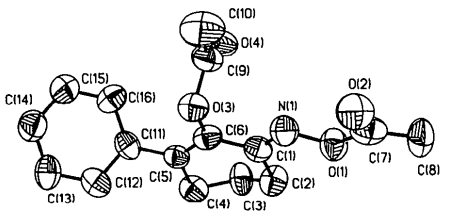

Fig. 1. A diagram of the title molecule viewed with 50% probability ellipsoids.

Related literature. The complete synthesis has been published (Tubergen, 1986). Examples of structurally similar oximes that may be used as comparisons are L-carvoxime (Kroon, van Gurp, Oonk, Baert & Fouret, 1976) and the oxime of 11-methyl-10-epieudesm-4-en-3-one (Huffman, Swain, Jacobus & McPhail, 1980).

Receipt of the material from Professor Robert D. Bach and Mark W. Tubergen (Wayne State University, Department of Chemistry) is gratefully acknowledged.

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Structure of (5*SR*,6*SR*)-4-Methoxy-7,7-bis(methoxycarbonyl)-5-[bis(methoxycarbonyl)(phenylthio)methyl]-1-oxaspiro[5.2]oct-3-en-2-one

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Abstract. $C_{23}H_{24}O_{11}S$, $M_r = 508{\cdot}496$, triclinic, $P\bar{1}$, $a = 14{\cdot}758$ (1), $b = 10{\cdot}522$ (1), $c = 8{\cdot}398$ Å, $\alpha = 106{\cdot}40$ (1), $\beta = 75{\cdot}80$ (1), $\gamma = 104{\cdot}05$ (1)°, $V = 1191{\cdot}5$ (1) Å^3, $Z = 2$, $D_x = 1{\cdot}417$ g cm^{-3}, Cu $K\alpha$ $\lambda = 1{\cdot}5418$ Å, $\mu = 16{\cdot}957$ cm^{-1}, $F(000) = 532$, $R = 0{\cdot}051$, $wR = 0{\cdot}054$ for 3375 observed reflections of 4068 unique data. The six-membered heterocyclic ring displays a distorted C_6 envelope conformation. The methoxy group is coplanar with the six-membered ring. The ester groups are planar and C10 and C34 are *trans*.

Experimental. The title compound was obtained by P. de March, M. Moreno-Manas and I. Ripoll of the Departamento de Química, Universidad Autonoma de Barcelona, Spain, who provided the crystals. Unit-cell parameters were obtained from least-squares refinement of 45 high-angle reflections (max. angle 60°) measured on a Philips PW1100 four-circle diffractometer; graphite-monochromated Cu $K\alpha$ radiation. Intensities were measured from a crystal of dimensions $0{\cdot}15 \times 0{\cdot}20 \times 0{\cdot}30$ mm on the same diffractometer for $2 < \theta < 65°$. ω–2θ scan technique. Two standard reflections measured every 100 reflections with no intensity variation. Of the 4008 measured independent reflections, 3375 were considered as observed with $I > 2\sigma(I)$, $0 < h < 17$, $-12 < k < 12$, $-10 < l < 10$. Lorentz, polarization and absorption (Walker & Stuart, 1983) corrections were applied. The min. and max. transmision factors are 0·867 and 1·324 respectively.

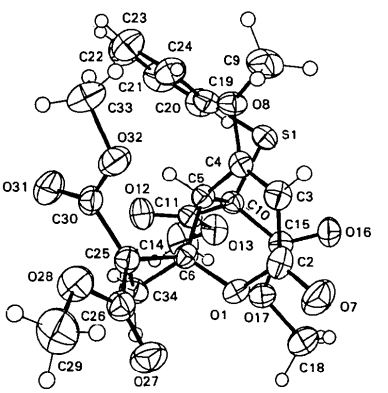

Fig. 1. A view of the molecule with the numbering scheme.

