

Fig. 3. $X-N$ map for 2-thiopyridone at 293 K. Contour interval: $0.1 \text{ e } \text{Å}^{-3}$. Positive density: full lines; zero density: dotted lines; negative density: dashed lines.

to each other by two $N-H \cdots S$ hydrogen bonds through a crystallographic centre of symmetry. For the distance $N-S$ we found $3.289(2) \text{ Å}$, and for the angle at H, 164° . Thus, the hydrogen bond is bent.

The $X-N$ map, shown in Fig. 3, gives a first impression of the deformation density in the molecule. Since thermal smearing is large at room temperature, the bond peaks are not very high ($0.15\text{--}0.25 \text{ e } \text{Å}^{-3}$) and a little irregular. The pronounced non-spherical minimum of $-0.35 \text{ e } \text{Å}^{-3}$ at the S atom, with the accompanying peaks at either side, is probably due to a discrepancy in the thermal parameters of the S atom, as derived from the X-ray and neutron data. The β_{11} and β_{22} components of the S atom each differ by about 5% of their magnitude, whereas the β_{33} com-

ponents are nearly equal. This discrepancy (referring only to two directions of space) indicates that the neutron parameters β_{11} and β_{22} do not fit well to the X-ray data and, hence, cause a systematic error in the representation of the electron-density distribution ($X-N$ map).

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References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
 HAMILTON, W. C. (1969). *Acta Cryst.* **A25**, 194–204.
 HIRSHFELD, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KOESTER, L. (1977). *Springer Tracts Mod. Phys.* **80**, 1–55.
 KVICK, Å. & BOOLES, S. S. (1972). *Acta Cryst.* **B28**, 3405–3409.
 PENFOLD, B. R. (1953). *Acta Cryst.* **6**, 707–713.
 SCHERINGER, C. (1978). *Acta Cryst.* **A34**, 428–431.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.

Acta Cryst. (1982). **B38**, 834–838

Structures of Two Sesquiterpene Lactones: Argophyllin-A and (8S)-Methacryloxy 1,10;4,5-diepoxykostenolide

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Abstract

Argophyllin-A (1a), $C_{20}H_{28}O_7$ ($M_r = 380.44$), isolated from *Helianthus argophyllus*, and (8S)-methacryloxy-1,10;4,5-diepoxykostenolide (2), $C_{19}H_{24}O_6$ ($M_r = 348.4$), isolated from *Vernonia jonesii*, are germacranolide-type sesquiterpene lactones. The space

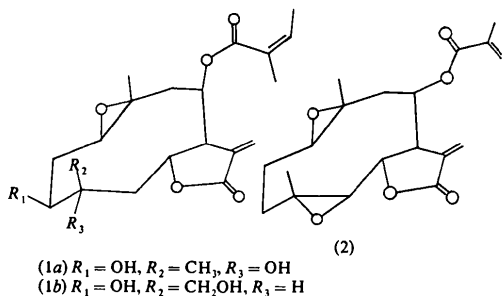
group for both compounds is $P2_12_12_1$, with $a = 11.506(4)$, $b = 17.273(5)$, $c = 9.999(4) \text{ Å}$, $Z = 4$, $V = 1987(1) \text{ Å}^3$, $d_c = 1.272 \text{ Mg m}^{-3}$ for (1a) and $a = 12.296(2)$, $b = 18.595(4)$, $c = 7.735(1) \text{ Å}$, $Z = 4$, $V = 1769.6(7) \text{ Å}^3$, $d_c = 1.308 \text{ Mg m}^{-3}$ for (2). The structures were solved by direct methods and refined by a full-matrix least-squares technique to final R values of 0.060 and 0.068 utilizing 1760 and 1779 reflexions, respectively. Thermal parameters for the nonhydrogen

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atoms were refined anisotropically. The two ten-membered rings adopt approximate chair-chair conformations, but the torsion angles differ by an average of 20°. The germacradiene skeleton normally contains C(1)–C(10) and C(4)–C(5) *trans* double bonds. In compound (2) both double bonds are epoxidized while in (1a) C(1)–C(10) is epoxidized and C(4)–C(5) is saturated. Epoxidation imparts the same conformational requirements as does the double bond; however, saturation of the C(4)–C(5) bond transmits conformational changes around the ten-membered ring. The C(8) side chain in (1a) is β while that in (2) is α . The exocyclic double bond in compound (2) has chemotaxonomic significance since the American *Vernonia* usually contain sesquiterpenes with endocyclic double bonds while terpenoids of the African *Vernonia* exhibit exocyclic double bonds.

