Studies on Alismatis Rhizoma. III.[1)]
Stereostructures of New Protostane-Type Triterpenes, Alisols H, I, J-23-Acetate, K-23-Acetate, L-23-Acetate, M-23-Acetate, and N-23-Acetate, from the Dried Rhizome of *Alisma orientale*

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New protostane-type triterpenes termed alisols H, I, J-23-acetate, K-23-acetate, L-23-acetate, M-23-acetate, and N-23-acetate were isolated from Alismatis Rhizoma, the rhizome of *Alisma orientale* Juzep. Their stereostructures were determined on the basis of physicochemical evidence.

Key words   alisol H; Alismatis Rhizoma; *Alisma orientale*; protostane-type triterpene; alisol N-23-acetate

We previously reported that the methanolic extract of Alismatis Rhizoma showed inhibitory activities against experimental models of type I, II, III, and IV allergies: that is, 48 h homologous passive cutaneous anaphylaxis in rats, reversed cutaneous anaphylaxis in rats, direct passive Arthus reaction in rats, and picryl chloride-induced contact dermatitis in mice.[2)] As the constituents responsible for anti-allergic activity of this natural medicine, four protostane-type triterpenes, alisols A (**1**)[3)] and B (**3**)[3)] and their monoacetates (**2**, **4**),[3)] and two sesquiterpenes, alismol[4)] and alismoxide,[4)] were characterized.[2)] The methanolic extract of Alismatis Rhizoma was also found to exhibit anti-complementary activities and to inhibit complement-induced hemolysis and hypotonic shock-induced hemolysis. Furthermore, we have found that four principal triterpene constituents (**1**—**4**) inhibited the complement-induced hemolysis, while two sesquiterpenes, alismol and alismoxide, were ineffective.[1)]

As a continuing part of our studies on Alismatis Rhizoma, we have isolated seven new protostane-type triterpenes called alisols H (**10**), I (**11**), J-23-acetate (**12**), K-23-acetate (**13**), L-23-acetate (**14**), M-23-acetate (**15**), and N-23-acetate (**16**) from the methanolic extract with anti-allergic and anti-complementary activities. In this paper, we elucidate the structure of these new protostane-type triterpenes (**10**—**16**).

The methanolic extract of Alismatis Rhizoma was partitioned into a mixture of ethyl acetate and water to furnish the ethyl acetate-soluble portion and the water-soluble portion as described in previous papers.[1,2)] The ethyl acetate-soluble portion was subjected to silica gel and octadecyl silica (ODS) column and finally HPLC to give alisols H (**10**), I (**11**), J-23-acetate (**12**), K-23-acetate (**13**), L-23-acetate (**14**), M-23-acetate (**15**), and N-23-acetate (**16**) together with **1**—**4**, alismol, alismoxide, 11-deoxyalisols B (**5**) and B-23-acetate (**6**),[5)] 11-deoxyalisols C (**7**)[6)] and C monoacetate (**8**),[7)] and 11-deoxyalisol D (**9**).[7)]

Alisol H (**10**) showed absorption bands at 3481, 1705, 1700, and 1665 cm^{-1} assignable to hydroxyl, ketone, and enone functions in its IR spectrum. The UV spectrum of **10** showed absorption maximum at 243 nm (log ε 3.8) suggestive of an enone function. In the negative-ion FAB-MS of **10**, a quasimolecular ion peak was observed at *m/z* 469 (M−

H)$^{-}$, while its positive-ion FAB-MS showed quasimolecular ion peaks at *m/z* 471 (M+H)$^{+}$ and 493 (M+Na)$^{+}$. High-resolution MS analysis of the quasimolecular ion peak (M+H)$^{+}$ in the positive-ion FAB-MS revealed the molecular formula of **10** to be $C_{30}H_{46}O_4$.

The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **10**, which were assigned with the aid of various NMR analytical methods,[8)] showed signals assignable to two isolated methylenes [δ 1.80, 2.44 (both d, *J*=19.5 Hz, 15-H$_2$), 2.52, 2.54 (both d, *J*=20.3 Hz, 24-H$_2$)] and two methylenes [δ 2.30, 2.64 (both m, 2-H$_2$), 2.66, 2.98 (both m, 22-H$_2$)] adjacent to a ketocarbonyl group together with seven tertiary methyls, a secondary methyl, three ketocarbonyls, and a tetrasubstituted olefin. The plane structure of **10** including the positions of the three ketocarbonyl groups and an olefin function was clarified by a heteronuclear multiple bond correlation (HMBC) experiment on **10**, which showed long-range correlations between the following protons and carbons: 3-C and 2-H$_2$, 28-H$_3$, 29-H$_3$; 16-C and 15-H$_2$; 23-C and 22-H$_2$, 24-H$_2$; 13-C and 18-H$_3$; 17-C and 20-H, 21-H$_3$, 22-H$_2$ (Fig. 1 A). The protostane-type stereostructure of **10** was confirmed by a nuclear Overhauser effect spectroscopy (NOESY) spectrum as shown in Fig. 2 a. Furthermore, the carbon signals in the ^{13}C-NMR spectrum of **10** were found to be superimposable on those of 11-deoxyalisol C (**7**),[6)] except for the signals due to the side chain moiety (C-22—27), so that the structure of alisol H (**10**) was determined as shown.

