a fully extended all-*trans* conformation.

The overall structure of the crystal is a multilamellar assembly of bilayers. The single bilayers are built in a head-to-head arrangement (Fig. 2). Two adjacent bilayers are related through the twofold screw axis. In the hydrophilic region of the molecule, the layers are connected through hydrogen bonds whereas the hydrophobic parts are held together only by the weak van der Waals interactions at the end of the polymethylene chain. This arrangement is common in the micellar bilayer structures of amphiphilic aggregates (Fuhrhop & Köning, 1994).

There are six different intermolecular hydrogen bonds in the head-group region (Table 2). The first connects the adjacent amide groups ($N4-H4N \cdots O4'$) in the usual way. The second is unusual since it contains a methine donor group; such hydrogen bonds are rarely observed. In our case, however, the distance of $2.33(2)$ Å between the α -methine H atom and the neighbouring carboxylic O atom ($C2-H2 \cdots O11'$), as well as the $170(1)^\circ$

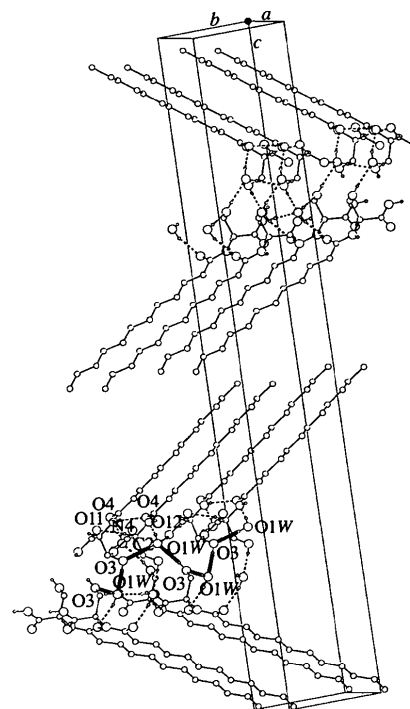


Fig. 2. A view (SCHAKAL88; Keller, 1988) of the crystal structure of the title compound. The coil is highlighted.

angle typical for a hydrogen bridge, clearly support this assumption. Note that the position of the α -H atom was located from the X-ray data. Compared to Jeffrey & Maluszynska's (1983) survey of the hydrogen-bond geometries of amino acids, this hydrogen bond is short and its angle is exceptionally linear. Thus, two different chains are formed which are oriented in opposite directions along the crystallographic *a* axis.

A third and fourth hydrogen bond form a sequence of the *AB* type, which runs perpendicular to those described above. They consist of two $O-H \cdots O$ bridges. The third connects the hydroxyl group, $O3-H3O$, of the serine head group and the O atom of the water molecule. The sequence is continued *via* the water H atom, H1W, to the hydroxyl O3 atom of a neighbouring molecule, being related by a 180° turn along the screw axis in the *b* direction, thus forming a helical arrangement. This sequence links both layers of the bilayer crystal and also two adjacent layers in the crystallographic *c* direction. The lengths are $2.01(3)$ and $1.92(2)$ Å, respectively.

The above hydrogen-bond sequence between the hydroxyl group of the serine moiety and the water molecule is surprisingly similar to the hydrogen-bond sequence between the hydroxyl groups in anhydrous L-serine (Kistenmacher, Rand & Marsh, 1974) and thus different from the L-serine monohydrate structure (Frey, Lehmann, Koetzle & Hamilton, 1973). In anhydrous L-serine, the neighbouring molecules are associated directly without water connections but these neighbours are also related by a twofold screw axis.

The remaining two hydrogen bonds again involve the water molecule. One links the water H atom H2W with the carbonyl O4 atom of the amide group, with a length of 1.85 (4) Å and an angle of 164 (3)°. The second is a connection of the donor carboxyl O12 atom to the acceptor water O1W atom with a length and angle of 1.73 (3) Å and 168 (3)°, respectively.

The six hydrogen bonds form a network which can be seen as layers of closely packed coils of O—H···O hydrogen bonds parallel to the *ab* plane. These coils, pointing in the *y* direction, are connected to the nearest uninvolved neighbours *via* the water molecules, through a series of the two hydrogen bridges characterized in the previous paragraph. According to the geometric properties of the tetrahedral O atom in a water molecule, these bonds are nearly perpendicular to each other. This shows the important role of the crystal water molecule. Nevertheless, this structure is more related to anhydrous L-serine than to L-serine monohydrate. In addition, all neighbouring molecules in the crystallographic *a* direction are connected by the sequence of strong amide- and methine-to-carboxyl hydrogen bonds.

