

Sesquiterpenoids. XXV.* X-ray Crystal Structure Analysis of Costunolide

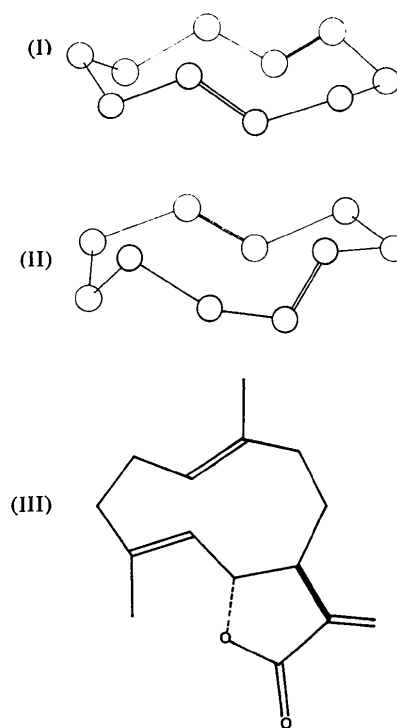
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The germacranolide costunolide, $C_{15}H_{20}O_2$, crystallizes in the orthorhombic space group $P2_12_12_1$, with $a=11.03$, $b=15.40$, $c=7.99$ Å, $Z=4$. The atomic coordinates were obtained by multiresolution direct phasing of 1398 independent reflexions, measured on a four-circle diffractometer, and refined to $R=4.3\%$ by full-matrix least squares. The torsion angles around the double bonds in the *trans,trans*-cyclodeca-1,5-diene ring are 156° and 165° and can be compared with the ideal value of 180° for an unstrained double bond and values of 169° calculated by molecular-mechanics methods for the C=C bonds in the isolated macrocycle. The C=C-C=O torsion angle of the α -methylene γ -lactone is -10° .

The detailed molecular topology of sesquiterpenoids has received considerable attention in recent years, (Mathieson, 1972; Cameron, 1973; Sim, 1974) with subsequent rationalization of some of the peculiarities (White & Sim, 1973; Yoshioka, Renold & Mabry, 1970). Two distinct conformations of the *trans,trans*-cyclodeca-1,5-diene ring have been observed among the germacranolides; (I) is typified by germacatriene (Allen & Rogers 1967), elephantol (McPhail & Sim, 1972), and costunolide in its silver nitrate complex (Sorm, Suchý, Holub, Líněk, Hadire & Novák, 1970), and (II) by dihydromokanolide (Cox & Sim, 1974), shiromodiol (McLure, Sim, Coggon & McPhail, 1970), and glaucolide-A (Cox & Sim, 1975), but it has yet to be established which is the more stable conformation. Indeed, apart from preliminary molecular-mechanics calculations (Buemi, Zuccarello & Favini, 1974), there has been little interest in this ring system in comparison with other cyclic alkenes (Ermer & Lifson, 1973; Allinger & Sprague, 1975). The conformation found for costunolide in its silver nitrate complex has also been deduced for the sesquiterpenoid molecule in solution, by NOE measurements (Tori, Horibe, Tamura & Tada, 1973). We undertook an X-ray study of costunolide (III) to confirm the adoption of conformation I in the solid state, to define the shape of the α -methylene γ -lactone, and to obtain details of the deformation of the *trans* double bonds in the ten-membered ring. The absolute configuration of costunolide is known to be as shown in (III) (Herout & Sorm, 1959; Bhattacharyya, Kelkar & Rao, 1959; Herout, Suchý & Sorm, 1961).



The double bonds in the ten-membered ring of the germacranolides are not deformed to the same extent; one C=C-C torsion angle is consistently smaller (*i.e.* deviates further from 180°) than the other (Table 8). The question posed here is whether the effect is a feature of an isolated *trans,trans*-cyclodeca-1,5-diene ring or an artefact introduced by the substituents and/or fusion of the lactone ring. In principle the question could be answered by an X-ray analysis of a minimally substituted cyclodeca-1,5-diene derivative, but molecular-mechanics calculations offer an

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elegant and less time-consuming alternative. To this end, the molecular geometries and relative steric energies of conformations I and II of the cyclic diene have been computed with two independent force fields.

Experimental

Crystal data

Costunolide, $C_{15}H_{20}O_2$, $M=232.3$. Orthorhombic, $a=11.03$, $b=15.40$, $c=7.99$ Å, $U=1356$ Å³, $Z=4$, $D_c=1.14$, $D_m=1.16$ g cm⁻³, $F(000)=504$, space group $P2_12_12_1$, $\mu(Cu K\alpha)=5.9$ cm⁻¹.

Crystallographic measurements

Cell dimensions were initially determined from precession photographs and subsequently adjusted to minimize the discrepancies between calculated and observed setting angles measured on a Hilger & Watts Y290 four-circle computer-controlled diffractometer. The intensities were obtained by the ω - 2θ step scan procedure with background intensity measurements at each end of the scan range and periodic monitoring of two standard reflexions. Initially, 900 intensities were obtained with Mo $K\alpha$ radiation; at a later stage a slightly larger crystal, $1.0 \times 0.5 \times 0.5$ mm, was irradiated with Cu $K\alpha$ radiation and 1398 intensities with $I > 3\sigma(I)$ were obtained.