Introduction

Extracts of *Helianthus argophyllus* (Tribe Heliantheae, Fam. Compositae) yielded two new germacranolide-type sesquiterpene lactones, argophyllin-A (1a) and argophyllin-B (1b). The two sesquiterpene lactones exhibit anti-auxin activity (Watanabe, Ohno, Yoshioka & Mabry, 1981). The structure of argophyllin-A was elucidated by X-ray diffraction techniques. *Vernonia jonesii* B. L. Turner (Section Leipidonia, Tribe Vernoniaeae, Fam. Compositae) is a recently described new species found in Mexico. The species is of interest because some or all of the isolated germacranolide-type sesquiterpene lactones contain exocyclic double bonds which are characteristic of the African *Vernonia*. The American *Vernonia* species contain the unique glaucolide-series of germacranolides with endocyclic double bonds. The differences in chemistry or the differences in phyletic origin are currently under investigation (Mabry, 1981). The structure of (8*S*)-methacryloxy-1,10;4,5-diepoxykostenolide (2) is described.



Structure determination and refinement

All intensity data were collected on a Syntex P2₁ diffractometer by the $\theta:2\theta$ scanning technique using a variable scan speed, a graphite monochromator and Cu

K α radiation ($\lambda = 1.54178 \text{ \AA}$). Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. For both compounds systematic absences were consistent with space group $P2_12_12_1$. Periodically monitored reflexions showed no significant

Table 1. Positional parameters ($\times 10^4$, for H $\times 10^3$) for (1a)

	x	y	z	U_{eq}^* or $U (\text{\AA}^2 \times 10^3)$
C(1)	4674 (4)	3086 (3)	4761 (4)	5.9 (2)
O(1)	5137 (3)	2496 (2)	5636 (4)	6.8 (1)
C(2)	3901 (5)	3685 (3)	5375 (4)	7.0 (3)
C(3)	3814 (5)	4426 (3)	4594 (4)	6.2 (2)
O(3)	3308 (4)	4986 (2)	5482 (3)	8.1 (2)
C(4)	3107 (3)	4404 (2)	3270 (4)	5.1 (2)
O(4)	3089 (3)	5216 (2)	2895 (3)	6.7 (2)
C(5)	3781 (3)	3962 (2)	2194 (3)	4.8 (2)
C(6)	3441 (3)	3129 (2)	1927 (3)	4.4 (1)
O(6)	2509 (2)	3130 (2)	918 (3)	5.8 (1)
C(7)	4395 (3)	2599 (2)	1372 (3)	4.4 (2)
C(8)	4482 (3)	1814 (2)	2069 (4)	5.0 (2)
O(8)	3302 (2)	1512 (1)	2066 (3)	5.3 (1)
C(9)	5004 (3)	1821 (2)	3477 (3)	5.6 (2)
C(10)	4368 (3)	2267 (3)	4548 (3)	5.6 (2)
C(11)	4048 (3)	2501 (2)	-73 (3)	4.7 (1)
C(12)	2867 (3)	2802 (2)	-233 (4)	5.2 (2)
O(12)	2235 (3)	2772 (2)	-1200 (3)	7.6 (2)
C(13)	4648 (4)	2195 (3)	-1063 (4)	6.3 (2)
C(14)	1867 (4)	4140 (3)	3489 (5)	6.3 (2)
C(15)	3224 (5)	1955 (4)	5024 (5)	7.2 (3)
C(16)	3152 (4)	743 (2)	2098 (5)	6.6 (3)
O(16)	3971 (4)	302 (2)	2150 (7)	10.2 (4)
C(17)	1906 (5)	536 (3)	2135 (5)	7.3 (3)
C(18)	1050 (5)	1100 (4)	1563 (8)	9.3 (4)
C(19)	1605 (7)	-124 (4)	2734 (7)	10.6 (4)
C(20)	2378 (2)	-692 (5)	3391 (2)	15.3 (8)
H(1)	529 (5)	323 (3)	417 (7)	8 (2)
H(2a)	435 (10)	388 (8)	614 (14)	18 (4)
H(2b)	309 (6)	341 (4)	550 (6)	9 (2)
H(3a)	456 (5)	460 (3)	453 (5)	6 (1)
H(3b)	314 (7)	543 (5)	492 (8)	11 (2)
H(4)	260 (7)	524 (4)	236 (8)	11 (2)
H(5a)	465 (4)	392 (3)	243 (5)	7 (1)
H(5b)	360 (3)	422 (2)	136 (4)	4 (1)
H(6)	308 (4)	287 (3)	273 (4)	5 (1)
H(7)	524 (4)	283 (3)	150 (5)	6 (1)
H(8)	493 (4)	153 (3)	150 (5)	5 (1)
H(9a)	564 (4)	194 (2)	336 (4)	5 (1)
H(9b)	496 (5)	134 (3)	369 (6)	8 (1)
H(13a)	557 (6)	189 (4)	-89 (7)	10 (2)
H(13b)	430 (5)	229 (4)	-201 (7)	8 (2)
H(14a)	157 (4)	415 (3)	279 (6)	5 (1)
H(14b)	178 (5)	365 (4)	391 (6)	8 (1)
H(14c)	151 (6)	442 (4)	430 (8)	9 (2)
H(15a)	339 (6)	138 (4)	520 (7)	10 (2)
H(15b)	261 (5)	190 (3)	432 (7)	8 (2)
H(15c)	301 (7)	218 (4)	577 (9)	10 (2)
H(18a)	138 (9)	130 (6)	62 (12)	14 (3)
H(18b)	23 (6)	81 (4)	153 (7)	9 (2)
H(18c)	97 (7)	158 (6)	222 (10)	15 (3)
H(19)	61 (7)	-32 (6)	273 (9)	13 (3)

