Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1092). Services for accessing these data are described at the back of the journal.

References

Burton, S. D., Kumara Swamy, K. C., Holmes, J. M., Day, R. O. & Holmes, R. R. (1990). *J. Am. Chem. Soc.* **112**, 6104–6115.
Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *User's Manual*. University of Western Australia, Australia.
McArdle, P. (1995). *ORTEX5j*. UCG Crystallography Centre, University College Galway, Ireland.
Said, M. A., Kumara Swamy, K. C., Veith, M. & Huch, V. (1995). *J. Chem. Soc. Perkin Trans.* 1, pp. 2945–2951.
Said, M. A., Pülm, M., Herbst-Irmer, R. & Kumara Swamy, K. C. (1996). *J. Am. Chem. Soc.* **118**, 9841–9849.
Said, M. A., Pülm, M., Herbst-Irmer, R. & Kumara Swamy, K. C. (1997). *Inorg. Chem.* **36**, 2044–2051.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1999). C**55**, 112–114

Scalarolide and scalarin, sesterterpenes from Cacospongia and Ircinia sponges

Richard C. Cambie, Clifton E. F. Rickard, P. Stewart Rutledge and Xiao-Shuang Yang

Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: c.rickard@auckland.ac.nz

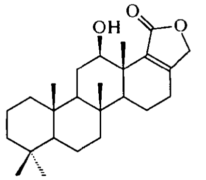
(*Received 2 April 1998; accepted 26 August 1998*)

Abstract

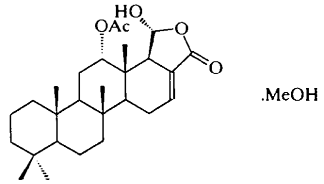
The structures of scalarolide (12β-hydroxyscalar-17-en-24,25-olide) [alternative name (5α,12β)-17a,17-lactone-12-hydroxy-17-(hydroxymethyl)-4,4,8-trimethyl-D-homoandrost-17-ene-17a-carboxylic acid], $C_{25}H_{38}O_3$, from a Cacospongia sponge and scalarin (12α-acetoxy-25α-hydroxyscalar-16-en-25,24-olide) methanol solvate {alternative name [5α,12α,17aβ(R)]-γ-lactone-12-(acetyloxy)-17a-(dihydroxymethyl)-4,4,8-trimethyl-D-homoandrost-16-ene-17-carboxylic acid methanol solvate}, $C_{27}H_{40}O_5\cdot CH_4O$, from an Ircinia sponge have been verified.

Comment

Tetracyclic sesterterpenes with a scalarane skeleton occur frequently as metabolites of sponges of the family Thorectidae (order dictyoceratida) (Faulkner, 1997) which includes the genera Cacospongia and Ircinia. Such compounds have biological importance (Rueda *et al.*, 1997) and their investigation has attracted much interest. During an investigation of the dictyoceratida sponges we have examined the constituents of two unnamed sponges of the genera Cacospongia and Ircinia which have yielded the known scalarane sesterterpenes scalarolide (Walker *et al.*, 1980) and scalarin (Fattorusso *et al.*, 1972), respectively. The structures and relative stereochemistry of the title compounds (I) and (II) have been verified by X-ray crystallography.



(I)



(II)

Compounds with a scalarane-type skeleton which have been examined by this method previously include the homoscalarane 22-acetoxy-24-methyl-12,24-dioxoscalar-16-en-25-al (Kazlauskas *et al.*, 1980), the bishomoscalaranes (20S,24S)-20-acetoxy-12β-hydroxy-20,24-dimethyl-25-norscalar-17-ene-18,24-carbolactone (Croft *et al.*, 1983), methyl 12α-acetoxy-20,24-dimethyl-16,24-dioxoscalara-14,17-dien-25-oate (Declercq *et al.*, 1985) and 24-O-methyl scalardysin-B (16β-acetoxy-24α-methoxy-20,24-dimethyl-12-oxoscalar-24,25-oxide) (Kitagawa *et al.*, 1989), heteronemin (16β,25α-diacetoxy-12β-hydroxyscalar-17(24)-en-24,25-oxide) (Patil *et al.*, 1991), 12-deacetoxyscalaradial, (scalar-16-en-24,25-dicarboxaldehyde) (De Rosa *et al.*, 1994), scalaradial (Puliti *et al.*, 1995) and 3β,25α-dihydroxy-20,24-dimethylscalar-16-en-24,25-oxide (Jaspers *et al.*, 1997).

The structure determinations verify the chemical composition and relative stereochemistry. The figures show the same absolute stereochemistry as scalarane (Kazlauskas *et al.*, 1980). Both molecules show a skeletal distortion similar to that observed for (20S,24S)-20-acetoxy-12β-hydroxy-20,24-dimethyl-25-norscalar-17-ene-18,24-carbolactone (Croft *et al.*, 1983) in that the distances between atoms in the sequence C4, C5, C10, C9, C8, C14, C13, C18 tend to be longer than expected (see Tables 1 and 2). In addition, the angles around C5, C9 and C14 tend to be larger than the tetrahedral value. This has been rationalized in terms of non-bonded hydrogen contacts (Croft *et al.*, 1983). Both molecules also show the bend in the molecular skeleton as found for scalaradial which has been ascribed to interactions between the axial methyl groups (Puliti *et al.*, 1995). An indication of the degree of bending is given by the angle between the mean planes of the *A* and *C* rings, 26.4 (2) and 30.4 (1)° for scalarolide (I) and scalarin (II), respectively.