The IR spectrum of alisol I (**11**) showed an absorption band at 1705 cm^{-1} ascribable to the ketone function. In the electron impact-mass spectrum (EI-MS) of **11**, a molecular ion peak was observed at *m/z* 454 (M$^+$) and the molecular formula $C_{30}H_{46}O_3$ was determined by high-resolution MS measurement. The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **11**[8)] showed signals assignable to three methines bearing an oxygen function [δ 4.47 (dd-like, 16-H), 3.53 (ddd, *J*=2.1, 7.9, 12.2 Hz, 23-H), 2.71 (d, *J*=7.9 Hz, 24-H)] together with seven tertiary methyls, a secondary methyl, a ketocarbonyl, and a tetrasubstituted olefin. Comparison of the ^{1}H- and ^{13}C-NMR spectra for **11** with those for alisol F[9)] and 16,23-oxidoalisol B[7)] allowed us to presume the presence of the 24,25-oxide and 16,23-oxide rings in the protostane-

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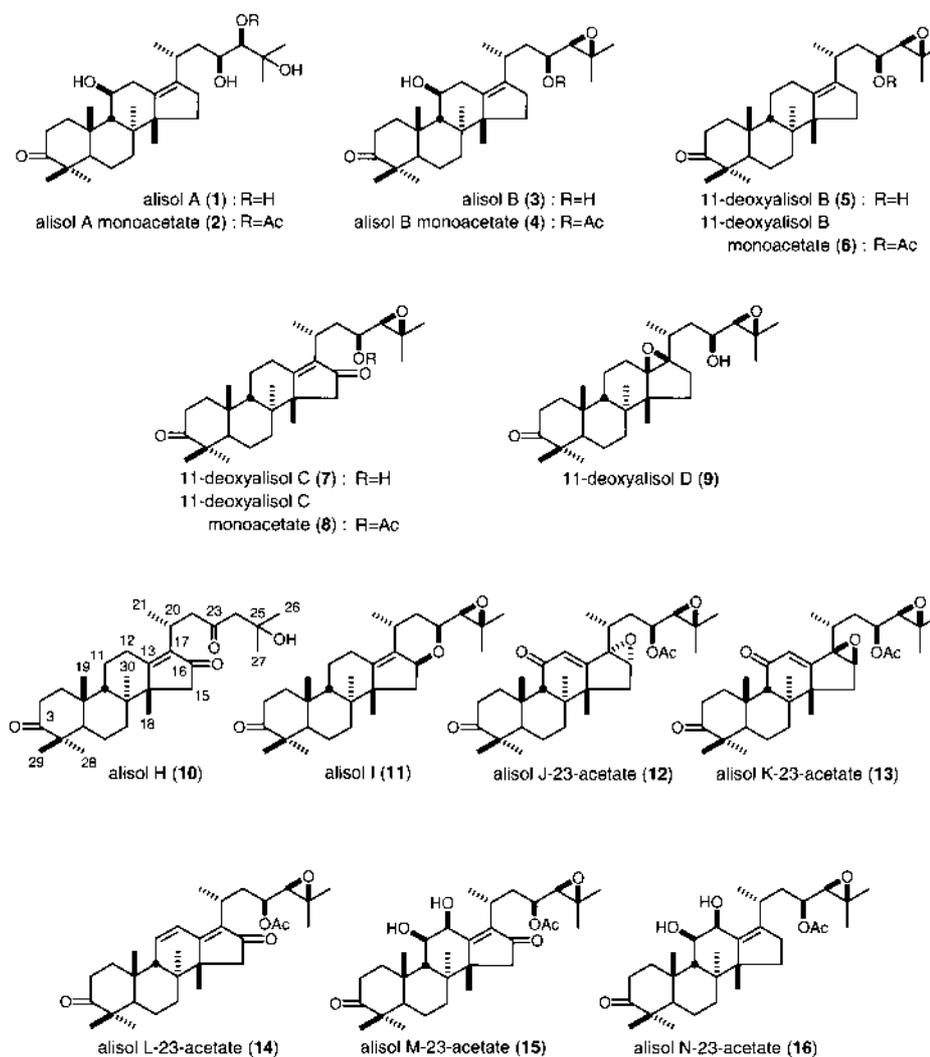
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Chart 1

