

Fig. 2. Stereoscopic view of the unit cell showing the intermolecular hydrogen bonding.

intermolecular interaction and by van der Waals interactions. The hydrogen bond is between the O(3)—H hydroxyl group of the molecule at $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ and the O(6) carbonyl group. The O(3)···O(6) and H(3A)···O(6) distances are 2.936 (9) and 2.06 Å and the O(3)—H(3A)···O(6) angle is 155.9°.

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3-Oxograndolide, a Guaiane Type of Sesquiterpene Lactone, C₁₅H₂₀O₄

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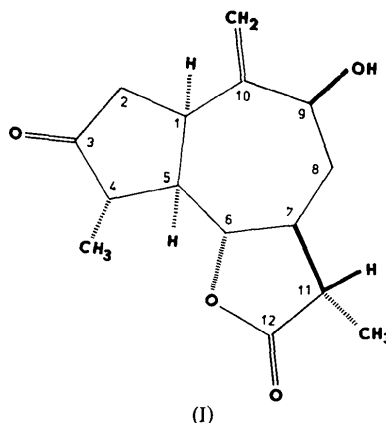
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Abstract. $M_r = 264.3$, orthorhombic, $P2_12_12_1$, $a = 6.2941$ (9), $b = 7.6749$ (7), $c = 28.278$ (4) Å, $V = 1366.0$ (3) Å³, $Z = 4$, $D_m = 1.26$, $D_x = 1.28$ Mg m⁻³, $\lambda(\text{Cu K}\alpha) = 1.54184$ Å, $\mu = 0.76$ mm⁻¹, $F(000) = 568$, $T = 295$ K, $R = 0.047$ for 1051 observed reflections. The three-ring guaianolide system contains a twist-chair *exo*-methylenecycloheptane moiety *cis*-fused with the cyclopentanone [at C(1)—C(5)] and *trans*-annulated with the γ -lactone at C(6)—C(7). The secondary hydroxyl group is at C(9) and is β -oriented; it participates in an intermolecular hydrogen bond with the cyclopentane keto group, O···O 2.976 (3) Å.

Introduction. The sesquiterpene lactone 3-oxograndolide was isolated from the aerial part of the species *Arctotis grandis* Thunb. (family Compositae, tribe Arctoteae) and *Vernonia angusticeps* Michaux. (family Compositae, tribe Vernoniaeae). On the basis of physical methods, mainly ¹H NMR spectroscopy, the structure (I) for 3-oxograndolide was deduced (Phuong,

Perez, Buděšínský, Šaman, Grabarczyk, Drożdż, Rychlewska & Holub, 1984). Since substitution at C(9) is relatively rare in sesquiterpene lactones, it was essential to check the proposed structure of this native lactone by X-ray structural analysis.



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Experimental. Crystal 0.25 × 0.30 × 0.35 mm, D_m by flotation, Syntex $P2_1$ diffractometer, θ - 2θ scan, variable scan rate, graphite-monochromated Cu $K\alpha$ radiation, cell parameters by least-squares refinement of setting angles of 15 reflections, 1108 reflections, $2\theta \leq 115^\circ$, h 0-6, k 0-8, l 0-30, background and integrated intensity for each reflection evaluated from profile analysis according to Lehmann & Larsen (1974) using *PRARA* program (Jaskólski, 1981). Two standard reflections, 4% intensity variation, no absorption correction, 1054 reflections with $I \geq 1.96 \sigma(I)$ considered significant, three additional reflections omitted; structure solved with *MULTAN* (Germain, Main & Woolfson, 1971), refined with *SHELX76* (Sheldrick, 1976), most H atoms placed in calculated positions and refined using a 'riding model', methyl groups refined as rigid groups, the two methylene hydrogen atoms and hydroxyl hydrogen located from difference Fourier synthesis, hydroxyl hydrogen allowed to refine freely. Isotropic temperature factor for methyl hydrogen atoms refined to 0.097 (6) Å², common isotropic temperature factor for remaining hydrogen atoms converged at $U = 0.063$ (3) Å²; function minimized $\sum w(|F_o| - |F_c|)^2$, $w = 1/(\sigma_F^2 + 0.001F^2)$, $R = 0.047$ ($wR = 0.064$); standard deviation of an observation of unit weight $S = 1.95$ for $m = 1051$ observations and $n = 180$ refined parameters; in final cycle of refinement average and max. shift/error 0.02 and 0.26 respectively; residual fluctuations in difference map $\pm 0.2 e \text{ \AA}^{-3}$; atomic scattering factors of *SHELX76* used.