* $U_{\text{eq}} = (U_1 U_2 U_3)^{1/3}$.

changes in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were made. The direct-methods program *MULTAN78* (Main, Lessinger, Woolfson, Germain & Declercq, 1978) was used to calculate phases for the $|E|$ values greater than 1.4. In both cases the phase set with the highest combined figure of merit was selected, and the E map computed with these phases revealed the

positions of all non-hydrogen atoms except one. After several cycles of least-squares refinement the H atoms were located in a difference Fourier map. The structures were refined by a full-matrix least-squares technique using anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for the H atoms. Refinements were terminated when the R factors converged; $R = \sum |F_o| - |F_c| / \sum |F_o|$. The function minimized in the refinements was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(I)$ was determined from counting statistics. Reflexions showing significant secondary extinctions were omitted during the final cycles of refinement.

Table 2. *Positional parameters* ($\times 10^4$, for H $\times 10^3$) for (2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^* or $U (\text{\AA}^2 \times 10^3)$
C(1)	8458 (2)	1715 (1)	5001 (4)	3.3 (1)
O(1)	8898 (2)	2170 (1)	3673 (3)	5.0 (1)
C(2)	8322 (3)	924 (2)	4649 (4)	4.5 (1)
C(3)	7881 (3)	544 (1)	6235 (4)	4.4 (1)
C(4)	6779 (3)	869 (1)	6755 (5)	4.3 (1)
O(4)	6502 (3)	818 (1)	8539 (4)	6.4 (2)
C(5)	6827 (2)	1510 (1)	7861 (3)	3.3 (1)
C(6)	5966 (2)	2092 (1)	7751 (3)	2.6 (1)
O(6)	5225 (2)	2009 (1)	9191 (3)	4.0 (1)
C(7)	6447 (2)	2870 (1)	7892 (3)	2.7 (1)
C(8)	6621 (2)	2196 (1)	6083 (3)	2.9 (1)
O(8)	6597 (1)	3976 (1)	6280 (2)	3.3 (1)
C(9)	7721 (2)	3012 (1)	5262 (4)	3.4 (1)
C(10)	7796 (2)	2304 (1)	4270 (3)	3.3 (1)
C(11)	5612 (2)	3218 (1)	9073 (3)	3.2 (1)
C(12)	4919 (2)	2658 (2)	9801 (4)	4.0 (1)
O(12)	4202 (2)	2708 (2)	10846 (4)	6.4 (1)
C(13)	5506 (3)	3890 (2)	9600 (4)	5.0 (1)
C(14)	5869 (3)	719 (2)	5580 (7)	6.3 (3)
C(15)	6950 (4)	2200 (2)	2889 (4)	5.7 (2)
C(16)	6221 (2)	4341 (1)	4869 (3)	3.3 (1)
O(16)	5887 (3)	4045 (1)	3589 (2)	4.8 (1)
C(17)	6249 (2)	5132 (1)	5059 (4)	3.6 (1)
C(18)	5708 (3)	5542 (2)	3666 (4)	5.4 (2)
C(19)	6728 (4)	5437 (2)	6426 (5)	5.9 (2)
H(1)	876 (3)	174 (2)	647 (5)	4 (1)
H(2a)	910 (3)	70 (2)	448 (5)	5 (1)
H(2b)	786 (6)	79 (3)	364 (7)	8 (2)
H(3a)	843 (3)	69 (2)	728 (5)	4 (1)
H(3b)	791 (3)	-1 (2)	592 (5)	4 (1)
H(5)	761 (5)	169 (3)	778 (7)	7 (1)
H(6)	558 (3)	212 (2)	680 (6)	4 (1)
H(7)	705 (4)	288 (2)	842 (5)	4 (1)
H(8)	599 (3)	308 (2)	544 (4)	2 (1)
H(9a)	830 (5)	290 (3)	630 (9)	7 (2)
H(9b)	798 (4)	355 (2)	460 (6)	5 (1)
H(13a)	487 (2)	392 (2)	1051 (5)	5 (1)
H(13b)	620 (6)	424 (4)	955 (9)	9 (2)
H(14a)	618 (8)	82 (5)	421 (12)	12 (3)
H(14b)	567 (6)	26 (4)	570 (9)	8 (1)
H(14c)	534 (10)	91 (5)	587 (15)	13 (3)
H(15a)	667 (4)	250 (3)	202 (7)	6 (1)
H(15b)	601 (6)	211 (4)	352 (9)	9 (2)
H(15c)	728 (6)	182 (5)	227 (11)	12 (2)
H(18a)	588 (4)	605 (3)	383 (7)	6 (1)
H(18b)	497 (5)	541 (4)	374 (9)	8 (2)
H(18c)	589 (6)	547 (3)	259 (7)	8 (2)
H(19a)	701 (7)	518 (4)	756 (9)	10 (2)
H(19b)	686 (5)	601 (3)	602 (9)	8 (1)

* $U_{eq} = (U_1 U_2 U_3)^{1/3}$.

Argophyllin-A (1a)

A crystal of dimensions $0.55 \times 0.1 \times 0.3$ mm was used to collect 2037 independent reflexions ($2\theta < 140^\circ$) of which 1770 had intensities greater than $2\sigma(I)$. Ten reflexions showed significant secondary extinction. The structure was refined to an R factor of 0.060 utilizing 1760 reflexions. Only the H atoms of the C(20) methyl group could not be located in the difference Fourier map. A final difference map showed no peak larger than $0.3 e \text{\AA}^{-3}$ and the average shift/error during the final cycle of refinement was 0.13.

