Crystal structure of (2*S*,3*S*,4a*R*,6a*S*,7a*R*,7b*R*)-methyl 2,3-dimethoxy-2,3-dimethyl-3,4a,6a,7,7a,7b-hexahydro-2*H*-cyclopropa[3,4]benzo-[1,2-b]dioxine-6-carboxylate, $C_{15}H_{22}O_6$

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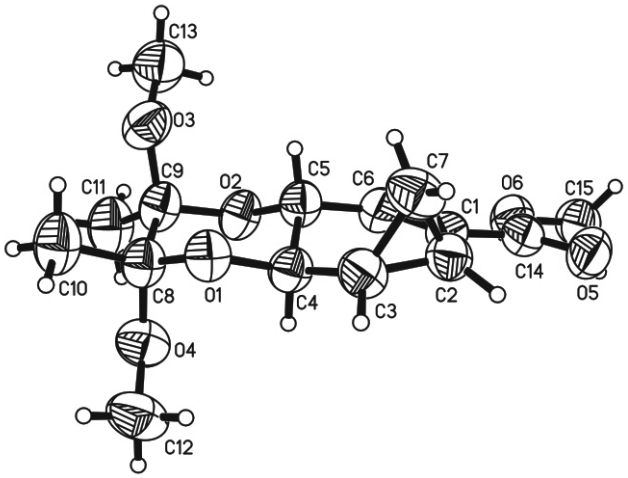

Abstract

$C_{15}H_{22}O_6$, orthorhombic, $P2_12_12$ (no. 18), a = 7.3483(9) Å, b = 31.0853(8) Å, c = 6.800(3) Å, V = 1553.3 Å^3, Z = 4, $R_{gt}(F)$ = 0.060, $wR_{ref}(F^2)$ = 0.176, T = 293 K.

Source of material

Based on the literature procedure [1], $Pd(OAc)_2$ (16.0 mg, 0.07 mmol) was added to a solution of (2*S*,3*S*,4a*R*,8a*R*)-methyl 2,3-dimethoxy-2,3-dimethyl-2,3,4a,8a-tetrahydrobenzo[b]-[1,4]dioxine-6-carboxylate (200 mg, 0.70 mmol) in freshly destilled Et_2O (2.0 mL). The orange mixture was cooled in an ice bath and stirred very slowly. A freshly prepared 0.4 M ethereal diazomethane solution (39.0 mL, 15.6 mmol) was added dropwise via an additional funnel. After about half the addition, the cloudy mixture was filtered through a pad of Celite, washed with Et_2O (20.0 mL) and concentrated under vacuum. The residue was dissolved in Et_2O (2.0 mL) and $Pd(OAc)_2$ (16.0 mg, 0.07 mmol) was added again. After addition of the remaining diazomethane solution and complete conversion, the excess diazomethane was destroyed by vigorous stirring. The solution was filtered, concentrated and purified by column chromatography. The resulting mixture of both monocyclopropanated products (88:12) were separated by means of MPLC (petroleum ether/EtOAc; 90:10). The title compound (141 mg, 0.48 mmol, 68 %) was obtained after recrystallization from *n*-pentane as colourless crystals (m. p. 89 °C; $[\alpha]_D^{20} = +108°$, c = 0.6 in $CHCl_3$).

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Experimental details

H atoms were located on difference Fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C—H) ranging from 0.93 to 0.98 Å. In addition, methyl groups were allowed to rotate but not to tip. For better overview the displacement parameters are drawn with 40 % probability. The Flack parameter is 0.1(5), which is in accordance with the absolute configuration resulting from the synthetic pathway.

Discussion

The title compound crystallizes with one independent molecule. The double bond C1=C6 of the cyclohexenyl moiety could be clearly identified by the distance of 1.329(6) Å. The cyclopropane has a nearly perpendicular orientation to the cyclohexene ring. The angle between their best planes is 80.2(3)°. In contrast, the methylester function has a nearly coplanar orientation to the cyclohexenyl moiety indicated by an angle of 14.0(1)° between their best planes. The methoxy functions show an axial orientation in relation to the bicyclic ring system. Consequently, both methyl groups have an equatorial orientation. The packing diagramm of the cellplot shows an antiparallel orientation of the molecules. This yields a bilayer-type pattern built up by the methoxy- and the methyl groups on the one side and the bicyclic ring systems on the other side in the *ac*-plane stacking along the *b*-axis.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.4 × 0.5 × 0.6 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	8.21 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	129.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6542, 2588
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1627
$N(param)_{refined}$:	196
Programs:	SHELXS-97, SHELXL-97, SHELXTL [2]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2)	4*c*	0.3100	0.0052	0.2211	0.090
H(3)	4*c*	0.3721	0.0759	0.1101	0.090
H(4)	4*c*	0.4798	0.1001	0.4215	0.079
H(5)	4*c*	0.1170	0.1063	0.5549	0.080
H(6)	4*c*	0.2527	0.0468	0.7789	0.084
H(7A)	4*c*	0.0744	0.0475	0.0768	0.104

