ORGANIC COMPOUNDS

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Diosbulbin B, a constituent of *Dioscorea pentaphylla*†

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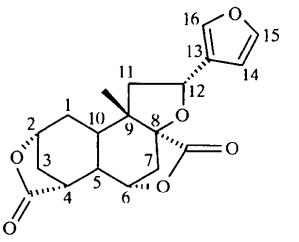
Abstract

The isolation of diosbulbin B, $C_{19}H_{20}O_6$, from *Dioscorea pentaphylla* is described. Both six-membered carbon rings have chair conformations. The absolute structure has not been determined.

Comment

Plants belonging to the genus *Dioscorea* (family *Dioscoreaceae*) are climber-bearing tubers, a few of which are used in the Indian indigenous system of medicine to remove swellings and also as a diuretic (Barua *et al.*, 1954). Dimethylbatatasin IV and 3,5,4′-trihydroxydibenzyl, both possessing antifungal and antimicrobial activities, have been isolated from *Dioscorea bulbifera* and *D. dumentorum* (Adesanya *et al.*, 1989). Dihydrodioscorine, an alkaloid isolated from *D. bulbifera*, has been found to inhibit five species of pathogenic fungi (Adeleye & Ikotun, 1989). The plant extract of *D. dumentorum* showed a strong hypoglycaemic activity in rats (Iwu *et al.*, 1990). We have carried out the phytochemical investigation of *Dioscorea pentaphylla* and have isolated diosbulbin B, (I), from this species for the first time; it had been isolated previously, from *D. bulbifera* (Wij & Rangaswami, 1978; Kawasaki & Komori, 1968; Komori *et al.*, 1968), but enough support had not been provided to confirm its structure fully. In view of the number of functionalities and stereogenic centres present in the molecule, and the interesting biological activities associated with several compounds isolated from this genus, we have confirmed the structure by X-ray diffraction.

† Chemical Abstracts name: [2*R*-(2α,3aβ,6β,6aβ,7β,10β,11aα,11bβ)]-2-(3-furanyl)octahydro-11b-methyl-4*H*-3a,6:7,10-dimethanofuro[2,3-*c*]-oxepino[4,5-*e*]oxepin-4,8(6*H*)-dione.



(I)

The structure of the title compound is illustrated in Fig. 1. All bond lengths and angles are unexceptional (Allen *et al.*, 1987). The two six-membered carbon rings share a common side and both have chair conformations. The two ester groupings occupy axial positions with respect to the cyclohexane rings, and thereby form γ-lactone rings. The terminal furan ring plane (r.m.s. 0.002 Å) is inclined at an angle of 81.3 (1)° to the plane of the adjacent five-membered ring (r.m.s. 0.19 Å).

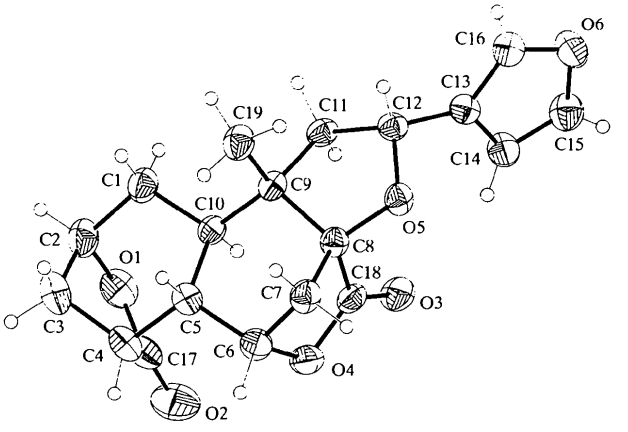


Fig. 1. View of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level, and H atoms are shown as spheres of an arbitrary radius.

Experimental

Dioscorea pentaphylla was collected from the forests around Shillong (Meghalaya, India). The rhizomes were crushed, air-dried and extracted in a Soxhlet apparatus with methanol. The dried extract (35 g) was subjected to silica column chromatography, and on elution with 5% methanol:chloroform, diosbulbin B was obtained as a white solid. It crystallized from methanol:chloroform as colourless needles (142 mg, m.p. 558–560 K). Spectroscopic data for (I): IR (KBr, ν_{max}/cm^{-1}): 3024, 2988, 2946, 1776, 1509, 1459, 1333, 1288, 1169, 1150, 1047, 963, 901, 866, 805, 760, 673, 601; ^{1}H NMR (250 MHz, acetone-d_6, p.p.m.): δ 1.24 (*s*, 3H, C19-H), 1.61 (*dd*, J = 13.8 Hz, 1H, C1-H$_{ax}$), 1.79 (*d*, J = 11.7 Hz, 1H, C3-H$_{eq}$), 1.92 (*d*, J = 11.1 Hz, 1H, C5-H$_{ax}$), 1.96 (*ddd*, J = 0.9, 5.5, 11.8 Hz, 1H, C11-H$_{eq}$), 2.07 (*m*, 1H, C1-H$_{eq}$), 2.13 (*dd*, J = 11.2, 11.8 Hz, 1H, C11-H$_{ax}$), 2.14 (*d*, J = 11.6 Hz, 1H, C7-

