

## Refinement

Refinement on $F$	$(\Delta/\sigma)_{\max} = 0.60$
Final $R = 0.063$	$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
$wR = 0.069$	$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$
517 reflections	Atomic scattering factors
89 parameters	from <i>International Tables</i>
H-atom parameters not refined	for <i>X-ray Crystallography</i>
	(1974, Vol. IV)
$w = [\sigma^2(F) + 0.001F^2]^{-1}$	

The density was determined by flotation in a dioxane/ $\text{CCl}_4$  solution. A linear correction was made for the decay in intensity of the three standard reflections. The structure was solved by direct methods using *MULTAN80* (Main *et al.*, 1980). As a result of the large decay in intensity (few observed reflections) and disorder in the tetrabutylammonium ion (large displacement parameters), rigid-body least-squares refinement was used for the ring system in the phthalimidato group with structural parameters taken from *N, N'*-biphthalimide (Aprea, Foces-Foces, Cano & Garcia-Blanco, 1978). All H atoms were placed in calculated positions and assigned an isotropic displacement parameter identical to that of the corresponding C atom. Br, N and O atoms were refined with anisotropic displacement parameters. The disorder in one of the butyl groups was interpreted as statistical with the occupancy factors fixed at 0.5. The *SHELX76* program system (Sheldrick, 1976) was used in the refinement.

We would like to thank Professor C. P. Brock for a useful discussion and for providing us with the results of her work prior to publication.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55227 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1007]

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## Structure of an Intermediate in the Synthesis of Corymbolone

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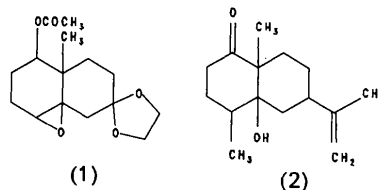
(Received 15 April 1992; accepted 8 July 1992)

## Abstract

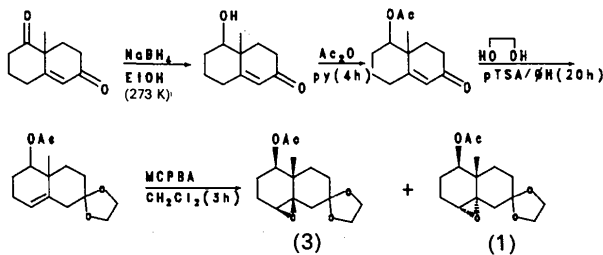
In the title compound, 7,7-ethylenedioxy-4 $\alpha$ , $\beta$ -methyl-1 $\alpha$ , $\beta$ ,2,4 $\alpha$ ,4 $\alpha$ ,5,6,7,8-octahydro-3*H*-naphth-[1,8*a-b*]oxiren-4-yl acetate, the epoxide ring is *trans* to the axial methyl group of the ring junction, which is *cis* to the equatorial acetate group. The six-membered rings are *trans*-fused, one in a chair and the other in a sofa conformation.

## Comment

The title compound (1) is a key intermediate in the synthesis of sesquiterpenoid natural products such as corymbolone (2) (Gambarino, Gambaro & Chamy, 1985).



It was prepared in four stages as shown in the scheme below.



Compound (1) was obtained together with a minor amount of its isomer (3). The isomeric mixture was

separated by column chromatography (silica gel 60, *n*-hexane:ethyl acetate 7:3 as eluent). The structure determination of (1) was undertaken to determine unambiguously its stereochemistry; this is necessary to predict successive reaction pathways.

The C(1)–C(12) ring is in a chair conformation: C(1) and C(8) are displaced by 0.655 (4) and –0.647 (4) Å from the best plane through C(6), C(7), C(11) and C(12). The C(1)–C(6) ring is in a sofa conformation with C(2) 0.688 (4) Å out of the best plane through C(1), C(3), C(4), C(5) and C(6). The five-membered ring is in an envelope conformation with O(3) 0.341 (4) Å out of the plane.