Table 3. *Interatomic distances* (\AA)

	Compound (1a)	Compound (2)
C(1)—O(1)	1.445 (5)	1.437 (3)
C(1)—C(2)	1.496 (7)	1.506 (4)
C(1)—C(10)	1.475 (6)	1.476 (4)
C(2)—C(3)	1.504 (7)	1.516 (5)
C(3)—O(3)	1.437 (6)	—
C(3)—C(4)	1.554 (6)	1.537 (5)
C(4)—O(4)	1.451 (4)	1.424 (5)
C(4)—C(5)	1.530 (5)	1.468 (4)
C(4)—C(14)	1.514 (6)	1.469 (6)
O(4)—C(5)	—	1.446 (3)
C(5)—C(6)	1.515 (6)	1.516 (3)
C(6)—O(6)	1.472 (4)	1.447 (3)
C(6)—C(7)	1.534 (5)	1.566 (3)
C(7)—C(8)	1.528 (5)	1.540 (3)
C(7)—C(11)	1.508 (5)	1.520 (3)
C(8)—O(8)	1.453 (4)	1.458 (3)
C(8)—C(9)	1.531 (5)	1.532 (3)
C(9)—C(10)	1.508 (5)	1.527 (4)
C(10)—O(1)	1.457 (5)	1.452 (3)
C(10)—C(15)	1.500 (7)	1.504 (5)
C(11)—C(12)	1.464 (5)	1.459 (4)
C(11)—C(13)	1.318 (6)	1.321 (4)
C(12)—O(6)	1.347 (5)	1.348 (3)
C(12)—O(12)	1.211 (5)	1.199 (4)
O(8)—C(16)	1.339 (5)	1.366 (3)
C(16)—O(16)	1.213 (6)	1.204 (3)
C(16)—C(17)	1.478 (7)	1.478 (3)
C(17)—C(18)	1.499 (9)	1.478 (4)
C(17)—C(19)	1.334 (9)	1.337 (5)
C(19)—C(20)	1.478 (14)	—

(8*S*)-Methacryloxy-1,10;4,5-diepoxykostenolide (2)

A crystal of dimensions 0.55 × 0.50 × 0.60 mm was used to collect 1797 independent reflexions ($2\theta < 140^\circ$) of which 1785 had intensities greater than $2\sigma(I)$. Six reflexions showed significant secondary extinction. The structure was refined to an *R* factor of 0.068 utilizing 1779 reflexions. A final difference Fourier map showed no peak larger than 0.4 e \AA^{-3} and the average shift/error during the final cycle of refinement was 0.40.

Table 4. Valence angles ($^\circ$)

	Compound (1a)	Compound (2)
O(1)C(1)C(2)	117.3 (3)	119.2 (2)
