atoms with C—H 1·00 (2) Å. Blocked full-matrix least-squares calculations with *SHELX76* (Sheldrick, 1976) on F with anisotropic thermal parameters for C and O atoms and common isotropic thermal parameters for the toluene, methyl and all other H atoms converged at $R = 0{\cdot}069$, unit weights. The plumbazeylanone and toluene molecules were refined in alternate least-squares calculations such that the maximum number of parameters refined was 400. The high R value is due to some unresolved disorder, as indicated by high temperature factors and distorted geometries, in the toluene molecule. Atomic scattering factors from *SHELX76*. Final $\Delta/\sigma \leq 0{\cdot}01$, final $\Delta\rho$ max. = 0·3, $\Delta\rho$ min. = $-0{\cdot}3$ e Å^{-3}. Molecular geometries were generated by the *GX* package (Mallinson & Muir, 1985).

Atomic coordinates are listed in Table 1, bond lengths and valency angles in Table 2.* The atomic arrangement is shown in Fig. 1.

Related literature. The isolation of plumbazeylanone (Gunaherath, Gunatilaka & Thomson, 1984) and a preliminary report of the plumbazeylanone toluene solvate (Gunaherath, Gunatilaka, Cox, Howie & Thomson, 1988) have been published. The crystal structure of plumbagin is also known (Vijayalakshmi, Rajan & Srinivasan, 1987) as are related structures such as 2,5-dihydroxy-3,8-dimethyl-1,4-naphthalenedione (Cowe, Cox, Cordell, Che, Fong, & Howie 1986), 5,8-dihydroxy-2-methyl-1,4-naphthoquinone (Cradwick, Hall & Wood, 1977) and 3-hydroxy-2-methyl-1,4-naphthoquinone (Gaultier & Hauw, 1965).

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* Lists of structure factors, anisotropic thermal parameters, H-atom positions and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52703 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1990). C**46**, 1351–1353

Structure of (±)-(1*R**,4*S**,6*S**)-1-Benzyloxy-4,8,11,11-tetramethyl-6-phenylthiobicyclo[5.3.1]undec-7-en-3-one

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Abstract. $C_{28}H_{34}O_2S$, $M_r = 434{\cdot}64$, triclinic, $P\bar{1}$, $a = 8{\cdot}9868\,(7)$, $b = 11{\cdot}2933\,(11)$, $c = 12{\cdot}3497\,(6)$ Å, $\alpha = 80{\cdot}937\,(6)$, $\beta = 73{\cdot}108\,(5)$, $\gamma = 87{\cdot}405\,(7)^\circ$, $V = 1184{\cdot}32\,(15)$ Å^3, $Z = 2$, $D_x = 1{\cdot}22$ g cm^{-3}, $\mu = 1{\cdot}509$ cm^{-1}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $F(000) = 468$, $T = 298$ K, $R = 0{\cdot}0583$ for 6924 reflections $[F_o \geq 4\sigma(F_o)]$. The cyclooctane portion of the [5.3.1] ring system is in the boat-chair conformation while the cyclohexene portion assumes the boat conformation. The carbonyl group and the alkene group are nearly parallel in the molecule with a dihedral angle of 14·9 (1)° between planes through the two groups. Ring strain appears to cause distortion in the alkene functionality. The bond length [C7—C8 1·343 (2) Å] is long for an isolated C—C double bond. The torsion angles deviate between 3·7 (2) and 18·39 (14)° (absolute values) from ideality. This twist in the alkene group is reflected in the non-planarity of the group [max. deviation −0·177 (2) Å for C9] and in the dihedral angle between the nearly planar portions (C6,C7,C8,C11 and C7,C8,C9,C16) which is 12·1 (1)°.

Experimental. The bicyclo[5.3.1] undecene (1), which possesses the key structural subunit that is present in the Taxane diterpenes (Martin, White & Wagner, 1982) was obtained by the alkylation of the enolate of (1) with methyl iodide (Martin, White, Wagner,

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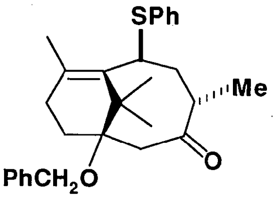
Guinn, Tanaka, Assercq, Gluchowski, Austin & Dantanarayana, 1989). Crystals of (1) were obtained by slow evaporation from an ether–hexane solution.



