Table 2. *Selected geometric parameters* (Å, °)

S—C2	1.742 (3)	C8—N9	1.375 (4)
S—C11	1.821 (3)	N9—C1′	1.456 (4)
N1—C2	1.364 (4)	C10—C11	1.496 (5)
N1—C6	1.396 (4)	C1′—O4′	1.407 (3)
N1—C10	1.473 (4)	C1′—C2′	1.531 (3)
C2—N3	1.311 (4)	C2′—O2′	1.406 (3)
N3—C4	1.360 (4)	C2′—C3′	1.522 (4)
C4—N9	1.359 (4)	C3′—O3′	1.424 (3)
C4—C5	1.386 (4)	C3′—C4′	1.537 (4)
C5—N7	1.382 (4)	C4′—O4′	1.446 (4)
C5—C6	1.424 (4)	C4′—C5′	1.508 (4)
C6—O6	1.233 (4)	C5′—O5′	1.410 (4)
N7—C8	1.308 (4)		
C2—S—C11	91.36 (15)	C4—N9—C8	106.2 (2)
C2—N1—C6	124.5 (2)	C4—N9—C1′	128.8 (2)
C2—N1—C10	114.6 (2)	C8—N9—C1′	125.0 (2)
C6—N1—C10	120.7 (2)	N1—C10—C11	107.7 (3)
N3—C2—N1	125.6 (2)	C10—C11—S	106.7 (2)
N3—C2—S	121.6 (2)	O4′—C1′—N9	108.2 (2)
N1—C2—S	112.8 (2)	O4′—C1′—C2′	105.3 (2)
C2—N3—C4	111.8 (2)	N9—C1′—C2′	114.9 (2)
N9—C4—N3	127.0 (3)	O2′—C2′—C3′	115.7 (2)
N9—C4—C5	105.8 (2)	O2′—C2′—C1′	114.8 (2)
N3—C4—C5	127.2 (3)	C3′—C2′—C1′	101.3 (2)
N7—C5—C4	110.6 (2)	O3′—C3′—C2′	110.9 (2)
N7—C5—C6	129.7 (3)	O3′—C3′—C4′	109.0 (2)
C4—C5—C6	119.7 (2)	C2′—C3′—C4′	103.1 (2)
O6—C6—N1	119.8 (3)	O4′—C4′—C5′	107.6 (2)
O6—C6—C5	129.0 (3)	O4′—C4′—C3′	106.4 (2)
N1—C6—C5	111.1 (3)	C5′—C4′—C3′	115.5 (3)
C8—N7—C5	104.0 (2)	C1′—O4′—C4′	109.6 (2)
N7—C8—N9	113.3 (3)	O5′—C5′—C4′	113.1 (3)

Table 3. *Contact distances* (Å)

A	H	*D*	*A*···H	*D*···*A*
N3	H5O′	O5′	2.21 (6)	3.045 (4)
O^{i}	H3O′	O3′	1.93 (4)	2.725 (4)
O6	H1	O	2.03 (4)	2.784 (3)
O3′^{ii}	H2	O3	1.98 (6)	2.826 (4)
O5′^{i}	H2O′	O2′	1.98 (4)	2.742 (3)

Symmetry codes: (i) $x, y, 1-z$; (ii) $1-x, y, 1+z$.

Dispersion corrections and absorption coefficients were taken from *International Tables for Crystallography* (1992, Vol. C, Tables 6.1.1.4, 4.2.6.8 and 4.2.4.2). Since (I) crystallizes in a polar space group, polar-axis restraints were applied by the method of Flack & Schwarzenbach (1988) and the absolute structure of the crystal was established as described by Flack (1983), which is consistent with the known absolute configuration of β-D-ribofuranose. Data collection and cell refinement: Rigaku AFC-5 software. Data reduction: *NRCVAX* (Gabe, Lee & Le Page, 1985). Program used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *ORTEP* (Johnson, 1971). Software used to prepare material for publication: *SHELXL*; *NRCVAX*.