type triterpene structure of **11**. The positions of the ketocarbonyl and tetrasubstituted olefin function in the protostane structure of **11** were characterized by an HMBC experiment. Namely, long-range correlations were observed between the following protons and carbons: 3-C and 2-H$_2$, 27-H$_3$, 28-H$_3$; 13-C and 12-H$_2$, 18-H$_3$; 17-C and 16-H$_2$, 20-H, 21-H$_3$, 28-H$_3$ (Fig. 1 B). The stereostructure of **11** was characterized from an NOESY experiment as depicted in Fig. 2 b and by comparison of the ^{1}H–^{1}H coupling pattern of the 23 and 24-protons in the ^{1}H-NMR spectrum of **11** with those for known protostane-type triterpenes having the 24,25-epoxide function.[5—7,9)] Consequently, the structure of alisol I (**11**) was elucidated as shown.

The IR spectra of alisols J-23-acetate (**12**) and K-23-acetate (**13**) were similar and showed absorption bands due to ester, ketone, and enone functions. In the UV spectrum of **12**, an absorption maximum was observed at 246 nm (log ε 3.8), which suggested the presence of an enone function. Alisols J-23-acetate (**12**) and K-23-acetate (**13**) were formed to have the same molecular formula C$_{32}$H$_{46}$O$_6$, which was obtained from the positive- and negative-ion FAB-MS [quasimolecular ion peak m/z: 527 (M+H)$^+$, 549 (M+Na)$^+$, 525 (M−H)$^-$] and by high-resolution MS measurement. The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **12**[8)] showed sig-

