organic compounds

5-(4-Methoxy-5-methyl-6-oxo-6H-pyran-2-yl)-3-methylhexa-2,4-dienoic acid

Stephen J. Bloor,[a] Douglas R. Crump[a] and Graeme J. Gainsford[b]*

[a]BioDiscovery NZ Ltd, 24 Balfour Road, Parnell, Auckland, New Zealand, and [b]Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
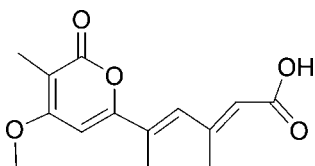Correspondence e-mail: g.gainsford@irl.cri.nz

The nearly planar molecule of the fungal metabolite infecto-pyrone, $C_{14}H_{16}O_5$, with an r.m.s. deviation of 0.040 (2) Å from the plane through all atoms, is linked tail-to-tail by strong O—H···O hydrogen bonds into dimers. Weaker C—H···O hydrogen bonds link the pyran-2-one 'head' groups.

Related literature

For general background see: Christensen *et al.* (2005); Larsen *et al.* (2003). For related structures, see: Allen (2002); Bernstein *et al.* (1995); Brassy *et al.* (1982); Garson *et al.* (1990); Kruger *et al.* (1979); McCabe *et al.* (1982); Norrestam (1978); Suh *et al.* (1996).

Experimental

Crystal data

$C_{14}H_{16}O_5$
$M_r = 264.27$
Monoclinic, $P2_1/c$
$a = 13.0563$ (15) Å
$b = 6.9804$ (6) Å
$c = 14.6138$ (17) Å
$\beta = 106.237$ (3)°

$V = 1278.8$ (2) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 169$ (2) K
$0.37 \times 0.05 \times 0.03$ mm

Data collection

Bruker–Nonius APEX2 CCD area detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.536$, $T_{max} = 1.000$
(expected range = 0.534–0.997)

9363 measured reflections
3718 independent reflections
1972 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.156$
$S = 1.00$
3718 reflections
179 parameters

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O5[i]	0.92 (3)	1.70 (3)	2.623 (2)	176.4 (18)
C5—H5···O2[ii]	0.95	2.59	3.448 (3)	151
C8—H8B···O2[ii]	0.98	2.47	3.318 (3)	144
C10—H10C···O2[ii]	0.98	2.55	3.490 (3)	162

Symmetry codes: (i) $-x - 1, -y, -z + 1$; (ii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* in *WinGX* (Farrugia, 1997); *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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supplementary materials

5-(4-Methoxy-5-methyl-6-oxo-6*H*-pyran-2-yl)-3-methylhexa-2,4-dienoic acid

S. J. Bloor, D. R. Crump and G. J. Gainsford

Comment

During our search for microbial metabolites with agroactivity, we isolated the known α-pyrone compounds, infectopyrone (Larsen *et al.*, 2003) and 4*Z*-infectopyrone (Christensen *et al.*, 2005)) from the fungus *Pyrenophora teres*. Both infectopyrone and the 4*Z*-isomer show mild antifungal activity *versus*. Botrytis, Colletotrichum, Fusarium and Rhizopus spp. The culture of Pyrenophora teres was obtained from the Landcare Research NZ International Collection of Micro-organisms from Plants (ICMP collection No.10948, see http://www.landcareresearch.co.nz/databases/) and was originally isolated from barley.

The asymmetric unit of the title compound (I) contains one independent 5-(4-Methoxy-5-methyl-6-oxo-6*H*-pyran-2-yl)-3-methyl-hexa-2,4-dienoic acid unit (Fig. 1, Table 1). There are no compounds reported with this binding to the −2*H*-pyran-2-one ring (sometimes called α-pyrone or −6*H*-pyran-6-one) in the Cambridge Structural Database (Allen, 2002; CSD Version 5.27). Somewhat similar compounds based on the 4-methoxy-5-methyl-2*H*-pyran-2-one have been reported (CSD codenames are given): Asteltoxin, ASTOXN, Kruger *et al.* (1979); Aurovertin B tetrahydrate, AURVER, Norrestam (1978); Citreomontanine, BEPNAL, Brassy *et al.*(1982); Isomalabaricane, BIFJAB, McCabe *et al.*(1982) and (-)-Citreoviridin, NETMAA, Suh *et al.*(1996). One similar compound based on 3,5-dimethyl-4-hydroxy-2*H*-pyran-2-one is (9*S*,11S,13*S*)-Pectinatone, KEGPER, Garson *et al.* (1990). Distances and angles here are similar to these compounds.