(1)

The data crystal was a large colorless block that was cut from a larger crystal and had approximate dimensions 0·40 × 0·47 × 0·59 mm. The data were collected at room temperature on a Picker diffractometer automated by Krisel Control Corporation using a graphite monochromator. Lattice parameters were obtained from the least-squares refinement of 19 reflections with $25{\cdot}2 < 2\theta < 33{\cdot}9°$. The data were collected using the ω-scan technique (13 848 reflections, of which 6924 were unique, $R_{\rm int} = 0{\cdot}0267$), with a 2θ range 4·0–60·0°, with a 1·0° ω scan at a constant 6° min^{-1} ($h = -12 \rightarrow 12$, $k = -15 \rightarrow 15$, $l = -17 \rightarrow 17$). Four reflections (200, 050, 004, $1\overline{3}\overline{3}$) were remeasured every three hours to monitor instrument and crystal stability (maximum correction on I was < 1%). The data were also corrected for Lp effects but not for absorption. The decay correction was applied according to Henslee & Davis (1975), while the data reduction was performed as described by Riley & Davis (1976). Reflections having $F_o < 4\sigma(F_o)$ were considered unobserved (1416 reflections). The structure was solved by the heavy-atom method (Sheldrick, 1976) and refined by full-matrix least squares (Sheldrick, 1976). The non-H atoms were refined with anisotropic thermal parameters. All H-atom positions were obtained from a ΔF map and refined with isotropic thermal parameters. In all, 416 parameters were refined in blocks of 233 (atoms C1 to C16 and the appropriate H atoms) and 184 (S17 to C31 and the appropriate H atoms) parameters with the scale factor refined in each block. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma(F_o)]^2$ and $\sigma(F_o) = 0{\cdot}5kI^{-1/2}\{[\sigma(\mathrm{I})]^2 + (0{\cdot}02I)^2\}^{1/2}$. The intensity, I, is given by $(I_{\rm peak} - I_{\rm background}) \times$ (scan rate), where 0·02 is a factor to downweight intense reflections and to account for instrument instability and k is the correction due to Lp effects and decay. $\sigma(I)$ was estimated from counting statistics; $\sigma(I) = [(I_{\rm peak} + I_{\rm background})^{1/2} \times \text{(scan rate)}]$. The final $R = 0{\cdot}0583$ for 6924 reflections, with $wR = 0{\cdot}0508$ ($R_{\rm all} = 0{\cdot}0927$, $wR_{\rm all} = 0{\cdot}0548$) and a goodness of fit = 1·867. The maximum $|\Delta/\sigma| < 0{\cdot}1$ in the final refinement cycle and the minimum and maximum peaks in the final ΔF map were $-0{\cdot}24$ and 0·43 e Å^{-3}, respectively. The scattering factors for the non-H atoms were taken from Cromer & Mann (1968), with the anomalous-dispersion corrections taken from the work of Cromer & Liberman (1970). The scattering factors for the H atoms were obtained from Stewart, Davidson & Simpson (1965). Values used to calculate the linear absorption coefficient are from *International Tables for X-ray Crystallography* (1974). Figures were generated using *SHELXTL-Plus* (Sheldrick, 1987). The least-squares-planes program was supplied by Cordes (1983). The positional and thermal parameters for non-H atoms are listed in Table 1,* while the bond lengths and angles for the non-H atoms are listed in Table 2. The atom labeling scheme is shown in Fig. 1. Other computer programs used in this work are listed in reference 11 of Gadol & Davis (1982).

