For all compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structure: *CRYSTAN-GM* (Edwards, Gilmore, Mackay & Stewart, 1995); program(s) used to refine structure: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1017). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allinger, N. L. (1977). *J. Am. Chem. Soc.* **99**, 8127–8134.

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1995). *CRYSTAN-GM*. Version 6.2. *Computer Program for the Solution and Refinement of Crystal Structures*. MacScience, Japan.

Kawata, T., Okuda, M., Ohba, S., Umehara, M., Honnami, H. & Hishida, S. (1993). *Acta Cryst.* C**49**, 410–413.

Rigaku Corporation (1993). *AFC/MSC Diffractometer Control System*. Rigaku Corporation, Tokyo, Japan.

Umehara, M., Honnami, H., Hishida, S., Kawata, T., Ohba, S. & Zen, S. (1993). *Bull. Chem. Soc. Jpn*, **66**, 562–567.

Acta Cryst. (1997). C**53**, 620–624

(*E*)-*o*-Stilbenecarboxylic Acid and its *p*-Methyl, Chloro and Methoxy Derivatives

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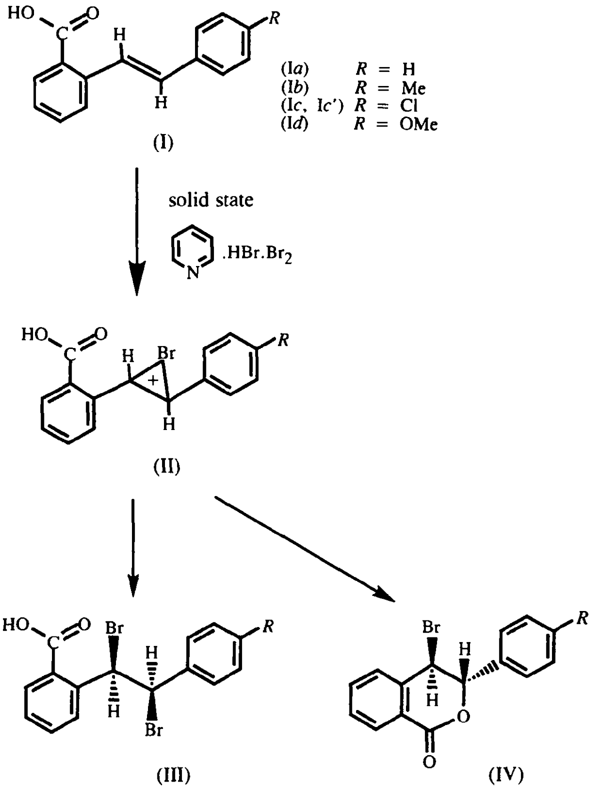
Abstract

The crystal structures of the title compounds, (*E*)-stilbene-1-carboxylic acid, $C_{15}H_{12}O_2$, (I*a*), (*E*)-4′-methylstilbene-1-carboxylic acid, $C_{16}H_{14}O_2$, (I*b*), (*E*)-4′-chlorostilbene-1-carboxylic acid, $C_{15}H_{11}ClO_2$, (I*c*) and (I*c*′), and (*E*)-4′-methoxystilbene-1-carboxylic acid, $C_{16}H_{14}O_3$, (I*d*), have been determined. The chloro derivative shows polymorphism, with prisms, (I*c*), being obtained from ether/hexane solution and needle crystals, (I*c*′), being obtained from ethanol solution. The latter is isostructural with (I*d*). The selectivities of the products to the addition reaction of bromine are different, however, suggesting that the bromonium ion intermediate is stabilized by a resonance contribution of the *p*-MeO group.

