Vulgarone B

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The crystal structure of vulgarone B (2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undec-10-en-9-one), a carbocyclic sesquiterpene with the formula $C_{15}H_{22}O$, is reported. All intramolecular geometric parameters are as expected. The molecule contains a four-membered ring, in which all atoms are stereogenic. The 1,3 and 2,4 atoms of this cyclobutane are bridgehead C atoms which form part of six-membered and seven-membered rings.

Comment

Continuing our structural and synthetic studies of the effects of ring strain on the properties of carbocyclic natural products (White & Lee, 1997), we report here the structure of vulgarone B, (I). This sesquiterpene was isolated as the major terpenoid component (*ca* 40%) of the essential oil of *Artemisia douglasiana* Bess., a plant that occurs widely in Western Oregon. An extract of this plant has been found to possess potent insecticidal and gastropod repellent activity. Previously, vulgarone B was isolated along with its isomer vulgarone A as a minor constituent of the oil of the medicinal plant *Chrysanthemum vulgare* (L.) Bernh, [*Tanacetum vulgare* (L)] (Uchio *et al.*, 1977). It has also been obtained from the volatile oil of cultivars of *Santolina chamaecyparcissus* L. (Baig *et al.*, 1989).

(I)
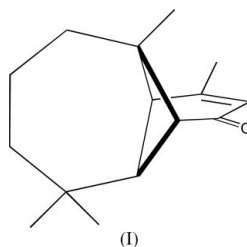
The structure of vulgarone B, including its absolute configuration, had earlier been deduced from spectroscopic evidence and by chemical correlation with the related sesquiterpene (+)-α-longipinene (Uchio, 1978). The results from our X-ray single-crystal diffraction experiment confirm the assigned structure. We also attempted to determine the absolute configuration of vulgarone B from the diffraction data, but, due to the small magnitude of the anomalous scattering components, the refined value of the absolute structure parameter could not be reliably determined. This is reflected in the fact that the model shown in Fig. 1 yields a value of −0.7 (6) for this parameter, whereas the inverted model yields a value of 1.7 (6). Further, since the absolute structure derived
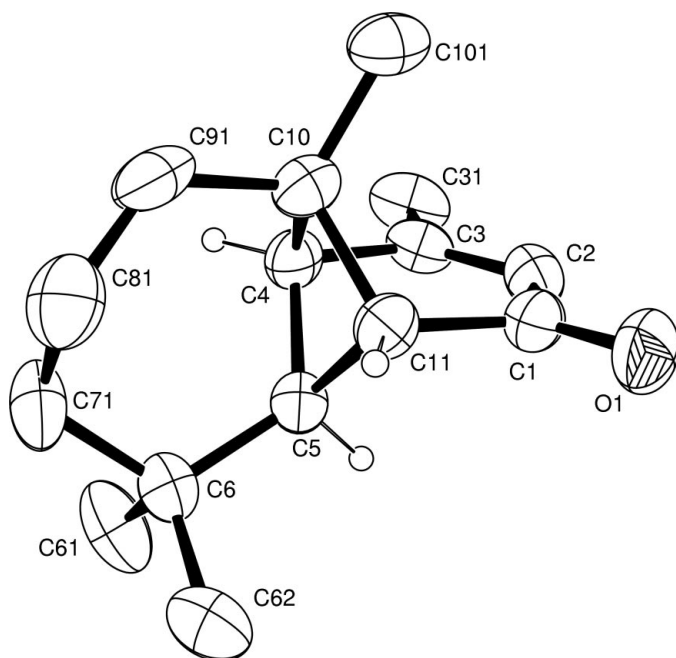
Figure 1
View of (I) illustrating the numbering scheme (30% probability displacement ellipsoids). The minor fraction of the disordered atoms C71, C81 and C91 have been omitted.

from the model shown is identical to the previously deduced configuration for this molecule (Uchio, 1978), we find it reasonable to conclude that this is the true configuration of vulgarone B.

