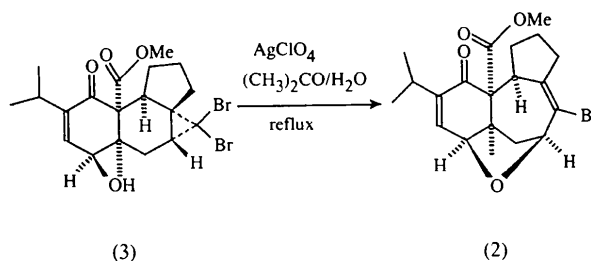


- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1994). *SHELXTL*. Release 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994). *XSCANS Users Manual*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Temussi, P. A., Salvadori, S., Amodeo, P., Guerrini, R., Tomatis, R., Lazarus, L. H., Picone, D. & Tancredi, T. (1994). *Biochem. Biophys. Res. Commun.* **198**, 933–939.
- Wilkes, B. C. & Schiller, P. W. (1995). *Biopolymers (Peptide Sci.)*, **37**, 391–400.

plex rearrangement reaction catalyzed by silver(I) salts in polar solvents (Brocksom, Pesquero & Lopes, 1990) leading to the crystalline product (2). Although the macroscopic sample is racemic, the crystal selected by hand turned out to be a single enantiomer and is the subject of the present paper. This three-dimensional structure determination is absolutely essential for successful planning of the total synthesis and cannot be accomplished by conventional spectroscopic means such as high-field NMR measurements.



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## Intermediates in the Synthesis of *Daphniphyllum* Alkaloids. I. A Tetracyclic Oxygen Analogue

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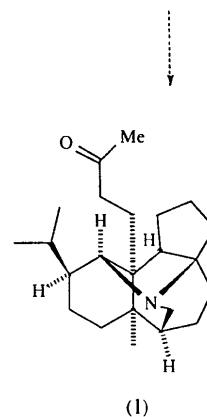
(Received 28 February 1997; accepted 4 April 1997)

### Abstract

In methyl (3*S*,5*S*,6*S*,10*R*,11*R*)-2-bromo-3,6-epoxy-8-isopropyl-5-methyl-9-oxotricyclo[9.3.0.0<sup>5,10</sup>]tetradeca-1,7-diene-10-carboxylate, C<sub>20</sub>H<sub>25</sub>BrO<sub>4</sub>, the seven-membered ring is half-chair shaped, the six-membered ring adopts a boat conformation and the five-membered rings both adopt envelope conformations. The molecule adopts an overall hemispherical conformation.

### Comment

In our projected synthesis of *Daphniphyllum* alkaloids, such as methyl homodaphniphyllate, (1), we have developed a route to an oxygen analogue, (2), containing many of the same structural features. We have previously presented the X-ray structure determination of a tetracyclic intermediate, (3) (Castellano, Brocksom & Ceschi, 1994), and this compound undergoes a com-



A *ZORTEP* (Zsolnai, 1995) illustration of the formula unit showing the relative stereochemistry is presented in Fig. 1 and selected bond distances and angles are given in Table 1. Compound (2) has an ether bridge in a tetracyclic structure containing fused six-, seven- and five-membered carbocyclic skeletons, analogous to the nitrogen-bridged *Daphniphyllum* alkaloids. The structure is heavily influenced by the ether bridge which forces the molecule to adopt an overall hemispherical conformation. The six-membered ring is in a slightly distorted boat conformation, with C<sub>6</sub> and C<sub>9</sub> lying at distances of 0.516 (6) and 0.408 (5) Å, respectively, from the least-squares plane through atoms C<sub>5</sub>, C<sub>7</sub>, C<sub>8</sub> and C<sub>10</sub>; both five-membered rings adopt envelope conformations, with C<sub>13</sub> and C<sub>5</sub> occupying the flap positions at distances of 0.526 (7) and −0.696 (5) Å from the least-squares plane made up of the remaining four atoms in the cyclopentane and furan rings, respectively. The molecules are joined through C—H···O interactions: C<sub>11</sub>···O<sub>1</sub><sup>i</sup> 3.410 (7), H<sub>11</sub>···O<sub>1</sub><sup>i</sup> 2.53 Å and

C11—H11...O1<sup>i</sup> 149°; C4...O1<sup>i</sup> 3.377 (8), H4B...O1<sup>i</sup> 2.43 Å and C4—H4B...O1<sup>i</sup> 166° [symmetry code: (i)  $-x, \frac{1}{2} + y, 2 - z$ ].