The 2*H*-pyran-2-one ring is planar (mean out of plane distance 0.0065 (14) Å) with atoms O2, O3, C7 & C9 slightly out of plane by 0.033 (3), 0.013 (3), −0.053 (3) & −0.036 (3)Å respectively. Likewise atoms of the alkene chain C9, C11, C12, & C13 are coplanar (mean deviation 0.0055 (13) Å). The carboxylate group is planar, but tipped slightly out of the plane of the rest of the molecule by 3.2 (2)°. This is consistent with the main packing interaction (Table 2, entry 1) which involves a strong hydrogen bonding interaction between inversion related molecules (tail-to-tail and dimer-forming) approximately along the *a* axis; this is described by the H-bonding code $R^2_2(8)$ (Bernstein *et al.*, 1995). Other weaker C—H···O interactions utilizing the pyran-2-one oxygen (O2) as donor to adjacent pyran-2-one H—C bound atoms provides additional linking in the lattice (Table 2, entries 2–4).

Experimental

Isolated from the fungus *Pyrenophora teres* (see Comment) and recrystallized from methanol/water in a *v/v* ratio of 70/30.

Refinement

All carbon-bound H atoms were constrained to their expected geometries [C—H 0.95,0.98 Å]; methyl H atoms were free to rotate (HFIX 137). All methyl/other H atoms were refined with U_{iso} 1.5/1.2 times the U_{eq} of their parent atom. Positional parameters of H4 (on O4) were refined with $U_{eq}(H) = 1.2U_{eq}(O)$.
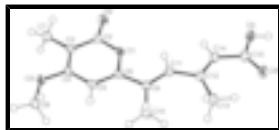
supplementary materials

Figures

Fig. 1. Molecular structure of (I) at the 50% ellipsoid probability level.

5-(4-methoxy-5-methyl-6-oxo-6*H*-pyran-2-yl)-3-methylhexa-2,4-dienoic acid

Crystal data

$C_{14}H_{16}O_5$	$F_{000} = 560$
$M_r = 264.27$	$D_x = 1.373$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1338 reflections
$a = 13.0563$ (15) Å	$\theta = 2.9$–$26.2°$
$b = 6.9804$ (6) Å	$\mu = 0.10$ mm^{-1}
$c = 14.6138$ (17) Å	$T = 169$ (2) K
$\beta = 106.237$ (3)°	Needle, yellow
$V = 1278.8$ (2) Å^3	$0.37 \times 0.05 \times 0.03$ mm
$Z = 4$	

Data collection

Bruker–Nonius APEX2 CCD area detector diffractometer	3718 independent reflections
Radiation source: fine-focus sealed tube	1972 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.062$
Detector resolution: 8.192 pixels mm^{-1}	$\theta_{max} = 30.3°$
$T = 169(2)$ K	$\theta_{min} = 2.9°$
φ and ω scans	$h = -18 \rightarrow 18$
Absorption correction: multi-scan (SADABS; Bruker, 2005)	$k = -4 \rightarrow 9$
$T_{min} = 0.536$, $T_{max} = 1.0$	$l = -20 \rightarrow 20$
9363 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.156$	$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} = <0.001$

3718 reflections

$\Delta\rho_{max} = 0.58$ e Å^{-3}

179 parameters

$\Delta\rho_{min} = -0.29$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

Special details

Experimental. Crystal decay was monitored by repeating the initial 10 frames at the end of the data collection and analyzing duplicate reflections. The standard 0.8 mm diameter collimator was used.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.10144 (11)	0.2841 (2)	0.57868 (10)	0.0175 (3)
O2	0.19047 (12)	0.3035 (2)	0.73065 (10)	0.0265 (4)
O3	0.36898 (11)	0.4085 (2)	0.49980 (10)	0.0225 (4)
O4	−0.37707 (13)	0.0672 (3)	0.58161 (11)	0.0301 (4)
H4	−0.444 (2)	0.020 (3)	0.5780 (17)	0.036*
O5	−0.43291 (12)	0.0605 (2)	0.42206 (11)	0.0290 (4)
C2	0.19664 (17)	0.3147 (3)	0.64914 (15)	0.0184 (5)
C3	0.28925 (16)	0.3544 (3)	0.61887 (15)	0.0169 (5)
C4	0.27910 (16)	0.3663 (3)	0.52368 (15)	0.0170 (5)
C5	0.17898 (16)	0.3357 (3)	0.45395 (15)	0.0167 (4)
H5	0.1733	0.3449	0.3879	0.020*
C6	0.09272 (16)	0.2934 (3)	0.48395 (14)	0.0153 (4)
C7	0.39381 (18)	0.3807 (3)	0.69235 (16)	0.0261 (5)
H7A	0.4286	0.4969	0.6781	0.039*
H7B	0.4396	0.2697	0.6918	0.039*
H7C	0.3819	0.3927	0.7554	0.039*
C8	0.36396 (18)	0.4367 (4)	0.40137 (15)	0.0258 (5)
H8A	0.3177	0.5462	0.3762	0.039*
H8B	0.3350	0.3214	0.3650	0.039*
H8C	0.4358	0.4617	0.3956	0.039*
C9	−0.01593 (16)	0.2532 (3)	0.42302 (15)	0.0174 (5)
C10	−0.03073 (19)	0.2571 (4)	0.31750 (17)	0.0340 (6)
H10A	−0.0487	0.3875	0.2935	0.051*
H10B	−0.0886	0.1698	0.2859	0.051*
H10C	0.0355	0.2165	0.3041	0.051*
C11	−0.09169 (16)	0.2175 (3)	0.46801 (16)	0.0174 (5)

