Bioactive Saponins and Glycosides. XVIII.[1] Nortriterpene and Triterpene Oligoglycosides from the Fresh Leaves of *Euptelea polyandra* Sieb. et Zucc. (2): Structures of Eupteleasaponins VI, VI Acetate, VII, VIII, IX, X, XI, and XII

Toshiyuki Murakami, Hideo Ominami, Hisashi Matsuda, and Masayuki Yoshikawa*

Kyoto Pharmaceutical University, Misasagi, Yamashina-ku, Kyoto 607–8412, Japan.
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Following the elucidation of eupteleasaponins I, II, III, IV, V, and V acetate, eupteleasaponins VI, VI acetate, VII, VIII, IX, X, XI, and XII were isolated from the fresh leaves of *Euptelea polyandra* Sieb. et Zucc. The structures of eupteleasaponins VI—XII were determined on the basis of chemical and physicochemical evidence.

Key words eupteleasaponin; *Euptelea polyandra*; nortriterpene oligoglycoside; Eupteleaceae; eupteleogenin

In the course of our studies in search of bioactive saponins and glycosides from medicinal foodstuffs and natural medicines,[1,2] we found that the saponin fraction from the fresh leaves of *Euptelea* (*E.*) *polyandra* Sieb. et Zucc. (Eupteleaceae) showed potent gastroprotective activity. From the saponin fraction, we have isolated fourteen nortriterpene and triterpene oligoglycosides called eupteleasaponins I (**1**), II (**2**), III (**3**), IV (**4**), V (**5**), V acetate (**6**), VI (**7**), VI acetate (**8**), VII (**9**), VIII (**10**), IX (**11**), X (**12**), XI (**13**), and XII (**14**). In the preceding paper,[3] we reported the gastroprotective effect of the saponin fraction and the structure elucidation of eupteleasaponins I (**1**), II (**2**), III (**3**), IV (**4**), V (**5**), and V acetate (**6**). This paper deals with the structure elucidation of the remaining eight new nortriterpene and triterpene oligoglycosides (**7**—**14**) from the fresh leaves of *E. polyandra.*

Structures of Eupteleasaponins VI (7), VI Acetate (8), VII (9), VIII (10), IX (11), X (12), XI (13), and XII (14) Eupteleasaponin VI (**7**) was isolated as colorless fine crystals of mp 184—187 °C from $CHCl_3$–MeOH. The IR spectrum of **7** showed absorption bands at 1775 and 1658 cm^{-1} due to γ-lactone and *exo*-methylene functions and strong absorption bands at 3453 and 1055 cm^{-1} suggestive of an oligoglycosidic structure. In the positive-ion FAB-MS of **7**, a quasimolecular ion peak was observed at *m/z* 947 $(M+Na)^+$ and the high-resolution MS analysis revealed the molecular formula of **7** to be $C_{47}H_{72}O_{18}$. Acid hydrolysis with 5% aqueous sulfuric acid (H_2SO_4)–1,4-dioxane (1 : 1, v/v) of **7** liberated D-glucose and L-rhamnose,[4] which were identified by GLC analysis of the thiazolidine derivatives.[5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra of **7**, which were assigned with the aid of various NMR analytical methods,[6] showed signals due to the presence of two β-D-glucopyranosyl moieties [δ 4.80 (d-like, 1′-H), 5.08 (d, J=7.0 Hz, 1‴-H)], an α-L-rhamnopyranosyl moiety [δ 1.65 (d, J=5.3 Hz, 6″-H_3), 6.36 (br s, 1″-H)] along with a nortriterpene sapogenol moiety [δ 2.33 (dd-like, 18-H), 3.03 (br s, 11-H), 3.14 (d-like, 12-H), 3.38 (dd-like, 3-H), 4.73 (m, 29-H_2)]. The carbon signals due to the nortriterpene sapogenol moiety were very similar to those of eupteleogenin moiety in known eupteleasaponin V (**5**) and V acetate (**6**).[3] The structures of the eupteleogenin and 3-*O*-triglycoside moieties were confirmed by HMBC experiments on **7**, which showed long-range correlations between the following protons and carbons: 23, 24-H_3 and 3, 4, 5-C; 25-H_3 and 1, 5, 9, 10-C; 26-H_3 and 7, 8, 9, 14-C; 27-H_3 and 8, 13, 14, 15-C; 18-H and 13, 17, 19-C; 29-H_2 and 19, 21-C; 1′-H and 3-C; 1″-H and 2′-C; 1‴-H and 3′-C. The stereostructure of the eupteleogenin moiety in **5** was also confirmed by a pROESY experiment, which showed NOE correlations between the following proton pairs (11β-H and 25-H_3; 12β-H and 11β, 18β-H, 26-H_3). Consequently, the structure of eupteleasaponin VI was determined to be eupteleogenin 3-*O*-α-L-rhamnopyranosyl(1→2)-[β-D-glucopyranosyl(1→3)]-β-D-glucopyranoside (**7**).