Structure analysis

The structure was elucidated from the Mo $K\alpha$ intensities by the direct phasing procedures in the X-RAY 70 suite of programs. Full-matrix least-squares

Table 1. Fractional atomic coordinates ($\times 10^4$) with *e.s.d.*'s ($\times 10^4$) in parentheses

	x	y	z
C(1)	876 (2)	6935 (1)	1874 (3)
C(2)	-116 (2)	6850 (2)	3117 (4)
C(3)	73 (2)	6014 (2)	4177 (4)
C(4)	1345 (2)	6021 (1)	4881 (3)
C(5)	2222 (2)	5671 (1)	3959 (2)
C(6)	3533 (2)	5880 (1)	4067 (2)
C(7)	4125 (2)	6064 (1)	2351 (2)
C(8)	4083 (2)	7009 (1)	1742 (3)
C(9)	2919 (2)	7313 (1)	836 (3)
C(10)	1841 (2)	7448 (1)	1951 (2)
C(11)	5381 (2)	5709 (1)	2628 (3)
C(12)	5322 (2)	5093 (1)	4052 (4)
C(13)	6414 (3)	5851 (2)	1855 (5)
C(14)	1566 (3)	6526 (2)	6435 (3)
C(15)	1967 (3)	8182 (2)	3166 (4)
O(1)	4218 (1)	5144 (1)	4768 (2)
O(2)	6080 (2)	4591 (1)	4551 (4)
H(1)	951 (22)	6544 (16)	1014 (32)
H(21)	-49 (26)	7476 (19)	3876 (37)
H(22)	-944 (29)	6786 (22)	2608 (45)
H(31)	-574 (32)	5978 (23)	5088 (55)
H(32)	-114 (39)	5484 (27)	3342 (58)
H(5)	1972 (21)	5289 (14)	2937 (30)
H(6)	3712 (20)	6360 (15)	4868 (32)
H(7)	3717 (26)	5699 (20)	1526 (39)
H(81)	4256 (30)	7465 (23)	2759 (44)
H(82)	4772 (29)	7079 (21)	1043 (41)
H(91)	3098 (24)	7905 (17)	222 (35)
H(92)	2775 (22)	6848 (16)	-1 (33)
H(131)	7251 (39)	5485 (27)	2284 (59)
H(132)	6429 (19)	6113 (14)	1318 (29)
H(141)	2401 (29)	6544 (20)	6770 (42)
H(142)	1045 (30)	6359 (23)	7281 (44)
H(143)	1362 (32)	7123 (25)	6224 (51)
H(151)	1236 (43)	8261 (32)	3903 (64)
H(152)	2435 (38)	8662 (30)	2776 (58)
H(153)	2492 (53)	8000 (38)	4211 (73)

Table 2. Components of the atomic vibration tensors ($U_{ij} \times 10^4$) for the carbon and oxygen atoms and isotropic temperature factors ($U \times 10^4$) for the hydrogen atoms, *e.s.d.*'s ($\times 10^4$) in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	824 (12)	800 (11)	734 (11)	21 (10)	-172 (10)	60 (10)
C(2)	693 (11)	1059 (16)	1112 (16)	81 (11)	-80 (13)	204 (15)
C(3)	676 (11)	1014 (16)	1148 (18)	51 (11)	147 (12)	253 (15)
C(4)	735 (10)	770 (10)	751 (11)	77 (9)	141 (9)	201 (10)
C(5)	683 (9)	615 (9)	698 (10)	-6 (8)	94 (9)	64 (8)
C(6)	684 (9)	579 (8)	618 (9)	29 (7)	26 (8)	34 (7)
C(7)	697 (9)	645 (9)	618 (9)	-85 (8)	39 (8)	0 (8)
C(8)	798 (12)	796 (12)	883 (14)	-144 (10)	23 (11)	213 (12)
C(9)	1011 (14)	878 (13)	694 (11)	-42 (12)	7 (12)	248 (10)
C(10)	898 (12)	676 (9)	645 (9)	-14 (10)	-123 (9)	107 (9)
C(11)	704 (10)	695 (10)	883 (13)	-41 (8)	120 (10)	-97 (10)
C(12)	698 (10)	763 (11)	1095 (16)	64 (10)	-6 (12)	20 (12)
C(13)	894 (16)	1169 (20)	1444 (25)	-88 (15)	358 (18)	110 (21)
C(14)	1059 (17)	1209 (19)	702 (13)	289 (16)	208 (12)	45 (13)
C(15)	1381 (23)	818 (14)	1061 (18)	-198 (15)	48 (19)	-117 (14)
O(1)	773 (7)	809 (8)	889 (9)	137 (6)	66 (7)	236 (8)
O(2)	875 (10)	1078 (12)	1754 (22)	289 (10)	-13 (13)	301 (15)
	U		U		U	
H(1)	590 (61)		H(7)	584 (79)	H(141)	781 (89)
H(21)	822 (81)		H(81)	937 (98)	H(142)	859 (100)
H(22)	897 (96)		H(82)	827 (87)	H(143)	935 (112)
H(31)	884 (114)		H(91)	694 (68)	H(151)	1267 (159)
H(32)	1074 (143)		H(92)	624 (64)	H(152)	1238 (132)
H(5)	458 (57)		H(131)	1287 (146)	H(153)	1670 (210)
H(6)	440 (57)		H(132)	563 (53)		