nals assignable to a trisubstituted olefin [δ 5.84 (s, 12-H)], a methine bearing an acetoxyl group [δ 2.08 (s, 23-OAc), 4.86 (ddd, J=2.8, 8.6, 15.0 Hz, 23-H)], and two methines bearing an oxygen function [δ 3.67 (d-like, 16-H), 2.78 (d, J=8.6 Hz, 24-H)] together with seven tertiary methyls, a secondary methyl, and two ketocarbonyl carbons. The plane structure of **12** including the positions of a ketone, an enone, two epoxides, and an acetoxyl function was confirmed by an HMBC experiment as shown in Fig. 1 C. The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **13**,[8)] in contrast, showed the presence of the same functional groups as **12** and also, in the HMBC experiment on **13** (Fig. 1 C), the same long-range correlations as **12** were observed. This evidence confirmed for us that **12** and **13** were stereoisomers at the 16,17-epoxide moiety. The stereostructures of the 16,17-epoxide in **12** and **13** were clarified by NOESY experiments, which showed NOE correlations between the following protons [**12**: 16-H and 15β-H, 21-H$_3$; 15α-H and 30-H$_3$; 23-H and 26-H$_3$; 24-H and 27-H$_3$ (Fig. 2 c). **13**: 16-H and 15α-H; 15α-H and 30-H; 23-H and 26-H$_3$; 24-H and 27-H$_3$ (Fig. 2 d)]. The proton and carbon signals of the side chain moiety (C-20—C-27) were found to be very similar to those of known protostane-type triterpenes (ex. **4**, **6**, **8**) having the 23β-acetoxyl and the 24β,25-epoxyl function. On the basis of the above evidence,
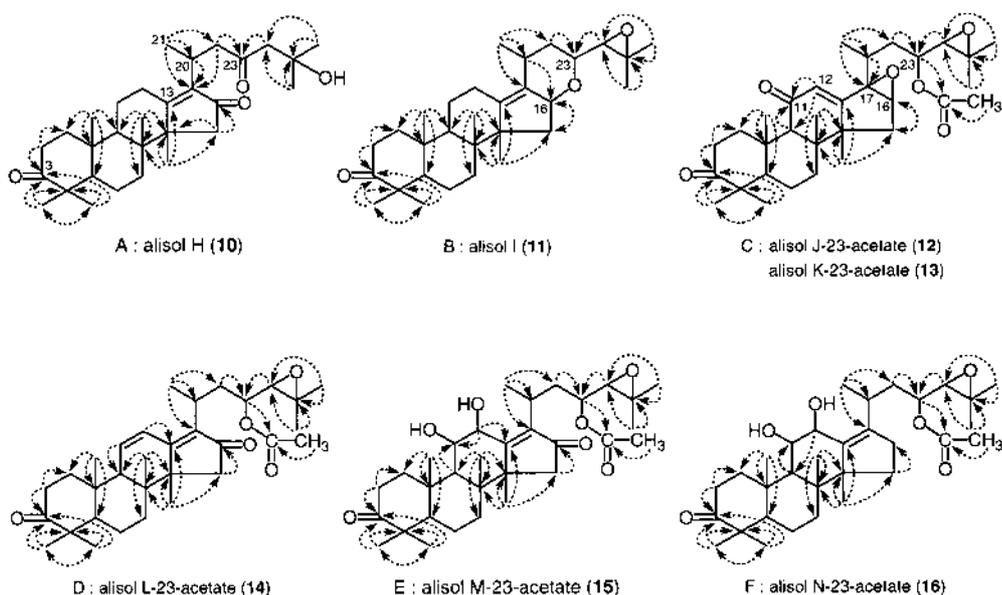
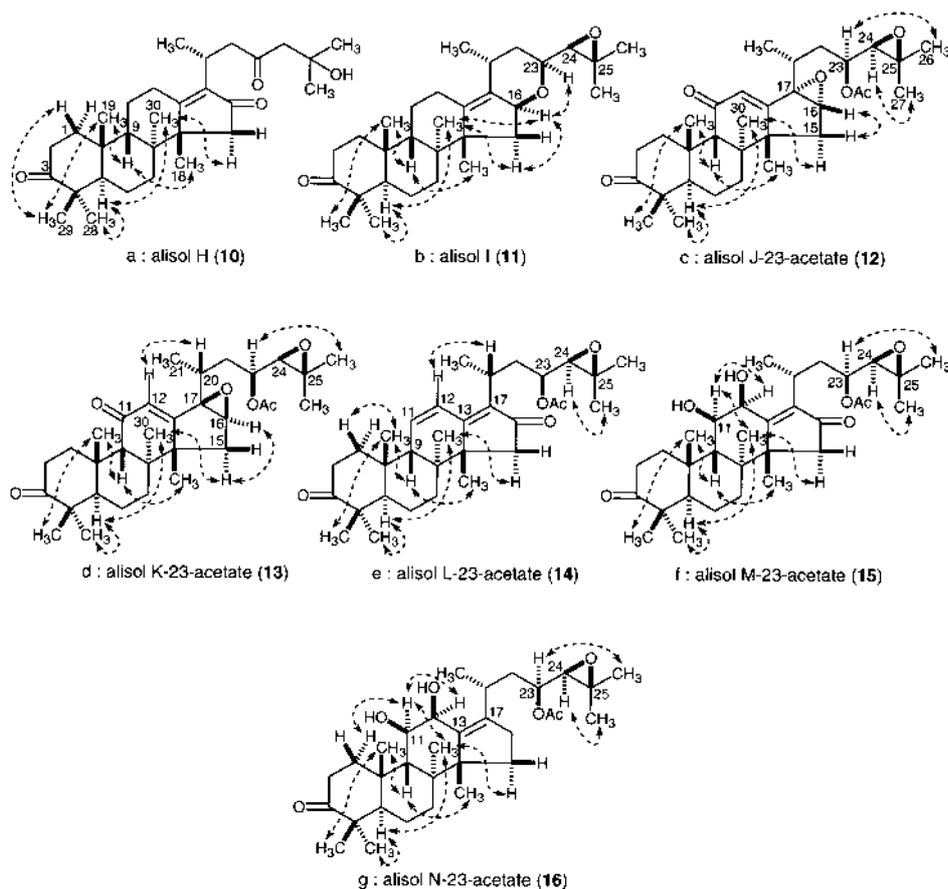Fig. 1.   Long-Range Correlations in the HMBC Spectra of **10**—**16**

Fig. 2.   NOE Correlations in the NOESY Spectra of **10**—**16**

the structures of alisol J-23-acetate (**12**) and alisol K-23-acetate (**13**) were characterized as shown.

Alisol L-23-acetate (**14**) showed absorption bands due to acetyl, ketone, and enone functions in the IR spectrum, while its UV spectrum showed absorption maximum at 285 nm (log ε 3.4) suggestive of a dienone function. In the positive- and negative-ion FAB-MS of **14**, quasimolecular ion peaks were observed at *m/z* 511 (M+H)$^+$, 533 (H+Na)$^+$, and 509

(M−H)$^-$ and the molecular formula $C_{32}H_{46}O_5$ of **14** was clarified by the high-resolution MS measurement. The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **14**[8)] showed signals assignable to a dienone [δ 6.48 (dd, *J*=3.7, 10.4 Hz, 11-H), 6.14 (dd, *J*=1.8, 10.4 Hz, 12-H)], a methine bearing an acetoxyl group [δ 2.06, (s, 23-OAc), 4.57 (ddd, *J*=2.8, 8.3, 11.3 Hz, 23-H)], a methine bearing an oxygen function [δ 2.73 (d, *J*=8.3 Hz, 24-H)], and an isolated meth-