Comment

Reaction of (*E*)-*o*-stilbenecarboxylic acid, (I*a*), with bromine in solution gives *trans*-4-bromo-3-phenyl-3,4-dihydroisocoumarin, (IV*a*), as the major product through the intramolecular attack of a carboxylic acid O atom on the carbenium ion C atom of the bromonium ion intermediate (II*a*), along with *erythro*-1,2-dibromo-1,2-dihydro-*o*-stilbenecarboxylic acid, (III*a*) (Berti, 1958). When the bromination was carried out in AcOH, $CHCl_3$ and CH_2Cl_2, compound (IV*a*) was produced as the major product, although the reaction in CCl_4 at 263 K gave compound (III*a*) as the major product. Nevertheless, it is difficult to control the reaction in solution completely. On the other hand, the reaction can be controlled perfectly when carried out in the solid state. Treatment of powdered (I*a*) with bromine vapour or with powdered pyridine.HBr.Br_2 complex in the solid state at room temperature gave compound (III*a*) selectively. Reactions of the *p*-methyl, (I*b*), and *p*-chloro, (I*c*), derivatives of (*E*)-*o*-stilbenecarboxylic acid with the pyridine.HBr.Br_2 complex in the solid state also gave only compounds (III*b*) and (III*c*), respectively. However, the *p*-methoxy derivative, (I*d*), gave mainly compound (IV*d*).



In compounds (I*a*)–(I*d*), the orientation of the carboxylic acid group with respect to the central C=C double bond of the stilbene moiety is essentially the same. The carboxylic acid groups form cyclic hydrogen-bonded dimers related by an inversion centre in all the crystals. The O1—C3—C4—C9 torsion angles are 27.3 (2), 24.2 (1), 12.4 (2), −0.6 (6) and −2.7 (2)° for compounds (I*a*), (I*b*), (I*c*), (I*c*′) and (I*d*), respectively. The O101—C103—C104—C109 angle of the second molecule in (I*c*) is 0.1 (2)°. These slight differences in conformation do not seem to affect the selectivity of the reaction. In fact, both (I*c*) and (I*c*′) lead to (III*c*) in 100% yield, but (I*d*) gives 20% (III*d*) and 80% (IV*d*). The addition reaction of bromine may occur at crystal surfaces, where the molecules vibrate greatly.

The specificity of the solid-state reaction of (I*d*) is attributed to the resonance effect of the methoxyl group, which may prolong the half-life time of intermediate (II) and makes the intramolecular attack of the carboxylic acid oxygen on the cationic centre possible.

