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An Enantiospecific Hetero-Diels–Alder Product

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Abstract. Methyl (3a*S*,4*S*,7a*R*)-(+)-4-(4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]hept-1-ylcarbonyloxy)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-5-carboxylate, $C_{19}H_{24}O_8$, $M_r = 380{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}056$ (1), $b = 14{\cdot}434$ (6), $c = 21{\cdot}298$ (4) Å, $U = 1862$ Å^3, $Z = 4$, $D_x = 1{\cdot}357$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}099$ mm^{-1}, $F(000) = 808$, $T = 298$ K, $R = 0{\cdot}058$ for 1991 reflections. The title compound is the main product of an enantioselective Diels–Alder reaction. Its absolute configuration is deduced from the known configuration of the camphanoyl group. The ring conformations correspond to established minimum-energy conformations of five- and six-membered rings.

Experimental. Crystal size 0·3 × 0·2 × 0·4 mm. Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation, profile-fitting mode (Clegg, 1981). 2626 reflections, $2\theta_{max}$ 45°, $+h+k+l$ and $-h+k+l$, three check reflections with no intensity change. 2431 unique data ($R_{int} = 0{\cdot}022$), of which 1991 with $F > 3\sigma(F)$ (Friedel opposites not merged) used for all calculations; program system *SHELXTL* (Sheldrick, 1978). Index ranges $|h| \le 6$, $k \le 15$, $l \le 22$. Cell constants refined from $\pm 2\theta$ values of 32 reflections in the range 20–25°. Absorption and extinction corrections unnecessary.

Table 1. *Atomic coordinates* (×10^4) *and isotropic thermal parameters* (Å^2 × 10^3)

	x	*y*	*z*	U_{eq}*
O(1)	−876 (4)	8832 (2)	2058 (1)	56 (1)
C(2)	270 (7)	8346 (3)	2475 (2)	48 (2)
C(3)	2339 (7)	8020 (3)	2395 (2)	42 (2)
C(4)	3470 (7)	8143 (3)	1787 (2)	44 (2)
C(4a)	2535 (7)	8967 (3)	1437 (2)	48 (2)
C(5)	3130 (7)	9908 (3)	1703 (3)	58 (2)
C(6)	1296 (8)	10523 (3)	1469 (3)	78 (2)
O(7)	−510 (5)	9908 (2)	1288 (2)	66 (1)
C(7a)	40 (7)	9019 (4)	1441 (2)	51 (2)
C(8)	3481 (7)	7528 (3)	2905 (2)	49 (2)
O(9)	2298 (5)	7484 (2)	3428 (1)	64 (1)
C(10)	3212 (9)	7034 (4)	3971 (2)	70 (2)
O(11)	5301 (5)	7214 (3)	2859 (2)	82 (2)
O(12)	2985 (4)	7308 (2)	1418 (1)	53 (1)
C(13)	4558 (7)	6927 (3)	1069 (2)	40 (2)
O(14)	6394 (5)	7229 (2)	1010 (1)	57 (1)
C(15)	3627 (6)	6093 (3)	755 (2)	35 (1)
O(16)	5436 (4)	5601 (2)	436 (1)	42 (1)
C(17)	4735 (6)	4713 (3)	351 (2)	43 (2)
C(18)	2407 (6)	4658 (3)	586 (2)	39 (1)
C(19)	1099 (6)	5259 (3)	110 (2)	47 (2)
C(20)	1901 (6)	6251 (3)	244 (2)	47 (2)
C(21)	2607 (6)	5316 (3)	1163 (2)	35 (1)
C(22)	4221 (7)	4965 (3)	1670 (2)	49 (2)
C(23)	398 (6)	5540 (3)	1473 (2)	49 (2)
C(24)	1545 (8)	3694 (3)	692 (2)	59 (2)
O(25)	5885 (4)	4135 (2)	110 (1)	58 (1)

* U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

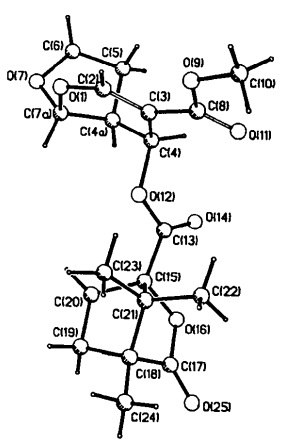

Fig. 1. The asymmetric unit of the title compound, showing the numbering scheme.

Structure solution by multisolution direct methods. Refinement on F to $R = 0{\cdot}058$, $wR = 0{\cdot}056$; all non-H atoms anisotropic, H atoms included using a riding model [C—H 0·96 Å, $U(H) = 1{\cdot}2\,U_{eq}(C)$], 256 parameters, $S = 1{\cdot}18$, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00069F^2$ which gave a featureless analysis of variance, max. $\Delta/\sigma = 0{\cdot}07$, max. and min. height in the final $\Delta\rho$ map 0·31 and −0·38 e Å^{-3} respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The atomic parameters

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Table 2. *Bond lengths* (Å) *and bond angles* (°)