Experimental

N-Dodecanoyl-L-serine was synthesized, with a 70% overall yield, by the aminolysis of an *N*-hydroxysuccinic ester of dodecanoic acid with L-serine, which was first described by Anderson, Zimmerman & Callahan (1963, 1964). The crystals were grown at room temperature from a 1:1 mixture of water and ethanol. Elemental analysis and ¹H NMR spectroscopy confirmed the structure of *N*-dodecanoyl-L-serine monohydrate.

Crystal data

C₁₅H₂₉NO₄·H₂O
M_r = 305.41
 Orthorhombic
*P*2₁2₁2₁
a = 4.934 (2) Å
b = 7.422 (1) Å
c = 48.561 (1) Å
V = 1778.3 (8) Å³
Z = 4
D_x = 1.141 Mg m⁻³
D_m not measured

Ni-filtered Cu *K*α radiation
 λ = 1.54180 Å
 Cell parameters from 67 reflections
 θ = 30–40°
 μ = 0.689 mm⁻¹
T = 293 (2) K
 Plate
 1.05 × 0.32 × 0.04 mm
 Colourless

Data collection

Stoe four-circle diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical, program *ABSORB* in *Xtal2.2* (Hall, Flack & Stewart, 1992)
 T_{\min} = 0.803, T_{\max} = 0.974
 3852 measured reflections
 3217 independent reflections

2596 reflections with $F_o > 4\sigma(F_o)$
 R_{int} = 0.021
 θ_{max} = 67.91°
 h = 0 → 5
 k = 0 → 8
 l = -58 → 58
 3 standard reflections
 frequency: 90 min
 intensity decay: 3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.034
 $wR(F^2)$ = 0.088
 S = 1.091
 3217 reflections
 313 parameters
 All H atoms refined
 $w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.2463P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}}$ = 0.034
 $\Delta\rho_{\text{max}}$ = 0.162 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.141 e Å⁻³

Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.0022 (3)
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute configuration: Flack (1983)
 Flack parameter = 0.0 (2)

Table 1. Selected geometric parameters (Å, °)

O11—C1	1.196 (2)	C6—C7	1.521 (3)
O12—C1	1.321 (2)	C7—C8	1.519 (3)
O3—C3	1.418 (3)	C8—C9	1.518 (3)
O4—C4	1.242 (2)	C9—C10	1.518 (3)
N4—C4	1.337 (2)	C10—C11	1.523 (3)
N4—C2	1.453 (2)	C11—C12	1.509 (3)
C1—C2	1.507 (2)	C12—C13	1.514 (3)
C2—C3	1.527 (3)	C13—C14	1.491 (4)
C4—C5	1.507 (3)	C14—C15	1.518 (5)
C5—C6	1.511 (3)		
C4—N4—C2—C1	-157.8 (2)	C1—C2—C3—O3	-61.9 (2)
O12—C1—C2—N4	178.4 (2)	H4N—N4—C4—O4	170.2 (3)
N4—C2—C3—O3	60.9 (2)		

Table 2. Hydrogen-bonding parameters (Å, °)

	<i>D</i> ··· <i>A</i>	<i>H</i> ··· <i>A</i>	<i>D</i> — <i>H</i> ··· <i>A</i>	<i>H</i> ··· <i>A</i> — <i>X</i>
O12—H12O···O1W ⁱ	2.649 (2)	1.73 (3)	168 (3)	114 (2)† 115 (2)‡
C2—H2···O11 ⁱⁱ	3.325 (3)	2.33 (2)	170 (1)	128.5 (4)
O1W—H1W···O3 ⁱⁱⁱ	2.704 (2)	1.92 (3)	171 (3)	120.4 (9)
O3—H3O···O1W ⁱⁱⁱ	2.774 (2)	2.01 (3)	163 (3)	108 (2)† 124 (3)‡
N4—H4N···O4 ^{iv}	3.063 (2)	2.24 (2)	160 (2)	154.1 (5)
O1W—H2W···O4	2.768 (2)	1.85 (4)	164 (3)	123 (1)

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

† *X* = H1W. ‡ *X* = H2W.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1977) and *SCHAKAL88* (Keller, 1988). Software used to prepare material for publication: *SHELXL93 ACTA* (Sheldrick, 1993).