Table 3. Bond lengths (Å) with *e.s.d.*'s ($\times 10^3$) in parentheses

O(1)—C(6)	1.473 (2)	C(2)—H(21)	1.121 (31)
O(1)—C(12)	1.348 (2)	C(2)—H(22)	1.007 (32)
O(2)—C(12)	1.204 (3)	C(3)—H(31)	1.028 (34)
C(1)—C(2)	1.485 (3)	C(3)—H(32)	1.063 (35)
C(1)—C(10)	1.326 (3)	C(5)—H(5)	1.046 (21)
C(2)—C(3)	1.555 (3)	C(6)—H(6)	0.990 (21)
C(3)—C(4)	1.512 (3)	C(7)—H(7)	0.975 (26)
C(4)—C(5)	1.329 (2)	C(8)—H(81)	1.088 (37)
C(4)—C(14)	1.487 (3)	C(8)—H(82)	0.947 (32)
C(5)—C(6)	1.483 (2)	C(9)—H(91)	1.061 (28)
C(6)—C(7)	1.544 (2)	C(9)—H(92)	0.999 (26)
C(7)—C(8)	1.536 (2)	C(13)—H(131)	1.104 (36)
C(7)—C(11)	1.506 (2)	C(13)—H(132)	0.702 (30)
C(8)—C(9)	1.546 (3)	C(14)—H(141)	0.984 (30)
C(9)—C(10)	1.500 (3)	C(14)—H(142)	0.931 (31)
C(10)—C(15)	1.496 (3)	C(14)—H(143)	0.956 (34)
C(11)—C(12)	1.483 (3)	C(15)—H(151)	1.012 (44)
C(11)—C(13)	1.315 (3)	C(15)—H(152)	0.989 (43)
C(1)—H(1)	0.974 (27)	C(15)—H(153)	1.023 (53)

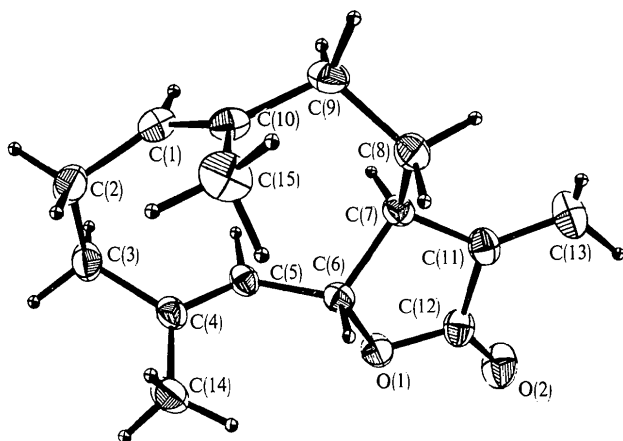
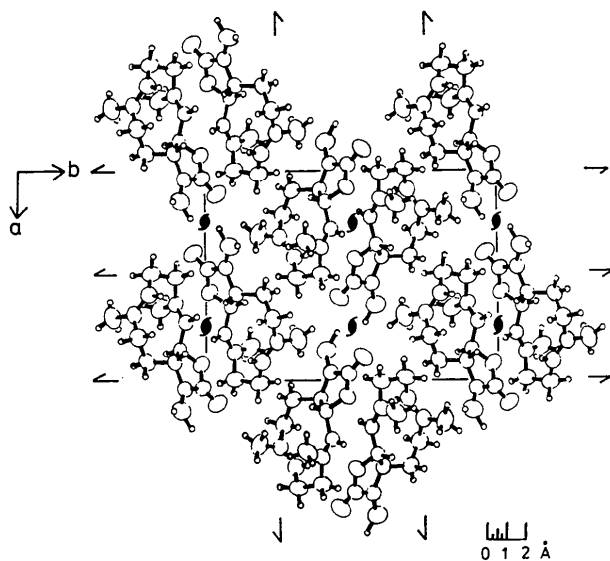


Fig. 1. A view of the molecule.

Fig. 2. The crystal packing viewed down *c*.

adjustment of the positional and anisotropic thermal parameters of the C and O atoms converged at $R=12\%$. At this stage the Cu $K\alpha$ data were obtained and the analysis was continued with these data. The H atoms were placed approximately from stereochemical considerations and their positional and isotropic thermal parameters refined by full-matrix least squares, which also included as variables the positional and anisotropic thermal parameters of the C and O atoms. These calculations converged at $R=4.3\%$. The weighting scheme was $\omega=3.05 \sin \theta/2.1|F|$ if $|F| < 3.05$ and $\omega=\sin \theta/2.1$ if $|F| > 3.05$. No correction was made for absorption.

Table 4. Intermolecular distances (Å) < 4.0 Å

The Roman numerals i to v refer to the following transformations of the atomic coordinates:

(i)	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$	(iv)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(ii)	$\frac{3}{2}-x$	$1-y$	$\frac{1}{2}+z$	(v)	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$-z$
(iii)	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$1-z$				

C(3) \cdots C(4 ⁱ)	3.859	O(2) \cdots C(2 ⁱ)	3.764
C(3) \cdots C(13 ⁱⁱ)	3.938	O(2) \cdots C(13 ⁱⁱⁱ)	3.389
C(4) \cdots C(7 ⁱ)	3.803	C(8) \cdots C(14 ⁱⁱⁱ)	3.835
C(4) \cdots C(11 ⁱⁱⁱ)	3.941	C(12) \cdots C(15 ⁱⁱⁱ)	3.910
C(14) \cdots C(12 ⁱ)	3.864	C(9) \cdots O(2 ^{iv})	3.691
C(14) \cdots O(1 ⁱ)	3.802	C(15) \cdots O(2 ^{iv})	3.748
O(1) \cdots C(1 ⁱ)	3.618	C(8) \cdots C(1 ^v)	3.860
O(1) \cdots C(5 ⁱ)	3.912	C(13) \cdots C(9 ^v)	3.921
O(2) \cdots C(1 ⁱ)	3.691		