The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain,

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Declercq & Woolfson, 1980) and Fourier synthesis. Refinement with full-matrix least squares on F. All H atoms were located in a difference Fourier map. Refinement using anisotropic and isotropic temperature factors for non-H and H atoms respectively yielded $R = 0.05$ and $wR = 0.054$ with w calculated by an empirical scheme fitted so as to give no trends in $\langle w\Delta^2 F_o \rangle$ *vs* $\langle \sin\theta/\lambda \rangle$. Number of variables 412, max. $\Delta/\sigma = 0.02$. Highest peak in final difference synthesis 0·16 e Å^{-3}, $S = 1.78$.

Table 1. *Coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^4)

$U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
S1	0·59942 (5)	0·15297 (7)	0·92744 (9)	382 (3)
O1	0·68614 (13)	0·48022 (19)	0·60524 (23)	354 (7)
C2	0·62953 (20)	0·55280 (28)	0·73744 (39)	385 (11)
C3	0·63146 (20)	0·54692 (28)	0·90640 (37)	356 (10)
C4	0·67662 (18)	0·46127 (25)	0·93320 (32)	301 (9)
C5	0·72492 (19)	0·36432 (25)	0·78799 (32)	287 (9)
C6	0·75924 (18)	0·43587 (26)	0·64417 (32)	300 (9)
O7	0·58277 (18)	0·61512 (26)	0·70153 (32)	598 (11)
O8	0·68932 (14)	0·45452 (19)	1·08271 (22)	361 (7)
C9	0·65147 (30)	0·54834 (38)	1·23060 (41)	521 (15)
C10	0·66197 (19)	0·22042 (26)	0·74031 (32)	206 (9)
C11	0·72358 (20)	0·11897 (27)	0·62860 (34)	338 (10)
O12	0·80832 (15)	0·13819 (20)	0·60910 (29)	475 (9)
O13	0·66941 (15)	0·00490 (20)	0·56377 (28)	478 (8)
C14	0·71649 (37)	−0·10284 (42)	0·45674 (70)	712 (19)
C15	0·58176 (20)	0·22479 (26)	0·65613 (35)	332 (10)
O16	0·50499 (14)	0·24643 (23)	0·73362 (27)	484 (9)
O17	0·61038 (14)	0·20743 (21)	0·49106 (24)	425 (8)
C18	0·54470 (31)	0·22564 (56)	0·39891 (53)	630 (16)
C19	0·69160 (22)	0·09025 (30)	0·96970 (36)	407 (11)
C20	0·68838 (23)	−0·04809 (33)	0·92421 (45)	527 (14)
C21	0·75804 (32)	−0·09919 (41)	0·95750 (52)	634 (17)
C22	0·82907 (32)	−0·01469 (43)	1·03579 (56)	661 (18)
C23	0·83064 (31)	0·12218 (42)	1·08502 (54)	633 (17)
C24	0·76256 (25)	0·17556 (36)	1·05288 (43)	503 (14)
C25	0·85670 (19)	0·53245 (27)	0·63709 (38)	331 (10)
C26	0·91150 (19)	0·53912 (29)	0·76813 (38)	369 (11)
O27	0·97260 (17)	0·47660 (27)	0·74875 (32)	610 (11)
O28	0·87940 (15)	0·62115 (22)	0·91322 (27)	463 (9)
C29	0·92115 (37)	0·63437 (59)	1·05700 (57)	693 (21)
C30	0·87259 (20)	0·65909 (29)	0·57797 (37)	375 (11)
O31	0·83407 (17)	0·67446 (23)	0·47747 (30)	535 (10)
O32	0·94058 (16)	0·75111 (22)	0·64683 (30)	513 (9)
C33	0·96805 (37)	0·87539 (43)	0·58961 (73)	680 (20)
C34	0·83841 (22)	0·40286 (31)	0·50231 (37)	380 (11)

Table 2. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°)