Relevant intermolecular C—H···O interactions are O(4)···C(10) 3.486 (7), O(4)···H'(C10) 2.735 (7) Å, C(10)—H'(C10)···O(4) 132 (1)° and O(5)···C(9) 3.486 (8), O(5)···H(C9) 2.583 (8) Å, C(9)—H(C9)···O(5) 159 (1)°.

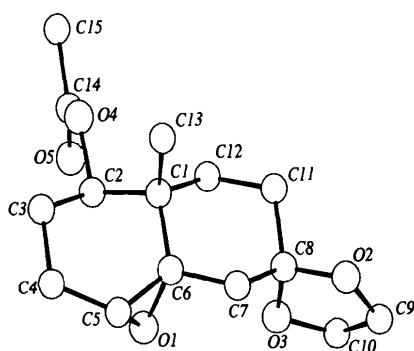


Fig. 1. View of  $C_{15}H_{22}O_5$  showing the atom labelling.

## Experimental

### Crystal data

$C_{15}H_{22}O_5$

$M_r = 282.3$

Monoclinic

$P2_1/c$

$a = 10.046 (2) \text{ \AA}$

$b = 12.365 (2) \text{ \AA}$

$c = 12.065 (2) \text{ \AA}$

$\beta = 111.60 (2)^\circ$

$V = 1393.6 (9) \text{ \AA}^3$

$Z = 4$

$D_x = 1.346 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 7-18^\circ$

$\mu = 0.09 \text{ mm}^{-1}$

$T = 292 \text{ K}$

Irregular

$0.45 \times 0.30 \times 0.18 \text{ mm}$

Colourless

### Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction: none

2167 measured reflections

2067 independent reflections

1207 observed reflections

$[I > 3\sigma(I)]$

$R_{int} = 0.017$

$\theta_{max} = 25^\circ$

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 14$

$l = 0 \rightarrow 14$

3 standard reflections

frequency: 30 min

intensity variation: 1.3%

## Refinement

Refinement on  $F$

Final  $R = 0.055$

$wR = 0.062$

$S = 1.30$

1207 reflections

182 parameters

$w = [\sigma^2(|F_o|) + 0.002|F_o|^2]^{-1}$   
 $(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.23 \text{ e \AA}^{-3}$