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H_{ax}), 2.55 (*ddd*, *J* = 1.7, 5.5, 11.7 Hz, 1H, C3-H_{ax}), 2.60 (*ddd*, *J* = 0.9, 5.7, 11.6 Hz, 1H, C7-H_{eq}), 2.74 (*d*, *J* = 5.5 Hz, 1H, C4-H_{eq}), 4.69 (*d*, *J* = 5.7 Hz, 1H, C6-H_{eq}), 4.86 (*dd*, *J* = 4.9 Hz, 1H, C2-H_{eq}), 5.29 (*dd*, *J* = 5.5, 11.2 Hz, 1H, C12-H_{ax}), 6.93 (*ddd*, *J* = 0.3, 0.9, 1.7 Hz, 1H, C14-H), 7.39 (*ddd*, *J* = 0.2, 0.4, 1.7 Hz, 1H, C15-H), 7.55 (*ddd*, *J* = 0.4, 0.5, 0.9 Hz, 1H, C16-H); ^{13}C NMR (62.5 MHz, acetone-d_6, p.p.m.): δ 16.56 (C19), 29.55 (C1), 37.26 (C7), 38.45 (C10), 39.30 (C3), 41.70 (C11), 42.00 (C4), 42.74 (C5), 45.61 (C9), 75.18 (C12), 76.28 (C2), 89.18 (C8), 109.90 (C14), 124.94 (C13), 141.25 (C16), 143.30 (C15), 175.03 (C18), 176.13 (C17); EIMS (electron impact MS), *m/z* (relative intensity): 344 (M^+, 100), 316 (2), 300 (80), 272 (7), 255 (15), 219 (4), 206 (57), 178 (22), 161 (37), 148 (24), 121 (25), 111 (77), 94 (52), 91 (17), 81 (13), 55 (7); CIMS (chemical ionization MS), *m/z* (relative intensity): 345 (M^+, 78), 317 (100), 299 (10), 293 (5), 251 (4), 239 (4), 225 (5), 207 (3), 195 (4), 175 (2), 151 (3), 145 (2), 113 (5), 97 (21), 85 (3).

Crystal data

$C_{19}H_{20}O_6$
M_r = 344.35
Orthorhombic
$P2_12_12_1$
a = 8.915 (4) Å
b = 10.623 (4) Å
c = 17.243 (5) Å
V = 1633.0 (10) Å^3
Z = 4
D_x = 1.401 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 4018 reflections
θ = 2.25–25.00°
μ = 0.104 mm^{-1}
T = 190 (2) K
Needle
0.30 × 0.16 × 0.15 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
8492 measured reflections
2872 independent reflections
2376 reflections with $I > 2\sigma(I)$

R_{int} = 0.057
θ_{max} = 24.99°
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 9$
$l = -20 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.097
S = 1.106
2872 reflections
228 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 0.5866P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0090 (12)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.3 (13)

Table 1. *Selected bond and torsion angles (°)*

C2—C3—C4	98.8 (2)	C8—C7—C6	97.4 (2)
C17—C4—C3	99.8 (2)		
C1—C2—C3—C4	−71.8 (3)	C6—C5—C10—C9	−49.7 (3)
C6—C7—C8—C9	72.7 (2)	C4—C5—C10—C1	48.9 (3)

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected 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 of 10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Coverage of the unique set was over 95% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections, and was found to be negligible. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement factors were used for all non-H atoms; H atoms were given isotropic displacement factors equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they were attached. Standard uncertainties on C—C bonds do not exceed 0.004 Å. The observed Flack parameter (Flack, 1983) of 0.3 (13) indicates that the absolute structure cannot be determined reliably from this experiment.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at the Daresbury Laboratory (Fletcher *et al.*, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). We also wish to thank the Council for Scientific Research (CSIR, New Delhi, India) for the award of a research fellowship (to AS).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1291). Services for accessing these data are described at the back of the journal.

