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(1*S*,7*S*,8*R*,10*S*)-3-Oxoguaia-4,11(13)-dien-8,12-olide, $C_{15}H_{18}O_3$

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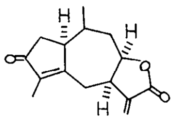
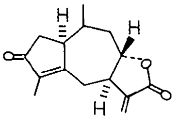
Abstract. $M_r = 246{\cdot}31$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}558\,(2)$, $b = 22{\cdot}365\,(7)$, $c = 7{\cdot}435\,(2)$ Å, $V = 1256{\cdot}7\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}302$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}96$ cm^{-1}, $F(000) = 528$, room temperature (295 K), $R = 0{\cdot}046$ for 1138 independent observed reflections. The title compound, 8-epixerantholide, (1) with a *cis*-fused lactone ring and the isomeric xerantholide (2) with a *trans*-fused lactone ring were isolated from *Decachaeta scabrella*. The difference in lactone ring fusion leads to significantly different conformations. The seven-membered ring in (1) exhibits a twist-boat conformation while that in (2) is in an almost ideal chair form. The pentenone ring in both compounds is almost planar; however, the conformation of the lactone ring in (1) is a flattened envelope while that in (2) is a half-chair.

Introduction. *Decachaeta scabrella* (B. L. Robinson) King et H. Robinson var. *scabrella* was investigated as part of our continuing chemotaxonomic study of the tribe Eupatorieae. In the genus *Decachaeta, D. scabrella* has been placed in the subgenus *Polydenia* (King & Robinson, 1969). So far only two other species have been studied from this subgenus: *D. thieleana* (Alvarado, Ciccio, Calzada, Zabel & Watson, 1979; Castro, Ciccio, Alvarado, Bohlmann, Schmeda-Hirschmann & Jakupovic, 1983) and *D. ovatifolia* (de Luengo, Miski, Gage, Mabry, Kashyap & Watson, 1985). *D. thieleana* afforded several 7,8-guaianolides, including 8-epixerantholide (1), while *D. ovatifolia* yielded 7α-hydroxysesquiterpene lactones of several skeletal types, including a 6,7-guaianolide derivative.

The CH_2Cl_2 extract of leaves of *D. scabrella* yielded 7,8-guaianolides, including 8-epixerantholide (1) and xerantholide (2), similar to the results for *D. thieleana*.



(1)



(2)

We now report in detail on the structure of 8-epixerantholide (1) and its correlation with xerantholide (2).

Experimental. Molecular formula of (1) by mass spectrometry, transparent prismatic-shaped crystal, 0·75 × 0·43 × 0·25 mm, mounted along the *c* axis (long dimension) on a Syntex $P2_1$ diffractometer, θ:2θ scan, variable scan rate, all accessible independent reflections collected within range $2\theta \leq 50°$, graphite-monochromated radiation; lattice parameters from least-squares refinement of 15 reflections ($6{\cdot}6 \leq 2\theta \leq 22{\cdot}4°$) with angles measured by a centering routine associated with the diffractometer system, systematic absences (h, k or $l = 2n + 1$ for $h00$, $0k0$, and $00l$) consistent with space group $P2_12_12_1$; a monitored reflection (012) showed no change in intensity larger than $2\sigma(I)$; 1283 independent reflections ($0 \leq h \leq 8$; $0 \leq k \leq 23$; $0 \leq l \leq 8$); 1138 had intensities greater than $3\sigma(I)$, equivalent reflections showed deviations of less than $2\sigma(I)$ and were discarded without averaging; no Friedel pairs collected since absolute configuration known from biosynthetic considerations; Lorentz and polarization corrections, no absorption correction; direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) located 17 non-H atoms; the missing non-H atom and all H atoms located in difference Fourier map, H-atom positions refined during isotropic cycles but held fixed during anisotropic refinement and finally fixed at 1·08 Å by scaling (for better evaluation of intramolecular contacts and comparison with results of molecular-mechanics calculations); full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F_o)$ [derived from counting statistics evaluated by Syntex (1976) routine]; 163 parameters refined, final $R = 0{\cdot}046$, $wR = 0{\cdot}055$, $S = 2{\cdot}76$, $(\Delta/\sigma)_{\max} = 0{\cdot}38$, $(\Delta/\sigma)_{\mathrm{av}} = 0{\cdot}078$, highest peak in final difference Fourier map 0·17 e Å^{-3}; locally written programs for data reduction, *ORTEP* (Johnson, 1971), *MULTAN*78 for direct-methods calculations, and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) for all others; atomic scattering factors for C and O from Cromer & Mann (1968) corrected for anomalous dispersion (real and imaginary), those for H from