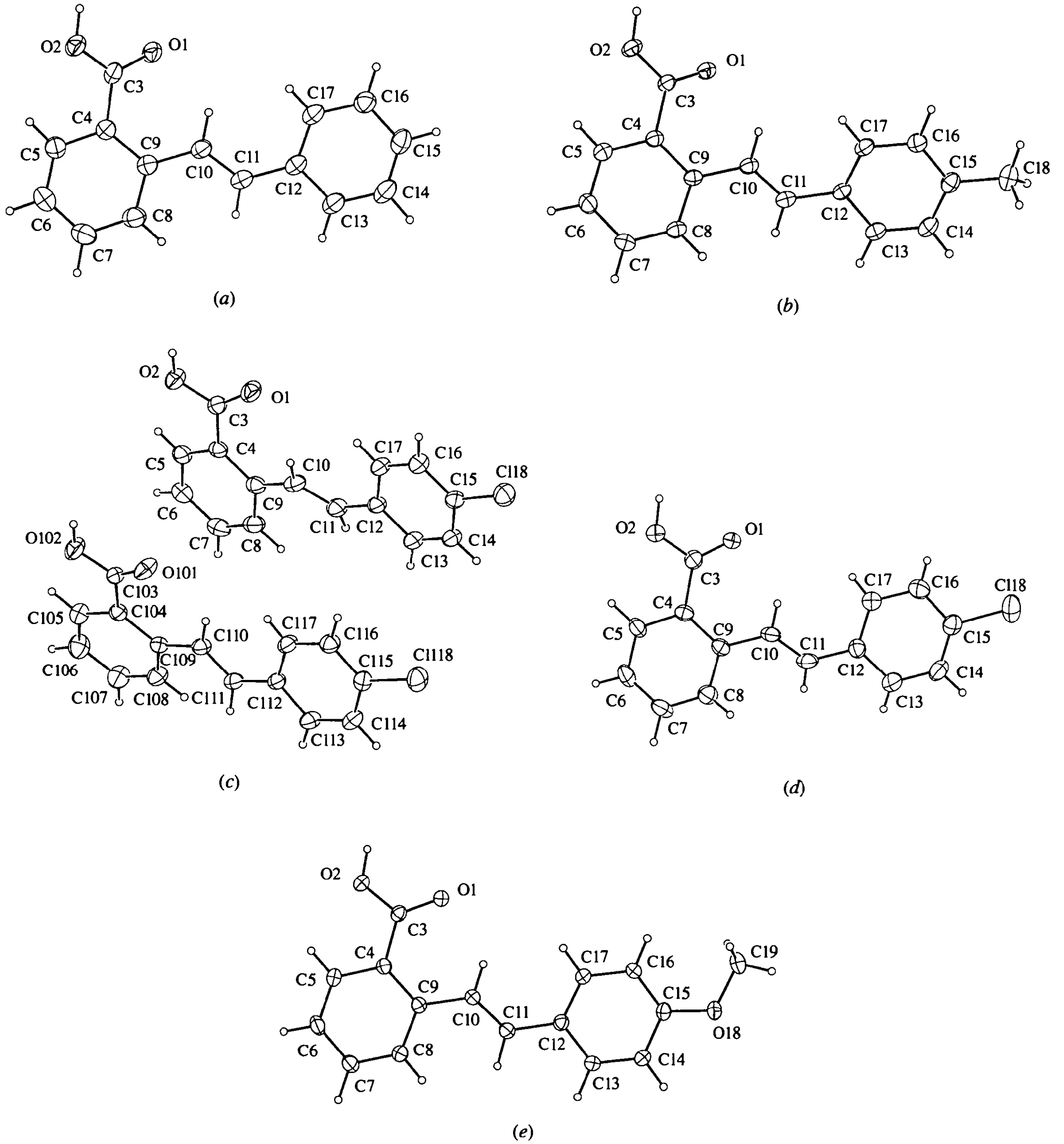


Fig. 1. The molecular structures of (*a*) compound (I*a*), (*b*) compound (I*b*), (*c*) compound (I*c*), (*d*) compound (I*c*′) and (*e*) compound (I*d*), with displacement ellipsoids at the 20% probability level. H atoms are represented by circles of radius 0.1 Å.

Structure checks at the Chester office indicated that there is a local pseudo-centre of symmetry for (I*c*) relating the atoms of the two independent molecules. Pseudo-inversion centres were studied by Desiraju, Calabrese & Harlow (1991) utilizing the Cambridge Structural Database (Allen *et al.*, 1991).

Experimental

Crystals of (I*c*) were grown from ether/hexane solution, while those of (I*c*′) were grown from ethanol.

Compound (I*a*)

Crystal data

$C_{15}H_{12}O_2$
$M_r = 224.26$
Monoclinic
$P2_1/n$
$a = 6.159\ (2)$ Å
$b = 8.332\ (3)$ Å
$c = 23.306\ (2)$ Å
$\beta = 90.93\ (2)°$
$V = 1195.8\ (6)$ Å^3
$Z = 4$
$D_x = 1.246$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.9$–$15.0°$
$\mu = 0.082$ mm^{-1}
$T = 300$ K
Prism
0.6 × 0.5 × 0.5 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
ω scans
Absorption correction: none
2314 measured reflections
2106 independent reflections
1421 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 9$
$l = -27 \rightarrow 27$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0468$
$wR = 0.0422$
$S = 1.24$
1421 reflections
199 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\rm max} = 0.04$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C3	1.244 (2)	C9—C10	1.466 (3)
O2—C3	1.291 (2)	C10—C11	1.318 (3)
C3—C4	1.476 (3)	C11—C12	1.459 (3)
O1—C3—O2	121.2 (2)	C3—C4—C9	123.3 (2)
O1—C3—C4	123.3 (2)	C9—C10—C11	126.3 (2)
O2—C3—C4	115.5 (2)	C10—C11—C12	127.6 (2)
C3—C4—C5	116.7 (2)		