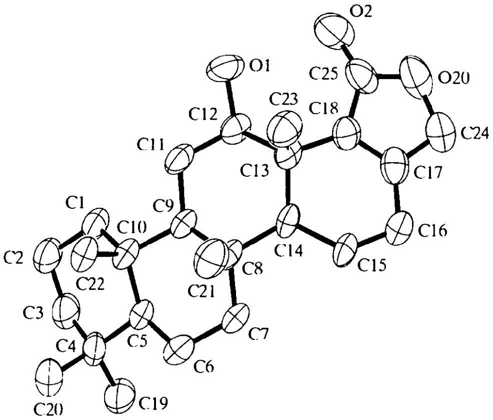


Fig. 1. Structure of scalarolide (I) showing 50% probability displacement ellipsoids. The H atoms are omitted for clarity.

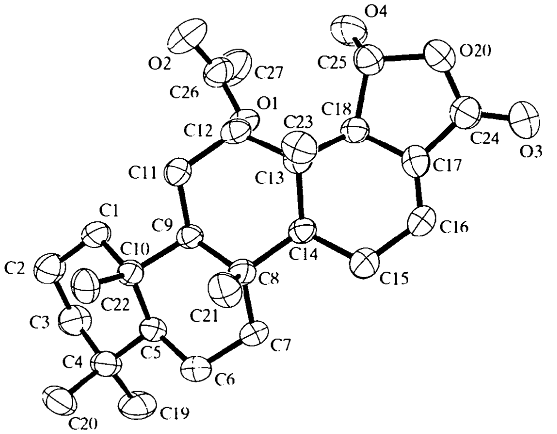


Fig. 2. Structure of scalarin (II) showing 50% probability displacement ellipsoids. The solvent molecule and H atoms are omitted for clarity.

There is an intramolecular hydrogen bond in scalarolide (I) in which the hydroxyl-O1 atom makes an approach of 2.727 (7) Å to O2. The methanol molecule in (II) is hydrogen bonded to two scalarin molecules. The hydroxyl-O4 atom, makes an approach of 2.666 (4) Å to the O5 methanol atom, and O5 also makes an approach of 2.763 (4) Å to O3(1−*x*, *y*−0.5, 1.5−*z*) of an adjacent molecule.

Experimental

Scalarolide was obtained by extraction of Cacospongia sponges with methanol and flash chromatography on silica gel of the dichloromethane-soluble portion. Crystallization from hexane/dichloromethane yielded colourless plates (m.p. 565–567 K).

Scalarin was obtained by extraction of Ircinia 'oanui' with dichloromethane and flash chromatography on silica gel and further purification by preparative TLC. Crystallization from methanol/acetone yielded colourless plates (m.p. 421–422 K).

Compound (I)

Crystal data

$C_{25}H_{38}O_3$
$M_r = 386.55$
Monoclinic
$C2$
$a = 13.7343\,(2)$ Å
$b = 6.1274\,(2)$ Å
$c = 25.2459\,(7)$ Å
$\beta = 92.2770\,(10)°$
$V = 2122.91\,(10)$ Å^3
$Z = 4$
$D_x = 1.209$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6037 reflections
$\theta = 2–25°$
$\mu = 0.077$ mm^{-1}
$T = 203\,(2)$ K
Plate
0.42 × 0.38 × 0.08 mm
Colourless

Data collection

Siemens SMART diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.968$, $T_{\max} = 0.994$
6254 measured reflections

3179 independent reflections
2339 reflections with $I > \sigma(I)$
$R_{\rm int} = 0.057$
$\theta_{\max} = 25.00°$
$h = -15 \rightarrow 15$
$k = -6 \rightarrow 6$
$l = 0 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.085$
$wR(F^2) = 0.245$
$S = 1.072$
3179 reflections
259 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1134P)^2 + 2.8087P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.264$ e Å^{-3}
$\Delta\rho_{\min} = -0.262$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.010 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

C4—C5	1.533 (8)	C9—C10	1.544 (8)
C5—C10	1.586 (8)	C13—C18	1.533 (8)
C8—C14	1.555 (8)	C13—C14	1.552 (7)
C8—C9	1.572 (7)		
C4—C5—C6	113.8 (5)	C10—C9—C8	117.4 (4)
C4—C5—C10	117.6 (4)	C13—C14—C8	117.0 (4)
C6—C5—C10	108.4 (5)	C13—C14—C15	109.3 (4)
C11—C9—C10	115.0 (4)	C8—C14—C15	113.8 (4)
C11—C9—C8	110.2 (4)		

Compound (II)