This work was supported by the National Science Council of the Republic of China (NSC81-0203-B001-14 to the Institute of Molecular Biology and NSC79-042-B016-136 to J-WC).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71785 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1058]

References

Chern, J.-W., Lin, G.-S. & Chen, C.-F. (1990). *Chin. Pharm. J.* **42**, 451-454.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876-881.
Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* A**44**, 499-506.
Gabe, E. J., Lee, F. L. & Le Page, Y. (1985). *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 167-174. Oxford: Clarendon Press.
Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467-473.
Sheldrick, G. M. (1994). *J. Appl. Cryst.* In preparation.
Wolfe, S. (1972). *Acc. Chem. Res.* **5**, 102.

Acta Cryst. (1994). C**50**, 736–738

Absolute Stereostructure of 13,17-Epoxyalisol B 23-Acetate Isolated from *Alisma orientale*

KENTARO YAMAGUCHI, YOSHITERU IDA, YOSHIJIROH NAKAJIMA, YOHKO SATOH AND JUNZO SHOJI

School of Pharmaceutical Sciences, Showa University, 1-5-8 Hatanodai, Shinagawa-ku, Tokyo 142, Japan

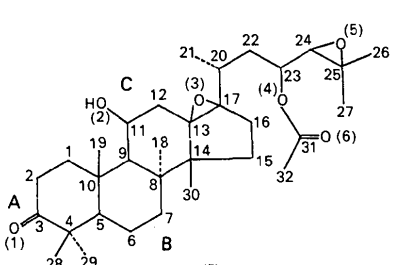
(*Received* 10 *August* 1993; *accepted* 2 *November* 1993)

Abstract

The absolute configration of the epoxy group in 13β,17β:-24(*R*),25-diepoxy-1β-hydroxydammar-3-one 23(*S*)-acetate, $C_{32}H_{50}O_6$, m.p. 472-474 K, $[\alpha]_D$ +139.4° (c = 0.96, $CHCl_3$), isolated from *Alisma orientale* rhizomes, was established to be the β orientation by X-ray crystallographic analysis. The *A*, *B* and *C* rings have chair forms. An intermolecular hydrogen bond is observed between O2 and O6′ with a distance of 3.148 (6) Å.

Comment

13,17-Epoxyalisol B 23-acetate (I) was isolated from *Alisma orientale* rhizomes along with 20 related triterpenes of the protostane type (Nakajima, Mikoshiba, Ida & Shoji, 1984; Ida, Satoh, Nakajima, Yamaguchi & Shoji, 1989).



(I)

The basic structure was established on the basis that the compound was obtained as the sole product with quantitative yield from arisol B 23-acetate (Murata, Shinohara & Miyamoto, 1970) on oxidation with *m*-chloroperbenzoic acid (Nakajima, Mikoshiba, Ida & Shoji, 1984; Ida, Satoh, Nakajima, Yamaguchi & Shoji, 1989; Fukuyama, Pei-Wu, Rei, Yamada & Nakagawa, 1988). It has been proposed that the epoxide group has the β orientation on the basis of the following considerations: the epoxide is formed stereospecifically as the sole product from the double bond of alisole B 23-acetate and the oxidation reaction seems to prefer the β side of the double bond rather than the α side, since the estimated electrostatic potential is higher on the β side than on the α side, according to our theoretical calculations (Nakajima, Mikoshiba, Ida & Shoji, 1984; Ida, Satoh, Nakajima, Yamaguchi & Shoji, 1989). The X-ray crystallographic analysis justified this proposal.

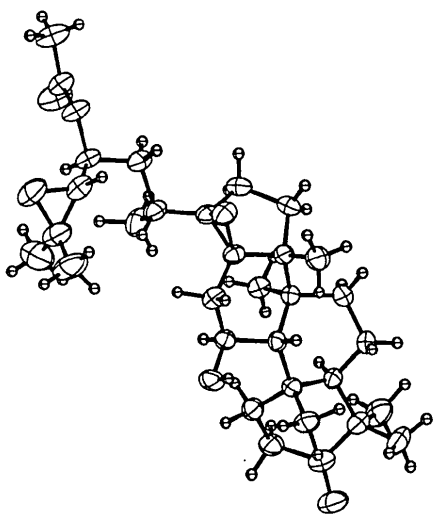


Fig. 1. Displacement-ellipsoid plot of the title molecule. Ellipsoids are drawn at the 50% probability level with isotropic H-atom parameters represented by spheres of arbitrary size.

Experimental

The title compound was isolated from a crude sample of the Chinese drug 'Zexie'.