Eupteleasaponin VI acetate (**8**) was also obtained as colorless fine crystals from $CHCl_3$–MeOH of mp 180—184 °C, and its IR spectrum showed absorption bands due to hydroxyl, γ-lactone, and *exo*-methylene functions. In the negative- and positive-ion FAB-MS of **8**, quasimolecular ion peaks were observed at *m/z* 965 $(M-H)^-$ and *m/z* 989 $(M+Na)^+$ and the molecular formula $C_{49}H_{74}O_{19}$ was deter-

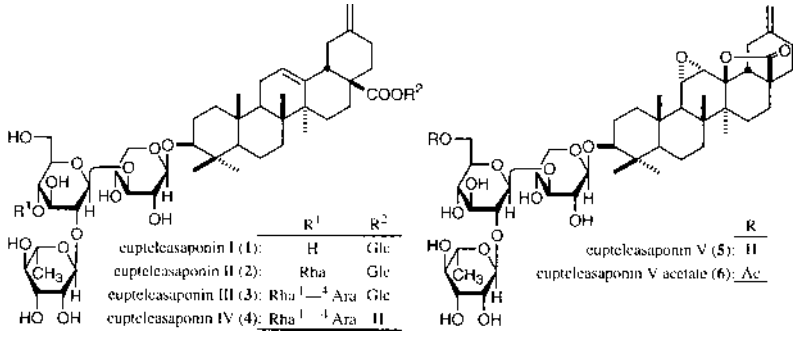

Chart 1

* To whom correspondence should be addressed. e-mail: shoyaku@mb.kyoto-phu.ac.jp

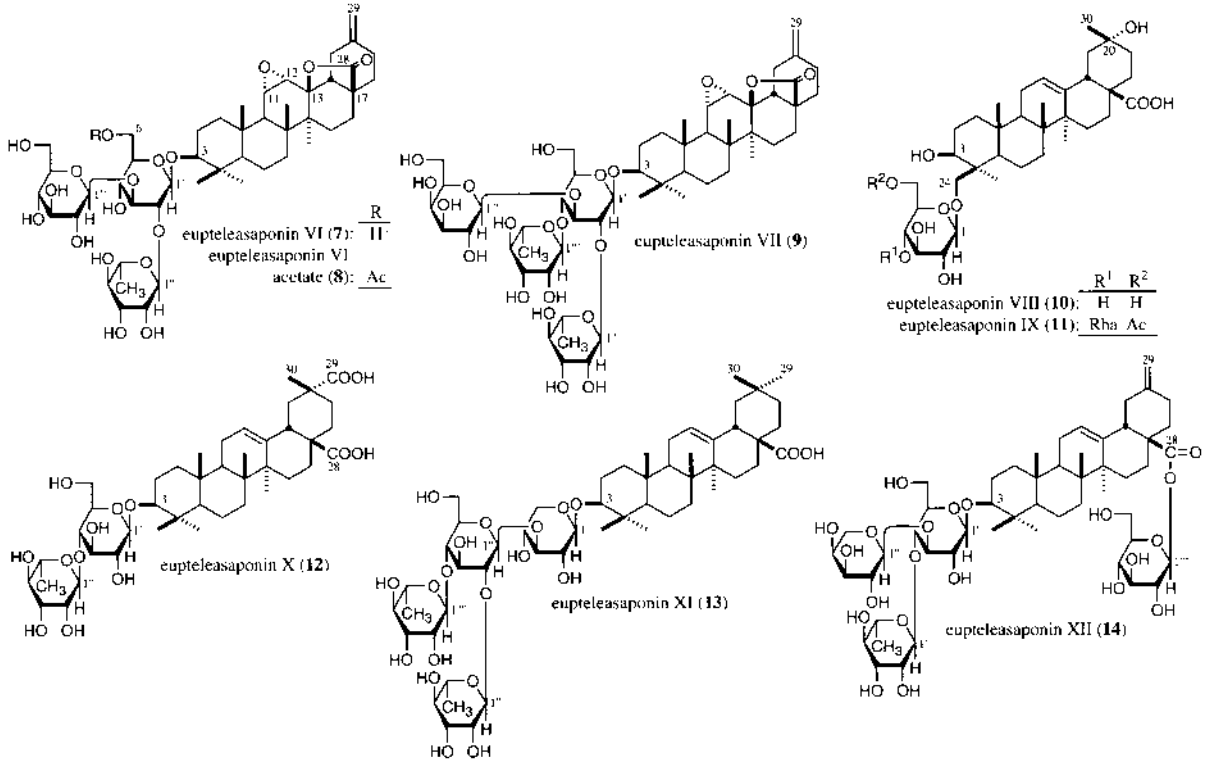

Chart 2

Table 1. ^{13}C-NMR Data for Eupteleasaponins VI (**7**), VI Acetate (**8**), VII (**9**), VIII (**10**), IX (**11**), X (**12**), XI (**13**), and XII (**14**)