Table 1. ^{13}C-NMR Data of Alisols H (**10**), I (**11**), J-23-Acetate (**12**), K-23-Acetate (**13**), L-23-Acetate (**14**), M-23-Acetate (**15**), and N-23-Acetate (**16**) (CDCl$_3$, 125 MHz)

	10	**11**	**12**	**13**	**14**	**15**	**16**
C-1	31.7	31.6	32.3	32.5	32.3	30.8	31.0
C-2	33.6	33.7	33.7	33.7	33.3	33.7	33.8
C-3	219.5	220.1	219.5	219.3	219.1	219.6	220.2
C-4	47.0	47.0	47.0	47.0	47.2	46.9	47.0
C-5	48.0	47.8	48.0	48.3	46.1	48.8	48.9
C-6	19.9	20.0	19.7	20.1	19.3	20.0	20.2
C-7	34.6	33.7	32.9	33.4	31.2	34.7	34.0
C-8	40.4	40.8	41.5	44.7	47.7	40.2	41.3
C-9	42.8	43.9	55.7	55.2	47.7	44.4	45.9
C-10	36.2	36.3	37.1	37.2	36.0	36.7	36.8
C-11	22.1	23.0	199.5	199.5	121.6	70.7	71.2
C-12	24.5	22.4	123.3	124.7	138.5	66.4	66.4
C-13	179.2	139.6	167.1	167.1	171.5	175.8	141.4
C-14	50.0	55.3	56.8	50.2	39.3	49.2	56.9
C-15	45.8	40.0	36.0	33.2	44.6	46.7	31.3
C-16	208.3	79.8	64.0	63.2	207.6	208.6	29.1
C-17	138.8	131.7	70.7	69.4	137.7	140.1	140.4
C-18	22.9	24.4	25.5	25.3	23.8	25.2	26.5
C-19	23.7	23.5	25.1	25.1	24.8	25.5	25.5
C-20	25.8	26.6	28.8	26.9	26.1	27.4	28.1
C-21	19.3	18.4	15.4	18.3	19.8	20.2	20.6
C-22	48.2	34.9	35.8	34.4	35.7	35.9	37.5
C-23	212.6	72.5	71.9	72.0	71.9	73.8	72.5
C-24	53.4	65.7	64.6	64.9	65.0	64.3	64.5
C-25	69.6	57.1	59.2	59.1	58.6	59.0	59.0
C-26	29.2$^{a)}$	19.3	19.8	19.7	19.4	19.1	19.2
C-27	29.3$^{a)}$	25.0	24.6	24.7	24.7	24.6	24.7
C-28	29.4	29.3	29.4	29.4	29.3	29.6	29.1
C-29	19.7	19.7	19.4	19.4	19.2	20.1	20.2
C-30	22.0	22.7	24.9	24.7	21.9	22.9	23.7
Ac-1			170.3	170.3	170.0	173.1	172.6
Ac-2			21.2	21.2	21.1	21.4	21.3

a) May be interchangeable.

ylene adjacent to a carbonyl function [δ 1.90, 2.36 (both d, $J=18.3$ Hz, 15-H$_2$)] together with methyls and methylenes due to protostane-type triterpene skeleton. The plane structure of **14** was determined by an HMBC experiment, which showed long-range correlations between the following protons and carbons: 3-C and 2-H$_2$, 28-H$_3$, 29-H$_3$; 9-C and 11-H, 30-H$_3$; 13-C and 12-H; 16-C and 15-H$_2$; 17-C and 21-H$_3$; 24-C and 23-H, 26-H$_3$, 27-H$_3$; 25-C and 26-H$_3$, 27-H$_3$; acetyl carbonyl-C and 23-H, acetyl-H$_3$ (Fig. 1 D). The carbon signals in the ^{13}C-NMR spectrum of **14** were very similar to those of **8**, except for the signals due to the disubstituted olefin of the C-ring part in **14**. The stereostructure of **14** was deduced by a NOESY experiment, and the stereostructure of the side chain bonded to the 17-position was deduced to be the same as that of **4**, **6**, and **8** by comparison of the ^{1}H- and ^{13}C-NMR data. Consequently, the structure of alisol L-23-acetate (**14**) was elucidated as shown.