O(1)C(1)C(10)	59.9 (3)	59.8 (2)
C(2)C(1)C(10)	125.5 (4)	126.5 (2)
C(1)O(1)C(10)	61.1 (3)	61.5 (2)
C(1)C(2)C(3)	114.5 (4)	110.4 (3)
C(2)C(3)O(3)	106.2 (3)	—
C(2)C(3)C(4)	117.2 (4)	110.1 (2)
O(3)C(3)C(4)	109.3 (4)	—
C(3)C(4)O(4)	101.7 (3)	116.0 (3)
C(3)C(4)C(5)	110.2 (3)	115.9 (3)
C(3)C(4)C(14)	112.2 (3)	115.8 (3)
O(4)C(4)C(5)	107.9 (3)	60.0 (2)
O(4)C(4)C(14)	108.4 (3)	113.9 (3)
C(5)C(4)C(14)	115.4 (7)	123.1 (3)
C(4)O(4)C(5)	—	61.5 (2)
C(4)C(5)O(4)	—	58.5 (2)
C(4)C(5)C(6)	117.8 (3)	121.3 (2)
O(4)C(5)C(6)	—	117.6 (2)
C(5)C(6)O(6)	107.9 (3)	108.7 (2)
C(5)C(6)C(7)	116.5 (3)	113.0 (2)
O(6)C(6)C(7)	105.9 (3)	106.4 (2)
C(6)O(6)C(12)	111.3 (3)	110.5 (2)
C(6)C(7)C(8)	114.3 (3)	110.7 (2)
C(6)C(7)C(11)	102.9 (3)	100.3 (2)
C(8)C(7)C(11)	110.7 (3)	118.2 (2)
C(7)C(8)O(8)	104.9 (3)	107.1 (2)
C(7)C(8)C(9)	115.9 (3)	114.3 (2)
O(8)C(8)C(9)	111.8 (3)	106.5 (2)
C(8)C(9)C(10)	117.9 (3)	117.1 (2)
C(9)C(10)O(1)	112.0 (3)	111.4 (2)
C(9)C(10)C(15)	117.9 (4)	115.2 (2)
O(1)C(10)C(1)	59.1 (3)	58.8 (2)
C(1)C(10)C(9)	118.5 (3)	118.7 (2)
O(1)C(10)C(15)	113.2 (3)	113.4 (2)
C(1)C(10)C(15)	120.6 (4)	123.9 (2)
C(7)C(11)C(12)	108.1 (3)	108.8 (2)
C(7)C(11)C(13)	129.8 (3)	130.9 (3)
C(12)C(11)C(13)	123.1 (3)	119.9 (3)
O(6)C(12)C(11)	109.8 (3)	109.9 (2)
O(6)C(12)O(12)	121.1 (3)	120.7 (3)
C(11)C(12)O(12)	129.1 (4)	129.3 (3)
C(8)O(8)C(16)	118.4 (3)	114.7 (2)
O(8)C(16)O(16)	121.5 (4)	123.0 (2)
O(8)C(16)C(17)	111.4 (4)	114.0 (2)
O(16)C(16)C(17)	126.9 (4)	123.0 (2)
C(16)C(17)C(18)	118.1 (5)	115.5 (2)
C(16)C(17)C(19)	118.1 (5)	120.7 (2)
C(18)C(17)C(19)	123.9 (6)	123.8 (2)
C(17)C(19)C(20)	127.6 (8)	—