H11	−0.0658	0.2225	0.5355	0.021*
C12	−0.20516 (17)	0.1728 (3)	0.43339 (16)	0.0182 (5)
C13	−0.26249 (18)	0.1644 (3)	0.32974 (16)	0.0246 (5)
H13A	−0.3389	0.1461	0.3216	0.037*
H13B	−0.2349	0.0571	0.3004	0.037*
H13C	−0.2513	0.2844	0.2991	0.037*
C14	−0.25189 (17)	0.1393 (3)	0.50414 (17)	0.0221 (5)
H14	−0.2065	0.1516	0.5672	0.027*
C15	−0.36170 (17)	0.0872 (3)	0.49665 (16)	0.0229 (5)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0175 (7)	0.0202 (8)	0.0162 (8)	−0.0004 (6)	0.0069 (6)	0.0015 (6)
O2	0.0251 (9)	0.0401 (10)	0.0160 (8)	−0.0018 (7)	0.0086 (7)	0.0015 (7)
O3	0.0176 (8)	0.0335 (9)	0.0184 (8)	−0.0043 (7)	0.0084 (6)	0.0003 (7)
O4	0.0223 (9)	0.0445 (11)	0.0247 (9)	−0.0112 (8)	0.0085 (7)	0.0021 (8)
O5	0.0200 (8)	0.0395 (10)	0.0271 (9)	−0.0082 (8)	0.0058 (7)	0.0009 (8)
C2	0.0199 (11)	0.0166 (11)	0.0190 (11)	0.0007 (9)	0.0059 (9)	0.0014 (9)
C3	0.0175 (11)	0.0178 (10)	0.0163 (11)	−0.0010 (8)	0.0059 (9)	0.0001 (9)
C4	0.0172 (11)	0.0139 (10)	0.0221 (12)	0.0006 (8)	0.0092 (9)	0.0005 (9)
C5	0.0209 (11)	0.0159 (10)	0.0140 (10)	0.0009 (9)	0.0063 (9)	0.0009 (9)
C6	0.0200 (11)	0.0121 (10)	0.0149 (10)	0.0025 (8)	0.0066 (9)	0.0005 (8)
C7	0.0226 (12)	0.0370 (14)	0.0191 (11)	−0.0022 (10)	0.0063 (9)	−0.0007 (10)
C8	0.0221 (12)	0.0399 (14)	0.0177 (12)	−0.0085 (11)	0.0093 (10)	−0.0015 (11)
C9	0.0178 (11)	0.0140 (10)	0.0206 (11)	0.0010 (8)	0.0057 (9)	−0.0015 (8)
C10	0.0201 (12)	0.0594 (18)	0.0243 (13)	0.0004 (12)	0.0090 (10)	−0.0031 (12)
C11	0.0181 (11)	0.0143 (10)	0.0201 (11)	−0.0010 (8)	0.0056 (9)	0.0015 (9)
C12	0.0199 (11)	0.0088 (9)	0.0266 (12)	−0.0006 (8)	0.0077 (9)	0.0003 (9)
C13	0.0181 (11)	0.0275 (12)	0.0281 (13)	−0.0056 (10)	0.0062 (10)	−0.0004 (11)
C14	0.0181 (11)	0.0181 (11)	0.0299 (13)	−0.0008 (9)	0.0062 (10)	−0.0024 (10)
C15	0.0221 (12)	0.0198 (11)	0.0265 (13)	−0.0020 (9)	0.0066 (10)	0.0000 (10)

Geometric parameters (Å, °)

O1—C6	1.358 (2)	C8—H8A	0.9800
O1—C2	1.391 (2)	C8—H8B	0.9800
O2—C2	1.219 (3)	C8—H8C	0.9800
O3—C4	1.347 (2)	C9—C11	1.355 (3)
O3—C8	1.435 (2)	C9—C10	1.500 (3)
O4—C15	1.319 (3)	C10—H10A	0.9800
O4—H4	0.92 (3)	C10—H10B	0.9800
O5—C15	1.233 (3)	C10—H10C	0.9800
C2—C3	1.426 (3)	C11—C12	1.459 (3)
C3—C4	1.363 (3)	C11—H11	0.9500
C3—C7	1.494 (3)	C12—C14	1.360 (3)
C4—C5	1.431 (3)	C12—C13	1.491 (3)
C5—C6	1.351 (3)	C13—H13A	0.9800
C5—H5	0.9500	C13—H13B	0.9800