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Stewart, Davidson & Simpson (1965). Table 1 lists atomic positional parameters and U_{eq} values while Table 2 lists interatomic distances, valence angles, and selected torsion angles. Experimental details and atomic parameters for compound (2) (Tables 6 and 7) are included in the deposited material.*

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* U_{eq} (Å^2 $\times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha].$$

	x	y	z	U_{eq}
C(1)	−3088 (3)	3397 (1)	2630 (4)	35 (2)
C(2)	−1253 (4)	3425 (1)	3518 (5)	47 (2)
C(3)	−705 (4)	4067 (1)	3400 (4)	43 (2)
O(3)	715 (3)	4269 (1)	3882 (4)	61 (1)
C(4)	−2156 (4)	4415 (1)	2610 (4)	36 (2)
C(5)	−3503 (3)	4046 (1)	2229 (4)	32 (1)
C(6)	−5250 (3)	4209 (1)	1451 (4)	34 (1)
C(7)	−5907 (4)	3765 (1)	26 (4)	36 (2)
C(8)	−6254 (4)	3123 (1)	699 (5)	41 (2)
O(8)	−8007 (3)	2961 (1)	3 (4)	58 (1)
C(9)	−6314 (4)	3045 (1)	2709 (5)	44 (2)
C(10)	−4510 (4)	3058 (1)	3685 (4)	38 (2)
C(11)	−7642 (4)	3942 (1)	−767 (4)	43 (2)
C(12)	−8833 (4)	3424 (1)	−787 (5)	48 (2)
O(12)	−10296 (3)	3378 (1)	−1370 (4)	70 (2)
C(13)	−8173 (5)	4458 (2)	−1347 (8)	90 (3)
C(14)	−4777 (5)	3288 (2)	5566 (4)	53 (2)
C(15)	−1988 (4)	5072 (1)	2311 (5)	48 (2)

Discussion. Fig. 1 is an *ORTEP* (Johnson, 1971) drawing of the title compound (1). The *cis* and *trans* ring fusions in the isomeric xerantholides (1) and (2) (Rychlewska, 1981) lead to significantly different conformations for the seven-membered ring and the lactone ring. Force-field calculations (*MM*2, Allinger & Yuh, 1980) were used to assess the factors which lead to differences in structural properties. The *cis* isomer (1) is calculated to have slightly more than 4 kJ of strain energy than isomer (2). Five bond lengths in the two isomers differ by more than 3σ; however, an independent structure determination in this laboratory of compound (2) shows four of these bonds to be statistically equivalent to those in (1). Force-field calculations suggest only differences in the C(7)–C(8) bond distances should be significant. The calculated values of 1·546 and 1·533 Å are consistent with the observed values of 1·546 (4) Å (1) and 1·524 (5) Å (2) (Rychlewska, 1981). We find the value for compound

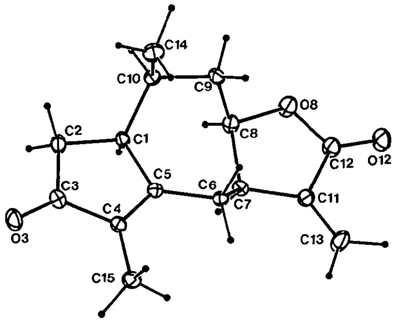

Fig. 1. *ORTEP* drawing of 8-epixerantholide (1). Thermal ellipsoids are drawn at the 35% probability level. H atoms are drawn at arbitrary size for clarity.

