C21—C11—N1	121,8 (3)	C33—C43—C53	120,0 (4)
C61′—C11—N1	115 (1)	C33—C43—O*M*3	120,2 (5)
C11—C21—C31	119,8 (4)	C53—C43—O*M*3	119,8 (5)
C41—C31—C21	121,1 (4)	C43—C53—C63	119,8 (4)
C51′—C41—C31	115 (1)	C13—C63—C53	120,1 (4)
C51′—C41—O*M*1	122 (1)	C73″—C73—O*M*3	42 (3)
C31—C41—O*M*1	120,4 (4)	C73—C73″—O*M*3	113 (5)
C51′—C41—C51	26 (1)		

Code de symétrie: (i) $1 - x, 1 - y, -z$.

La largeur de balayage est $(0{,}71 + 0{,}67\tan\theta)^\circ$. Les intensités ont été corrigées des facteurs de Lorentz–polarisation. La structure a été résolue par les méthodes directes (*SHELXS*86; Sheldrick, 1985) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4 *EXPRESS* (Macicek & Yordanov, 1992). Affinement des paramètres de la maille: *CAD*-4 *EXPRESS*. Réduction des données: *MolEN* (Fair, 1990). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL*93.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: DU1176). Les processus d'accès à ces archives est donné au dos de la couverture.

Références

Averbuch-Pouchot, M. T. & Durif, A. (1989). *C. R. Acad. Sci.* **308**, 1699–1702.

Averbuch-Pouchot, M. T. & Durif, A. (1990*a*). *Acta Cryst.* C**46**, 179–181.

Averbuch-Pouchot, M. T. & Durif, A. (1990*b*). *Acta Cryst.* C**46**, 965–968.

Bagieu-Beucher, M. & Rzaigui, M. (1991). *Acta Cryst.* C**47**, 1789–1791.

Ben Salah, A., Daoud, A., Constant, G., Jaud, J. & Galy, J. (1983). *Acta Cryst.* C**39**, 63–66.

Elmokhtar, O. S. M., Abid, S., Rzaigui, M. & Durif, A. (1995). *Mater. Chem. Phys.* **42**, 225–230.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, Les Pays-Bas.

Macicek, J. & Yordanov, A. (1992). *J. Appl. Cryst.* **25**, 73–80.

Mahoui, A., Lapasset, J. & Moret, J. (1994). *Acta Cryst.* C**50**, 358–362.

Schulke, U. & Kayser, R. (1985). *Z. Anorg. Allg. Chem.* **531**, 167–176.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Université de Göttingen, Allemagne.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Université de Göttingen, Allemagne.

Soumhi, E. H. & Jouini, T. (1996). *Acta Cryst.* C**52**, 434–436.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 159.

Acta Cryst. (1998). C**54**, 816–818

Absolute Configuration of a Tetrachloro Monoterpene from *Plocamium cartilagineum*

PATRICIO RIVERA,[a] VICTOR MANRÍQUEZ[b] AND OSCAR WITTKE[c]

[a]*Ingenieria Forestal, Facultad de Ciencias Silvoagropecuarias, Universidad Mayor, Americo Vespucio 357, Santiago, Chile,* [b]*Departamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile, and* [c]*Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago, Chile. E-mail: vmanriqu@abello.dic.uchile.cl*

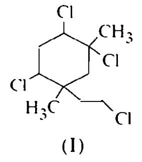
(*Received 23 October 1996; accepted 27 November 1997*)

Abstract

The molecular structure of the naturally occurring title compound, 2,4,5-trichloro-1-chloroethenyl-1,5-dimethylcyclohexane, $C_{10}H_{14}Cl_4$, consists of a cyclohexane ring in a chair conformation with three Cl atoms, two tertiary methyl groups and a chlorovinyl group as substituents. The absolute configuration was determined by the Flack test to be (1*S*,2*R*,4*R*,5*S*,1′*E*)-1,2,4-trichloro-5-(2′-chloroethenyl-1,5-dimethylcyclohexane). This compound is then a diastereomer of that isolated from *Plocamium hamatum* J. Agardh. This species is noted for its insecticidal activity.

Comment

The title compound, (I), was isolated from an acetonic extract of the red algae *Plocamium cartilagineum* collected along the central coast of Chile. Red algae of the genera *Plocamium* and *Chondrococcus* have been shown to be a rich source of polyhalogenated aliphatic and alicyclic monoterpenes. The major components of the monoterpene mixture isolated from materials collected from the central coast of Chile are monocyclic monoterpenes belonging predominantly to two skeletal classes: violacene and mertecene. They have been shown to possess a range of biological activities: antimicrobial (Rovirosa *et al.*, 1990), insecticidal (Crews *et al.*, 1976), antifeedant (Paul *et al.*, 1980) and cytotoxic (Fuller *et al.*, 1992). The title compound has shown insecticidal activity (San-Martin *et al.*, 1991).