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3-Cyano-5-(4-methoxybenzyl)-6-(4-methoxyphenyl)-4-methylthio-2*H*-pyran-2-one†

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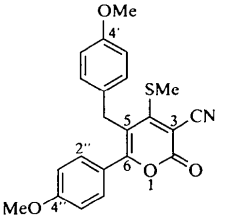
Abstract

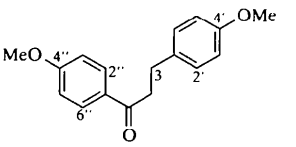
The synthesis of the title compound, $C_{22}H_{19}NO_4S$, is described. The methyl group of the methylthio substituent points towards the CN group, as has been noted before when bulky substituents occupy the 5-position. The phenyl groups in the 5- and 6-positions are twisted at angles of 75.7 (1) and 36.5 (1)°, respectively, from the plane of the pyrone ring.

Comment

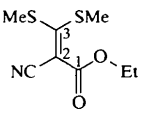
Substituted δ-lactones are useful intermediates in the synthesis of various bioactive, naturally occurring, pyrones such as anibine, phenylcoumalin, paracotoin, *etc.* (Tominaga *et al.*, 1977, 1984, 1987). We have synthesized several 3-cyano-4-methylthio-6-aryl-2*H*-pyran-2-ones as synthons for the synthesis of different classes of heterocyclic systems such as pyrazoles, isoxazoles, pyrazolo/isoxazolocoumarins and triazoles (Singh *et al.*, 1995; Kumar *et al.*, 1996). Such δ-lactones, with a benzyl group at the C-5 position, have not been reported previously, but we have synthesized several novel 3-cyano-5-benzyl-4-methylthio-6-aryl-2*H*-pyran-2-ones, with a view to screening them for antibacterial and antifungal activities and in order to study structure–activity relationships. This paper reports the synthesis of a novel lactone, (I), prepared by the addition of the enolate anion derived from 1,3-bis(4-methoxyphenyl)propanone, (II), to ethyl 2-cyano-3,3-bis(methylthio)acrylate, (III). The structure of this novel δ-lactone is confirmed by single-crystal X-ray diffraction.



(I)



(II)



(III)

The molecular structure of the title compound (I) is illustrated in Fig. 1. The bond lengths and angles are largely unexceptional (Allen *et al.*, 1987). The Csp^2—S distance [1.742 (2) Å] is shorter than the Csp^3—S distance [1.789 (3) Å]; this behaviour has been previously noted (Azim *et al.*, 1997) and is indicative of some double bonding in the sp^2 case. The structure of the 3-cyano-4-methylthio-2*H*-pyran-2-one fragment has been reported previously by our group (Kumar *et al.*, 1996; Malhotra *et al.*, 1997; Azim *et al.*, 1997), and in all cases the methylthio substituent is approximately co-planar with the pyrone ring [in this instance, the C8—S1—C4—C5 torsion angle is 169.09 (18)°]. As in the title compound, bulky substituents in the 5-position cause the methyl group to point towards the CN group. In com-

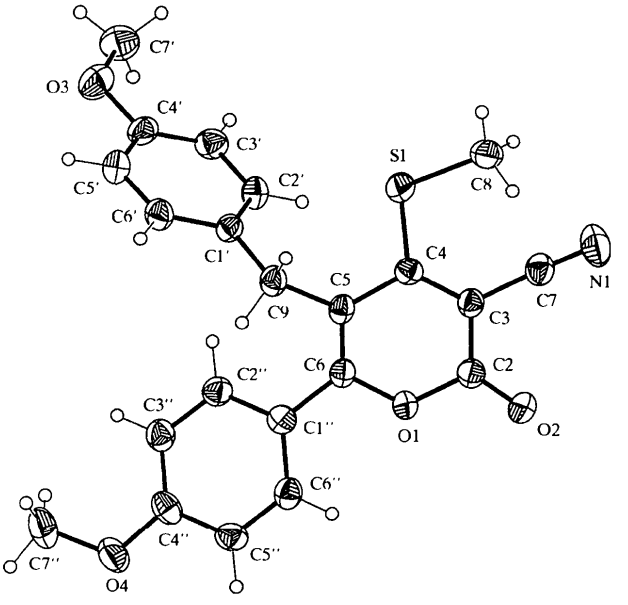


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of an arbitrary radius.

† IUPAC name: 5-(4-methoxybenzyl)-6-(4-methoxyphenyl)-4-methylthio-2-oxo-2*H*-pyran-3-carbonitrile.

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