	7	**8**	**9**	**10**	**11**	**12**	**13**	**14**		**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
C-1	38.8	38.8	38.8	39.0	39.2	38.7	39.1	38.9	C-1′	104.9	104.9	104.9	105.6	105.2	106.6	104.8	107.3
C-2	26.4	26.3	26.4	28.1	28.3	26.5	26.6	26.7	C-2′	77.1	76.9	77.3	75.0	75.1	75.9	74.9	71.9
C-3	88.4	88.5	88.5	79.4	79.3	89.0	88.3	88.8	C-3′	89.3	89.9	89.1	78.2	76.5	77.0	81.8	84.5
C-4	39.6	39.5	39.5	43.0	43.2	39.5	39.6	39.6	C-4′	69.9	69.9	78.2	71.5	79.2	78.7	68.1	78.5
C-5	55.3	55.3	55.3	56.6	56.7	55.9	56.1	56.0	C-5′	77.8	75.1	77.8	78.3	73.7	77.0	64.8	77.3
C-6	17.8	17.7	17.8	19.2	19.6	18.5	18.6	18.6	C-6′	62.2	64.5	61.5	62.6	63.6	61.8		61.5
C-7	31.4	31.4	31.4	33.4	33.6	33.2	33.3	33.2	C-1″	101.6	101.6	101.8		102.8	102.8	104.4	106.1
C-8	41.7	41.6	41.7	39.6	39.8	39.8	39.8	40.0	C-2″	72.2	72.3	72.3		72.3	72.6	75.1	75.9
C-9	51.1	51.1	51.1	48.0	48.2	48.0	48.1	48.1	C-3″	72.4	72.5	72.5		72.6	72.8	76.4	76.5
C-10	36.5	36.4	36.4	37.0	37.3	37.1	37.1	37.0	C-4″	73.8	73.9	73.9		73.7	74.0	78.4	69.3
C-11	52.8	52.8	52.8	23.8	23.9	23.8	23.8	23.6	C-5″	69.8	69.7	69.8		70.7	70.3	77.3	66.9
C-12	57.2	57.2	57.2	122.4	122.7	122.7	122.6	122.7	C-6″	18.5	18.6	18.6		18.4	18.5	61.4	
C-13	87.0	87.0	87.0	144.1	144.3	144.4	144.8	143.5	C-1‴	104.0	104.5	103.7				101.9	102.7
C-14	41.0	41.0	41.0	41.9	42.1	42.2	42.2	42.2	C-2‴	75.1	74.9	75.3				72.4	72.5
C-15	27.1	27.0	27.1	28.2	28.4	28.3	28.4	28.2	C-3‴	78.5	78.1	76.5				72.6	72.8
C-16	32.3	32.3	32.3	23.7	23.9	23.8	23.8	23.8	C-4‴	71.4	71.5	69.9				74.0	74.0
C-17	44.1	44.1	44.1	46.6	46.8	46.6	46.7	47.4	C-5‴	78.2	77.8	77.2				70.1	70.4
C-18	54.8	54.8	54.8	44.2	44.4	41.1	42.0	47.7	C-6‴	62.7	62.7	62.7				18.6	18.5
C-19	34.7	34.7	34.7	47.8	48.1	41.1	46.5	41.7	C-1⁗			102.7				102.7	95.8
C-20	147.1	147.0	147.1	69.8	70.0	42.6	31.0	148.5	C-2⁗			72.4				72.5	74.1
C-21	30.2	30.2	30.2	35.9	36.2	29.3	34.3	30.2	C-3⁗			72.7				72.8	78.8
C-22	22.0	22.0	22.0	34.9	35.1	32.4	33.3	37.7	C-4⁗			73.9				74.0	71.3
C-23	27.7	27.7	27.7	23.3	28.5	28.3	28.2	28.2	C-5⁗			70.4				70.4	79.2
C-24	16.5	16.5	16.5	73.2	73.0	17.0	17.0	17.0	C-6⁗			18.5				18.4	62.4
C-25	17.4	17.3	17.5	15.6	15.7	15.5	15.6	15.6	Ac-1		170.8			170.5			
C-26	20.7	20.3	20.3	17.0	17.2	17.4	17.4	17.5	Ac-2		20.6			20.6			
C-27	18.9	18.9	18.9	25.8	26.0	26.1	26.2	26.1									
C-28	178.2	178.1	178.2	179.8	179.9	180.9	180.1	175.7									
C-29	109.9	109.8	109.8			184.3	33.3	107.3									
C-30				25.4	25.7	20.0	23.8										

500 MHz, pyridine-d_5.

mined by high-resolution MS measurement. A fragment ion peak was observed at *m/z* 923 $(M-C_2H_3O)^-$, which was derived by cleavage of the acetyl linkage, and was observed in the negative-ion FAB-MS of **8**. Upon acid hydrolysis with 5% aqueous H_2SO_4–1,4-dioxane, **8** gave D-glucose and L-rhamnose,[4,5] while alkaline treatment of **8** with 0.1% NaOMe–MeOH furnished eupteleasaponin VI (**7**). The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **8** showed signals assignable to an acetyl moiety [δ 2.17 (s, Ac-2)] together with a eupteleasaponin VI part [δ 1.66 (d, J=6.3 Hz, 6″-H_3), 2.32 (dd-like, 18-H), 3.02 (br s, 11-H), 3.14 (d-like, 12-H), 3.40 (dd, J=3.9, 11.0 Hz, 3-H), 4.73 (m, 29-H_2), 4.84 (d, J=7.3 Hz, 1′-H), 5.01 (d, J=7.6 Hz, 1‴-H), 6.37 (br s, 1″-H)]. The HMBC experiment of **8** showed a long-range correlation between the 6′-protons of the 3-*O*-glucopyranosyl moiety and the acetyl carbonyl carbon. Comparison of the ^{13}C-NMR data for **8** with that of **7** revealed an acetylation shift around the 6′-position of the glucose moiety in **8**. Consequently, the structure of eupteleasaponin VI was elucidated as eupteleogenin 3-*O*-[α-L-rhamnopyranosyl(1→2)][β-D-glucopyranosyl(1→3)]-6′-*O*-acetyl-β-D-glucopyranoside (**8**).

Eupteleasaponin VII (**9**) was isolated as colorless fine crystals from $CHCl_3$–MeOH of mp 168—172 °C. The IR spectrum of **9** showed absorption bands due to hydroxyl, γ-lactone, and *exo*-methylene functions at 3432, 1775, and 1654 cm^{-1}. In the negative- and positive-ion FAB-MS of **9**, a quasimolecular ion peak was observed at *m/z* 1069 $(M-H)^-$, *m/z* 1093 $(M+Na)^+$, and 1115 $(M+2Na-H)^+$, and the high-resolution MS analysis revealed the molecular formula of **9** to be $C_{53}H_{82}O_{22}$. Furthermore, fragment ion peaks were observed at *m/z* 923 $(M-C_6H_{11}O_4)^-$ and *m/z* 761 $(M-C_{12}H_{23}O_9)^-$. Acid hydrolysis of **9** liberated D-glucose, L-rhamnose, and D-galactose.[4,5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **9** showed the presence of an eupteleogenin moiety [δ 2.35 (dd, J=3.7, 13.8 Hz, 18-H), 3.01 (br s, 11-H), 3.14 (d, J=2.3 Hz, 12-H), 3.38 (dd, J=4.3, 11.9 Hz, 3-H), 4.71, 4.74 (both s, 29-H_2)], a β-D-glucopyranosyl moiety [δ 4.83 (d, J=7.3 Hz, 1′-H)], two α-L-rhamnopyranosyl moieties [δ 1.67, 1.69 (both d, J=6.1 Hz, 6⁗, 6″-H_3), 5.69, 6.37 (both br s, 1⁗, 1″-H)], and a β-D-galactopyranosyl moiety [δ 5.04 (d, J=7.9 Hz, 1‴-H)]. In the HMBC experiment of **9**, long-range correlations were observed between the following protons and carbons: 1′-H and 3-C; 1″-H and 2′-C; 1‴-H and 3′-C; 1⁗-H and 4′-C. Consequently, the structure of eupteleasaponin VII was determined to be eupteleogenin 3-*O*-[α-L-rhamnopyranosyl(1→2)][β-D-galactopyranosyl(1→3)][α-L-rhamnopyranosyl(1→4)]-β-D-glucopyranoside (**9**).