Crystal data

$C_{32}H_{50}O_6$
M_r = 530.75
Monoclinic
$P2_1$
a = 10.558 (1) Å
b = 20.351 (1) Å
c = 7.326 (2) Å
β = 106.22 (1)°
V = 1511.3 (6) Å^3
Z = 2
D_x = 1.166 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 28.0–30.5°
μ = 0.593 mm^{-1}
T = 297 K
Prism
0.55 × 0.35 × 0.11 mm
Clear

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans [width (1.3 + 0.14tanθ)° (in ω); speed 16° min^{-1}]
Absorption correction: none
2586 measured reflections
2323 independent reflections
2149 observed reflections [$F > 3\sigma(F)$]
R_{int} = 0.018
θ_{max} = 60°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 150 reflections
intensity variation: < 3%

Refinement

Refinement on F^2
$R(F)$ = 0.040
$wR(F^2)$ = 0.038
S = 1.98
2149 reflections
488 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F) + 0.007F^2]$
$(\Delta/\sigma)_{max}$ = 0.12
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	0.9375 (5)	0.0955	0.7525 (6)	0.045 (1)
C2	1.0266 (5)	0.1524 (3)	0.7189 (7)	0.051 (1)
C3	1.1155 (4)	0.1839 (3)	0.8955 (7)	0.048 (1)
C4	1.0531 (4)	0.2033 (3)	1.0520 (6)	0.045 (1)
C5	0.9239 (4)	0.1628 (3)	1.0272 (6)	0.036 (1)
C6	0.8689 (4)	0.1648 (4)	1.1998 (6)	0.046 (1)
C7	0.7231 (4)	0.1500 (3)	1.1346 (7)	0.048 (1)
C8	0.6848 (4)	0.0901 (3)	0.9950 (5)	0.035 (1)
C9	0.8104 (4)	0.0505 (3)	0.9866 (6)	0.033 (1)
C10	0.9304 (4)	0.0915 (3)	0.9602 (5)	0.036 (1)
C11	0.7696 (4)	−0.0079 (3)	0.8472 (6)	0.039 (1)
C12	0.6666 (4)	−0.0521 (3)	0.8942 (7)	0.042 (1)
C13	0.5565 (4)	−0.0157 (3)	0.9398 (6)	0.037 (1)
C14	0.5906 (4)	0.0437 (3)	1.0690 (5)	0.038 (1)
C15	0.4543 (4)	0.0753 (4)	1.0542 (7)	0.050 (1)
C16	0.3553 (4)	0.0490 (4)	0.8724 (8)	0.050 (1)
C17	0.4171 (4)	−0.0133 (3)	0.8245 (6)	0.040 (1)
C18	0.6119 (4)	0.1166 (3)	0.7953 (6)	0.040 (1)
C19	1.0568 (4)	0.0576 (4)	1.0799 (8)	0.047 (1)
C20	0.3589 (4)	−0.0498 (3)	0.6411 (6)	0.043 (1)
C21	0.3460 (6)	−0.0052 (4)	0.4678 (8)	0.064 (2)
C22	0.2258 (4)	−0.0798 (4)	0.6428 (7)	0.048 (1)
C23	0.1830 (4)	−0.1353 (3)	0.4982 (7)	0.044 (1)
C24	0.2738 (4)	−0.1926 (3)	0.5534 (8)	0.051 (1)
C25	0.3745 (5)	−0.2106 (3)	0.4574 (9)	0.063 (2)
C26	0.3892 (9)	−0.1763 (5)	0.2857 (13)	0.095 (3)
C27	0.4942 (6)	−0.2468 (5)	0.5763 (16)	0.089 (3)
C28	1.1532 (6)	0.1977 (4)	1.2487 (9)	0.064 (2)
C29	1.0156 (6)	0.2761 (4)	1.0154 (10)	0.066 (2)
C30	0.6541 (5)	0.0199 (4)	1.2750 (7)	0.056 (2)
C31	−0.0519 (4)	−0.1289 (3)	0.3885 (7)	0.047 (1)
C32	−0.1775 (5)	−0.1547 (4)	0.4149 (12)	0.065 (2)
O1	1.2284 (3)	0.1983 (3)	0.9033 (5)	0.072 (1)
O2	0.8803 (2)	−0.0488 (3)	0.8421 (5)	0.056 (1)
O3	0.4573 (3)	−0.0566 (3)	0.9900 (4)	0.051 (1)
O4	0.0530 (2)	−0.1588 (3)	0.5057 (4)	0.049 (1)
O5	0.2528 (3)	−0.2487 (3)	0.4273 (5)	0.068 (1)
O6	−0.0434 (3)	−0.0878 (3)	0.2753 (5)	0.067 (1)