Table 5. Bond angles ($^\circ$) with *e.s.d.*'s ($\times 10$) in parentheses

C(12)	O(1)	C(6)	110.4 (1)	C(10)	C(1)	C(2)	127.7 (2)
C(3)	C(2)	C(1)	109.8 (2)	C(4)	C(3)	C(2)	108.8 (1)
C(5)	C(4)	C(3)	117.9 (2)	C(14)	C(4)	C(3)	117.8 (2)
C(14)	C(4)	C(5)	123.8 (2)	C(6)	C(5)	C(4)	126.1 (1)
C(7)	C(6)	O(1)	105.2 (1)	C(5)	C(6)	O(1)	110.8 (1)
C(7)	C(6)	C(5)	113.7 (1)	C(8)	C(7)	C(6)	116.2 (1)
C(11)	C(7)	C(6)	101.2 (1)	C(11)	C(7)	C(8)	114.8 (1)
C(9)	C(8)	C(7)	117.4 (1)	C(10)	C(9)	C(8)	114.9 (1)
C(15)	C(10)	C(1)	123.8 (2)	C(9)	C(10)	C(1)	121.7 (1)
C(15)	C(10)	C(9)	114.5 (2)	C(12)	C(11)	C(7)	107.7 (1)
C(13)	C(11)	C(7)	131.5 (2)	C(13)	C(11)	C(12)	120.8 (2)
C(11)	C(12)	O(1)	109.1 (1)	C(11)	C(12)	O(2)	129.2 (2)
O(2)	C(12)	O(1)	121.7 (2)	H(1)	C(1)	C(2)	119.7 (15)
H(1)	C(1)	C(10)	111.7 (15)	H(22)	C(2)	C(1)	114.7 (19)
H(21)	C(2)	C(1)	103.1 (15)	H(21)	C(2)	C(3)	113.6 (16)
H(22)	C(2)	C(3)	105.7 (19)	H(22)	C(2)	H(21)	110.2 (24)
H(32)	C(3)	C(2)	104.3 (19)	H(31)	C(3)	C(4)	112.3 (19)
H(32)	C(3)	C(4)	113.5 (19)	H(31)	C(3)	C(2)	109.0 (17)
H(32)	C(3)	H(31)	108.5 (26)	H(5)	C(5)	C(4)	118.1 (11)
H(5)	C(5)	C(6)	114.9 (11)	H(6)	C(6)	C(7)	110.6 (12)
H(6)	C(6)	O(1)	103.3 (12)	H(6)	C(6)	C(5)	112.5 (11)
H(7)	C(7)	C(11)	108.4 (14)	H(7)	C(7)	C(6)	107.0 (15)
H(7)	C(7)	C(8)	108.7 (15)	H(81)	C(8)	C(9)	108.2 (18)
H(82)	C(8)	C(9)	110.7 (19)	H(82)	C(8)	C(7)	105.1 (19)
H(81)	C(8)	C(7)	110.5 (19)	H(82)	C(8)	H(81)	104.1 (27)
H(92)	C(9)	C(10)	112.1 (14)	H(91)	C(9)	C(8)	108.9 (15)
H(92)	C(9)	C(8)	103.2 (14)	H(91)	C(9)	C(10)	106.9 (15)
H(92)	C(9)	H(91)	110.8 (22)	H(131)	C(13)	C(11)	118.8 (19)
H(132)	C(13)	C(11)	120.1 (23)	H(132)	C(13)	H(131)	121.0 (30)
H(141)	C(14)	C(4)	113.1 (18)	H(142)	C(14)	C(4)	112.0 (19)
H(143)	C(14)	C(4)	107.2 (21)	H(142)	C(14)	H(141)	112.8 (26)
H(143)	C(14)	H(141)	105.0 (26)	H(143)	C(14)	H(142)	106.1 (27)
H(152)	C(15)	C(10)	114.3 (25)	H(153)	C(15)	C(10)	112.9 (30)
H(151)	C(15)	C(10)	111.5 (24)	H(152)	C(15)	H(151)	124.8 (34)
H(153)	C(15)	H(151)	90.8 (39)	H(153)	C(15)	H(152)	98.2 (39)

Results and discussion

The atomic coordinates, thermal parameters, bond lengths, intermolecular distances, valency angles, torsion angles, and deviations of the atoms from various planes in the molecule are listed in Tables 1–7.* The molecular and crystal structures are shown in Figs. 1 and 2. The bond lengths are unexceptional, with

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31931 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

mean $C_{sp^3}-C_{sp^3}$, $C_{sp^3}-C_{sp^2}$, and $C=C$ distances of 1.545, 1.500, and 1.323 Å respectively.

Discussion of conformational aspects of the germa-cranolide structure has been hampered in the past by lack of a reference geometry for the *trans,trans*-cyclo-deca-1,5-diene ring and we have remedied this by means of appropriate molecular-mechanics calculations. In order to ensure credible reference conformations the calculations were performed with two independent force fields (FF), namely, Allinger's alkene FF (Allinger & Sprague, 1972) and our own recently developed FF (see Appendix). The conformations resulting from these calculations are described by the torsion angles shown in Fig. 3 which also indicates the relative steric

Table 6. Torsion angles ($^{\circ}$) with *e.s.d.*'s ($\times 10$) in parentheses

The angle 1–2–3–4 is defined as positive if, when viewed along the 2–3 bond, atom 1 has to be rotated clockwise to eclipse atom 4.