The IR spectrum of alisol M-23-acetate (**15**) showed absorption bands at 3480, 1738, 1705, and 1695 cm^{-1} assignable to hydroxyl, acetyl, ketone, and enone functions, whereas an absorption maximum was observed at 244 nm (log ε 3.8) in its UV spectrum. Here again, the molecular formula C$_{32}$H$_{48}$O$_7$ was determined from the positive- and negative-ion FAB-MS [m/z 545 (M+H)$^+$, 567 (M+Na)$^+$, 543 (M−H)$^+$] and by high-resolution MS measurement. The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **15**$^{8)}$ showed the presence of two methines bearing a hydroxyl group [δ 3.86

(m, 11-H), 4.53 (br s, 12-H)], a methine bearing an acetoxyl group [δ 2.16 (s, 23-OAc), 4.57 (ddd, $J=2.2$, 8.9, 11.0 Hz, 23-H], an epoxide [δ 2.82 (d, $J=8.9$ Hz, 24-H)], and an isolated methylene adjacent to a ketocarbonyl function [δ 1.80, 2.47 (both d, $J=19.2$ Hz, 15-H$_2$)]. The plane structure of **15** was also determined from an HMBC experiment (Fig. 1 E) and its stereostructure including the vicinal diol moiety was clarified by an NOESY experiment, which showed NOE correlations between the 11-proton and the 12-proton and between the 11-proton and the 30-methyl protons (Fig. 2 f). This evidence and comparison of the ^{1}H- and ^{13}C-NMR data for **15** with those of known protostane-type triterpenes such as **8** and **14** led us to formulate the structure of alisol M-23-acetate (**15**) as shown.

Alisol N-23-acetate (**16**) showed absorption bands due to hydroxyl, ester, and ketone functions. The molecular formula C$_{32}$H$_{50}$O$_6$ was determined from the positive- and negative-ion FAB-MS [m/z 531 (M+H)$^+$, 553 (M+Na)$^+$, 529 (M−H)$^-$] and by high-resolution FAB-MS measurement. The ^{1}H-NMR (CDCl$_3$) and ^{13}C-NMR (Table 1) spectra of **16**$^{8)}$ showed the presence of a vicinal diol moiety [δ 3.73 (m, 11-H), 4.35 (br s, 12-H)], a methine bearing an acetoxyl group [δ 2.14 (s, 23-OAc), 4.75 (ddd-like, 23-H)], and an epoxide [δ 2.80 (d, $J=8.6$ Hz, 24-H)]. The carbon signals in the ^{13}C-NMR spectrum of **16** were superimposable on those of **15**, except for the signals due to the carbons on D-ring. The plane structure of **16** was determined by an HMBC experiment (Fig. 1 F) and its stereostructure was deduced by a NOESY experiment (Fig. 2 g). On the basis of the above evidence and comparison of the ^{1}H- and ^{13}C-NMR data for **16** with those for **4**, the structure of alisol N-23-acetate (**16**) was elucidated as shown.

rate: 9.0—10.0 ml/min] to furnish alisols H (**10**, 18.2 mg), I (**11**, 41.5 mg), J-23-acetate (**12**, 52.5 mg), K-23-acetate (**13**, 52.4 mg), L-23-acetate (**14**, 27.3 mg), M-23-acetate (**15**, 28.4 mg), and N-23-acetate (**16**, 19.7 mg) and 11-deoxyalisols B (**5**, 15 mg), B-23-acetate (**6**, 139 mg), C (**7**, 9 mg), and C-monoacetate (**8**, 115 mg). Known protostane-type triterpenes were identified by comparison with authentic samples (^{1}H- and ^{13}C-NMR, IR, and $[\alpha]_D$ data).

Alisol H (**10**): A white powder, $[\alpha]_D^{25}$ +59.1° (c=0.9, CHCl$_3$). High-resolution negative-ion FAB-MS: Calcd for C$_{30}$H$_{47}$O$_4$ (M+H)$^+$: 471.3474. Found: 471.3488. UV $\lambda_{\max}^{CHCl_3}$ nm (log ε): 243 (3.8). IR (KBr): 3481, 1705, 1700, 1665, 1462, 1379, 1238 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.88, 0.92, 1.06, 1.07, 1.18, 1.20, 1.24 (3H each, all s, 19, 30, 29, 28, 26, 27, 18-H$_3$), 1.16 (3H, d, J=7.0 Hz, 21-H$_3$), 1.49, 2.07 (1H each, both m, 1-H$_2$), 1.80, 2.44 (1H each, both d, J=19.5 Hz, 15-H$_2$), 1.83 (1H, s, 9-H), 1.98 (1H, m, 5-H), 2.30, 2.64 (1H each, both m, 2-H$_2$), 2.52, 2.54 (1H each, both d, J=20.3 Hz, 24-H$_2$), 2.66, 2.98 (1H each, both m, 22-H$_2$). ^{13}C-NMR (CDCl$_3$) δ_C: Given in Table 1. Positive-ion FAB-MS m/z: 471 (M+H)$^+$, 493 (M+Na)$^+$. Negative-ion FAB-MS m/z 469: (M−H)$^-$.