Table 2. *Selected geometric parameters* (Å, °)

C1—C10	1.546 (6)	C14—C15	1.552 (7)
C1—C2	1.553 (8)	C15—C16	1.542 (7)
C2—C3	1.513 (7)	C16—C17	1.512 (10)
C3—C4	1.526 (8)	C17—C20	1.508 (7)
C4—C28	1.535 (7)	C20—C21	1.534 (9)
C4—C29	1.537 (11)	C20—C22	1.536 (7)
C4—C5	1.560 (7)	C22—C23	1.529 (9)
C5—C6	1.532 (7)	C23—C24	1.490 (9)
C5—C10	1.541 (9)	C24—C25	1.477 (9)
C6—C7	1.509 (7)	C25—C26	1.483 (12)
C7—C8	1.570 (9)	C25—C27	1.511 (9)
C8—C18	1.547 (6)	C31—C32	1.488 (9)
C8—C9	1.568 (7)	O1—C3	1.213 (6)
C8—C14	1.574 (8)	O2—C11	1.445 (7)
C9—C11	1.548 (8)	O3—C17	1.462 (7)
C9—C10	1.573 (7)	O3—C13	1.463 (7)
C10—C19	1.540 (7)	O4—C31	1.342 (6)
C11—C12	1.523 (8)	O4—C23	1.469 (6)
C12—C13	1.493 (8)	O5—C24	1.448 (8)
C13—C17	1.479 (5)	O5—C25	1.463 (7)
C13—C14	1.516 (8)	O6—C31	1.198 (8)
C14—C30	1.547 (7)		
C10—C1—C2	113.1 (3)	C17—C13—C14	110.9 (5)
C3—C2—C1	116.1 (4)	C12—C13—C14	118.2 (4)
O1—C3—C2	120.7 (5)	C13—C14—C30	108.9 (5)
O1—C3—C4	121.8 (5)	C13—C14—C15	103.5 (3)
C2—C3—C4	117.2 (4)	C13—C14—C8	109.0 (4)
C3—C4—C28	111.0 (4)	C30—C14—C15	109.8 (4)
C3—C4—C29	105.3 (5)	C30—C14—C8	112.3 (3)
C3—C4—C5	108.8 (4)	C15—C14—C8	113.0 (5)
C28—C4—C29	108.1 (5)	C16—C15—C14	107.9 (5)
C28—C4—C5	114.8 (5)	C17—C16—C15	105.1 (4)
C29—C4—C5	108.3 (4)	O3—C17—C13	59.7 (3)
C6—C5—C10	110.5 (5)	O3—C17—C20	113.2 (5)
C6—C5—C4	114.2 (4)	O3—C17—C16	110.9 (4)
C10—C5—C4	114.8 (4)	C13—C17—C20	125.9 (5)
C7—C6—C5	108.7 (3)	C13—C17—C16	108.6 (4)
C6—C7—C8	114.6 (5)	C20—C17—C16	121.7 (4)
C18—C8—C9	110.1 (4)	C17—C20—C21	111.5 (5)
C18—C8—C7	108.4 (5)	C17—C20—C22	109.6 (4)
C18—C8—C14	109.8 (3)	C21—C20—C22	111.8 (4)
C9—C8—C7	111.0 (3)	C23—C22—C20	112.5 (4)
C9—C8—C14	109.1 (5)	O4—C23—C24	105.8 (5)
C7—C8—C14	108.3 (4)	O4—C23—C22	108.2 (4)
C11—C9—C8	109.8 (3)	C24—C23—C22	110.3 (4)
C11—C9—C10	114.3 (4)	O5—C24—C25	60.0 (4)
C8—C9—C10	116.8 (5)	O5—C24—C23	118.1 (4)
C19—C10—C5	110.4 (4)	C25—C24—C23	124.0 (5)
C19—C10—C1	108.2 (4)	O5—C25—C24	59.0 (4)
C19—C10—C9	107.0 (5)	O5—C25—C26	114.6 (5)
C5—C10—C1	106.5 (4)	O5—C25—C27	112.8 (6)
C5—C10—C9	110.6 (4)	C24—C25—C26	123.1 (6)
C1—C10—C9	114.2 (3)	C24—C25—C27	116.4 (6)
O2—C11—C12	107.4 (5)	C26—C25—C27	116.7 (6)
O2—C11—C9	112.5 (3)	O6—C31—O4	123.4 (4)
C12—C11—C9	112.9 (4)	O6—C31—C32	125.3 (5)
C13—C12—C11	114.0 (6)	O4—C31—C32	111.3 (5)
O3—C13—C17	59.6 (3)	C17—O3—C13	60.8 (3)
O3—C13—C12	115.5 (5)	C31—O4—C23	116.2 (5)
O3—C13—C14	111.0 (4)	C24—O5—C25	61.0 (4)
C17—C13—C12	126.9 (4)		