1–2–3–4				1–2–3–4			
C(12)O(1) C(6) C(5)	145.1 (1)	C(12)O(1) C(6) C(7)	21.8 (2)				
C(6) O(1) C(12)O(2)	172.7 (2)	C(6) O(1) C(12)C(11)	–8.6 (2)				
C(10)C(1) C(2) C(3)	–101.8 (2)	C(2) C(1) C(10)C(9)	164.6 (2)				
C(2) C(1) C(10)C(15)	–13.6 (3)	C(1) C(2) C(3) C(4)	52.0 (2)				
C(2) C(3) C(4) C(5)	–88.6 (2)	C(2) C(3) C(4) C(14)	82.9 (2)				
C(3) C(4) C(5) C(6)	155.9 (2)	C(14)C(4) C(5) C(6)	–15.1 (3)				
C(4) C(5) C(6) O(1)	110.5 (2)	C(4) C(5) C(6) C(7)	–131.2 (2)				
O(1) C(6) C(7) C(8)	–149.9 (1)	O(1) C(6) C(7) C(11)	–24.9 (1)				
C(5) C(6) C(7) C(8)	88.6 (2)	C(5) C(6) C(7) C(11)	–146.4 (1)				
C(6) C(7) C(8) C(9)	–83.9 (2)	C(11)C(7) C(8) C(9)	158.4 (1)				
C(6) C(7) C(11)C(12)	20.5 (2)	C(6) C(7) C(11)C(13)	–159.8 (2)				
C(8) C(7) C(11)C(12)	146.4 (1)	C(8) C(7) C(11)C(13)	–33.9 (3)				
C(7) C(8) C(9) C(10)	73.6 (2)	C(8) C(9) C(10)C(1)	–111.7 (2)				
C(8) C(9) C(10)C(15)	66.7 (2)	C(7) C(11)C(12)O(1)	–8.5 (2)				
C(7) C(11)C(12)O(2)	170.0 (2)	C(13)C(11)C(12)O(1)	171.8 (2)				
C(13)C(11)C(12)O(2)	–9.7 (4)	C(12)O(1) C(6) H(6)	–94.2 (12)				
C(10)C(1) C(2) H(21)	19.6 (16)	C(10)C(1) C(2) H(22)	139.4 (20)				
H(1) C(1) C(2) C(3)	66.4 (18)	H(1) C(1) C(2) H(21)	–172.2 (24)				
H(1) C(1) C(2) H(22)	–52.4 (27)	H(1) C(1) C(10)C(9)	–4.3 (17)				
H(1) C(1) C(10)C(15)	177.5 (17)	C(1) C(2) C(3) H(31)	174.8 (19)				
C(1) C(2) C(3) H(32)	–69.5 (19)	H(21)C(2) C(3) C(4)	–62.8 (17)				
H(21)C(2) C(3) H(31)	59.9 (26)	H(21)C(2) C(3) H(32)	175.7 (26)				
H(22)C(2) C(3) C(4)	176.2 (19)	H(22)C(2) C(3) H(31)	–61.0 (27)				
H(22)C(2) C(3) H(32)	54.7 (27)	H(31)C(3) C(4) C(5)	150.6 (20)				
H(31)C(3) C(4) C(14)	–37.8 (20)	H(32)C(3) C(4) C(5)	27.1 (21)				
H(32)C(3) C(4) C(14)	–161.4 (21)	C(3) C(4) C(5) H(5)	–12.3 (13)				
C(14)C(4) C(5) H(5)	176.7 (13)	C(3) C(4) C(14)H(141)	–176.2 (19)				
C(3) C(4) C(14)H(142)	55.0 (20)	C(3) C(4) C(14)H(143)	–61.0 (21)				
C(5) C(4) C(14)H(141)	–5.2 (19)	C(5) C(4) C(14)H(142)	–134.0 (20)				
C(5) C(4) C(14)H(143)	110.0 (21)	C(4) C(5) C(6) H(6)	–4.6 (13)				
H(5) C(5) C(6) O(1)	–80.9 (12)	H(5) C(5) C(6) C(7)	37.4 (12)				
H(5) C(5) C(6) H(6)	164.0 (18)	O(1) C(6) C(7) H(7)	88.5 (15)				
C(5) C(6) C(7) H(7)	–32.9 (15)	H(6) C(6) C(7) C(8)	–39.0 (13)				
H(6) C(6) C(7) C(11)	86.0 (13)	H(6) C(6) C(7) H(7)	–160.6 (20)				
C(6) C(7) C(8) H(81)	40.8 (20)	C(6) C(7) C(8) H(82)	152.6 (20)				
C(11)C(7) C(8) H(81)	–76.9 (20)	C(11)C(7) C(8) H(82)	34.9 (20)				
H(7) C(7) C(8) C(9)	36.8 (16)	H(7) C(7) C(8) H(81)	161.5 (26)				
H(7) C(7) C(8) H(82)	–86.7 (25)	H(7) C(7) C(11)C(12)	–91.9 (16)				
H(7) C(7) C(11)C(13)	87.8 (16)	C(7) C(8) C(9) H(91)	–166.5 (16)				
C(7) C(8) C(9) H(92)	–48.8 (15)	H(81)C(8) C(9) C(10)	–52.3 (20)				
H(81)C(8) C(9) H(91)	67.6 (26)	H(81)C(8) C(9) H(92)	–174.7 (25)				
H(82)C(8) C(9) C(10)	–165.8 (20)	H(82)C(8) C(9) H(91)	–45.9 (26)				
H(82)C(8) C(9) H(92)	71.9 (26)	H(91)C(9) C(10)C(1)	127.3 (16)				
H(91)C(9) C(10)C(15)	–54.3 (16)	H(92)C(9) C(10)C(1)	5.7 (16)				
H(92)C(9) C(10)C(15)	–175.9 (16)	C(1) C(10)C(15)H(151)	–3.1 (27)				
C(1) C(10)C(15)H(152)	–151.4 (27)	C(1) C(10)C(15)H(153)	97.4 (32)				
C(9) C(10)C(15)H(151)	178.6 (26)	C(9) C(10)C(15)H(152)	30.3 (27)				
C(9) C(10)C(15)H(153)	–80.9 (32)	C(7) C(11)C(13)H(131)	–177.5 (21)				
C(7) C(11)C(13)H(132)	2.7 (28)	C(12)C(11)C(13)H(131)	2.2 (22)				

energies and the torsion angles found for costunolide in the crystal.