Discussion. Final atomic coordinates are given in Table 1.* Bond lengths and angles and torsion angles are listed in Table 2. Fig. 1 shows a perspective view of the molecule (*PLUTO78*, Motherwell & Clegg, 1978). The X-ray analysis confirms that 3-oxograndolide has the

* Lists of structure factors, hydrogen-atom parameters and anisotropic thermal parameters for non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39929 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

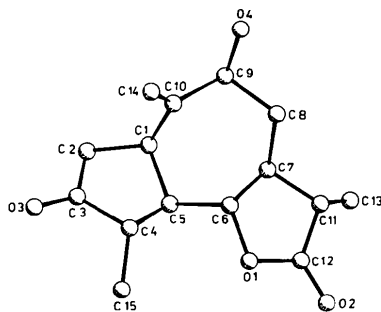


Fig. 1. View of the β -face of the molecule of 3-oxograndolide and atom-numbering scheme.

Table 1. Final fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
C(1)	3659 (5)	949 (4)	4279 (1)	420 (10)
C(2)	4642 (6)	-124 (4)	4678 (1)	512 (11)
C(3)	6768 (6)	-708 (4)	4501 (1)	479 (11)
C(4)	6913 (5)	-431 (4)	3974 (1)	459 (10)
C(5)	4642 (5)	103 (4)	3831 (1)	396 (9)
C(6)	4541 (5)	1305 (4)	3404 (1)	365 (8)
C(7)	2366 (4)	2182 (4)	3328 (1)	380 (9)
C(8)	2252 (6)	3991 (4)	3553 (1)	484 (10)
C(9)	2347 (6)	4029 (4)	4096 (1)	437 (10)
C(10)	4078 (5)	2908 (4)	4310 (1)	408 (10)
C(11)	2145 (5)	2206 (4)	2788 (1)	395 (9)
C(12)	3634 (5)	814 (4)	2624 (1)	423 (10)
C(13)	-94 (6)	1926 (5)	2611 (1)	525 (11)
C(14)	5771 (7)	3562 (5)	4510 (1)	607 (13)
C(15)	7878 (7)	-1949 (5)	3712 (1)	682 (13)
O(1)	4929 (3)	288 (3)	2979 (1)	458 (7)
O(2)	3759 (4)	159 (3)	2239 (1)	563 (9)
O(3)	8186 (5)	-1297 (4)	4747 (1)	710 (10)
O(4)	2589 (5)	5824 (3)	4217 (1)	548 (8)

Table 2. Bond distances (Å), valency angles ($^\circ$) and torsion angles ($^\circ$)