S1–C10	1·851 (3)	S1–C19	1·794 (4)
O1–C2	1·375 (3)	O1–C6	1·411 (4)
C2–C3	1·445 (5)	C2–O7	1·202 (5)
C3–C4	1·337 (5)	C4–C5	1·503 (3)
C4–O8	1·338 (4)	C5–C6	1·520 (4)
C5–C10	1·573 (3)	C6–C25	1·545 (3)
C6–C34	1·478 (4)	O8–C9	1·437 (4)
C10–C11	1·528 (4)	C10–C15	1·536 (5)
C11–O12	1·195 (4)	C11–O13	1·325 (3)
O13–C14	1·441 (5)	C15–O16	1·200 (3)
C15–O17	1·319 (3)	O17–C18	1·455 (6)
C19–C20	1·389 (5)	C19–C24	1·392 (5)
C20–C21	1·385 (7)	C21–C22	1·370 (6)
C22–C23	1·378 (6)	C23–C24	1·375 (7)
C25–C26	1·495 (5)	C25–C30	1·497 (5)
C25–C34	1·521 (4)	C26–O27	1·195 (4)
C26–O28	1·333 (3)	O28–C29	1·444 (6)
C30–O31	1·191 (5)	C30–O32	1·333 (4)
O32–C33	1·452 (6)		

Table 2 (*cont.*)

C10–S1–C19	101·6 (1)	C2–O1–C6	117·2 (2)
O1–C2–O7	116·7 (3)	O1–C2–C3	117·5 (3)
C3–C2–O7	125·8 (3)	C2–C3–C4	121·5 (3)
C3–C4–O8	126·5 (3)	C3–C4–C5	121·0 (3)
C5–C4–O8	112·4 (2)	C4–C5–C10	114·3 (2)
C4–C5–C6	105·5 (2)	C6–C5–C10	114·1 (2)
O1–C6–C5	113·3 (2)	C5–C6–C34	123·5 (3)
C5–C6–C25	118·0 (2)	O1–C6–C34	115·9 (2)
O1–C6–C25	115·9 (2)	C25–C6–C34	60·4 (2)
C4–O8–C9	117·6 (3)	S1–C10–C5	112·8 (2)
C5–C10–C15	111·1 (2)	C5–C10–C11	110·6 (2)
S1–C10–C15	104·3 (2)	S1–C10–C11	106·2 (2)
C11–C10–C15	111·6 (2)	C10–C11–O13	110·3 (3)
C10–C11–O12	124·5 (3)	O12–C11–O13	125·1 (3)
C11–O13–C14	117·5 (3)	C10–C15–O17	111·0 (3)
C10–C15–O16	123·4 (3)	O16–C15–O17	125·5 (3)
C15–O17–C18	116·3 (3)	S1–C19–C24	121·8 (3)
S1–C19–C20	118·2 (3)	C20–C19–C24	119·9 (3)
C19–C20–C21	119·3 (3)	C20–C21–C22	120·6 (4)
C21–C22–C23	120·0 (5)	C22–C23–C24	120·6 (4)
C19–C24–C23	119·6 (4)	C6–C25–C34	57·7 (2)
C6–C25–C30	120·8 (3)	C6–C25–C26	115·8 (2)
C30–C25–C34	114·7 (3)	C26–C25–C34	120·1 (3)
C26–C25–C30	115·6 (3)	C25–C26–O28	109·9 (3)
C25–C26–O27	125·5 (3)	O27–C26–O28	124·6 (3)
C26–O28–C29	117·5 (3)	C25–C30–O32	110·2 (3)
C25–C30–O31	125·6 (3)	O31–C30–O32	124·2 (3)
C30–O32–C33	115·7 (3)	C6–C34–C25	62·0 (2)