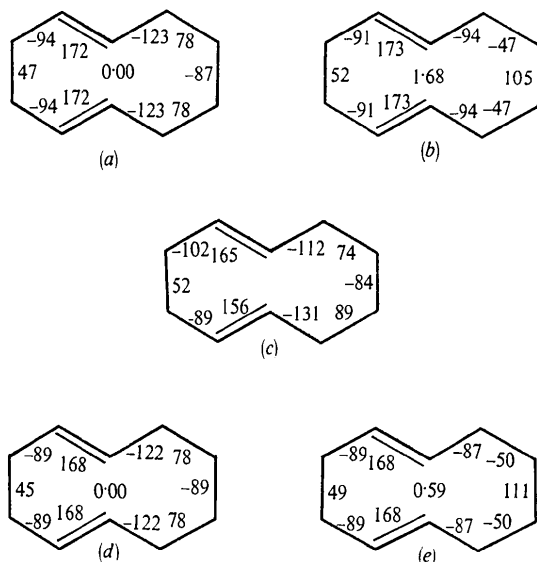


Fig. 3. Calculated torsion angles for the cyclodeca-1,5-diene ring. (a) Type I conformation; Allinger force field. (b) Type II conformation; Allinger force field. (c) Observed in costunolide (type I); White & Bovill force field. (d) Type I conformation; White & Bovill force field. (e) Type II conformation; White & Bovill force field. Steric energies are inset (kcal mol^{-1}).

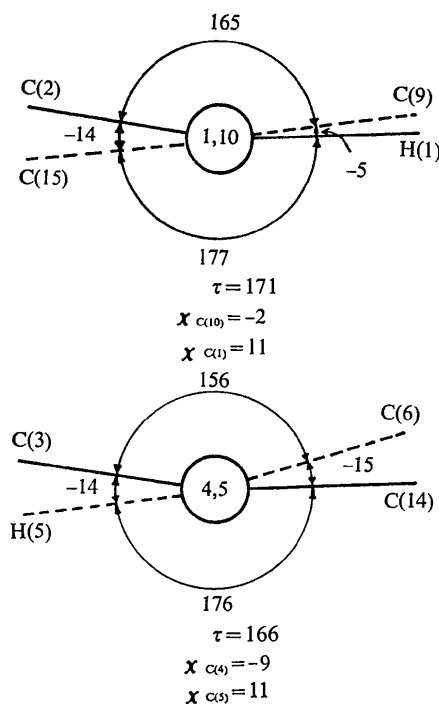


Fig. 4. Newman projections down C(1)-C(10) and C(4)-C(5) as observed in costunolide.

Table 7. Deviations of atoms from molecular best planes

Planes	Deviations (\AA)
(i) C(1), C(2), C(10)	H(1) 0.16
(ii) C(1), C(9), C(10)	C(15) 0.04
(iii) C(3), C(4), C(5)	C(14) -0.20
(iv) C(4), C(5), C(6)	H(5) -0.17
(v) C(11), C(12), O(1), O(2)	C(6) 0.19
	C(7) -0.23
	C(13) 0.16

Equations of the planes

$$\begin{aligned} \text{(i)} \quad & 0.0510X - 0.7222Y + 0.4672Z = -6.5200 \\ \text{(ii)} \quad & 0.4081X - 0.6021Y + 0.6863Z = -5.0081 \\ \text{(iii)} \quad & -0.1662X - 0.8870Y + 0.4308Z = -6.7909 \\ \text{(iv)} \quad & 0.1996X - 0.7199Y + 0.6837Z = -3.8317 \\ \text{(v)} \quad & 0.3448X + 0.7064Y + 0.6182Z = 9.5564 \end{aligned}$$

X , Y and Z are orthogonal coordinates in \AA (referred to a , b and c).

The results from both force fields are essentially identical, both in terms of conformation and relative energies. Conformations I and II for the hydrocarbon have C_2 symmetry and conformation I is the more stable by *ca* $1.0 \text{ kcal mol}^{-1}$. Indeed, conformation I has the lowest energy of all the conformations of *trans*, *trans*-cyclodeca-1,5-diene we have investigated to date. The conformation observed for costunolide in the crystal departs from C_2 symmetry, with differences of up to 16° between individual observed and calculated torsion angles. However, if the observed torsion angles are averaged to produce a C_2 symmetric conformation then this is indistinguishable, within the limits of experimental error, from the calculated conformation. The differential distortion of the endocyclic double bonds C(4)-C(5) and C(10)-C(1) is therefore a feature of the germacranolide conformation which is absent in the isolated cyclic diene.

Newman projections down C(4)-C(5) and C(10)-C(1) for the observed conformation are shown in Fig. 4 with the values of τ and χ describing the torsion and out-of-plane bending (Winkler & Dunitz, 1971). A detailed discussion of the individual values would be inappropriate because of the uncertainties associated with the positions of H(1) and H(5). However, X-ray structure analyses of eupatolide (Cox & Sim, 1976*b*), alatolide (Cox & Sim, 1976*c*), and onopordopicrin (Gilmore & Sim, 1976) reveal conformations of the ten-membered ring identical with that of costunolide and the values of τ and χ , based on fully refined H atom positions, for these molecules are compared with those for costunolide in Table 8. Rather strikingly, torsion and out-of-plane bending at the double bonds are relatively invariant from molecule to molecule with the widest scatter attached to χ for the unsubstituted trigonal C atoms. The deformations are partitioned almost equally between torsion and out-of-plane bending for the C(4)-C(5) double bond whilst there is almost no out-of-plane bending at C(10) for the other double bond. The out-of-plane bending at C(1), C(4) and C(5) is in such a sense as to push H(1), H(5) and

C(14) outwards from the ten-membered ring† and it is significant that the C(1)···C(4), C(1)···C(5) transannular distances of 2.8–2.9 Å are much shorter than C(10)···C(4) and C(10)···C(5) at 3.2–3.4 Å. Transannular repulsions involving C(1) and H(1) probably account, in part at least, for the out-of-plane bending at C(1), C(4) and C(5) and the relatively uncrowded steric environment of C(10) could account for the lack of out-of-plane bending at that centre.