Alisol I (**11**): A white powder, $[\alpha]_D^{25}$ +51.9° (c=2.1, CHCl$_3$). High-resolution EI-MS: Calcd for C$_{30}$H$_{46}$O$_3$ (M$^+$): 454.3447. Found: 454.3422. IR (KBr): 1705, 1458, 1377, 1242 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.82, 0.91, 1.03, 1.06, 1.20 (3H each, all s, 19, 30, 29, 28, 18-H$_3$), 1.15 (3H, d, J=7.8 Hz, 21-H$_3$), 1.31 (6H, s, 26, 27-H$_3$), 1.33, 2.30 (1H each, both m, 15-H$_2$), 1.42, 2.03 (1H each, both m, 1-H$_2$), 1.68 (1H, dd-like, 9-H), 2.03 (1H, m, 5-H), 2.30, 2.63 (1H each, both m, 2-H$_2$), 2.71 (1H, d, J=7.9 Hz, 24-H), 3.53 (1H, ddd, J=2.1, 7.9 12.2 Hz, 23-H), 4.47 (1H, dd-like, 16-H). ^{13}C-NMR (CDCl$_3$) δ_C: Given in Table 1. EI-MS m/z: 454 (M$^+$).

Alisol J-23-Acetate (**12**): A white powder, $[\alpha]_D^{25}$ +39.1° (c=2.6, CHCl$_3$). High-resolution positive-ion FAB-MS: Calcd for C$_{32}$H$_{47}$O$_6$ (M+H)$^+$: 527.3373. Found : 527.3386. UV $\lambda_{\max}^{CHCl_3}$ nm (log ε): 246 (3.8). IR (KBr): 1738, 1700, 1661, 1462, 1382, 1238 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.04 (3H, d, J=7.0 Hz, 21-H$_3$), 1.05, 1.08, 1.10, 1.17, 1.33, 1.36, 1.38 (3H each, all s, 29, 28, 25, 30, 18, 26, 27-H$_3$), 1.56, 1.58 (1H each, both d, J=3.4 Hz, 15-H$_2$), 1.92, 2.44 (1H each, both m, 1-H$_2$), 2.08 (3H, s, 23-OAc), 2.22 (1H, m, 5-H), 2.37, 2.68 (1H each, both m, 2-H$_2$), 2.58 (1H, m, 9-H), 2.78 (1H, d, J=8.6 Hz, 24-H), 3.67 (1H, d-like, 16-H), 4.86 (1H, ddd, J=2.8, 8.6, 15.0 Hz, 23-H), 5.84 (1H, s, 12-H). ^{13}C-NMR (CDCl$_3$) δ_C: Given in Table 1. Positive-ion FAB-MS m/z: 527 (M+H)$^+$, 549 (M+Na)$^+$. Negative-ion FAB-MS m/z: 525 (M−H)$^-$.

Alisol K-23-Acetate (**13**): A white powder, $[\alpha]_D^{25}$ +69.4° (c=2.6, CHCl$_3$). High-resolution positive-ion FAB-MS: Calcd for C$_{32}$H$_{47}$O$_6$ (M+H)$^+$: 527.3372. Found: 527.3386. IR (KBr): 1738, 1705, 1661, 1379, 1240 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 1.05, 1.08, 1.11, 1.17, 1.33, 1.34, 1.37 (3H each, all s, 29, 28, 19, 30, 27, 18, 26-H$_3$), 1.07 (3H, d, J=7.0 Hz, 21-H$_3$), 1.74, 2.02 (1H each, both dd-like, 15-H$_2$), 1.91, 2.45 (1H each, both m, 1-H$_2$), 2.09 (3H, s, 23-OAc), 2.15 (1H, m, 5-H), 2.30, 2.68 (1H each, both m, 2-H$_2$), 2.66 (1H, s, 9-H), 2.78 (1H, d, J=8.5 Hz, 24-H), 3.67 (1H, d, J=1.9 Hz, 16-H), 4.89 (1H, ddd, J=2.5, 8.5, 13.8 Hz, 23-H), 5.91 (1H, s, 12-H). ^{13}C-NMR (CDCl$_3$) δ_C: Given in Table 1. Positive-ion FAB-MS m/z: 527 (M+H)$^+$, 549 (M+Na)$^+$. Negative-ion FAB-MS m/z: 525 (M−H)$^-$.