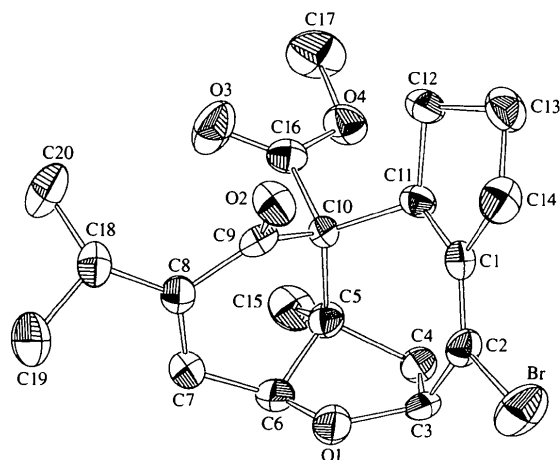


Fig. 1. The molecular structure of (2) showing the atom labelling; 50% probability displacement ellipsoids are shown.

## Experimental

The synthesis of (2) has been described by Ceschi (1994). Crystals were obtained by slow evaporation from a hexane/Et<sub>2</sub>O mixture at 269 K.

### Crystal data

C<sub>20</sub>H<sub>25</sub>BrO<sub>4</sub>  
*M<sub>r</sub>* = 409.319  
 Monoclinic  
*P*2<sub>1</sub>  
*a* = 7.9210 (9) Å  
*b* = 10.6680 (10) Å  
*c* = 10.7280 (10) Å  
 $\beta$  = 94.400 (10)°  
*V* = 903.86 (16) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.5040 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

### Data collection

Enraf-Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 Gaussian (PLATON; Spek,  
 1990)  
*T<sub>min</sub>* = 0.584, *T<sub>max</sub>* = 0.661  
 2402 measured reflections  
 2288 independent reflections

Mo *K* $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 25  
 reflections  
 $\theta$  = 9.54–19.35°  
 $\mu$  = 2.296 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Irregular  
 0.38 × 0.25 × 0.20 mm  
 Colourless

1473 reflections with  
 $F^2 > 2\sigma(F^2)$   
*R<sub>int</sub>* = 0.023  
 $\theta_{\max}$  = 27.97°  
*h* = -10 → 10  
*k* = 0 → 14  
*l* = 0 → 14  
 2 standard reflections  
 frequency: 60 min  
 intensity decay: 0.8%

### Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.117$   
*S* = 1.077  
 2288 reflections  
 230 parameters  
 H-atom parameters  
 constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0376P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.000$   
 $\Delta\rho_{\max} = 0.393 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.775 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)  
 Absolute configuration:  
 Flack (1983)  
 Flack parameter = 0.00 (2)

Table 1. Selected geometric parameters (Å, °)

Br—C2	1.906 (5)	C1—C11	1.523 (7)
O1—C6	1.439 (7)	C2—C3	1.500 (8)
O1—C3	1.457 (8)	C7—C8	1.323 (8)
O2—C9	1.212 (7)	C8—C9	1.479 (8)
C1—C2	1.325 (8)	C8—C18	1.524 (8)
C1—C14	1.499 (8)		
C6—O1—C3	108.5 (4)	C1—C2—Br	119.9 (4)
C2—C1—C14	125.9 (5)	C3—C2—Br	114.2 (4)
C2—C1—C11	124.9 (5)	C7—C8—C9	116.4 (5)
C14—C1—C11	109.1 (5)	C7—C8—C18	125.1 (6)
C1—C2—C3	125.9 (5)	C9—C8—C18	118.2 (5)

H atoms were refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.5 (for methyl H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1310). Services for accessing these data are described at the back of the journal.

## References

- Brocksom, T. J., Pesquero, E. T. C. & Lopes, F. T. (1990). *Synth. Commun.* **20**, 1181–1191.
- Castellano, E. E., Brocksom, T. J. & Ceschi, M. A. (1994). *Acta Cryst.* **C50**, 124–126.
- Ceschi, M. A. (1994). PhD thesis, Universidade Federal de São Carlos, SP, Brazil.
- Enraf-Nonius. (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34
- Zsolnai, L. (1995). *ZORTEP. An Interactive Molecular Graphics Program*. University of Heidelberg, Germany.