Table 2. *Interatomic distances* (Å), *valence angles* (degrees), *and selected torsion angles* (degrees) *for compounds* (1) *and* (2)

	(1)	(2)		(1)	(2)		(1)	(2)
C(1)–C(2)	1·537 (4)	1·552 (6)	C(4)–C(15)	1·493 (4)	1·485 (6)	C(9)–C(10)	1·545 (4)	1·551 (6)
C(1)–C(5)	1·515 (4)	1·508 (6)	C(5)–C(6)	1·487 (4)	1·498 (6)	C(10)–C(14)	1·503 (5)	1·508 (7)
C(1)–C(10)	1·530 (4)	1·535 (6)	C(6)–C(7)	1·534 (4)	1·527 (6)	C(11)–C(12)	1·469 (5)	1·485 (6)
C(2)–C(3)	1·497 (5)	1·513 (7)	C(7)–C(8)	1·542 (4)	1·529 (6)	C(11)–C(13)	1·295 (5)	1·296 (7)
C(3)–O(3)	1·218 (4)	1·217 (6)	C(7)–C(11)	1·492 (4)	1·497 (5)	C(12)–O(8)	1·344 (4)	1·367 (5)
C(3)–C(4)	1·467 (4)	1·474 (6)	C(8)–O(8)	1·468 (4)	1·488 (5)	C(12)–O(12)	1·192 (4)	1·191 (5)
C(4)–C(5)	1·341 (4)	1·330 (6)	C(8)–C(9)	1·505 (5)	1·484 (6)			
C(2)C(1)C(5)	103·4 (2)	103·0 (3)	C(1)C(5)C(6)	119·7 (2)	122·0 (4)	C(8)C(9)C(10)	115·9 (3)	112·4 (4)
C(2)C(1)C(10)	115·7 (3)	111·5 (4)	C(4)C(5)C(6)	127·2 (2)	123·8 (3)	C(1)C(10)C(9)	112·9 (3)	112·6 (3)
C(5)C(1)C(10)	115·4 (4)	117·3 (4)	C(5)C(6)C(7)	113·4 (2)	115·9 (3)	C(1)C(10)C(14)	112·7 (3)	112·0 (4)
C(1)C(2)C(3)	105·3 (2)	105·1 (3)	C(6)C(7)C(8)	115·7 (3)	112·9 (3)	C(9)C(10)C(14)	109·0 (3)	112·4 (4)
C(2)C(3)O(3)	125·6 (3)	125·2 (4)	C(6)C(7)C(11)	112·7 (2)	115·0 (3)	C(7)C(11)C(12)	109·5 (3)	107·1 (3)
C(2)C(3)C(4)	109·0 (2)	108·2 (3)	C(8)C(7)C(11)	103·1 (2)	102·0 (3)	C(7)C(11)C(13)	129·9 (3)	130·3 (4)
O(3)C(3)C(4)	125·4 (3)	126·6 (4)	C(7)C(8)C(9)	115·8 (3)	116·6 (3)	C(12)C(11)C(13)	120·6 (3)	122·6 (4)
C(3)C(4)C(5)	109·0 (2)	109·2 (4)	C(7)C(8)O(8)	105·6 (2)	103·5 (3)	O(8)C(12)C(11)	108·6 (3)	108·4 (4)
C(3)C(4)C(15)	121·2 (3)	122·2 (4)	O(8)C(8)C(9)	107·1 (3)	108·1 (3)	O(8)C(12)O(12)	121·5 (3)	130·7 (4)
C(5)C(4)C(15)	129·8 (3)	128·7 (4)	C(8)O(8)C(12)	112·5 (2)	109·7 (3)	C(11)C(12)O(12)	129·9 (3)	129·9 (3)
C(1)C(5)C(4)	113·0 (2)	114·2 (3)						
C(1)C(2)C(3)C(4)	3·7 (4)	−6·0 (5)	C(5)C(6)C(7)C(8)	63·0 (3)	62·8 (5)	C(7)C(11)C(12)O(8)	3·1 (4)	9·8 (5)
C(2)C(3)C(4)C(5)	−0·7 (4)	4·8 (5)	C(6)C(7)C(8)C(9)	13·5 (4)	−87·6 (4)	C(11)C(12)O(8)C(8)	2·8 (4)	10·4 (5)
C(3)C(4)C(5)C(1)	−2·9 (4)	−1·5 (5)	C(7)C(8)C(9)C(10)	−75·2 (3)	71·8 (5)	C(12)O(8)C(8)C(7)	−7·3 (4)	−25·9 (4)
C(4)C(5)C(1)C(2)	5·1 (3)	−2·3 (5)	C(8)C(9)C(10)C(1)	23·9 (4)	−64·6 (5)	O(8)C(8)C(7)C(11)	8·4 (3)	29·9 (4)
C(5)C(1)C(2)C(3)	5·0 (3)	4·9 (5)	C(9)C(10)C(1)C(5)	59·4 (3)	77·2 (5)	C(8)C(7)C(11)C(12)	−7·2 (3)	−24·7 (4)
C(1)C(5)C(6)C(7)	−39·6 (4)	−2·1 (6)	C(10)C(1)C(5)C(6)	−48·9 (4)	−60·8 (5)			