Compound (I*b*)

Crystal data

$C_{16}H_{14}O_2$
$M_r = 238.29$
Monoclinic
$P2_1/n$
$a = 7.138\ (2)$ Å
$b = 12.036\ (2)$ Å
$c = 14.874\ (2)$ Å
$\beta = 91.74\ (2)°$
$V = 1277.3\ (5)$ Å^3
$Z = 4$
$D_x = 1.239$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.8$–$15.0°$
$\mu = 0.081$ mm^{-1}
$T = 300$ K
Plate-like
0.6 × 0.6 × 0.5 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: none
2449 measured reflections
2256 independent reflections
1796 reflections with $|F_o| > 3\sigma(|F_o|)$

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 14$
$l = -17 \rightarrow 17$
3 standard reflections every 100 reflections intensity decay: 5.2%

Refinement

Refinement on F
$R = 0.0456$
$wR = 0.0510$
$S = 1.20$
1796 reflections
216 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\rm max} = 0.06$
$\Delta\rho_{\rm max} = 0.12$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

O1—C3	1.230 (2)	C9—C10	1.469 (2)
O2—C3	1.304 (2)	C10—C11	1.325 (2)
C3—C4	1.484 (2)	C11—C12	1.463 (2)
O1—C3—O2	122.4 (1)	C3—C4—C9	122.1 (1)
O1—C3—C4	122.8 (1)	C9—C10—C11	125.6 (1)
O2—C3—C4	114.8 (1)	C10—C11—C12	127.4 (1)
C3—C4—C5	117.6 (1)		

Compound (I*c*)

Crystal data

$C_{15}H_{11}ClO_2$
$M_r = 258.70$
Monoclinic
$P2_1/n$
$a = 12.977\ (5)$ Å
$b = 8.023\ (4)$ Å
$c = 25.171\ (3)$ Å
$\beta = 103.56\ (2)°$
$V = 2547.6\ (16)$ Å^3
$Z = 8$
$D_x = 1.349$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 14.7$–$15.0°$
$\mu = 0.290$ mm^{-1}
$T = 300$ K
Prism
0.6 × 0.4 × 0.4 mm
Pale yellow

Data collection

Rigaku AFC-5 diffractometer

$R_{\rm int} = 0.015$
$\theta_{\rm max} = 25°$

ω scans
Absorption correction: none
4706 measured reflections
4495 independent reflections
3033 reflections with $|F_o| > 3\sigma(|F_o|)$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 9$
$l = -29 \rightarrow 29$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0505$
$wR = 0.0452$
$S = 1.23$
3033 reflections
407 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\max} = 0.03$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. *Selected geometric parameters (Å, °) for (Ic)*

O1—C3	1.214 (3)	O101—C103	1.203 (3)
O2—C3	1.316 (3)	O102—C103	1.304 (3)
C3—C4	1.484 (3)	C103—C104	1.490 (3)
C9—C10	1.460 (3)	C109—C110	1.460 (3)
C10—C11	1.311 (4)	C110—C111	1.310 (3)
C11—C12	1.465 (4)	C111—C112	1.462 (3)
Cl18—C15	1.740 (3)	Cl118—C115	1.739 (2)
O1—C3—O2	121.0 (2)	O101—C103—O102	121.2 (2)
O1—C3—C4	124.7 (2)	O101—C103—C104	126.3 (2)
O2—C3—C4	114.3 (2)	O102—C103—C104	112.5 (2)
C3—C4—C5	118.5 (2)	C103—C104—C105	117.6 (2)
C3—C4—C9	122.0 (2)	C103—C104—C109	122.9 (2)
C9—C10—C11	127.3 (3)	C109—C110—C111	127.6 (2)
C10—C11—C12	127.2 (3)	C110—C111—C112	126.7 (2)