All the observed intramolecular distances and angles are well within the expected values. The most interesting feature of the molecule is the four-membered ring, in which all four atoms are stereogenic. Opposite corners of this ring are the bridgehead C atoms that are components of two other rings, *i.e.* a seven-membered cycle and a six-membered ring. The six-membered ring contains a C=C—C=O moiety, which should force five of the six atoms in the ring to be planar. This is found to be correct; atoms O1, C1, C2, C3, C31, C4 and C11 are nearly coplanar, with a maximum deviation from the mean plane of 0.028 (2) Å by atom C2. This geometric constraint also causes a slight distortion of the four-membered ring, in which the bridgehead C atoms of the six-membered ring have moved toward each other. This is reflected in the C—C—C angles within the ring, which are identical pairwise at about 84 and 89° as shown in Table 1.

Experimental

Crystals of the title compound were obtained by sublimation of a bulk sample under ambient pressure and temperature. Due to the high vapor pressure of the compound, it also sublimes during the diffraction experiment. Thus, in order to minimize the rate of sublimation, the crystal was completely encapsulated in a thin layer of epoxy glue. This strategy was sufficient to allow data collection over a period of a few days.

Crystal data

$C_{15}H_{22}O$	Cu $K\alpha$ radiation
$M_r = 218.33$	Cell parameters from 99
Orthorhombic, $P2_12_12_1$	reflections
$a = 6.628\ (1)$ Å	$\theta = 8.0\text{–}27.3°$
$b = 10.218\ (1)$ Å	$\mu = 0.50\ \text{mm}^{-1}$
$c = 19.889\ (1)$ Å	$T = 293\ (2)$ K
$V = 1347.0\ (3)$ Å^3	Block, colorless
$Z = 4$	$0.4 \times 0.4 \times 0.3$ mm
$D_x = 1.077\ \text{Mg m}^{-3}$	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.041$
$\omega/2\theta$ scans	$\theta_{max} = 67.6°$
Absorption correction: empirical	$h = -6 \rightarrow 7$
via ψ scans (North *et al.*, 1968)	$k = -12 \rightarrow 12$
using *XEMP* (Siemens, 1990)	$l = -23 \rightarrow 23$
$T_{min} = 0.827,\ T_{max} = 0.866$	3 standard reflections
2270 measured reflections	every 97 reflections
1911 independent reflections	intensity decay: 1%
1666 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R(F) = 0.050$	$\Delta\rho_{max} = 0.12$ e Å^{-3}
$wR(F^2) = 0.132$	$\Delta\rho_{min} = -0.14$ e Å^{-3}
$S = 1.07$	Extinction correction: *SHELXL*97
1911 reflections	Extinction coefficient: 0.0052 (12)
176 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = not reliably
$w = 1/[\sigma^2(F_o^2) + (0.0858P)^2$	determined [−0.7 (6)]
$+ 0.0511P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (°).

C5—C4—C10	89.24 (16)	C11—C10—C4	84.44 (15)
C4—C5—C11	84.03 (15)	C10—C11—C5	89.02 (15)

All data was employed in the refinement with the exception of the (1,1,2) reflection which had strongly negative intensity. During the course of the refinement, the disorder in the $C(Me)_2(CH_2)_3$ backbone of the seven-membered ring became apparent. This disorder was modelled by introducing two $(CH_2)_3$ moieties anchored at both ends to the undisordered fragment of the molecule (C71/C81/C91 and C72/C82/C92), the occupation factors of which were allowed to refine. While bond-length restraints were introduced during the initial phases of the disordered refinement to minimize the likelihood of a divergent refinement, these proved to be unnecessary and were removed during the final cycles of least-squares refinement. Though under this model the two methyl groups of the $C(Me)_2$ moiety may also be expected to be disordered, a model taking this aspect into account failed to yield lower residuals. H atoms were placed in geometrically idealized positions and given a common displacement parameter by class (methyl group H atoms, all others), which were allowed to refine. The final value of $U_{iso}(H)$ for the methyl group H atoms is 0.141 (4) Å^2, and for all other H atoms is 0.095 (3) Å^2.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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