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$$U_{\rm eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
C1	0·8332 (2)	0·28208 (13)	0·71469 (14)	0·0389 (6)
C2	0·9321 (2)	0·3181 (2)	0·5891 (2)	0·0442 (6)
C3	0·8446 (2)	0·35388 (15)	0·50058 (15)	0·0446 (6)
C4	0·8432 (2)	0·2718 (2)	0·4140 (2)	0·0477 (7)
C5	0·8265 (2)	0·1372 (2)	0·4571 (2)	0·0448 (7)
C6	0·6758 (2)	0·10030 (14)	0·55198 (15)	0·0411 (6)
C7	0·6532 (2)	0·17218 (13)	0·64942 (14)	0·0368 (5)
C8	0·5553 (2)	0·26585 (15)	0·65330 (14)	0·0414 (6)
C9	0·5585 (2)	0·3640 (2)	0·7228 (2)	0·0486 (7)
C10	0·7087 (2)	0·3750 (2)	0·7557 (2)	0·0476 (7)
C11	0·7554 (2)	0·15724 (13)	0·73147 (14)	0·0383 (6)
C12	0·6494 (3)	0·1243 (2)	0·8550 (2)	0·0516 (8)
C13	0·8805 (2)	0·0588 (2)	0·7156 (2)	0·0469 (7)
O14	0·79109 (15)	0·45513 (10)	0·48925 (11)	0·0567 (5)
C15	0·9947 (3)	0·2939 (2)	0·3160 (2)	0·0688 (10)
C16	0·4390 (3)	0·2935 (2)	0·5859 (2)	0·0590 (9)
S17	0·68684 (6)	–0·06396 (4)	0·57536 (4)	0·0525 (2)
C18	0·5232 (2)	–0·1202 (2)	0·68696 (15)	0·0458 (7)
C19	0·5246 (3)	–0·2437 (2)	0·7226 (2)	0·0586 (8)
C20	0·4028 (3)	–0·2986 (2)	0·8086 (2)	0·0737 (10)
C21	0·2779 (3)	–0·2324 (2)	0·8610 (2)	0·0750 (10)
C22	0·2755 (3)	–0·1115 (2)	0·8255 (2)	0·0725 (10)
C23	0·3967 (2)	–0·0543 (2)	0·7388 (2)	0·0598 (8)
O24	0·93598 (13)	0·26460 (10)	0·78652 (10)	0·0460 (4)
C25	1·0105 (2)	0·3662 (2)	0·8017 (2)	0·0514 (8)
C26	1·1024 (2)	0·3274 (2)	0·88495 (15)	0·0445 (6)
C27	1·1591 (2)	0·4118 (2)	0·9322 (2)	0·0581 (8)
C28	1·2458 (3)	0·3780 (3)	1·0085 (2)	0·0705 (10)
C29	1·2757 (3)	0·2595 (3)	1·0378 (2)	0·0744 (11)
C30	1·2208 (3)	0·1754 (3)	0·9925 (2)	0·0777 (11)
C31	1·1348 (3)	0·2089 (2)	0·9160 (2)	0·0623 (9)

Related literature. Distortions in ring systems induced by the presence of a bridgehead C as the terminus of a double bond are discussed by Wiseman (1967).

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* Tables of anisotropic thermal parameters, H-atom positional parameters, bond distances and angles involving the H atoms, torsion angles, selected least-squares planes, structure factor amplitudes and a unit-cell packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52693 (53 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *for the non*-H *atoms of* (1)