Eupteleasaponin VIII (**10**) was isolated as colorless fine crystals form $CHCl_3$–MeOH of mp 199—201 °C. The IR spectrum of **10** showed absorption bands at 3432, 1709, and 1078 cm^{-1} assignable to hydroxyl and carboxyl functions. In the positive-ion FAB-MS of **10**, a quasimolecular ion peak was observed at *m/z* 659 $(M+Na)^+$, and the molecular formula $C_{35}H_{56}O_{10}$ was determined by high-resolution MS measurement. Acid hydrolysis of **10**, with 5% aqueous H_2SO_4–1,4-dioxane, liberated D-glucose.[4,5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **10** indicated the presence of five methyl groups at δ 0.83, 0.92, 1.22, 1.36, and 1.38 (all s), an oxymethylene group at δ 4.30 and 4.48 (both m), an oxymethine group at δ 3.51 (dd-like), and an olefin function at δ 5.51 (br s) together with a β-D-glucopyranosyl moiety [δ 4.90 (d, J=7.6 Hz, 1′-H)]. The positions of two hydroxyl groups, an olefin function, and a glycosidic linkage were determined by HMBC and ^{1}H–^{1}H COSY experiments shown in Fig. 1. Long-range correlations were observed between the 23-protons [δ 1.36 (s)] and the 3, 4, 5, 24-carbons, between the 18-proton [δ 3.32 (m)] and the 13, 17, 19-carbons, between the 30-protons [δ 1.38 (s)] and the 19, 20, 21-carbons, and between the 1′-proton and the 24-carbon. The stereostructures of the 3, 4, and 20-positions were clarified by a pROESY experiment, which showed NOE correlations between the 3-proton and the 23-protons, between the 24-protons and the 25-protons [δ 0.83 (s)], and between the 26, 30-protons and the 18-proton (Fig. 1). Consequently, the structure of eupteleasaponin VIII was determined to be 3β,20α,24-trihydroxy-29-norolean-12-en-28-oic acid 24-*O*-β-D-glucopyranoside (**10**).

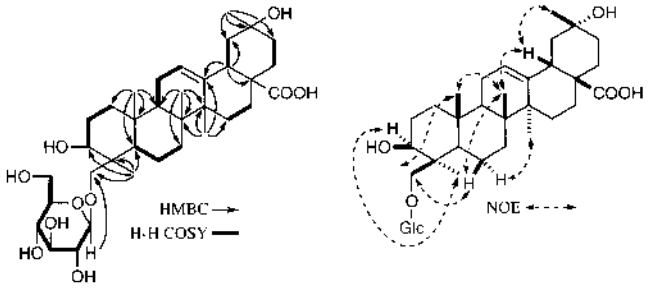

Fig. 1. H–H COSY, HMBC, and pROESY Correlations of Eupteleasaponin VIII (**10**)

Eupteleasaponin IX (**11**), isolated as colorless fine crystals from $CHCl_3$–MeOH of mp 221—225 °C, liberated D-glucose and L-rhamnose on acid hydrolysis,[4,5] and its IR spectrum showed absorption bands due to hydroxyl and carboxyl functions. Here again, the molecular formula $C_{43}H_{68}O_{15}$ of **11** was identified from its negative- and positive-ion FAB-MS [quasimolecular ion peaks: *m/z* 823 $(M-H)^-$, *m/z* 825 $(M+H)^+$, *m/z* 847 $(M+Na)^+$] and by high-resolution MS measurement. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **11** showed the presence of a 3β,20α,24-trihydroxy-29-norolean-12-en-28-oic acid moiety [δ 3.32 (dd-like, 18-H), 3.51 (dd, J=5.3, 10.2 Hz, 3-H), 4.55, 4.62 (both m, 24-H_2), 5.51 (br s, 12-H)], a β-D-glucopyranosyl moiety [δ 4.79 (d, J=7.6 Hz, 1′-H)], an α-L-rhamnopyranosyl moiety [δ 1.66 (d, J=5.9 Hz, 6″-H_3), 5.52 (br s, 1″-H)], and an acetyl moiety [δ 1.89 (s, Ac-2)]. The carbon signals assignable to the aglycone moiety in the ^{13}C-NMR spectrum of **11** were shown to be superimposable on those of **10**. In the HMBC experiment of **11**, long-range correlations were observed between the 1′-proton and the 24-carbon, between the 1″-proton and the 4′-carbon, and between the 6′-protons and the acetyl carbonyl carbon. Consequently, the structure of eupteleasaponin IX was determined to be 3β,20α,24-trihydroxy-29-norolean-12-en-28-oic acid 24-*O*-[α-L-rhamnopyranosyl(1→4)]-6′-*O*-acetyl-β-D-glucopyranoside (**11**).