Alisol L-23-Acetate (**14**): A white powder, $[\alpha]_D^{25}$ +86.7° (c=1.4, CHCl$_3$). High-resolution FAB-MS: Calcd for C$_{32}$H$_{47}$O$_5$ (M+H)$^+$: 511.3424. Found : 511.3430. UV $\lambda_{\max}^{CHCl_3}$ nm (log ε): 285 (3.4). IR (KBr): 1740, 1705, 1665, 1458, 1379, 1285 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.94, 0.96, 1.06, 1.09, 1.12, 1.27, 1.30 (3H each, all s, 19, 30, 29, 28, 18, 26, 27-H$_3$), 1.17 (3H, d, J=7.0 Hz, 21-H$_3$), 1.68, 2.06 (1H each, both m, 1-H$_2$), 1.90, 2.36 (1H each, both d, J=18.3 Hz, 15-H$_2$), 2.06 (3H, s, 23-OAc), 2.28, 2.71 (1H each, both m, 2-

H$_2$), 2.32 (1H, m, 5-H), 2.38 (1H, s, 9-H), 2.73 (1H, d, J=8.3 Hz, 24-H), 4.57 (1H, ddd, J=2.8, 8.3, 11.3 Hz, 23-H), 6.14 (1H, dd, J=1.8, 10.4 Hz, 12-H), 6.48 (1H, dd, J=3.7, 10.4 Hz, 11-H). ^{13}C-NMR (CDCl$_3$) δ_C: Given in Table 1. Positive-ion FAB-MS m/z: 511 (M+H)$^+$, 533 (M+Na)$^+$. Negative-ion FAB-MS m/z: 509 (M−H)$^-$.

Alisol M-23-Acetate (**15**): A white powder, $[\alpha]_D^{25}$ +35.4° (c=1.4, CHCl$_3$). High-resolution positive-ion FAB-MS: Calcd for C$_{32}$H$_{49}$O$_7$ (M+H)$^+$: 545.3479. Found: 545.3477. $\lambda_{\max}^{CHCl_3}$ nm (log ε): 244 (3.8). IR (KBr): 3480, 1738, 1705, 1675, 1462, 1381, 1238 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.88, 1.08, 1.09, 1.10, 1.17, 1.31, 1.48 (3H each, all s, 30, 29, 28, 19, 26, 27, 18-H$_3$), 1.16 (3H, d, J=6.2 Hz, 21-H$_3$), 1.80, 2.47 (1H each, both d, J=19.2 Hz, 15-H$_2$), 2.05 (1H, m, 5-H), 2.08 (1H, m, 9-H), 2.16 (3H, s, 23-OAc), 2.24 (2H, m, 1-H$_2$), 2.38, 2.65 (1H each, both m, 2-H$_2$), 2.82 (1H, d, J=8.9 Hz, 24-H), 3.86 (1H, m, 11-H), 4.53 (1H, br s, 12-H), 4.57 (1H, ddd, J=2.2, 8.9, 11.0 Hz, 23-H). ^{13}C-NMR (CDCl$_3$) δ_C: Given in Table 1. Positive-ion FAB-MS m/z: 545 (M+H)$^+$, 567 (M+Na)$^+$. Negative-ion FAB-MS m/z: 543 (M−H)$^-$.

Alisol N-23-Acetate (**16**): A white powder, $[\alpha]_D^{25}$ +52.9° (c=1.0, CHCl$_3$). High-resolution positive-ion FAB-MS: Calcd for C$_{32}$H$_{51}$O$_6$ (M+H)$^+$: 531.3678. Found : 531.3686. IR (KBr): 3503, 1739, 1705, 1462, 1377, 1242 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 0.95, 1.05, 1.06, 1.07, 1.31, 1.32, 1.33 (3H each, all s, 30, 19, 28, 29, 18, 26, 27-H$_3$), 1.01 (3H, d, J=9.2 Hz, 21-H$_3$), 1.28, 1.93 (1H each, both m, 15-H$_2$), 1.98 (1H, m, 9-H), 2.03 (1H, m, 5-H), 2.10, 2.22 (1H each, both m, 16-H$_2$), 2.14 (3H, s, 23-OAc), 2.22 (2H, m, 1-H$_2$). 2.37, 2.63 (1H each, both m, 2-H$_2$), 2.80 (1H, d, J=8.6 Hz, 24-H), 3.73 (1H, m, 11-H), 4.35 (1H, br s, 12-H), 4.75 (1H, ddd-like, 23-H). ^{13}C-NMR (CDCl$_3$) δ_C: given in Table 1. Positive-ion FAB-MS m/z: 531 (M+H)$^+$, 553 (M+Na)$^+$. Negative-ion FAB-MS m/z: 529 (M−H)$^-$.

References and Notes

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