1	2	3	1—2	1—2—3
C2	C1	C10	1·548 (2)	112·86 (14)
C2	C1	C11		110·87 (14)
C10	C1	C11	1·530 (2)	109·68 (13)
C10	C1	O24		110·1 (2)
C11	C1	O24	1·559 (2)	104·51 (12)
O24	C1	C2	1·444 (2)	108·49 (13)
C3	C2	C1	1·519 (3)	116·97 (14)
C4	C3	O14	1·524 (3)	119·1 (2)
C4	C3	C2		120·5 (2)
O14	C3	C2	1·223 (2)	119·7 (2)
C5	C4	C15	1·528 (2)	108·6 (2)
C5	C4	C3		117·4 (2)
C15	C4	C3	1·536 (3)	107·5 (2)
C6	C5	C4	1·535 (2)	114·72 (14)
C7	C6	C5	1·516 (3)	110·83 (15)
C7	C6	S17		121·53 (12)
S17	C6	C5	1·835 (2)	103·31 (11)
C8	C7	C11	1·343 (2)	117·9 (2)
C8	C7	C6		117·8 (2)
C11	C7	C6	1·540 (3)	123·54 (13)
C9	C8	C16	1·511 (3)	111·1 (2)
C9	C8	C7		122·1 (2)
C16	C8	C7	1·509 (3)	126·6 (2)
C10	C9	C8	1·534 (3)	116·1 (2)
C1	C10	C9		114·5 (2)
C12	C11	C13	1·543 (2)	105·42 (14)
C12	C11	C1		110·9 (2)
C12	C11	C7		108·41 (14)
C13	C11	C1	1·538 (2)	109·99 (14)
C13	C11	C7		117·0 (2)
C1	C11	C7		105·16 (12)
C18	S17	C6	1·760 (2)	108·73 (8)
C19	C18	C23	1·395 (3)	118·9 (2)
C19	C18	S17		114·99 (13)
C23	C18	S17	1·381 (3)	126·11 (14)
C20	C19	C18	1·375 (3)	120·6 (2)
C21	C20	C19	1·376 (4)	120·4 (2)
C22	C21	C20	1·368 (4)	119·2 (2)
C23	C22	C21	1·385 (3)	121·4 (2)
C18	C23	C22		119·6 (2)
C25	O24	C1	1·418 (3)	118·56 (13)
C26	C25	O24	1·500 (3)	108·96 (15)
C27	C26	C31	1·379 (3)	117·7 (2)
C27	C26	C25		120·0 (2)
C31	C26	C25	1·375 (3)	122·3 (2)
C28	C27	C26	1·388 (4)	121·0 (2)
C29	C28	C27	1·366 (4)	119·9 (3)
C30	C29	C28	1·353 (5)	119·9 (3)
C31	C30	C29	1·386 (4)	120·3 (3)
C26	C31	C30		121·2 (2)

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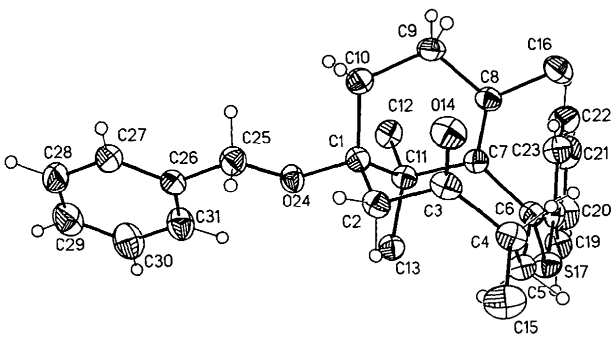

Fig. 1. View of (1) with the atomic labeling scheme showing the boat-chair conformation of the cyclooctane portion of the [5.3.1] ring system. The nearly parallel orientation of the carbonyl group and the alkene moiety can also be seen. The methyl-group H atoms were removed for clarity. Atom label for C18 has been omitted. Ellipsoids are scaled to the 30% probability level. H atoms are of arbitrary size.

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Structure of (±)-(1*S**,3*S**)-3-Hydroxy-8,11,11-trimethyl-9-oxobicyclo[5.3.1]undec-7-en-1-yl Benzoate

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(*Received* 27 *October* 1989; *accepted* 6 *February* 1990)

Abstract. $C_{21}H_{26}O_4$, $M_r = 342{\cdot}43$, monoclinic, $P2_1/n$, $a = 7{\cdot}211$ (2), $b = 19{\cdot}521$ (6), $c = 12{\cdot}674$ (3) Å, $\beta = 95{\cdot}04$ (2)°, $V = 1777{\cdot}2$ (8) Å^3, $Z = 4$, $D_x = 1{\cdot}28$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}8152$ cm^{-1}, $F(000) = 736$, $T = 163$ K, $R = 0{\cdot}0632$ for 3754 reflections [$F_o \geq 4\sigma(F_o)$]. The molecules exist

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