O(1)–C(2)	1·328 (5)	O(1)–C(7a)	1·452 (5)
C(2)–C(3)	1·348 (6)	C(3)–C(4)	1·476 (6)
C(3)–C(8)	1·470 (6)	C(4)–C(4a)	1·514 (6)
C(4)–O(12)	1·468 (5)	C(4a)–C(5)	1·516 (6)
C(4a)–C(7a)	1·513 (6)	C(5)–C(6)	1·506 (7)
C(6)–O(7)	1·461 (6)	O(7)–C(7a)	1·365 (6)
C(8)–O(9)	1·327 (5)	C(8)–O(11)	1·195 (5)
O(9)–C(10)	1·436 (6)	O(12)–C(13)	1·326 (5)
C(13)–O(14)	1·201 (5)	C(13)–C(15)	1·489 (6)
C(15)–O(16)	1·472 (5)	C(15)–C(20)	1·525 (5)
C(15)–C(21)	1·547 (6)	O(16)–C(17)	1·362 (5)
C(17)–C(18)	1·499 (5)	C(17)–O(25)	1·202 (5)
C(18)–C(19)	1·552 (6)	C(18)–C(21)	1·558 (6)
C(18)–C(24)	1·502 (6)	C(19)–C(20)	1·539 (6)
C(21)–C(22)	1·542 (6)	C(21)–C(23)	1·527 (5)
C(2)–O(1)–C(7a)	120·3 (3)	O(1)–C(2)–C(3)	125·9 (4)
C(2)–C(3)–C(4)	119·9 (4)	C(2)–C(3)–C(8)	120·9 (4)
C(4)–C(3)–C(8)	119·2 (4)	C(3)–C(4)–C(4a)	110·7 (3)
C(3)–C(4)–O(12)	106·2 (3)	C(4a)–C(4)–O(12)	107·8 (3)
C(4)–C(4a)–C(5)	115·6 (4)	C(4)–C(4a)–C(7a)	114·2 (4)
C(5)–C(4a)–C(7a)	101·0 (4)	C(4a)–C(5)–C(6)	103·3 (4)
C(5)–C(6)–O(7)	106·4 (4)	C(6)–O(7)–C(7a)	109·0 (3)
O(1)–C(7a)–C(4a)	112·2 (3)	O(1)–C(7a)–O(7)	107·3 (4)
C(4a)–C(7a)–O(7)	106·9 (4)	C(3)–C(8)–O(9)	112·9 (4)
C(3)–C(8)–O(11)	123·9 (4)	O(9)–C(8)–O(11)	123·2 (4)
C(8)–O(9)–C(10)	119·3 (4)	C(4)–O(12)–C(13)	119·7 (3)
O(12)–C(13)–O(14)	125·0 (4)	O(12)–C(13)–C(15)	108·3 (3)
O(14)–C(13)–C(15)	126·6 (4)	C(13)–C(15)–O(16)	108·4 (3)
C(13)–C(15)–C(20)	117·3 (4)	O(16)–C(15)–C(20)	104·7 (3)
C(13)–C(15)–C(21)	119·0 (3)	O(16)–C(15)–C(21)	101·9 (3)
C(20)–C(15)–C(21)	103·6 (3)	C(15)–O(16)–C(17)	106·5 (3)
O(16)–C(17)–C(18)	107·4 (3)	O(16)–C(17)–O(25)	122·0 (3)
C(18)–C(17)–O(25)	130·6 (4)	C(17)–C(18)–C(19)	103·4 (3)
C(17)–C(18)–C(21)	99·1 (3)	C(19)–C(18)–C(21)	102·3 (3)
C(17)–C(18)–C(24)	115·3 (4)	C(19)–C(18)–C(24)	116·0 (3)
C(21)–C(18)–C(24)	118·3 (4)	C(18)–C(19)–C(20)	103·8 (3)
C(15)–C(20)–C(19)	102·1 (3)	C(15)–C(21)–C(18)	91·8 (3)
C(15)–C(21)–C(22)	112·3 (3)	C(18)–C(21)–C(22)	113·6 (3)
C(15)–C(21)–C(23)	116·1 (3)	C(18)–C(21)–C(23)	113·7 (3)

are given in Table 1,* and bond lengths and angles in Table 2. Fig. 1 shows the molecule and numbering scheme.

Related literature. For the preparation of the compound see Tietze & Glüsenkamp (1983). For the preparation and structure of a related compound see Tietze, Glüsenkamp, Harms, Remberg & Sheldrick (1982).

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* Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42934 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Photolysis Product

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Abstract. Methyl (+)-1β-hydroxy-7α-methoxy-5β-trityloxymethyl-4aβ,7,8,8aβ-tetrahydro-1*H*,5*H*-pyrano-[4,3-*c*]pyran-4-carboxylate, $C_{31}H_{32}O_7$, $M_r = 516{\cdot}6$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}424$ (1), $b = 14{\cdot}773$ (2), $c = 22{\cdot}165$ (2) Å, $U = 2758$ Å^3, $Z = 4$, $D_x = 1{\cdot}244$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}077$ mm^{-1}, $F(000) = 1096$, $T = 298$ K, $R = 0{\cdot}079$ for 1447 reflections. The title compound is the main product of a photolysis reaction. Its absolute configuration is deduced from the known configuration at C(5) and C(7).

Experimental. Crystal size 0·1 × 0·1 × 0·3 mm. Stoe–Siemens four-circle diffractometer, monochromated

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