Table 5. Torsion angles ($^\circ$)

	Compound (1a)	Compound (2)
1-2-3-4	72.4 (6)	58.9 (3)
2-3-4-5	-72.5 (5)	-85.2 (3)
3-4-5-6	100.2 (4)	148.4 (2)
4-5-6-7	-153.2 (3)	-139.9 (2)
5-6-7-8	133.6 (3)	96.5 (2)
6-7-8-9	-73.2 (4)	-86.8 (2)
7-8-9-10	62.7 (4)	85.7 (3)
8-9-10-1	-90.9 (4)	-110.6 (3)
9-10-1-2	156.4 (4)	155.4 (3)
10-1-2-3	-131.0 (5)	-109.5 (3)
6-O(6)-12-11	3.9 (4)	-12.6 (3)
O(6)-12-11-7	5.5 (4)	-0.6 (3)
12-11-7-6	-11.8 (4)	11.8 (2)
11-7-6-O(6)	13.7 (3)	-18.7 (2)
7-6-O(6)-12	-11.5 (2)	20.2 (1)
O(12)-12-11-13	6.2 (7)	1.7 (5)
6-O(6)-12-O(12)	-177.5 (4)	170.4 (3)
7-11-12-O(12)	-173.0 (4)	176.1 (3)
8-O(8)-16-O(16)	1.2 (7)	3.2 (3)
8-O(8)-16-17	178.2 (3)	-177.3 (2)
O(8)-16-17-18	25.6 (3)	-171.8 (2)
O(8)-16-17-19	-151.2 (3)	7.5 (4)
O(16)-16-17-18	-157.7 (5)	7.6 (4)
O(16)-16-17-19	25.6 (9)	-173.0 (3)
16-17-19-20	0.3 (8)	—
18-17-19-20	-176.3 (9)	—

Atomic scattering factors were calculated by the XRAY76 program system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) while the real and imaginary contributions to the anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). Atomic positional parameters for argophyllin-A (1a) are presented in Table 1 while those for (2) are given in Table 2. Interatomic distances, valence angles and torsion angles for both compounds are presented in Tables 3, 4 and 5.*

Discussion

Figs. 1 and 2 are *ORTEP* drawings (Johnson, 1971) of argophyllin-A (1a) and (8*S*)-methacryloxy-1,10;4,5-diepoxykostenolide (2). The ten-membered rings adopt approximate chair-chair conformations; however, the torsion angles for the two rings differ by an average of 20° . For biogenetic reasons the ten-membered ring is expected to have C(1)–C(10) and C(4)–C(5) *trans* double bonds. A *trans* epoxide is conformationally equivalent to the double bond and ten-membered

