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.

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A Kaurane Derivative Isolated from *Alisma orientale*

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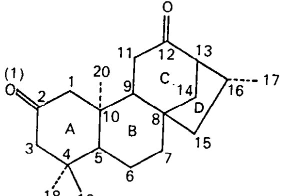
Abstract

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)°.

Comment

During phytochemical investigation of fresh rhizomes of *Alisma orientale* (Mikoshiba, Nakajima, Ida & Shoji, 1983; Nakajima, Mikoshiba, Ida & Shoji, 1984; Ida, Satoh, Nakajima, Yamaguchi & Shoji, 1989), the source material of a Chinese crude drug 'Zexie' (Alismatis rhizome) used for diabetes and swelling (diuretics), a new diterpene was isolated together with four sesquiterpenes and 21 triterpenoids. In order to establish its structure, the X-ray analysis was undertaken. The structure determined here as *ent*-kauren-2,12-dione, (I), is very rare, having ketones as the only functional group. This is the first isolation of a diterpene from the family of this plant, whereas kauranes (Fiagbe, Karlsson, Pilotti & Berg, 1979; Karle, 1972) have been found mainly in plants of the compositae, labiatae, polypodiaceae (genus Pteris) families.



(I)

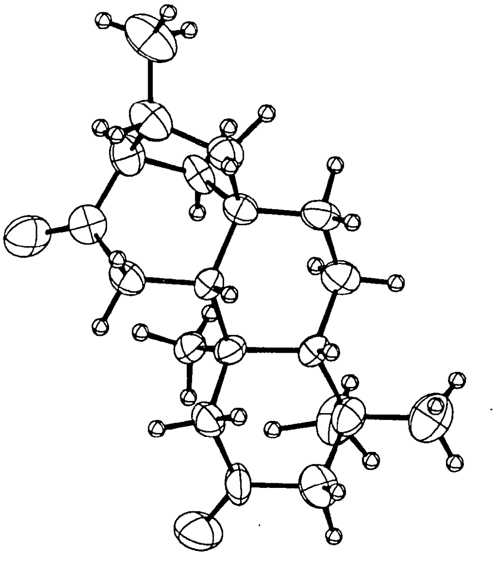


Fig. 1. Displacement-ellipsoid plot of the title molecule. Ellipsoids are drawn at the 50% probability level with isotropic H-atom parameters represented by spheres of arbitarary size.

Experimental

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

Crystal data

$C_{20}H_{30}O_2$
M_r = 302.46
Orthorhombic
$P2_12_12_1$
a = 11.252 (1) Å
b = 19.435 (1) Å
c = 7.880 (1) Å
V = 1723.4 (4) Å^3
Z = 4
D_x = 1.166 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 20 reflections
θ = 29.0–30.5°
μ = 0.531 mm^{-1}
T = 297 K
Prism
0.55 × 0.25 × 0.05 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
1557 measured reflections
1502 independent reflections
1029 observed reflections [$F > 3\sigma(F)$]

$\theta_{\max}$ = 60°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 150 reflections
intensity variation: < 3%

Refinement

Refinement on F^2
$R(F)$ = 0.061
$wR(F^2)$ = 0.060
S = 1.70
1029 reflections
318 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F) + 0.02F^2]$

$(\Delta/\sigma)_{\max}$ = 0.14
$\Delta\rho_{\max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\min}$ = −0.36 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)

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

	x	y	z	U_{eq}
C1	0.3411 (6)	0.1813 (3)	−0.1585 (11)	0.044 (2)
C2	0.3775 (7)	0.2490 (4)	−0.2370 (9)	0.050 (2)
C3	0.4641 (8)	0.2434 (4)	−0.3798 (11)	0.057 (3)
C4	0.5770 (7)	0.2042 (3)	−0.3284 (9)	0.048 (2)
C5	0.5432 (6)	0.1374 (3)	−0.2344 (9)	0.035 (2)
C6	0.6495 (7)	0.0934 (4)	−0.1789 (11)	0.046 (2)
C7	0.6092 (8)	0.0206 (4)	−0.1337 (12)	0.047 (3)
C8	0.5174 (6)	0.0186 (3)	0.0057 (9)	0.039 (2)
C9	0.4140 (6)	0.0693 (3)	−0.0336 (9)	0.037 (2)
C10	0.4522 (6)	0.1441 (3)	−0.0876 (9)	0.037 (2)
C11	0.3202 (6)	0.0682 (4)	0.1097 (10)	0.043 (2)
C12	0.3696 (7)	0.0580 (4)	0.2863 (10)	0.046 (2)
C13	0.4692 (7)	0.0063 (4)	0.2992 (10)	0.049 (2)
C14	0.5701 (6)	0.0309 (4)	0.1847 (11)	0.045 (2)
C15	0.4687 (8)	−0.0546 (3)	0.0289 (11)	0.049 (2)
C16	0.4320 (7)	−0.0625 (4)	0.2166 (12)	0.056 (3)
C17	0.4898 (11)	−0.1243 (5)	0.3076 (18)	0.081 (4)
C18	0.6587 (10)	0.2527 (5)	−0.2247 (13)	0.068 (3)
C19	0.6439 (11)	0.1876 (6)	−0.4944 (13)	0.071 (4)
C20	0.4979 (8)	0.1869 (3)	0.0655 (10)	0.041 (2)
O1	0.3381 (6)	0.3036 (2)	−0.1833 (9)	0.075 (2)
O2	0.3289 (5)	0.0876 (2)	0.4105 (7)	0.068 (2)