Compound (I*c*′)

Crystal data

$C_{15}H_{11}ClO_2$
$M_r = 258.70$
Monoclinic
$P2_1/n$
$a = 11.361$ (2) Å
$b = 5.066$ (3) Å
$c = 22.710$ (2) Å
$\beta = 98.45$ (1)°
$V = 1292.9$ (8) Å^3
$Z = 4$
$D_x = 1.329$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 10.1$–$13.8°$
$\mu = 0.285$ mm^{-1}
$T = 300$ K
Needle
0.70 × 0.25 × 0.15 mm
Colourless

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: by integration
$T_{\min} = 0.929$, $T_{\max} = 0.960$
2379 measured reflections
2258 independent reflections
975 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{\rm int} = 0.025$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 6$
$l = -26 \rightarrow 26$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0699$
$wR = 0.0531$
$S = 1.25$
975 reflections
204 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 4. *Selected geometric parameters (Å, °) for (Ic’)*

O1—C3	1.213 (8)	C10—C11	1.273 (11)
O2—C3	1.301 (8)	C11—C12	1.461 (10)
C3—C4	1.485 (9)	Cl18—C15	1.733 (7)
C9—C10	1.472 (9)		
O1—C3—O2	120.5 (6)	C3—C4—C9	122.2 (5)
O1—C3—C4	125.7 (6)	C9—C10—C11	130.4 (7)
O2—C3—C4	113.8 (6)	C10—C11—C12	130.4 (8)
C3—C4—C5	117.5 (6)		

Compound (I*d*)

Crystal data

$C_{16}H_{14}O_3$
$M_r = 254.29$
Monoclinic
$P2_1/n$
$a = 11.280$ (2) Å
$b = 5.273$ (2) Å
$c = 22.462$ (2) Å
$\beta = 103.00$ (1)°
$V = 1301.8$ (6) Å^3
$Z = 4$
$D_x = 1.297$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.9$–$14.6°$
$\mu = 0.089$ mm^{-1}
$T = 300$ K
Prism
0.7 × 0.4 × 0.1 mm
Pale yellow

Data collection

Rigaku AFC-5 diffractometer
θ–2θ scans
Absorption correction: none
2422 measured reflections
2297 independent reflections
1450 reflections with $|F_o| > 3\sigma(|F_o|)$
$R_{\rm int} = 0.013$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 6$
$l = -26 \rightarrow 26$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.0512$
$wR = 0.0463$
$S = 1.14$
1450 reflections
225 parameters
All H atoms refined
$w = 1/[\sigma^2(F) + 0.000225F^2]$
$(\Delta/\sigma)_{\max} = 0.04$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 5. *Selected geometric parameters (Å, °) for (Id)*

O1—C3	1.221 (3)	C10—C11	1.300 (3)
O2—C3	1.309 (3)	C11—C12	1.471 (3)
C3—C4	1.488 (3)	O18—C15	1.369 (3)
C9—C10	1.474 (3)	O18—C19	1.437 (4)
O1—C3—O2	120.6 (2)	C3—C4—C9	123.0 (2)
O1—C3—C4	124.9 (2)	C9—C10—C11	127.3 (3)
O2—C3—C4	114.4 (2)	C10—C11—C12	127.2 (2)
C3—C4—C5	117.6 (2)	C15—O18—C19	117.2 (2)

Carboxyl H atoms were located by difference syntheses and were restrained with an O—H distance of 0.96 Å.