C(1)-C(2)	1.528 (5)	C(7)-C(8)	1.528 (4)
C(1)-C(5)	1.551 (4)	C(7)-C(11)	1.533 (4)
C(1)-C(10)	1.529 (4)	C(8)-C(9)	1.538 (4)
C(2)-C(3)	1.497 (5)	C(9)-C(10)	1.514 (5)
C(3)-C(4)	1.509 (4)	C(9)-O(4)	1.428 (4)
C(3)-O(3)	1.217 (5)	C(10)-C(14)	1.307 (5)
C(4)-C(5)	1.540 (5)	C(11)-C(12)	1.495 (4)
C(4)-C(15)	1.509 (5)	C(11)-C(13)	1.512 (5)
C(5)-C(6)	1.522 (4)	C(12)-O(1)	1.355 (4)
C(6)-C(7)	1.540 (4)	C(12)-O(2)	1.200 (4)
C(6)-O(1)	1.454 (3)		
C(2)-C(1)-C(5)	102.4 (2)	C(6)-C(7)-C(8)	112.4 (2)
C(2)-C(1)-C(10)	114.7 (2)	C(6)-C(7)-C(11)	103.0 (2)
C(5)-C(1)-C(10)	112.9 (2)	C(8)-C(7)-C(11)	113.5 (2)
C(1)-C(2)-C(3)	106.1 (3)	C(7)-C(8)-C(9)	115.5 (2)
C(2)-C(3)-C(4)	109.9 (3)	C(8)-C(9)-C(10)	114.6 (2)
C(2)-C(3)-O(3)	125.2 (3)	C(8)-C(9)-O(4)	105.2 (2)
C(4)-C(3)-O(3)	124.8 (3)	C(10)-C(9)-O(4)	112.1 (2)
C(3)-C(4)-C(5)	103.9 (3)	C(9)-C(10)-C(1)	114.3 (2)
C(3)-C(4)-C(15)	113.6 (3)	C(1)-C(10)-C(14)	122.9 (3)
C(5)-C(4)-C(15)	116.8 (3)	C(9)-C(10)-C(14)	122.8 (3)
C(4)-C(5)-C(1)	105.5 (2)	C(7)-C(11)-C(12)	104.2 (2)
C(6)-C(5)-C(1)	112.1 (2)	C(7)-C(11)-C(13)	114.5 (2)
C(4)-C(5)-C(6)	114.1 (2)	C(12)-C(11)-C(13)	112.3 (2)
C(5)-C(6)-C(7)	114.4 (2)	C(11)-C(12)-O(1)	111.1 (2)
C(5)-C(6)-O(1)	108.9 (2)	C(11)-C(12)-O(2)	128.5 (2)
C(7)-C(6)-O(1)	105.6 (2)	C(6)-O(1)-C(12)	110.6 (2)
C(5)-C(1)-C(2)-C(3)	29.9 (3)	C(5)-C(6)-C(7)-C(8)	94.5 (3)
C(2)-C(1)-C(5)-C(4)	-35.1 (3)	C(5)-C(6)-C(7)-C(11)	-143.0 (3)
C(2)-C(1)-C(5)-C(6)	-159.9 (3)	C(5)-C(6)-O(1)-C(12)	140.2 (3)
C(10)-C(1)-C(2)-C(3)	-92.9 (3)	O(1)-C(6)-C(7)-C(8)	-145.8 (3)
C(2)-C(1)-C(10)-C(9)	-150.5 (3)	O(1)-C(6)-C(7)-C(11)	-23.3 (3)
C(2)-C(1)-C(10)-C(14)	28.5 (4)	C(7)-C(6)-O(1)-C(12)	17.0 (3)
C(10)-C(1)-C(5)-C(4)	88.8 (3)	C(6)-C(7)-C(8)-C(9)	-66.7 (3)
C(10)-C(1)-C(5)-C(6)	-35.9 (3)	C(6)-C(7)-C(11)-C(12)	21.3 (3)
C(5)-C(1)-C(10)-C(9)	92.7 (3)	C(6)-C(7)-C(11)-C(13)	144.2 (3)
C(5)-C(1)-C(10)-C(14)	-88.4 (4)	C(11)-C(7)-C(8)-C(9)	176.9 (3)
C(1)-C(2)-C(3)-C(4)	-14.1 (3)	C(8)-C(7)-C(11)-C(12)	143.0 (3)
C(1)-C(2)-C(3)-O(3)	164.9 (4)	C(8)-C(7)-C(11)-C(13)	-94.0 (3)
C(2)-C(3)-C(4)-C(5)	-8.0 (3)	C(7)-C(8)-C(9)-C(10)	46.7 (3)
C(2)-C(3)-C(4)-C(15)	-135.9 (4)	C(7)-C(8)-C(9)-O(4)	170.2 (3)
O(3)-C(3)-C(4)-C(5)	173.0 (4)	C(8)-C(9)-C(10)-C(1)	-72.2 (3)
O(3)-C(3)-C(4)-C(15)	45.1 (4)	C(8)-C(9)-C(10)-C(14)	108.9 (3)
C(3)-C(4)-C(5)-C(1)	26.7 (3)	O(4)-C(9)-C(10)-C(1)	168.0 (3)
C(3)-C(4)-C(5)-C(6)	150.3 (3)	O(4)-C(9)-C(10)-C(14)	-10.9 (4)
C(15)-C(4)-C(5)-C(1)	152.7 (3)	C(7)-C(11)-C(12)-O(1)	-12.3 (3)
C(15)-C(4)-C(5)-C(6)	-83.8 (3)	C(7)-C(11)-C(12)-O(2)	166.7 (3)
C(1)-C(5)-C(6)-C(7)	-46.6 (3)	C(13)-C(11)-C(12)-O(1)	-136.7 (3)
C(1)-C(5)-C(6)-O(1)	-164.5 (2)	C(13)-C(11)-C(12)-O(2)	42.3 (4)
C(4)-C(5)-C(6)-C(7)	-166.5 (3)	C(11)-C(12)-O(1)-C(6)	-2.9 (3)
C(4)-C(5)-C(6)-O(1)	75.7 (2)	O(2)-C(12)-O(1)-C(6)	178.0 (3)