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* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, and molecular-mechanics-calculated parameters for compounds (1) and (2) also, together with Tables 6 and 7, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42103 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(2) to be 1·529 (6) Å. There are a number of valence angles which differ significantly between structures (1) and (2), and in general, these differences are reflected in the calculated values. This implies the differences are real and reflect adjustments to ring strain and to intramolecular contacts induced by the different ring fusions. The torsion angles show the greatest discrepancies, and a twist-boat conformation is observed for the seven-membered ring in (1) and an almost ideal chair form for (2). The calculated and observed values show reasonable agreement; however, torsion angles more readily reflect the influence of intermolecular interactions which are neglected in the calcultions. The lactone ring in (1) is calculated to be more planar than observed and the cyclopentenone ring, although almost planar, with a different puckering pattern than observed. These small deviations from planarity again may reflect the influence of intermolecular interactions; however, there are only four intermolecular contacts, 2·38–2·44 Å, less than 3·00 Å.

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Structure of *cis-transoid-cis*-6,11-Dioxatricyclo[7.3.0.0^{4,8}]-dodec-2-en-5,5,7,7,10,10,12,12-octacarbonitrile, $C_{18}H_6N_8O_2$

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Abstract. $M_r = 366\cdot3$, monoclinic, $P2_1/c$, $a = 6\cdot771\,(2)$, $b = 16\cdot149\,(7)$, $c = 16\cdot407\,(9)$ Å, $\beta = 100\cdot08\,(5)°$, $V = 1766\,(1)$ Å^3, $Z = 4$, $D_x = 1\cdot377$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot09$ mm^{-1}, $F(000) = 744$, $T = 295$ K, $R = 0\cdot050$ for 824 observed reflexions. The structure determination shows that in the adduct formed from one molecule of benzene and two molecules of tetracyanoethylene oxide, the benzene ring has lost its aromatic character. Bond lengths and angles are normal.

Introduction. The reaction of benzene and tetracyanoethylene oxide (TCNEO) (Linn & Benson, 1965) gives two different cycloadducts, one of them a monoadduct and the other a bisadduct.

This bisadduct is formed by reaction of one benzene molecule and two of TCNEO. This result suggests olefinic, not aromatic, behaviour of benzene. The structure of the bisadduct was difficult to resolve by spectroscopic techniques (Brown & Cookson, 1968; Diez-Barra, Pardo, Arriau, Elguero & Fruchier, 1984). However, theoretical methods and simulations of ^{1}H NMR spectra have allowed us to exclude the structures formed by [$\pi^4 + \pi^4$] cycloaddition between the monoadduct and TCNEO; these methods, in fact, support the structure arising from [$\pi^4 + \pi^2$] cycloaddition.

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