$\Delta\rho_{min} = -0.22 \text{ e \AA}^{-3}$

Atomic scattering factors from SHELX76

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

	$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$			$B_{eq}$
	x	y	z	
O(1)	-0.0366 (3)	0.1387 (2)	0.2099 (2)	3.65 (9)
O(2)	-0.4207 (3)	0.3079 (3)	-0.0426 (3)	5.8 (1)
O(3)	-0.2921 (3)	0.2826 (3)	0.1543 (3)	4.8 (1)
O(4)	0.2716 (3)	0.3646 (3)	0.2150 (3)	3.68 (9)
O(5)	0.2806 (4)	0.4053 (3)	0.3995 (3)	5.1 (1)
C(1)	0.0368 (4)	0.2876 (3)	0.1030 (3)	2.7 (1)
C(2)	0.1808 (5)	0.2700 (3)	0.2066 (3)	3.0 (1)
C(3)	0.2600 (5)	0.1728 (4)	0.1879 (4)	3.7 (1)
C(4)	0.1732 (5)	0.0672 (4)	0.1703 (4)	4.4 (2)
C(5)	0.0139 (5)	0.0822 (3)	0.1281 (4)	3.4 (1)
C(6)	-0.0546 (5)	0.1884 (3)	0.0966 (4)	3.0 (1)
C(7)	-0.2093 (5)	0.1978 (4)	0.0142 (4)	3.6 (1)
C(8)	-0.2788 (5)	0.2969 (4)	0.0411 (4)	3.9 (2)
C(9)	-0.5127 (6)	0.3232 (6)	0.0178 (6)	6.7 (2)
C(10)	-0.4242 (5)	0.3267 (5)	0.1455 (5)	5.3 (2)
C(11)	-0.1917 (5)	0.3988 (4)	0.0427 (4)	4.2 (2)
C(12)	-0.0386 (5)	0.3866 (3)	0.1306 (4)	3.7 (1)
C(13)	0.0588 (5)	0.3010 (4)	-0.0150 (4)	3.8 (1)
C(14)	0.3130 (5)	0.4242 (4)	0.3152 (4)	3.5 (1)
C(15)	0.4038 (6)	0.5182 (4)	0.3075 (5)	5.4 (2)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O(1)—C(5)	1.445 (5)	O(1)—C(6)	1.448 (5)
O(2)—C(8)	1.418 (6)	O(2)—C(9)	1.385 (7)
O(3)—C(8)	1.431 (5)	O(3)—C(10)	1.402 (7)
O(4)—C(2)	1.464 (5)	O(4)—C(14)	1.344 (5)
O(5)—C(14)	1.200 (6)	C(1)—C(2)	1.540 (6)
C(1)—C(6)	1.517 (6)	C(1)—C(12)	1.539 (6)
C(1)—C(13)	1.528 (6)	C(2)—C(3)	1.504 (6)
C(3)—C(4)	1.541 (7)	C(4)—C(5)	1.502 (8)
C(5)—C(6)	1.466 (6)	C(6)—C(7)	1.510 (6)
C(7)—C(8)	1.504 (7)	C(8)—C(11)	1.530 (7)
C(9)—C(10)	1.469 (8)	C(11)—C(12)	1.521 (7)
C(14)—C(15)	1.501 (7)		
C(5)—O(1)—C(6)	60.9 (3)	C(8)—O(2)—C(9)	109.2 (4)
C(8)—O(3)—C(10)	107.3 (4)	C(2)—O(4)—C(14)	118.6 (3)
C(2)—C(1)—C(6)	107.3 (3)	C(2)—C(1)—C(12)	109.1 (3)
C(2)—C(1)—C(13)	110.9 (3)	C(6)—C(1)—C(12)	108.5 (3)
C(6)—C(1)—C(13)	109.4 (3)	C(12)—C(1)—C(13)	111.5 (4)
O(4)—C(2)—C(1)	108.6 (3)	O(4)—C(2)—C(3)	107.4 (3)
C(1)—C(2)—C(3)	112.5 (4)	C(2)—C(3)—C(4)	113.2 (4)
C(3)—C(4)—C(5)	114.9 (4)	O(1)—C(5)—C(4)	115.2 (4)
O(1)—C(5)—C(6)	59.7 (3)	C(4)—C(5)—C(6)	122.6 (4)
O(1)—C(6)—C(1)	115.6 (3)	O(1)—C(6)—C(5)	59.4 (3)
O(1)—C(6)—C(7)	113.3 (4)	C(1)—C(6)—C(5)	119.6 (4)
C(1)—C(6)—C(7)	115.4 (4)	C(5)—C(6)—C(7)	120.7 (4)
C(6)—C(7)—C(8)	111.6 (4)	O(2)—C(8)—O(3)	105.6 (4)
O(2)—C(8)—C(7)	110.5 (4)	O(2)—C(8)—C(11)	110.5 (4)
O(3)—C(8)—C(7)	108.6 (4)	O(3)—C(8)—C(11)	110.1 (4)
C(7)—C(8)—C(11)	111.4 (4)	O(2)—C(9)—C(10)	107.0 (5)
O(3)—C(10)—C(9)	105.0 (5)	C(8)—C(11)—C(12)	110.7 (4)
C(1)—C(12)—C(11)	112.3 (4)	O(4)—C(14)—O(5)	124.4 (4)
O(4)—C(14)—C(15)	111.3 (4)	O(5)—C(14)—C(15)	124.3 (5)

H atoms were included as fixed contributors at positions found in a difference synthesis and refined with a common isotropic temperature factor of  $0.077(3) \text{ \AA}^2$ .

Programs used were SHELX76 (Sheldrick, 1976), SHELXS86 (Sheldrick, 1985) and ORTEP (Johnson, 1965). The refinement

was by full-matrix least-squares methods. Most of the calculations were performed on a VAX 6420 computer at the Instituto de Física e Química de Sao Carlos.