Eupteleasaponin X (**12**) was also isolated as colorless fine crystals from $CHCl_3$–MeOH of mp 237—239 °C. The IR spectrum of **12** showed absorption bands at 1740 and 1655 cm^{-1} due to two carboxyl functions and the strong ab-

sorption bands at 3389 and 1076 cm^{-1} suggestive of an oligoglycosidic structure. Here again, the molecular formula $C_{42}H_{66}O_{14}$ of **12** was clarified from its negative- and positive-ion FAB-MS [quasimolecular ion peaks: *m/z* 793 $(M-H)^-$, *m/z* 795 $(M+H)^+$, *m/z* 817 $(M+Na)^+$] and by high-resolution MS measurement. A fragment ion peak was observed at *m/z* 647 $(M-C_6H_{11}O_4)^-$, which was derived by cleavage of the glycoside linkage at the rhamnose, in the negative-ion FAB-MS of **12**. Acid hydrolysis of **12** with 5% aqueous H_2SO_4–1,4-dioxane, liberated serratagenic acid,[7] D-glucose, and L-rhamnose.[5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **12** showed signals due to a serratagenic acid moiety [δ 3.33 (dd, *J*=4.0, 11.6 Hz, 3-H), 3.41 (dd, *J*=4.0, 14.2 Hz, 18-H), 5.53 (br s, 12-H)], a β-D-glucopyranosyl moiety [δ 4.83 (d, *J*=7.9 Hz, 1′-H)], and an α-L-rhamnopyranosyl moiety [δ 1.67 (d, *J*=6.3 Hz, 6″-H_3), 5.82 (br s, 1″-H)]. In the HMBC experiment of **12**, long-range correlations were observed between the 1′-proton and the 3-carbon and between the 1″-proton and the 4′-carbon. Consequently, the structure of eupteleasaponin X was determined to be serratagenic acid 3-*O*-α-L-rhamnopyranosyl(1→4)-β-D-glucopyranoside (**12**).

Eupteleasaponin XI (**13**), obtained as colorless fine crystals from $CHCl_3$–MeOH, liberated oleanolic acid, D-xylose, D-glucose, and L-rhamnose on acid hydrolysis[5] and its IR spectrum showed absorption bands due to hydroxyl and carboxyl functions. In the negative- and positive-ion FAB-MS of **13**, quasimolecular ion peaks were observed at *m/z* 1041 $(M-H)^-$ and *m/z* 1065 $(M+Na)^+$ and the molecular formula $C_{53}H_{86}O_{20}$ was determined by high-resolution MS measurement. Fragment ion peaks were observed at *m/z* 895 $(M-C_6H_{11}O_4)^-$ and *m/z* 749 $(M-C_{12}H_{21}O_8)^-$, which were derived by cleavage of the glycoside linkage at the rhamnose moiety, and were observed in the negative-ion FAB-MS of **13**. The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **13** showed the presence of an oleanolic acid moiety [δ 3.28 (dd-like, 18-H), 3.30 (dd-like, 3-H), 5.47 (br s, 12-H)], a β-D-xylopyranosyl moiety [δ 4.84 (1H, d, *J*=5.5 Hz, 1′-H)], a β-D-glucopyranosyl moiety [δ 5.00 (d, *J*=7.9 Hz, 1″-H)], and two α-L-rhamnopyranosyl moieties [δ 1.62, 1.67 (both d, *J*=6.1 Hz, 6‴, 6⁗-H_3), 5.76, 6.01 (both br s, 1‴, 1⁗-H)]. In the HMBC experiment of **13**, long-range correlations were observed between the following protons and carbons: 1′-H and 3-C; 1″-H and 3′-C; 1‴-H and 2″-C; 1⁗-H and 4″-C. On the basis of the above evidence, the structure of eupteleasaponin XI was determined to be oleanolic acid 3-*O*-{α-L-rhamnopyranosyl(1→2)-[α-L-rhamnopyranosyl(1→4)]-β-D-glucopyranosyl(1→3)}-β-D-xylopyranoside (**13**).

Eupteleasaponin XII (**14**) was also obtained as colorless fine crystals from $CHCl_3$–MeOH. The molecular formula $C_{52}H_{82}O_{21}$ was determined from the negative- and positive-ion FAB-MS [*m/z* 1041 $(M-H)^-$ and *m/z* 1065 $(M+Na)^+$] and by high-resolution MS measurement. Fragment ion peaks were observed at *m/z* 909 $(M-C_5H_9O_4)^-$, *m/z* 895 $(M-C_6H_{11}O_4)^-$, *m/z* 879 $(M-C_6H_{11}O_5)^-$, and *m/z* 733 $(M-C_{12}H_{23}O_9)^-$ were observed in the negative-ion FAB-MS of **14**. Acid hydrolysis of **14** with 5% aqueous H_2SO_4–1,4-dioxane (1 : 1, v/v) furnished D-xylose, L-rhamnose, and D-glucose.[5] The ^{1}H-NMR (pyridine-d_5) and ^{13}C-NMR (Table 1) spectra[6] of **14** showed signals assignable to an akebonoic acid moiety [δ 3.16 (dd, *J*=4.6, 13.2 Hz, 18-H), 3.36 (dd, *J*=4.3, 11.9 Hz, 3-H), 4.69, 4.75 (both s, 29-H_2), 5.44 (br s, 12-H)], two β-D-glucopyranosyl moieties [δ 4.73 (d, *J*=7.6 Hz, 1′-H), 6.24 (d, *J*=7.9 Hz, 1⁗-H)], an α-L-arabinopyranosyl moiety [δ 5.28 (d, *J*=7.9 Hz, 1″-H)], and an α-L-rhamnopyranosyl moiety [δ 1.67 (d, *J*=6.3 Hz, 6‴-H_3), 5.81 (br s, 1‴-H)]. The carbon signals due to the aglycone structure in the ^{13}C-NMR data were very similar to those of eupteleasaponins I (**1**), II (**2**), III (**3**), and IV (**4**).[3] In the HMBC experiment of **14**, long-range correlations were observed between the following protons and carbons: 1′-H and 3-C; 1″-H and 3′-C; 1‴-H and 4′-C; 1⁗-H and 28-C. Consequently, the structure of eupteleasaponin XII was determined to be 28-*O*-β-D-glucopyranosylakebonoic acid 3-*O*-α-L-arabinopyranosyl(1→3)-[α-L-rhamnopyranosyl(1→4)]-β-D-glucopyranoside (**14**).