C10–S1–C19–C20	−104·0 (3)	C10–S1–C19–C24	79·0 (3)
C19–S1–C10–C5	−80·7 (2)	C19–S1–C10–C15	158·6 (2)
C19–S1–C10–C11	40·6 (2)	C2–O1–C6–C25	−91·0 (3)
C2–O1–C6–C34	−158·9 (3)	C2–O1–C6–C5	50·0 (3)
C6–O1–C2–O7	164·0 (3)	C6–O1–C2–C3	−16·4 (4)
O1–C2–C3–C4	−8·4 (4)	O7–C2–C3–C4	171·1 (3)
C2–C3–C4–C5	−1·9 (4)	C2–C3–C4–O8	174·4 (3)
C3–C4–O8–C9	−0·3 (4)	C3–C4–C5–C6	31·7 (4)
C3–C4–C5–C10	−94·5 (3)	C5–C4–O8–C9	176·2 (3)
O8–C4–C5–C10	88·8 (3)	O8–C4–C5–C6	−145·0 (2)
C4–C5–C6–O1	−54·7 (3)	C4–C5–C10–S1	−45·4 (3)
C6–C5–C10–S1	−167·0 (2)	C4–C5–C10–C11	−164·2 (2)
C4–C5–C10–C15	71·3 (3)	C4–C5–C6–C25	85·4 (3)
C4–C5–C6–C34	156·8 (3)	C10–C5–C6–O1	71·6 (3)
C6–C5–C10–C11	74·3 (3)	C6–C5–C10–C15	−50·2 (3)
C10–C5–C6–C34	−76·9 (3)	C10–C5–C6–C25	−148·3 (2)
C5–C6–C34–C25	−105·8 (3)	O1–C6–C34–C25	106·4 (3)
C5–C6–C25–C26	4·0 (4)	O1–C6–C25–C26	143·1 (3)
C5–C6–C25–C30	−144·0 (3)	O1–C6–C25–C30	−4·9 (4)
C5–C6–C25–C34	114·6 (3)	O1–C6–C25–C34	−106·3 (3)
C34–C6–C25–C30	101·4 (3)	C34–C6–C25–C26	−110·6 (3)
C5–C10–C15–O16	−89·0 (3)	S1–C10–C15–O16	32·8 (3)
C5–C10–C15–O17	88·8 (3)	S1–C10–C15–O17	−149·9 (2)
C5–C10–C11–O12	14·3 (4)	S1–C10–C11–O12	−108·3 (3)
C5–C10–C11–O13	−168·1 (2)	S1–C10–C11–O13	68·6 (3)
C11–C10–C15–O16	147·1 (3)	C11–C10–C15–O17	−35·6 (3)
C15–C10–C11–O13	−44·5 (3)	C15–C10–C11–O12	138·6 (3)
C10–C11–O13–C14	−179·1 (3)	O12–C11–O13–C14	−2·2 (5)
C10–C15–O17–C18	−172·8 (3)	O16–C15–O17–C18	4·5 (5)
S1–C19–C24–C23	178·8 (3)	S1–C19–C20–C21	−179·2 (3)
C20–C19–C24–C23	1·9 (5)	C24–C19–C20–C21	−2·1 (5)
C19–C20–C21–C22	0·6 (6)	C20–C21–C22–C23	1·2 (7)
C21–C22–C23–C24	−1·5 (7)	C22–C23–C24–C19	−0·1 (6)
C30–C25–C34–C6	−112·1 (3)	C26–C25–C34–C6	103·3 (3)
C6–C25–C30–O31	−30·2 (5)	C6–C25–C30–O32	153·3 (3)
C6–C25–C26–O27	96·1 (4)	C6–C25–C26–O28	−81·2 (3)
C26–C25–C30–O31	−178·3 (3)	C26–C25–C30–O32	5·3 (4)
C30–C25–C26–O28	68·4 (3)	C30–C25–C26–O27	−114·3 (4)
C34–C25–C26–O28	−147·3 (3)	C34–C25–C26–O27	30·1 (5)
C34–C25–C30–O32	−141·0 (3)	C34–C25–C30–O31	35·5 (4)
C25–C26–O28–C29	176·9 (3)	O27–C26–O28–C29	−0·4 (5)
C25–C30–O32–C33	175·5 (3)	O31–C30–O32–C33	−1·0 (5)