This work has received partial support from CNPq, FAPESP, CAPES and FINEP.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55321 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1013]

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## D-Secoestrone Derivatives. II. 16-Cyano-3-methoxy-16,17-secoestra-1,3,5(10)-trien-17-yl *p*-Toluenesulfonate

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## Abstract

The asymmetric unit contains two molecules, which differ slightly in the geometry of their toluenesul-

fonyloxy moieties. The strong dipole–dipole repulsion between the sulfonyl and nitrile groups determines the conformation of these parts of the molecules.

## Comment

The title compound was synthesized as a crucial intermediate in the preparation of some 17-deoxy-17-halogeno-D-secoestrone derivatives (Petrović, Pejanović, Miljković & Hranisavljević, 1990). However, this compound did not show any estrogenic or antiestrogenic activity. The structures of the chloro, bromo and iodo derivatives have already been published (Stanković, Petrović, Miljković, Pejanović, Kovačević, Stefanović & Bruvo, 1992).

A perspective view of the symmetry-independent molecule *A*, computed from the final atomic coordinates listed in Table 1, is shown in Fig. 1. Selected bond lengths, angles and torsion angles are given in Table 2. As the starting material was synthesized from natural estrone, the absolute stereochemistry of which is known (Fieser & Fieser, 1967), it was assumed, for the purposes of the X-ray structure refinement, that the same enantiomorph occurs in the crystalline state.

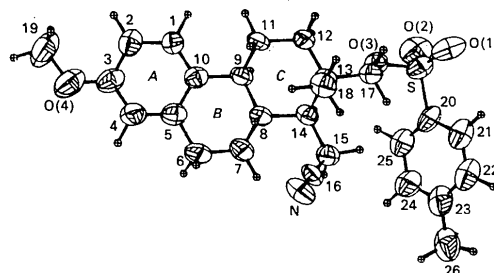


Fig. 1. A perspective view of the symmetry independent molecule *A*.

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$U_{eq} = \frac{1}{3} [(U_{11} + U_{33})\sin^2\beta + U_{22} + 2U_{13}\sin^{-2}\beta\cos\beta].$$

	x	y	z	$U_{eq}$
S(1A)	0.3532 (1)	0.3984 (3)	0.8754 (2)	0.071 (0)
O(1A)	0.3164 (2)	0.5155 (8)	0.8611 (5)	0.094 (2)
O(2A)	0.3943 (2)	0.4650 (8)	0.8479 (5)	0.096 (2)
O(3A)	0.3611 (1)	0.3375 (6)	1.0213 (4)	0.064 (1)
O(4A)	0.5066 (2)	-0.2589 (10)	1.8457 (6)	0.110 (2)
N(1A)	0.2852 (2)	-0.3127 (8)	1.2106 (6)	0.081 (2)
C(1A)	0.4589 (2)	0.0733 (10)	1.6176 (6)	0.063 (2)
C(2A)	0.4816 (2)	0.0039 (11)	1.7299 (7)	0.071 (2)
C(3A)	0.4849 (2)	-0.1764 (12)	1.7401 (8)	0.074 (2)
C(4A)	0.4670 (2)	-0.2736 (11)	1.6370 (8)	0.078 (2)
C(5A)	0.4451 (2)	-0.2032 (9)	1.5239 (7)	0.062 (2)
C(6A)	0.4245 (2)	-0.3189 (9)	1.4133 (7)	0.068 (2)
C(7A)	0.4125 (2)	-0.2291 (9)	1.2829 (6)	0.062 (2)
C(8A)	0.3854 (2)	-0.0680 (8)	1.3097 (6)	0.051 (1)
C(9A)	0.4150 (2)	0.0595 (8)	1.3921 (6)	0.055 (2)
C(10A)	0.4397 (2)	-0.0231 (9)	1.5122 (7)	0.057 (2)
C(11A)	0.3885 (2)	0.2186 (8)	1.4280 (6)	0.059 (2)