C6—C9	1.476 (3)	C13—H13C	0.9800
C7—H7A	0.9800	C14—C15	1.453 (3)
C7—H7B	0.9800	C14—H14	0.9500
C7—H7C	0.9800		
C6—O1—C2	123.37 (17)	H8B—C8—H8C	109.5
C4—O3—C8	119.39 (16)	C11—C9—C6	116.81 (19)
C15—O4—H4	112.1 (15)	C11—C9—C10	126.9 (2)
O2—C2—O1	115.10 (19)	C6—C9—C10	116.28 (18)
O2—C2—C3	127.5 (2)	C9—C10—H10A	109.5
O1—C2—C3	117.38 (18)	C9—C10—H10B	109.5
C4—C3—C2	118.67 (19)	H10A—C10—H10B	109.5
C4—C3—C7	122.34 (19)	C9—C10—H10C	109.5
C2—C3—C7	118.99 (19)	H10A—C10—H10C	109.5
O3—C4—C3	115.77 (18)	H10B—C10—H10C	109.5
O3—C4—C5	122.46 (18)	C9—C11—C12	132.8 (2)
C3—C4—C5	121.77 (19)	C9—C11—H11	113.6
C6—C5—C4	118.70 (19)	C12—C11—H11	113.6
C6—C5—H5	120.7	C14—C12—C11	113.6 (2)
C4—C5—H5	120.7	C14—C12—C13	124.1 (2)
C5—C6—O1	120.09 (18)	C11—C12—C13	122.2 (2)
C5—C6—C9	126.43 (19)	C12—C13—H13A	109.5
O1—C6—C9	113.48 (18)	C12—C13—H13B	109.5
C3—C7—H7A	109.5	H13A—C13—H13B	109.5
C3—C7—H7B	109.5	C12—C13—H13C	109.5
H7A—C7—H7B	109.5	H13A—C13—H13C	109.5
C3—C7—H7C	109.5	H13B—C13—H13C	109.5
H7A—C7—H7C	109.5	C12—C14—C15	129.0 (2)
H7B—C7—H7C	109.5	C12—C14—H14	115.5
O3—C8—H8A	109.5	C15—C14—H14	115.5
O3—C8—H8B	109.5	O5—C15—O4	122.7 (2)
H8A—C8—H8B	109.5	O5—C15—C14	126.1 (2)
O3—C8—H8C	109.5	O4—C15—C14	111.22 (19)
H8A—C8—H8C	109.5		
C6—O1—C2—O2	179.07 (17)	C4—C5—C6—C9	−178.58 (19)
C6—O1—C2—C3	−1.1 (3)	C2—O1—C6—C5	−0.6 (3)
O2—C2—C3—C4	−178.1 (2)	C2—O1—C6—C9	179.23 (16)
O1—C2—C3—C4	2.0 (3)	C5—C6—C9—C11	−178.7 (2)
O2—C2—C3—C7	2.1 (3)	O1—C6—C9—C11	1.4 (2)
O1—C2—C3—C7	−177.71 (18)	C5—C6—C9—C10	1.0 (3)
C8—O3—C4—C3	−175.79 (18)	O1—C6—C9—C10	−178.80 (18)
C8—O3—C4—C5	4.2 (3)	C6—C9—C11—C12	−179.9 (2)
C2—C3—C4—O3	178.53 (18)	C10—C9—C11—C12	0.3 (4)
C7—C3—C4—O3	−1.7 (3)	C9—C11—C12—C14	177.6 (2)
C2—C3—C4—C5	−1.5 (3)	C9—C11—C12—C13	−2.1 (3)
C7—C3—C4—C5	178.27 (19)	C11—C12—C14—C15	−178.6 (2)
O3—C4—C5—C6	179.81 (18)	C13—C12—C14—C15	1.1 (4)
C3—C4—C5—C6	−0.2 (3)	C12—C14—C15—O5	1.4 (4)
C4—C5—C6—O1	1.2 (3)	C12—C14—C15—O4	−179.8 (2)

Hydrogen-bond geometry (Å, °)

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H4$\cdots$O5[i]	0.92 (3)	1.70 (3)	2.623 (2)	176.4 (18)
C5—H5$\cdots$O2[ii]	0.95	2.59	3.448 (3)	151
C8—H8B$\cdots$O2[ii]	0.98	2.47	3.318 (3)	144
C10—H10C$\cdots$O2[ii]	0.98	2.55	3.490 (3)	162

Symmetry codes: (i) $-x-1$, $-y$, $-z+1$; (ii) x, $-y+1/2$, $z-1/2$.

Fig. 1