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(7B)	4*c*	0.0183	0.0664	0.2926	0.104
H(10A)	4*c*	0.3958	0.2438	0.4781	0.141
H(10B)	4*c*	0.2215	0.2255	0.3746	0.141
H(10C)	4*c*	0.4084	0.2257	0.2634	0.141
H(11A)	4*c*	0.4061	0.2235	0.8139	0.143
H(11B)	4*c*	0.5323	0.1834	0.8450	0.143
H(11C)	4*c*	0.3489	0.1872	0.9615	0.143
H(12A)	4*c*	0.8200	0.1680	0.3630	0.157

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(12B)	4*c*	0.6831	0.1997	0.2618	0.157
H(12C)	4*c*	0.6572	0.1499	0.2390	0.157
H(13A)	4*c*	–0.1090	0.1811	0.8009	0.160
H(13B)	4*c*	0.0506	0.2008	0.9246	0.160
H(13C)	4*c*	0.0395	0.1509	0.8924	0.160
H(15A)	4*c*	0.2749	–0.0722	0.9939	0.148
H(15B)	4*c*	0.3729	–0.0872	0.8009	0.148
H(15C)	4*c*	0.1599	–0.0874	0.8126	0.148

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*c*	0.3249(4)	0.14830(8)	0.3289(4)	0.084(2)	0.069(2)	0.056(2)	–0.003(1)	–0.004(2)	–0.001(1)
C(1)	4*c*	0.2561(6)	0.0205(1)	0.5167(7)	0.062(2)	0.065(2)	0.078(3)	0.002(2)	0.000(2)	–0.005(2)
O(2)	4*c*	0.3203(4)	0.12529(8)	0.7279(4)	0.098(2)	0.065(2)	0.056(2)	0.009(1)	–0.003(2)	–0.005(1)
C(2)	4*c*	0.2606(6)	0.0286(1)	0.3020(7)	0.073(3)	0.078(3)	0.074(3)	–0.008(2)	0.002(2)	–0.015(2)
O(3)	4*c*	0.1248(5)	0.1826(1)	0.6586(5)	0.093(2)	0.081(2)	0.081(2)	0.016(2)	0.016(2)	0.003(2)
C(3)	4*c*	0.3000(6)	0.0737(1)	0.2310(7)	0.079(3)	0.085(3)	0.061(3)	–0.013(2)	0.005(2)	–0.014(2)
O(4)	4*c*	0.5833(4)	0.1719(1)	0.4997(5)	0.077(2)	0.105(2)	0.076(2)	–0.006(2)	–0.003(2)	–0.004(2)
C(4)	4*c*	0.3505(6)	0.1042(1)	0.3913(6)	0.072(2)	0.067(2)	0.059(2)	0.001(2)	0.001(2)	–0.005(2)
O(5)	4*c*	0.2543(5)	–0.0552(1)	0.4720(6)	0.085(2)	0.079(2)	0.123(3)	0.014(2)	–0.023(2)	–0.024(2)
C(5)	4*c*	0.2441(7)	0.0981(1)	0.5777(6)	0.083(3)	0.063(2)	0.055(2)	–0.001(2)	0.008(2)	–0.002(2)
O(6)	4*c*	0.2640(5)	–0.02924(9)	0.7800(6)	0.099(2)	0.070(2)	0.098(3)	0.002(2)	0.006(2)	0.008(2)
C(6)	4*c*	0.2514(6)	0.0528(1)	0.6449(7)	0.078(2)	0.063(2)	0.069(3)	0.003(2)	0.002(2)	–0.003(2)
C(7)	4*c*	0.1137(6)	0.0553(2)	0.2082(8)	0.075(3)	0.113(4)	0.071(3)	–0.014(3)	–0.004(2)	–0.001(3)
C(8)	4*c*	0.3931(6)	0.1776(1)	0.4707(7)	0.085(3)	0.066(2)	0.060(3)	0.000(2)	0.000(2)	–0.003(2)
C(9)	4*c*	0.3109(7)	0.1699(1)	0.6754(7)	0.094(3)	0.061(2)	0.063(3)	0.007(2)	–0.001(2)	0.000(2)
C(10)	4*c*	0.3508(9)	0.2223(1)	0.3891(7)	0.128(4)	0.071(3)	0.082(3)	–0.001(3)	0.000(3)	0.007(2)
C(11)	4*c*	0.4084(9)	0.1931(2)	0.8388(8)	0.132(5)	0.084(3)	0.070(3)	–0.007(3)	–0.007(3)	–0.012(3)
C(12)	4*c*	0.6952(7)	0.1724(2)	0.3265(9)	0.086(3)	0.134(4)	0.095(4)	–0.021(3)	0.023(3)	–0.009(4)
C(13)	4*c*	0.0176(9)	0.1785(2)	0.8335(9)	0.121(4)	0.099(3)	0.100(4)	0.005(3)	0.046(4)	–0.001(3)
C(14)	4*c*	0.2562(6)	–0.0247(1)	0.5838(8)	0.061(2)	0.071(3)	0.099(4)	–0.002(2)	–0.006(3)	–0.008(3)
C(15)	4*c*	0.2683(8)	–0.0726(1)	0.8529(9)	0.091(3)	0.071(3)	0.133(5)	0.005(2)	0.003(4)	0.021(3)

References

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