The structures of principle eupteleasaponins are characterized by noroleanane-type triterpenoid aglycones and the 24-*O*-glycosidic structure. As far as we know, this is the first example of 24-*O*-glycosides. The noroleanane-type triterpene aglycone in eupteleasaponins VIII (**10**) and IX (**11**) has been placed as an intermediate in the biogenetic pathway from oleanolic acid to eupteleogenin in this plant as shown in Fig. 2.

Experimental

The following instruments were used to obtain physical data: specific rotations, Horiba SEPA-300 digital polarimeter (*l*=5 cm); IR spectra, Shimadzu FTIR-8100 spectrometer; ^{1}H-NMR spectra, JNM-LA500 (500 MHz)

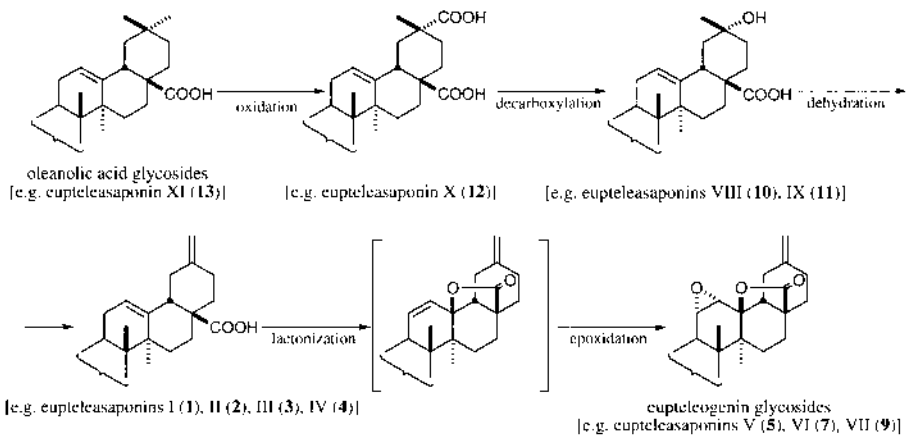

Fig. 2

spectrometer; ^{13}C-NMR spectra, JNM-LA500 (125 MHz) spectrometer with tetramethylsilane as an internal standard; MS and high-resolution MS, JEOL JMS-SX 102A mass spectrometer; HPLC, Shimadzu LC-10AS chromatograph.

The following experimental conditions were used for chromatography: normal-phase column chromatography; Silica gel BW-200 (Fuji Silysia Chemical, Ltd., 150—350 mesh), reversed-phase column chromatography; Chromatorex ODS DM1020T (Fuji Silysia Chemical, Ltd., 100—200 mesh): TLC, pre-coated TLC plates with Silica gel 60F_{254} (Merck, 0.25 mm) (normal-phase) and Silica gel RP-18 F_{254S} (Merck, 0.25 mm) (reversed-phase); HPTLC, pre-coated TLC plates with Silica gel RP-18 WF_{254S} (Merck, 0.25 mm) (reversed-phase). Detection was done by spraying with 1% aqueous $Ce(SO_4)_2$–10% aqueous H_2SO_4, followed by heating.

Isolation of Eupteleasaponins VI (7), VI Acetate (8), VII (9), VIII (10), IX (11), X (12), XI (13), and XII (14) from the Fresh Leaves of *E. polyandra* Eupteleasaponins VI (**7**), VI acetate (**8**), VII (**9**), VIII (**10**), IX (**11**), X (**12**), XI (**13**), and XII (**14**) were isolated from the fresh leaves of *E. polyandra* collected in the Kitayama area of Kyoto Prefecture, Japan, as described earlier.[1)]

Eupteleasaponin VI (**7**): Colorless fine crystals from $CHCl_3$–MeOH, mp 184—187 °C, $[\alpha]_D^{25}$ +46.8° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{47}H_{72}O_{18}Na$ $(M+Na)^+$: 947.4616. Found: 947.4642. IR (KBr): 3453, 1775, 1658, 1055 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.90, 1.09, 1.12, 1.18, 1.23 (3H each, all s, 25, 26, 24, 27, 23-H_3), 1.65 (3H, d, *J*=5.3 Hz, 6″-H_3), 2.33 (1H, dd-like, 18-H), 3.03 (1H, br s, 11-H), 3.14 (1H, d-like, 12-H), 3.38 (1H, dd-like, 3-H), 4.73 (2H, m, 29-H_2), 4.80 (1H, d-like, 1′-H), 5.08 (1H, d, *J*=7.0 Hz, 1‴-H), 6.36 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Positive-ion FAB-MS: *m/z* 947 $(M+Na)^+$.