Crystal data

$C_{27}H_{40}O_5 \cdot CH_4O$
$M_r = 476.63$
Orthorhombic
$P2_12_12_1$
$a = 6.3833\,(3)$ Å
$b = 10.9108\,(6)$ Å
$c = 37.2967\,(19)$ Å
$V = 2597.6\,(2)$ Å^3
$Z = 4$
$D_x = 1.219$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7137 reflections
$\theta = 2–25°$
$\mu = 0.084$ mm^{-1}
$T = 203\,(2)$ K
Plate
0.22 × 0.16 × 0.06 mm
Colourless

Data collection

Siemans SMART diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.982$, $T_{\max} = 0.995$
14889 measured reflections
4541 independent reflections
3191 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 25°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 44$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.135$
$S = 1.076$
4541 reflections
317 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0566P)^2 + 0.6084P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.013$
$\Delta\rho_{\max} = 0.184$ e Å^{-3}
$\Delta\rho_{\min} = -0.210$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (II)*

C4—C5	1.562 (5)	C9—C10	1.570 (4)
C5—C10	1.559 (4)	C13—C18	1.548 (4)
C8—C9	1.553 (4)	C13—C14	1.575 (4)
C8—C14	1.568 (4)		
C6—C5—C10	111.1 (3)	C8—C9—C10	117.3 (2)
C6—C5—C4	115.2 (3)	C15—C14—C8	113.4 (2)
C10—C5—C4	116.9 (3)	C15—C14—C13	111.7 (3)
C11—C9—C8	110.0 (2)	C8—C14—C13	116.7 (2)
C11—C9—C10	114.3 (3)		

Table 3. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*A*···O5	0.83	1.97	2.666 (4)	140.6
O5—H5···O3$^{\rm i}$	1.20 (5)	1.59 (5)	2.763 (4)	167 (3)

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

The data collection nominally covered over a hemisphere of reciprocal space by a combination of three sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.94 cm. In each case a total of 1271 frames was collected. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. Crystals of (I) were of poor quality, yielding a weak diffraction pattern and leading to a higher final residual.

H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom. The scalarin structure (II) also contains a methanol of solvation in which the hydroxyl-H atom was located from a difference map.

The absolute configuration could not be determined in either case and the figures depict the same absolute configuration as scalarane (Kazlauskas *et al.*, 1980).

For both compounds, data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1072). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Croft, K. D., Ghisalberti, E. L., Skelton, B. W. & White, A. H. (1983). *J. Chem. Soc. Perkin Trans.* 1, pp. 155–159.

Declercq, J. P., Van Meerssche, M., Braekman, J. C. & Daloze, D. (1985). *Acta Cryst.* C**41**, 1222–1224.

De Rosa, S., Puliti, R., Crispino, A., De Giulio, A., Mattia, C. A. & Mazzarella, L. (1994). *J. Nat. Prod.* **57**, 256–262.

Fattorusso, E., Magno, S., Santacroce, C. & Sica, D. (1972). *Tetrahedron*, **28**, 5993–5997.

Faulkner, D. J. (1997). *Nat. Prod. Rep.* **14**, 259–302, and previous reviews of this series.

Jaspars, M., Jackson, E., Lobkovsky, E., Clardy, J., Diaz, M. C. & Crews, P. (1997). *J. Nat. Prod.* **60**, 556–561.

Kazlauskas, R., Murphy, P. T., Wells, R. J. & Daly, J. J. (1980). *Aust. J. Chem.* **33**, 1783–1797.

Kitagawa, I., Kobayashi, M., Lee, N. K., Oyama, Y. & Kyogoki, Y. (1989). *Chem. Pharm. Bull.* **37**, 2078–2082.

Patil, A. D., Westley, J. W., Baures, P. W. & Eggleston, D. S. (1991). *Acta Cryst.* C**47**, 1250–1253.

Puliti, R., Mattia, C. A. & Mazzarella, L. (1995). *Acta Cryst.* C**51**, 1703–1707.

Rueda, A., Zubia, E., Ortega, M. J., Carballo, J. L. & Salva, J. (1997). *J. Org. Chem.* **62**, 1451–1485.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Siemens (1994). *SHELXTL.* Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1994). *SMART* and *SAINT. Area-Detector Control and Integration Software.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Walker, R. P., Thompson, J. E. & Faulkner, D. J. (1980). *J. Org. Chem.* **45**, 4976–4979.

Acta Cryst. (1999). C**55**, 114–116

9-Acetonyl-3-ethylidene-1,2,3,4-tetrahydrospiro[carbazole-1,2′-[1,3]dithiolan]-4-one

TUNCER HÖKELEK,[a]* SÜLEYMAN PATIR[b] AND NESİMİ ULUDAĞ[b]

[a]*Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and* [b]*Hacettepe University, Department of Science, Faculty of Education, 06532 Beytepe, Ankara, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr*

(*Received 13 July 1998; accepted 18 August 1998*)

Abstract

The title compound, $C_{18}H_{19}NO_2S_2$, consists of a carbazole skeleton with a pentacyclic dithiolane ring spiro-bonded at position 1 and acetonyl and ethylidene chains