Table 8. Twist (τ°) and out-of-plane bending (χ°) at the C(1)–C(10) and C(4)–C(5) double bonds for germacranolides with a type I ten-ring conformation

	τ_{3456}	$\chi_{C(4)}$	$\chi_{C(5)}$	τ_{91012}	$\chi_{C(1)}$	$\chi_{C(10)}$
Costunolide	166	–9	11	171	11	–2
Eupatolide	168	–9	18	176	15	–1
Alatolide	174	–6	6	179	26	0
Onopordopicrin	170	–10	13	176	13	–2

The γ -lactone ring has a half-chair conformation almost exactly midway between a C(6) and a C(7) envelope and may be described in terms of a puckering amplitude $q=0.25$ Å and a phase angle $\varphi=18.8^\circ$ (Cremer & Pople, 1975). The negative Cotton effect of the $n \rightarrow \pi^*$ transition of the α -methylene γ -lactone in costunolide is characteristic of a C(6),C(7)-*trans* lactone (Stöcklin, Waddell & Geissman, 1970). Beecham (1972) suggested that the sign of the Cotton effect is determined by the chirality of the C=C–C=O chromophore and X-ray results show that sesquiterpenoid C(6),C(7)-*trans* lactones generally have negative C=C–C=O torsion angles (McPhail & Sim, 1973). The exocyclic C=C–C=O and endocyclic C $_{\alpha}$ –C $_{\beta}$ –C $_{\gamma}$ –O torsion angles of the lactones are frequently paired in sign and this is the case in costunolide, where the angles are -10 and -25° respectively. This general correlation between these angles suggests that observation of the sign of the $n \rightarrow \pi^*$ transition of the C=C–C=O chromophore should enable conformational deductions to be made about the C $_{\beta}$ –C $_{\gamma}$ ring junction of sesquiterpenoid lactones in solution.

APPENDIX

We have included conformational and thermodynamic data calculated from two distinct force fields. An indication of the current quality of our yet unpublished force field is given by standard deviations in enthalpies of formation of 0.48 kcal mol $^{-1}$, mean deviation in bond lengths of 0.003 Å, bond angles of 1° , and torsion angles of 1.5° over some 50 diverse alkanes and alkenes for which experimental thermodynamic and/or structural data are available. We have also taken specific cognizance of what little experimental data are available

† cf. 2,7-Dibromo-3,8-dimethoxy-*trans,trans*-cyclodeca-1,6-diene (White, 1973).

for medium-ring dienes (e.g. Turner, Mallon, Tichy, Doering, Roth & Schröder, 1973).

We recognize that there is good experimental evidence for certain deficiencies in Allinger's force field (White & Bovill, 1976; Clark, Knox, Mackle & McKervery, 1975*a, b*) but these only become important when short H···H contacts are involved (White & Bovill, 1976), and such is not the case here. Our own force field does not suffer from defects in this respect and indeed it reproduces the molecular geometry of cyclodecane [where there are six very short and well characterized H···H contacts (Ermer, Dunitz & Bernal, 1973)] almost perfectly.

References

- ALLEN, F. H. & ROGERS, D. (1967). *Chem. Commun.* pp. 588–590.
- ALLINGER, N. L. & SPRAGUE, J. T. (1972). *J. Amer. Chem. Soc.* **94**, 5734–5747.
- ALLINGER, N. L. & SPRAGUE, J. T. (1975). *Tetrahedron*, **31**, 21–24.
- BEECHAM, A. F. (1972). *Tetrahedron*, **28**, 5543–5554.
- BHATTACHARYYA, S. C., KELKAR, G. R. & RAO, A. S. (1959). *Chem. Ind.* p. 1069.
- BUEMI, G., ZUCCARELLO, F. & FAVINI, G. (1974). *J. Mol. Struct.* **21**, 41–51.
- CAMERON, A. F. (1973). *Molecular Structure by Diffraction Methods*, Vol. 1, Part III, pp. 354–358. London: The Chemical Society.
- CLARK, T., KNOX, T. MCO., MACKLE, H. & MCKERVEY, M. A. (1975*a*). *Chem. Commun.* pp. 666–667.
- CLARK, T., KNOX, T. MCO., MACKLE, H. & MCKERVEY, M. A. (1975*b*). *J. Amer. Chem. Soc.* **97**, 3835–3836.
- COX, P. J. & SIM, G. A. (1974). *J. Chem. Soc. Perkin II*, pp. 1355–1359.
- COX, P. J. & SIM, G. A. (1975). *J. Chem. Soc. Perkin II*, pp. 455–458.
- COX, P. J. & SIM, G. A. (1976*a*). To be published.
- COX, P. J. & SIM, G. A. (1976*b*). In preparation.
- COX, P. J. & SIM, G. A. (1976*c*). In preparation.
- CREMER, D. & POPLE, J. A. (1975). *J. Amer. Chem. Soc.* **97**, 1354–1358.
- ERMER, O., DUNITZ, J. D. & BERNAL, I. (1973). *Acta Cryst.* **B29**, 2278–2285.
- ERMER, O. & LIFSON, S. (1973). *J. Amer. Chem. Soc.* **95**, 4121–4132.
- GILMORE, C. J. & SIM, G. A. (1976). In preparation.
- HEROUT, V. & SORM, F. (1959). *Chem. Ind.* pp. 1067–1068.
- HEROUT, V., SUCHÝ, M. & SORM, F. (1961). *Coll. Czech. Chem. Commun.* **26**, 2612–2623.
- MCLURE, R. J., SIM, G. A., COGGON, P. & MCPHAIL, A. T. (1970). *Chem. Commun.* pp. 128–129.
- MCPHAIL, A. T. & SIM, G. A. (1972). *J. Chem. Soc. Perkin II*, pp. 1313–1316.
- MCPHAIL, A. T. & SIM, G. A. (1973). *Tetrahedron*, **29**, 1751–1758.
- MATHIESON, A. MCL. (1972). *MTP Int. Rev. Sci. Chem. Crystallogr. Ser. 1*, **11**, 311–346.
- SIM, G. A. (1974). *Molecular Structure by Diffraction Methods*, Vol. 2, Part III, pp. 169–174; Vol. 3, Part III, pp. 203–209. London: The Chemical Society.
- SORM, F., SUCHÝ, M., HOLUB, M., LÍNEK, A., HADIRE, I. & NOVÁK, C. (1970). *Tetrahedron Lett.* pp. 1893–1896.