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

C1—C2	1.509 (11)	C8—C9	1.556 (10)
C1—C10	1.548 (10)	C9—C11	1.546 (10)

C2—C3	1.493 (11)	C9—C10	1.574 (9)
C3—C4	1.536 (12)	C10—C20	1.553 (10)
C4—C5	1.541 (10)	C11—C12	1.512 (11)
C4—C19	1.543 (13)	C12—C13	1.509 (11)
C4—C18	1.550 (13)	C13—C14	1.527 (11)
C5—C6	1.534 (10)	C13—C16	1.545 (11)
C5—C10	1.550 (10)	C15—C16	1.543 (13)
C6—C7	1.528 (11)	C16—C17	1.543 (14)
C7—C8	1.508 (12)	O1—C2	1.224 (10)
C8—C15	1.537 (10)	O2—C12	1.224 (10)
C8—C14	1.548 (11)		

C2—C1—C10	109.7 (6)	C11—C9—C8	110.9 (6)
O1—C2—C3	124.0 (7)	C11—C9—C10	113.4 (5)
O1—C2—C1	121.0 (7)	C8—C9—C10	115.8 (5)
C3—C2—C1	115.0 (7)	C1—C10—C5	107.7 (5)
C2—C3—C4	112.1 (6)	C1—C10—C20	107.3 (5)
C3—C4—C5	109.9 (6)	C1—C10—C9	108.0 (5)
C3—C4—C19	106.5 (7)	C5—C10—C20	113.9 (6)
C3—C4—C18	109.1 (7)	C5—C10—C9	107.7 (5)
C5—C4—C19	110.6 (7)	C20—C10—C9	112.0 (5)
C5—C4—C18	113.9 (6)	C12—C11—C9	115.0 (6)
C19—C4—C18	106.5 (8)	O2—C12—C13	122.4 (7)
C6—C5—C4	114.5 (6)	O2—C12—C11	122.5 (7)
C6—C5—C10	110.4 (6)	C13—C12—C11	115.0 (6)
C4—C5—C10	116.8 (5)	C12—C13—C14	107.6 (6)
C7—C6—C5	110.6 (6)	C12—C13—C16	110.3 (6)
C8—C7—C6	113.4 (7)	C14—C13—C16	102.9 (6)
C7—C8—C15	110.8 (6)	C13—C14—C8	101.9 (6)
C7—C8—C14	113.4 (6)	C8—C15—C16	107.5 (6)
C7—C8—C9	110.5 (6)	C17—C16—C15	114.2 (8)
C15—C8—C14	99.9 (6)	C17—C16—C13	111.4 (8)
C15—C8—C9	110.1 (6)	C15—C16—C13	104.2 (6)
C14—C8—C9	111.8 (5)		

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 *SAPI85* (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).

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References

Fiagbe, N., Karlsson, B., Pilotti, A. M. & Berg, J. E. (1979). *Acta Cryst.* B35, 236-239.

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

Karle, I. L. (1972). *Acta Cryst*, B**28**, 585-589.

Mikoshiba, K., Nakajima, Y., Ida, Y. & Shoji, J. (1983). *30th Ann. Meet. Jpn. Soc. Pharmacogn. Tokushima*, p. 43. Abstract.

Nakajima, Y., Mikoshiba, K., Ida, Y. & Shoji, J. (1984). *104th 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.

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Triphenylphosphoranylideneammonium Azide, $[Ph_3P{=}NH_2][N_3]$

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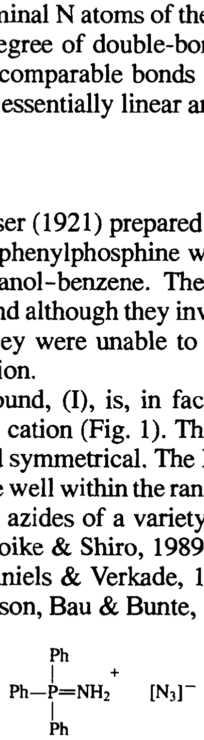
Abstract

The structure consists of $[Ph_3P{=}NH_2]^+$ cations and $[N_3]^-$ anions, which are linked together into polymeric chains by hydrogen bonding between the cationic NH_2 groups and the terminal N atoms of the anions. The P=N bond has a high degree of double-bond character and is shorter than most comparable bonds in other structures. The azide anion is essentially linear and symmetrical.

Comment

Staudinger & Hauser (1921) prepared the title compound by treatment of triphenylphosphine with hydrogen azide in solution in ethanol-benzene. They formulated it as $Ph_3P{=}NH.N_3H$ and although they investigated a number of its reactions, they were unable to deduce the precise chemical constitution.

The title compound, (I), is, in fact, the azide salt of the $[Ph_3P{=}NH_2]^+$ cation (Fig. 1). The azide anion is essentially linear and symmetrical. The N—N bond lengths (mean 1.164 Å) are well within the range (1.136-1.188 Å) reported for linear azides of a variety of organic cations (Kimura, Anan, Koike & Shiro, 1989; Bracuti & Extine, 1990; Woning, Daniels & Verkade, 1990; Lex & Linke, 1976; Christe, Wilson, Bau & Bunte, 1992).



$\mathrm{Ph{-}P(Ph)_2{=}NH_2^{+}\quad [N_3]^-}$

(I)

The cation has a pseudo-tetrahedral P atom and a trigonal planar N atom (at least within the accuracy to which the two H atoms have been placed), consistent with partial P=N double bonding. The $Ph_3P{=}N$ unit is