(I)

ISSN 0108-2701

The molecular structure of this monocyclic monoterpene exhibits the characteristic violacene skeleton with a cyclohexane ring in a chair conformation possessing as substituents three Cl atoms, two tertiary methyl groups and a chlorovinyl group as a side chain. The chair form of the cyclohexane ring is slightly distorted, with C2 −0.667 (3) and C5 −0.571 (2) Å out of the mean plane defined by atoms C1, C3, C4 and C6. The Cl atom at C2 and the methyl group at C1 are both equatorial, the tertiary methyl group at C1 is axial and the Cl atoms at C2 and C5 are in *trans*-axial configurations. The Flack (1983) parameter was refined to 0.00 (7). The absolute configuration of compound (I) was deduced to be (1*S*,2*R*,4*R*,5*R*,1′*E*)-1,2,4-trichloro-5-(2′-chloroethenyl-1,5-dimethylcyclohexane) which is a diastereomer of (1*R**,2*R**,4*S**,5*R**,1′*E*)-1,2,4-trichloro-5-(2′-chloroethenyl-1,5-dimethylcyclohexane) isolated from *Plocamium hamatum* J. Agardh and collected from the Palm Island group, Australia (Coll *et al.*, 1988). The crystal packing results in H· · ·Cl contacts, the shortest of these being Cl3· · ·H6*A*($-x$, $y-\frac{1}{2}$, $2-z$) at 2.897 (2) Å.

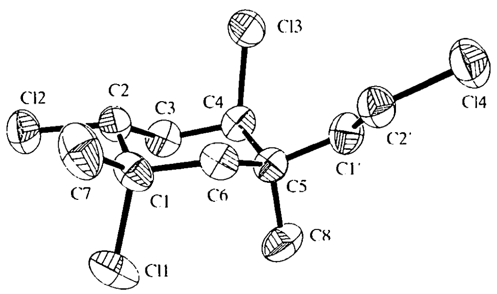


Fig. 1. A perspective drawing of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was crystallized from acetone.

Crystal data

$C_{10}H_{14}Cl_4$
$M_r = 276.01$
Monoclinic
$P2_1$
$a = 7.269\ (1)$ Å
$b = 8.030\ (2)$ Å
$c = 11.055\ (2)$ Å
$\beta = 103.76\ (3)°$
$V = 626.8\ (2)$ Å^3
$Z = 2$
$D_x = 1.462$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–$12.5°$
$\mu = 0.905$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.92 × 0.64 × 0.60 mm
Colourless

Data collection

Siemens *R*3*m* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2534 measured reflections
2159 independent reflections (including Friedel pairs)
2100 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.010$
$\theta_{\rm max} = 27.56°$
$h = -5 \rightarrow 5$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$
3 standard reflections every 47 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.072$
$S = 1.090$
2158 reflections
128 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 0.0833P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.183$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.173$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.006 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.00 (7)

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

Cl1—C1	1.817 (2)	C1—C7	1.529 (3)
Cl2—C2	1.800 (2)	C1—C6	1.537 (3)
Cl3—C4	1.823 (2)	C2—C3	1.518 (3)
Cl4—C2′	1.745 (2)	C3—C4	1.520 (3)
C1′—C2′	1.302 (3)	C4—C5	1.531 (4)
C1′—C5	1.516 (3)	C5—C8	1.541 (3)
C1—C2	1.523 (4)	C5—C6	1.543 (3)
C2′—C1′—C5	127.5 (2)	C2—C3—C4	110.2 (2)
C1′—C2′—Cl4	121.8 (2)	C3—C4—C5	113.8 (2)
C2—C1—C7	112.1 (2)	C3—C4—Cl3	107.5 (2)
C2—C1—C6	108.7 (2)	C5—C4—Cl3	111.23 (14)
C7—C1—C6	109.2 (2)	C1′—C5—C4	108.2 (2)
C2—C1—Cl1	109.57 (15)	C1′—C5—C8	107.2 (2)
C7—C1—Cl1	106.4 (2)	C4—C5—C8	107.4 (2)
C6—C1—Cl1	110.9 (2)	C1′—C5—C6	110.6 (2)
C3—C2—C1	112.9 (2)	C4—C5—C6	110.2 (2)
C3—C2—Cl2	109.4 (2)	C8—C5—C6	113.0 (2)
C1—C2—Cl2	113.25 (14)	C1—C6—C5	118.1 (2)

The collimator aperture was 1 mm. The only suitable single crystal was one with dimensions at the limit of the collimator aperture. The single crystal was not cut to avoid its destruction, but special care was taken in its alignment. H atoms were placed at calculated positions with C—H = 0.97 Å.

Data collection: *P3/P4-PC* (Siemens, 1991). Cell refinement: *P3/P4-PC*. Data reduction: *XDISK* in *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

This research was financed by the following grants: Fundacion Andes C-10810/2; Universidad Mayor, Chile.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1027). Services for accessing these data are described at the back of the journal.