Eupteleasaponin VI Acetate (**8**): Colorless fine crystals from $CHCl_3$–MeOH, mp 180—184 °C, $[\alpha]_D^{26}$ +31.9° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{49}H_{74}O_{19}Na$ $(M+Na)^+$: 989.4722. Found: 989.4716. IR (KBr): 3453, 1761, 1658, 1060 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.91, 1.09, 1.13, 1.17, 1.24 (3H each, all s, 25, 26, 24, 27, 23-H_3), 1.66 (3H, d, *J*=6.3 Hz, 6″-H_3), 2.17 (3H, s, Ac-2), 2.32 (1H, dd-like, 18-H), 3.02 (1H, br s, 11-H), 3.14 (1H, d-like, 12-H), 3.40 (1H, dd, *J*=3.9, 11.0 Hz, 3-H), 4.73 (2H, m, 29-H_2), 4.84 (1H, d, *J*=7.3 Hz, 1′-H), 5.01 (1H, d, *J*=7.6 Hz, 1‴-H), 6.37 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 965 $(M-H)^-$, 923 $(M-C_2H_3O)^-$. Positive-ion FAB-MS: *m/z* 989 $(M+Na)^+$.

Eupteleasaponin VII (**9**): Colorless fine crystals from $CHCl_3$–MeOH, mp 168—172 °C, $[\alpha]_D^{26}$ +14.6° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{53}H_{82}O_{22}Na$ $(M+Na)^+$: 1093.5195. Found: 1093.5184. IR (KBr): 3432, 1775, 1654, 1068 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.90, 1.10, 1.13, 1.18, 1.25 (3H each, all s, 25, 26, 24, 27, 23-H_3), 1.67, 1.69 (3H each, both d, *J*=6.1 Hz, 6‴, 6″-H_3), 2.35 (1H, dd, *J*=3.7, 13.8 Hz, 18-H), 3.01 (1H, br s, 11-H), 3.14 (1H, d, *J*=2.3 Hz, 12-H), 3.38 (1H, dd, *J*=4.3, 11.9 Hz, 3-H), 4.71, 4.74 (1H each, both s, 29-H_2), 4.83 (1H, d, *J*=7.3 Hz, 1′-H), 5.04 (1H, d, *J*=7.9 Hz, 1‴-H), 5.69, 6.37 (1H each, both br s, 1⁗, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 1069 $(M-H)^-$, 923 $(M-C_6H_{11}O_4)^-$, 761 $(M-C_{12}H_{23}O_9)^-$. Positive-ion FAB-MS: *m/z* 1093 $(M+Na)^+$, 1115 $(M+2Na-H)^+$.

Eupteleasaponin VIII (**10**): Colorless fine crystals from $CHCl_3$–MeOH, mp 199—201 °C, $[\alpha]_D^{26}$ +73.9° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{35}H_{56}O_{10}Na$ $(M+Na)^+$: 659.3771. Found: 659.3785. IR (KBr): 3432, 1709, 1078 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.83, 0.92, 1.22, 1.36, 1.38 (3H each, all s, 25, 26, 27, 23, 30-H_3), 3.32 (1H, m, 18-H), 3.51 (1H, dd-like, 3-H), 4.30, 4.48 (1H each, both m, 24-H_2), 4.90 (1H, d, *J*=7.6 Hz, 1′-H), 5.51 (1H, br s, 12-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Positive-ion FAB-MS: *m/z* 659 $(M+Na)^+$.

Eupteleasaponin IX (**11**): Colorless fine crystals from $CHCl_3$–MeOH, mp 221—225 °C, $[\alpha]_D^{26}$ +34.9° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{43}H_{69}O_{15}$ $(M+H)^+$: 825.4637. Found: 825.4644. IR (KBr): 3432, 1730, 1042 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.91, 0.97, 1.22, 1.48, 1.56 (3H each, all s, 25, 26, 27, 23, 30-H_3), 1.66 (1H, d, *J*=5.9 Hz, 6″-H_3), 1.89 (3H, s, Ac-2), 3.32 (1H, dd-like, 18-H), 3.51 (1H, dd, *J*=5.3, 10.2 Hz, 3-H), 4.55, 4.62 (1H each, both m, 24-H_2), 4.79 (1H, d, *J*=7.6 Hz, 1′-H), 5.51 (1H, br s, 12-H), 5.52 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 823 $(M-H)^-$, 781 $(M-C_2H_3O)^-$, 677 $(M-C_6H_{11}O_4)^-$, 635 $(C_8H_{13}O_5)^-$, 473 $(M-C_{14}H_{23}O_9)^-$. Positive-ion FAB-MS: *m/z* 825 $(M+H)^+$, 847 $(M+Na)^+$.

Eupteleasaponin X (**12**): Colorless fine crystals from $CHCl_3$–MeOH, mp 237—239 °C, $[\alpha]_D^{26}$ +12.1° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{42}H_{66}O_{14}Na$ $(M+Na)^+$: 817.4350. Found: 817.4366. IR (KBr): 3389, 1740, 1655, 1076 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.84, 0.98, 1.00, 1.57 (3H each, all s, 25, 24, 26, 30-H_3), 1.30 (6H, s, 23, 27-H_3), 1.67 (3H, d, *J*=6.3 Hz, 6″-H_3), 3.33 (1H, dd, *J*=4.0, 11.6 Hz, 3-H), 3.41 (1H, dd, *J*=4.0, 14.2 Hz, 18-H), 4.83 (1H, d, *J*=7.9 Hz, 1′-H), 5.53 (1H, br s, 12-H), 5.82 (1H, br s, 1″-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 793 $(M-H)^-$, 647 $(M-C_6H_{11}O_4)^-$. Positive-ion FAB-MS: *m/z* 795 $(M+H)^+$, 817 $(M+Na)^+$.