stereochemistry shown in (I). If the usual assumption is made that the C(7) equatorial substituent is β as in all sesquiterpene lactones of authenticated stereochemistry (Fisher, Olivier & Fisher, 1979), then (I) also represents the absolute configuration of 3-oxograndolide. The ring junctions in this tricyclic molecule are *cis* at C(1)–C(5) and *trans* at C(6)–C(7). The cycloheptane ring adopts a twist-chair conformation with approximate C_2 symmetry, the approximate twofold axis passing through C(5) and the midpoint of the C(8)–C(9) bond. For an isolated methylenecycloheptane moiety, this conformer is, of course, indistinguishable from one in which the C_2 axis passes through C(8) and the midpoint of the C(1)–C(5) bond, and represents one of the calculated energy minima (but not the calculated global minimum) for this species (Bovill, Guy, Sim, White & Herz, 1979). This approximate C_2 symmetry is also observed in related guaian-6,12-olides having one five-membered ring *cis*-fused and the other *trans*-fused to a methylenecycloheptane ring (Thiessen & Hope, 1970; Stevens & Wong, 1982; Rychlewska & Hodgson, unpublished observations).

As has been noted by Hendrickson (1963), this C_2 conformation allows both 1,2-*cis*-diequatorial and 1,3-*trans*-diequatorial substituents. In a substituted methylenecycloheptane system, it becomes possible to distinguish between the two approximately C_2 conformers alluded to above. As stated earlier, the present compound has the C_2 axis passing through C(5). Consequently, the *cis*-fused cyclopentanone ring [at C(1)–C(5)] is diequatorial and the C(6)–O(1) and C(1)–C(2) bonds are *trans* and equatorial. Moreover, the calculated preferred dihedral angle at C(6)–C(7) is 23° (Hendrickson, 1963) which is easily accommodated by the five-membered γ -lactone ring; the observed value in the present compound is $23.3(5)^\circ$. The same conformer was found in solstitialin (Thiessen & Hope, 1970), but the related species acroptilin (Stevens & Wong, 1982) and linichlorin B (Rychlewska & Hodgson, unpublished observations) adopt the other C_2 conformation, in which the approximate C_2 axis passes through C(8).

The cyclopentanone ring is present in a half-chair conformation with the approximate twofold axis passing through the C(3)=O(3) bond and the midpoint of the C(1)–C(5) bond. The average magnitude of the five endocyclic torsion angles is 22.8° .

The γ -lactone ring is slightly less puckered. The average torsion-angle magnitude is 15.4° and the ring approximates an envelope conformation with C(7) as the flap, a conformation common among saturated γ -lactones (McPhail & Onan, 1976).

The β -hydroxy function present in the structure participates in an intermolecular hydrogen bond with the 3-keto group; the O(4)···O(3) and H(O4)···O(3) distances are 2.976 (3) and 0.92 (3) Å respectively, and the O(4)–H(O4)···O(3) angle is $174(3)^\circ$.

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4,4'-Dichlorobenzophénone à 293 K (Phase I), C₁₃H₈Cl₂O

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Abstract. $M_r = 251.11$, monoclinic, $C2/c$, $a = 1.473 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha_1) = 0.7093 \text{ \AA}$, $\mu = 25.161(9)$, $b = 6.104(2)$, $c = 7.535(8) \text{ \AA}$, $\beta = 0.546 \text{ mm}^{-1}$, $F(000) = 512$, $T = 293 \text{ K}$, $R = 0.08$ for $101.98(9)^\circ$, $V = 1132(3) \text{ \AA}^3$, $Z = 4$, $D_x = 635$ significant reflections. The title compound is a

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