Initial structure analysis was performed with a continuous process connected to the data collection using the fully automatic procedure *FASE* (Yamaguchi, 1993). Data collection and cell refinement were performed using *AFD* (Rigaku Corporation, 1985*a*); data reduction was by *FASE*. The structure was solved by direct methods, included in *FASE*, and with *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985), and refined using *RCRYSTAN* (Rigaku Corporation, 1985*b*). Molecular graphics were obtained using *ACV* (Stardent Computer Inc., 1990) and the material for publication was prepared with *XPACK* (Yamaguchi, 1987).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71803 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1083]

References

Fukuyama, Y., Pei-Wu, G., Rei, W., Yamada, T. & Nakagawa, K. (1988). *Plant Med.* **54**, 445-447.

Ida, Y., Satoh, Y., Nakajima, Y., Yamaguchi, K. & Shoji, J. (1989). 109*th Ann. Meet. Jpn. Soc. Pharm. Sci. Nagoya*, p. 207. Abstract.

Murata, T., Shinohara, M. & Miyamoto, M. (1970). *Chem. Pharm. Bull.* **18**, 1369-1384.

Nakajima, Y., Mikoshiba, K., Ida, Y. & Shoji, J. (1984). 104*th Ann. Meet. Jpn. Soc. Pharm. Sci. Sendai*, p. 151. Abstract.

Rigaku Corporation (1985*a*). *AFD. Diffractometer Control Program System*. Rigaku Corporation, Tokyo, Japan.

Rigaku Corporation (1985*b*). *RCRYSTAN. X-ray Analysis Program System*. Rigaku Corporation, Tokyo, Japan.

Stardent Computer Inc. (1990). *ACV. Application Chemistry Viewer*. Stardent Computer Inc., Mewton, Massachusetts, USA.

Yamaguchi, K. (1987). *XPACK. Programs for X-ray Parameters Report*. Showa Univ., Tokyo, Japan.

Yamaguchi, K. (1993). *Chem. Pharm. Bull.* **41**, 424-429

Yao, J.-X., Zheng, C.-D., Qian., J.-Z., Han, F.-S., Gu, Y.-X. & Fan, H.-F. (1985). *SAPI85. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

Acta Cryst. (1994). C**50**, 738–740

A Kaurane Derivative Isolated from *Alisma orientale*

KENTARO YAMAGUCHI, YOSHITERU IDA, YOHKO SATOH, YOSHIJIROH NAKAJIMA AND JUNZO SHOJI

School of Pharmaceutical Sciences, Showa University, 1-5-8 Hatanodai, Shinagawa-ku, Tokyo 142, Japan

(*Received* 10 *August* 1993; *accepted* 2 *November* 1993)

Abstract

The structure of a new diterpene, $C_{20}H_{30}O_2$, m.p. 452-453 K, $[\alpha]_D$ −28.4° (*c* = 1.0, acetone), isolated from fresh rhizomes of *Alisma orientale* (Alismataceae) was established to be 16(*R*)-(-)-kaurane-2,12-dione by means of X-ray crystallographic analysis and its optical rotation. The *A*, *B* and *C* rings have chair conformations. The puckering parameter of the bridging *D* ring, the angle between the planes C(14)—C(13)—C(16)—C(15) and C(15)—C(8)—C(14), is 39.4 (7)°.