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36407 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

germacradienes and epoxidized germacradienes adopt similar conformations (Watson, Zabel, Mabry & Yabuta, 1982). The torsion angles of compound (2) are consistent with this observation and differ from the averaged values of the germacradienes and the epoxide derivatives by about 7° . However, saturation of the

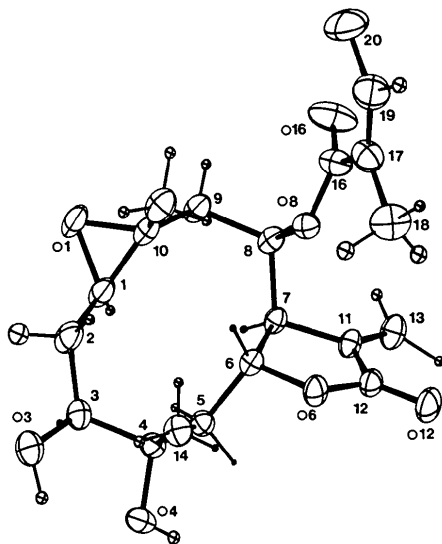


Fig. 1. ORTEP drawing of argophyllin-A. Ellipsoids are drawn at the 35% probability level while H atoms are represented by arbitrary-size spheres.

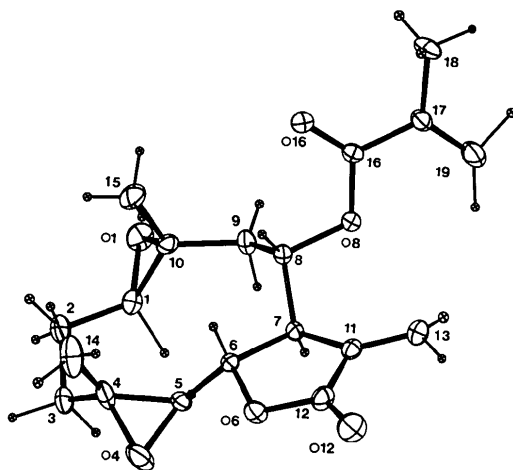


Fig. 2. ORTEP drawing of (8*S*)-methacryloxy-1,10;4,5-diepoxy-costunolide. Ellipsoids are drawn at the 35% probability level while H atoms are represented by arbitrary-size spheres.

C(4)—C(5) bond leads to conformational changes transmitted around the ten-membered ring. The torsion angles differ from the averaged values of the germacradienes and the epoxide derivatives by an average of 22° . Conformational changes are also transmitted into the five-membered ring. While the two lactone rings have torsion angles of approximately the same magnitude, they are of opposite sign.

The C(8) side chain in (2) is approximately planar while that in (1*a*) deviates from planarity by a twist about the C(16)—C(17) bond. If the absolute configuration at C(6) is assumed to be that with the H oriented β [(6*S*) in (2) and (6*R*) in (1*a*)] (Neidle & Rogers, 1972), the two structures differ in the configuration at C(8). Compound (1*a*) exhibits a β or (8*R*) oriented side chain while compound (2) exhibits an α or (8*S*) oriented side chain. Whether the differences in biological activity can be attributed to differences in conformation, configuration or epoxidation cannot be assessed at this time. Compound (2) is of phytochemical interest since all American *Vernonia* contain sesquiterpenoids with a C(7)—C(11) endocyclic double bond while the African *Vernonia* contain a C(11)—C(13) exocyclic double bond. The botanical significance of this observation is currently under investigation (Mabry, 1981).

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References

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1971). *ORTEP II*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.
- MABRY, T. J. (1981). Private communication; manuscript in preparation.
- MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- NEIDLE, S. & ROGERS, D. (1972). *J. Chem. Soc. Chem. Commun.* pp. 142–143.
- STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). XRAY76. Tech. Rep. TR-441. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WATANABE, K., OHNO, N., YOSHIOKA, H. & MABRY, T. J. (1981). *Phytochemistry*. In the press.
- WATSON, W. H., ZABEL, V., MABRY, T. J. & YABUTA, G. (1982). *Acta Cryst.* B38, 511–514.