- STÖCKLIN, W., WADDELL, T. G. & GEISSMAN, T. A. (1970). *Tetrahedron*, **26**, 2397–2409.
- TORI, K., HORIBE, I., TAMURA, Y. & TADA, H. (1973). *Chem. Commun.* pp. 620–621.
- TURNER, R. B., MALLON, B. J., TICHY, M., DOERING, W. VON E., ROTH, W. R. & SCHRÖDER, G. (1973). *J. Amer. Chem. Soc.* **95**, 8605–8610.
- WHITE, D. N. J. (1973). *Helv. Chim. Acta*, **56**, 1348–1351.
- WHITE, D. N. J. & BOVILL, M. J. (1976). *J. Mol. Struct.* **33**, 273–277.
- WHITE, D. N. J. & SIM, G. A. (1973). *Tetrahedron*, **29**, 3933–3938.
- WINKLER, F. K. & DUNITZ, J. D. (1971). *J. Mol. Biol.* **59**, 169–182.
- YOSHIOKA, H., RENOLD, W. & MABRY, T. J. (1970). *Chem. Commun.* pp. 148–149.

Acta Cryst. (1976). B32, 3209

Une Méthode de Résolution Structurale Adaptée aux Polytypes. Application au Polytype de Sulfure de Titane 26H

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A new method for polytypic structure determination is described. It consists of a trial and error method in which randomly chosen hypotheses are fitted to experimental results by the comparison of Patterson functions. The determination of fairly long elementary sequences may be carried out by this method with a short computation time and without any auxiliary information on the stacking sequence. This method was used for the structure determination of a 26H Ti-S polytype.

Introduction

La connaissance des structures des polytypes revêt une importance particulière dans la mesure où les relations qui peuvent exister entre elles peuvent permettre de déduire ou de confirmer le mécanisme commun qui a causé leur formation. Ainsi, la connaissance des structures rhomboédriques 12R et 24R (Tronc & Huber, 1973; Moret & Huber, 1976) rencontrées en coalescence syntaxique avec le polytype 4H dans le système Ti-S a permis d'entrevoir un mécanisme de formation expliquant l'existence de telles structures (Legendre, Moret, Tronc & Huber, 1975b). De façon analogue, la connaissance des structures des polytypes hexagonaux 8H, 10H 12H (Tronc & Huber, 1973) dont l'existence est liée à celle de 2H a permis de vérifier la validité pour les structures hexagonales du mécanisme de formation déjà proposé pour les structures rhomboédriques (Legendre, 1976).

Cette vérification a été poursuivie par l'étude structurale d'un polytype 26H qui a été identifié récemment.

Méthode de résolution structurale

La résolution des structures polytypiques de période moyenne comme le 26H se heurte à certains problèmes particuliers dûs aux caractéristiques cristallographiques de ces composés.

En effet, même si l'on fait abstraction des difficultés entraînées par la coalescence de structures différentes

lors de la mesure des intensités ainsi que de la proximité des faisceaux diffractés, la résolution du problème des phases ne peut s'effectuer systématiquement par les méthodes les plus couramment utilisées.

Les méthodes à atome lourd s'avèrent inefficaces en raison du nombre souvent important d'atomes de même poids qui compliquent considérablement la fonction de Patterson obtenue à partir des intensités diffractées.

Les méthodes directes sont inapplicables en raison de la grande symétrie des structures étudiées.

En ce qui concerne les méthodes issues de l'étude de la fonction de Patterson, des tentatives fructueuses ont été faites par différents auteurs (Tokonami & Hosoya, 1965; Kakinoki, Kodera & Aikami, 1969; Farkas-Jahnke & Dornberger-Schiff, 1970; Dornberger-Schiff & Farkas-Jahnke, 1970) mais elles nécessitent l'obtention d'une fonction de Patterson entachée de peu d'erreur, ce qui limite leurs possibilités d'utilisation.

Les méthodes d'essais et erreurs, facilement programmables, sont les plus fréquemment utilisées surtout pour la détermination des structures à courte période. Par contre, leur emploi semble peu souhaitable sans modification pour les périodes moyennes ou longues dans la mesure où le nombre de calculs à effectuer croît très vite avec le nombre de couches par période.

Etant donné que les seuls renseignements qu'on peut connaître sur la structure recherchée sont sa période et le type de son réseau, la recherche systématique