For all compounds, data collection: *AFC/MSC Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSC Diffractometer Control System*; data reduction: local programs; program(s) used to solve structure: *CRYSTAN-GM* (Edwards, Gilmore, Mackay & Stewart, 1995); program(s) used to refine structure: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

This work was supported by the Grant-in-Aid on Priority Areas Nos. 06242101 and 07231229 from the Ministry of Education, Science, Sports and Culture, Japan.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: OA1018). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Allen, F. H., Davies, J. E., Galloy, J. J., Johnson, O., Kennard, O., Macrae, C. F., Mitchell, E. M., Mitchell, G. F., Smith, J. M. & Watson, D. G. (1991). *J. Chem. Inf. Comput. Sci.* **31**, 187–204.

Berti, G. (1958). *Tetrahedron*, **4**, 393–402.

Desiraju, G. R., Calabrese, J. C. & Harlow, R. L. (1991). *Acta Cryst.* B**47**, 77–86.

Edwards, C., Gilmore, C. J., Mackay, S. & Stewart, N. (1995). *CRYSTAN*-GM. Version 6.2. *Computer Program for the Solution and Refinement of Crystal Structures.* MacScience, Japan.

Rigaku Corporation (1993). *AFC/MSC Diffractometer Control System.* Rigaku Corporation, Tokyo, Japan.

Acta Cryst. (1997). C**53**, 624–626

1α,5α-Dihydroxymanoyl Oxide, a Novel Diterpene from *Satureja gilliesii*

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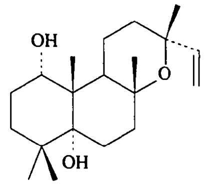
Abstract

The structure of the title diterpene, $C_{20}H_{34}O_3$ (8α,13*R*-epoxylabd-14-ene-1α,5α-diol), exhibits a very uncommon oxidation pattern, with two axially disposed hydroxyl substituents at C1 and C5, and five tertiary methyl groups.

Comment

The title compound, (I), was isolated, along with other diterpenoids, from the aerial parts of *Satureja gilliesii* (Labiatae), a small shrub endemic to central Chile. This species and other members of the genus display an uncommon natural resistance to insect attack (Lincoln & Lagenheim, 1981; Montenegro, Jordán & Aljaro, 1980). The chemical studies on the genus have been restricted to mainly the essential oil contents (Navarro, Zarzuelo, Jiménez & Duarte, 1989; Lincoln & Lagenheim, 1981), thus, it was of interest to investigate the other constituents of the extract in order to identify the metabolites responsible for the antifeedant behaviour of *S. gilliesii*. The isolation of some rare mono- and sesquiterpenoids from this species have been reported previously (Manríquez, Labbé, Castillo, von Schnering & Peters, 1990; Labbé, Castillo & Connolly, 1993).



(I)

The combined spectroscopic data of the title compound revealed a manoyl oxide diterpene derivative, with five tertiary methyl groups and two hydroxyl substituents (one secondary and one tertiary). However, the hydroxyl groups could not be located unequivocally from the spectroscopic data alone. The present single-crystal X-ray analysis establishes the molecular structure of this compound as shown in Fig. 1.

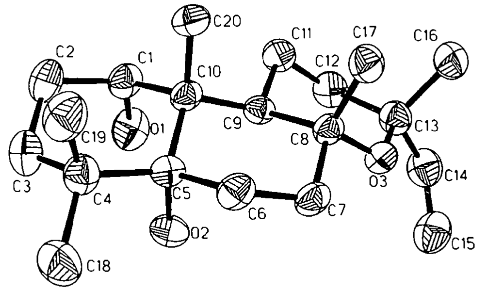


Fig. 1. A perspective drawing of the title molecule with H atoms omitted, displacement ellipsoids at the 50% probability level and atom site labels.

The three fused six-membered rings have a chair conformation; both hydroxyl substituents, α-secondary at C1 and α-tertiary at C5, are axially disposed on one side of the molecule and four of the five methyl groups are axially disposed on the other side, giving