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 312 Vectorial Membrane Processes), the FNK of the Free University and the Fonds der Chemischen Industrie.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1078). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.
- Anderson, G. W., Zimmerman, J. E. & Callahan, F. M. (1963). *J. Am. Chem. Soc.* **85**, 3030–3039.
- Anderson, G. W., Zimmerman, J. E. & Callahan, F. M. (1964). *J. Am. Chem. Soc.* **86**, 1839–1842.
- Cody, V. (1985). *Chemistry and Biochemistry of the Amino Acids*, edited by G. C. Barrett, p. 649. London: Chapman & Hall.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Frey, M. N., Lehmann, M. S., Koetzle, T. F. & Hamilton, W. C. (1973). *Acta Cryst.* **B29**, 876–884.
- Fuhrhop, J.-H. & Köning, J. (1994). *Membranes and Molecular Assemblies: The Synkinetic Approach*, p. 3. Cambridge: The Royal Society of Chemistry.
- Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 Reference Manual*. Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
- Jeffrey, G. A. & Maluszynska, H. (1983). *Int. J. Biol. Macromol.* **4**, 173–185.
- Johnson, C. K. (1977). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA. (Modified for *Xtal* by G. Davenport, S. Hall & W. Dreissig.)
- Keller, E. (1988). *SCHAKAL88. Fortran Program for the Graphic Representation of Molecular and Crystallographic Models*. University of Freiburg, Germany.
- Kistenmacher, T. J., Rand, G. A. & Marsh, R. E. (1974). *Acta Cryst.* **B30**, 2573–2578.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Stoe & Cie (1991a). *DIF4. Diffractometer Control Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1991b). *REDU4. Data Reduction Program*. Version 7.08. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1997). **C53**, 1073–1075

6-Methyl-3-phenylthiochroman-4-one and 6-Methoxy-3-phenylthiochroman-4-one: Configurational Preference of the Phenylthio Group at the Third Position due to Remote Substitution

D. SRIRAM,^a S. SRINIVASAN,^a K. C. SANTHOSH^b AND K. K. BALASUBRAMANIAN^b

^aDepartment of Physics, Indian Institute of Technology, Madras 600 036, India, and ^bDepartment of Chemistry, Indian Institute of Technology, Madras 600 036, India. E-mail: phy13@iitm.ernet.in

(Received 2 September 1996; accepted 4 March 1997)

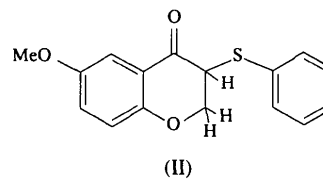
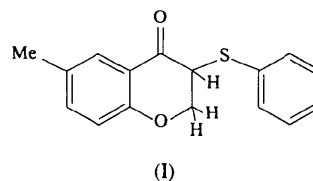
Abstract

The pyran ring adopts a distorted sofa conformation in the title compounds, 6-methyl-3-phenylthiochroman-

4-one (C₁₆H₁₄O₂S), (I), and 6-methoxy-3-phenylthiochroman-4-one (C₁₆H₁₄O₃S), (II). The S atom substituted at the third position is attached equatorially in (II) and axially in (I). High-resolution proton NMR studies could not provide a conclusive explanation for this feature.

Comment

Isoflavanoids, the compounds based on a 3-phenylchroman skeleton, belong to the family Papilionoidae of the Leguminosae of the plant kingdom. They exhibit a large number of structural variations (Dewick, 1988). The title compounds, (I) and (II), belong to the series of 3-phenylchromanones, synthesized by our group, with S as the bridge between the phenyl ring and the C atom at the third position of the heterocycle of the chroman ring system. The bond lengths in the pyran ring (involving atoms O1, C2, C3, C4, C9 and C9') are normal with negligible variations in their values in both compounds. The bond angles around C4 differ significantly from the ideal *sp*² values. Similarly, the bond angles around C9 deviate from the ideal 120°. The bond angle C3—S—C10 in (I) is 3.4° lower than in (II).



The dihedral angles between the planes of the phenyl rings C5–C9 and C10–C15 are 31.9 (4) and 67.1 (9)° in (I) and (II), respectively. In both compounds, the pyran ring adopts a distorted sofa conformation, with C2 deviating from the mean plane formed by the other atoms of this ring [0.651 for (I) and 0.663 Å for (II)], the normal conformation of the pyran ring being half chair (Alex *et al.*, 1993). As seen from the torsion angle O2—C4—C3—S, the S atom is axially connected to the C3 atom in (I) whereas it is connected equatorially in (II). The crystal structures are stabilized by intermolecular van der Waals interactions, although compound (II), which has a relatively higher density, is marked by tighter packing. However, the only difference between the two compounds is the substitution of a methyl group at a remote site (C5) in (I) instead of a methoxy group in (II).