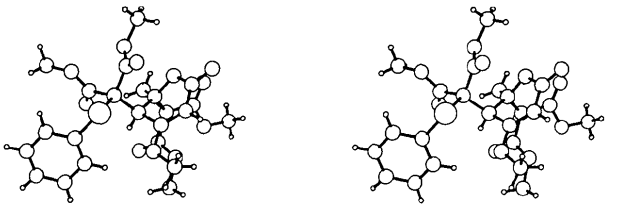

Fig. 2. Stereoview along the *a* axis.

The computations were made with *XRAY76* (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), *PARST* (Nardelli, 1983) and *PESOS* (Martínez-Ripoll & Cano, 1975) programs on a VAX 11/750 computer. Scattering and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic coordinates are given in Table 1* and bond lengths and angles in Table 2. Fig. 1 shows the structure with the numbering scheme used and Fig. 2 a stereoview of the structure. Asymmetric parameters for the six-membered heterocyclic ring are: $q_2 = 0{\cdot}393$ (3), $q_3 = 0{\cdot}240$ (2) Å, $\varphi = -77{\cdot}9$ (3), $\theta = 58{\cdot}6$ (3)°, $Q_T = 0{\cdot}461$ (3) Å (Cremer & Pople, 1975).

Related literature. The synthesis of the title compound and other related compounds is discussed by de March, Moreno-Manas, Ripoll, Florencio, García-Blanco & Martínez-Carrera, 1986). Structure determinations of related compounds are reported by Mascarenhas & Gottlieb (1977), Okuyama, Yamazaki, Kobayashi & Sakurai (1983) and Florencio & García-Blanco (1987).

* Lists of structure factors, anisotropic thermal parameters, bond distances, bond angles, torsion angles, least-squares planes, asymmetry parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44063 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(–)-Platynecine, a Pyrrolizidine Necine Base

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Abstract. $C_8H_{15}NO_2$, $M_r = 157{\cdot}2$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}810$ (1), $b = 8{\cdot}348$ (1), $c = 12{\cdot}459$ (1) Å, $V = 812{\cdot}3$ Å^3, $Z = 4$, $D_x = 1{\cdot}28$ g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 7{\cdot}07$ cm^{-1}, $F(000) = 344$, $T = 291$ K, final $R = 0{\cdot}030$ for 766 observed reflections. (–)-Platynecine adopts an *exo–endo* conformation with ring *A* *exo*-buckled with a puckering angle of 35·1 (3)° whilst the *endo* ring, *B*, has a puckering angle of 150·2 (4)°. These ring pucker values, as well as the dihedral angle of 125·6 (4)° between the planes defined by atoms C(1), C(8), N(4), C(3) and C(5), N(4), C(8), C(7), are in close agreement with values reported for other pyrrolizidine alkaloid nuclei. The hydroxyl group on C(9) is involved in two intermolecular hydrogen bonds: O(1)···O(2) 2·835 (3) and O(1)···N(4) 2·777 (3) Å. Their respective hydrogen-bond angles are O(1)···H(O2)–O(2) 165 (6)° and O(1)–H(O1)···O(2) 168 (9)°.

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Experimental. Hydrolysis of retrorsine, obtained from *Senecio isatideus* plants, yielded retronecine (2) (Robins & Sweeney, 1981). Hydrogenation of retronecine in ethanol using Adam's catalyst afforded (–)-platynecine (1) (*cf.* Adams & Rogers, 1941). Colourless, needle-shaped crystals grown by slow evaporation from aqueous acetone, crystal *ca* 0·6 × 0·3 × 0·2 mm used in data collection, CAD-4 diffractometer. Systematic absences from Weissenberg photographs indicated the crystals to be orthorhombic, $P2_12_12_1$. 989 independent intensities, θ limit 75°, $\omega/2\theta$ scan. Two standard

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