Eupteleasaponin XI (**13**): Colorless fine crystals from $CHCl_3$–MeOH, mp 241—245 °C, $[\alpha]_D^{26}$ +11.6° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{53}H_{86}O_{20}Na$ $(M+Na)^+$: 1065.5610. Found: 1065.5619. IR (KBr): 3432, 1705, 1085 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.86, 0.96, 1.00, 1.02, 1.11, 1.18, 1.31 (3H each, all s, 25, 29, 26, 30, 24, 23, 27-H_3), 1.62, 1.67 (3H each, both d, *J*=6.1 Hz, 6‴, 6⁗-H_3), 3.28 (1H, dd-like, 18-H), 3.30 (1H, dd-like, 3-H), 4.84 (1H, d, *J*=5.5 Hz, 1′-H), 5.00 (1H, d, *J*=7.9 Hz, 1″-H), 5.47 (1H, br s, 12-H), 5.76, 6.01 (1H each, both br s, 1⁗, 1‴-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 1041 $(M-H)^-$, 895 $(M-C_6H_{11}O_4)^-$, 749 $(M-C_{12}H_{21}O_8)^-$. Positive-ion FAB-MS: *m/z* 1065 $(M+Na)^+$.

Eupteleasaponin XII (**14**): Colorless fine crystals from $CHCl_3$–MeOH, mp 175—177 °C, $[\alpha]_D^{25}$ +33.9° (*c*=0.1, MeOH). High-resolution positive-ion FAB-MS: Calcd for $C_{52}H_{82}O_{21}Na$ $(M+Na)^+$: 1065.5246. Found: 1065.5264. IR (KBr): 3348, 1745, 1655, 1076 cm^{-1}. ^{1}H-NMR (500 MHz, pyridine-d_5) δ: 0.88, 0.98, 1.08, 1.25, 1.30 (3H each, all s, 25, 24, 26, 23, 27-H_3), 1.67 (3H, d, *J*=6.3 Hz, 6‴-H_3), 3.16 (1H, dd, *J*=4.6, 13.2 Hz, 18-H), 3.36 (1H, dd, *J*=4.3, 11.9 Hz, 3-H), 4.69, 4.75 (1H each, both s, 29-H_2), 4.73 (1H, d, *J*=7.6 Hz, 1′-H), 5.28 (1H, d, *J*=7.9 Hz, 1″-H), 5.44 (1H, br s, 12-H), 5.81 (1H, br s, 1‴-H), 6.24 (1H, d, *J*=7.9 Hz, 1⁗-H). ^{13}C-NMR (125 MHz, pyridine-d_5) δ_C: given in Table 1. Negative-ion FAB-MS: *m/z* 1041 $(M-H)^-$, 909 $(M-C_5H_9O_4)^-$, 895 $(M-C_6H_{11}O_4)^-$, 879 $(M-C_6H_{11}O_5)^-$, 733 $(M-C_{12}H_{23}O_9)^-$. Positive-ion FAB-MS: *m/z* 1065 $(M+Na)^+$.

Acid Hydrolysis of Eupteleasaponins VI (7), VI Acetate (8), VII (9), VIII (10), IX (11), X (12), XI (13), and XII (14) A solution of eupteleasaponins (**7**—**14**, 5 mg each) in 5% aq. H_2SO_4–1,4-dioxane (1 : 1, v/v, 2 ml) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and residue was removed by filtration. After removal of the solvent from the filtrate *in vacuo*, the residue was transferred to a Sep-Pak C18 cartridge with H_2O and MeOH. The MeOH eluate from **12** and **13** was concentrated and the residue was purified by normal-phase silica gel column chromatography [1.0 g, $CHCl_3$–MeOH–H_2O (10 : 3 : 1, v/v)] to give sapogenols [serratagenic acid (2.5 mg, 82% from **12**) and oleanolic acid (1.7 mg, 78% from **13**)], which were identified by physical data comparison with an authentic sample or a reported value.[7)] The H_2O eluate was concentrated and the residue was treated with L-cysteine methyl ester hydrochloride (4 mg) in pyridine (0.5 ml) at 60 °C for 1 h. After reaction, the solution was treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.2 ml) at 60 °C for 1 h. The supernatant was then subjected to GLC analysis to identify the derivatives of D-glucose (i) form **7**—**14**, L-rhamnose (ii) from **7**, **8**, **9**, **11**—**14**, D-galactose (iii) from **9**, D-xylose (iv) from **13**, L-arabinose (v) from **14**; GLC conditions: Supeluco STB™-1, 30 m×0.25 mm (i.d.) capillary column, column temperature 230 °C, He flow rate 15 ml/min, t_R: i (24.2 min), ii (15.4 min), iii (24.6 min), iv (19.4 min), v (15.0 min).

Alkaline Hydrolysis of Eupteleasaponin VI Acetate (8) with 0.1% NaOMe–MeOH Giving Eupteleasaponin VI (7) A solution of **8** (20 mg) in 0.1% NaOMe–MeOH (2 ml) was stirred under reflux for 2 h. The reaction mixture was neutralized with Dowex HCR W2 (H^+ form) and the resin was removed by filtration. Evaporation of the solvent from filtrate *in vacuo* yielded a product which was separated by normal-phase silica gel column chromatography [200 mg, $CHCl_3$–MeOH–H_2O (7 : 3 : 1, lower layer, v/v)] to give eupteleasaponin VI (**7**, 17 mg). **7** was identified on the basis of TLC, $[\alpha]_D$, and ^{1}H- and ^{13}C-NMR spectra comparisons with an authentic sample.

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6) The ^{1}H- and ^{13}C-NMR spectra of **7**—**14** were assigned with the aid of homo- and hetero-correlation spectroscopy (^{1}H–^{1}H, ^{1}H–^{13}C COSY), distortionless enhancement by polarization transfer (DEPT), homo- and hetero-nuclear Hartmann–Hahn spectroscopy (^{1}H–^{1}H, ^{1}H–^{13}C HOHAHA), heteonuclear multiple bond correlation (HMBC), and phase-sensitive rotating nuclear Overhauser effect (pROESY) experiments.

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