References

Coll, J. C., Skelton, B. W., White, A. H. & Wright, A. D. (1988). *Aust. J. Chem.* **41**, 1743–1753.
Crews, P., Kho, E. & Pace, C. (1976). *Phytochemistry*, **45**, 1707–1711.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fuller, R. W., Cardellina, J. H. II, Kato, Y., Brinen, L. S., Clardy, J., Snader, K. & Boyd, M. R. (1992). *J. Med. Chem.* **35**, 3007–3011.
Paul, J. V., McConnell, D. J. & Fenical, W. (1980). *J. Org. Chem.* **45**, 3401–3434.
Rovirosa, J., Sanchez, I., Palacios, Y., Darias, J. & San-Martin, A. (1990). *Bol. Soc. Chil. Quim.* **35**, 131–135.
San-Martin, A., Negrete, R. & Rovirosa, J. (1991). *Phytochemistry*, **30**, 2165–2169.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1994). *SHELXTL. Structure Determination Programs*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 818–820

Polysulfonylamines. CI. 1,4,7,10-Tetraoxacyclododecane–Di(benzenesulfonyl)amine (1/2)[†]

KARNA WIJAYA, OLIVER MOERS, PETER G. JONES* AND ARMAND BLASCHETTE

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany. E-mail: jones@xray36.anchem.nat.tu-bs.de

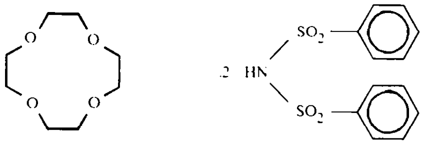
(*Received 6 January 1998; accepted 9 February 1998*)

Abstract

In the centrosymmetric formula unit of the title complex, $C_8H_{16}O_4.2C_{12}H_{11}NO_4S_2$, the disulfonylamine molecules are linked to 12-crown-4 *via* a slightly bent N—H···O hydrogen bond [N···O 2.771 (2) Å]. The macrocycle adopts the [66] conformation and the $(PhSO_2)_2NH$ molecules have an open pseudo-C_2 symmetric conformation with the phenyl groups lying on opposite sides of the S–N–S plane.

Comment

Hydrogen-bond-mediated crystalline complexes between uncharged molecules and coronands, especially 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6), have attracted much attention since the first representatives were reported in 1971 (Pedersen, 1971). It was alleged in a review article that 'guests containing monodentate acidic OH groups...do not associate directly with 18-crown-6'; instead, ternary complexes having water molecules inserted between the substrate and the hexafunctional 18-crown-6 ring were reported to be formed preferentially (Goldberg, 1989; for updated references *cf.* Henschel, Blaschette & Jones, 1995). In contrast to these findings and using di(organosulfonyl)amines, $(RSO_2)_2NH$, as substrates, we were able to demonstrate that binary hydrogen-bonded complexes of 18-crown-6 with mono-acidic guests can indeed be isolated despite the donor–acceptor disparity of their molecular components. Thus, N—H···O-bonded adducts of 18-crown-6 with di(methanesulfonyl)amine (3:2) and bis(2-naphthalenesulfonyl)amine (1:2) were obtained by co-crystallization from anhydrous methanol or 2-propanol, respectively, and structurally characterized by low-temperature X-ray diffraction (Blaschette *et al.*, 1994; Henschel, Näveke *et al.*, 1995). As an extension of this work, we now present the first example, (1), of a binary complex in which a disulfonylamine is directly attached to the smaller coronand 1,4,7,10-tetraoxacyclododecane (12-crown-4).



(1)

The centrosymmetric formula unit of the title complex is shown in Fig. 1; selected intramolecular geometric data are listed in Table 1. A slightly bent N—H···O hydrogen bond, in which the N···O distance is *ca* 0.17 Å shorter than the sum of the van der Waals radii (2.94 Å; Emsley, 1991), links the N—H acids to the crown ether [N—H01 0.80 (2), H01···O34 1.98 (2), N···O34 2.771 (2) Å and N—H01···O34 170 (2)°]. Together with the analogous adducts 12-crown-4.2D, where D = Ph_3SiOH (Babaian *et al.*, 1990) or $(EtSO_2)_2CH_2$ (Michalides *et al.*, 1995), compound (1) forms a series of binary complexes displaying O—H···O, C—H···O or N—H···O interactions.

The macrocycle in (1) adopts the C_i-symmetric [66] conformation that also occurs in pure crystalline 12-crown-4 (Groth, 1978), in the aforementioned molecular 1:2 complexes and in a number of other structures [for systematic conformational analyses of the coronand in its complexes *cf.* Raithby *et al.* (1997) and Hay *et al.* (1995)]. The C—O [average 1.431 (2) Å] and C—C distances [average 1.499 (3) Å] are normal, as are the C—O—C angles [average 114.59 (14)°], the O—C—C angles [average 110.2 (2)°] and the 'bite' of the

---

[†] Part C: Moers *et al.* (1998).

ISSN 0108-2701