Studies on the Constituents of Leguminous Plants. XI.[1] The Structures of New Triterpenoids from *Wistaria brachybotrys* SIEB. *et* ZUCC.[2]

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Two new triterpenoids (wistariasapogenols A and B) were obtained from the knots of *Wistaria brachybotrys* (Leguminosae), and characterized as 22-oxo-3β,24,30-trihydroxyolean-12-ene (1) and 3β,22β,24,30-tetrahydroxyolean-12-ene (8) by analysis of the two-dimensional nuclear magnetic resonance spectra (^{1}H–^{1}H correlation spectroscopy (COSY), ^{1}H–^{13}C COSY and ^{1}H–^{13}C long-range COSY) and the difference nuclear Overhauser effect spectra.

Keywords triterpene; 22-oxo-3β,24,30-trihydroxyolean-12-ene; 3β,22β,24,30-tetrahydroxyolean-12-ene; wistariasapogenol A; wistariasapogenol B; *Wistaria brachybotrys*; Leguminosae; 2D-NMR; difference NOE

The knots of *Wistaria brachybotrys* SIEB. *et* ZUCC. (Leguminosae) have been used in Japanese folk medicine for the treatment of gastric cancer. A few phytosterols and isoflavonoids have been isolated from *W. floribunda* and reported.[3,4] In a previous paper, we reported the anti-tumor promoting effects of isoflavonoids from the knots of *W. brachybotrys*.[5] As a continuation of our chemical studies on the constituents of leguminous plants and on the potential anti-tumor promoting activities of crude drugs, we have now isolated two new triterpenes named wistariasapogenol A (**1**) and B (**8**), together with a known triterpene, soyasapogenol B (**3**),[6] obtained by acid hydrolysis of the crude saponin fraction. In this paper, we describe the structure elucidation of these triterpenoids.

The crude saponin fraction was fractionated by column chromatography on silica gel to obtain four fractions, I, II, III and IV. From fractions I and II, soyasaponin I and soyasaponin II[6a,7] were isolated and identified, respectively. Fraction III was hydrolyzed with 20% H_2SO_4 in ethanol to yield wistariasapogenol A, $C_{30}H_{48}O_4$, (**1**) as colorless prisms. In the infrared (IR) spectrum (1697 cm^{-1}) and the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (at δ216.01), **1** showed the presence of a carbonyl group. Acetylation of **1** with pyridine and acetic anhydride afforded a triacetate (**4**). In the mass spectra (MS) of **1** and **4**, retro Diels–Alder type fragment ion[8] peaks (from the A, B rings at *m/z* 224 and 308, and from the D, E rings at *m/z* 248 and 290, respectively) were observed, suggesting the presence of two hydroxy groups on the A, B rings and one hydroxy group and carbonyl group on the D, E rings. From the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **4** and the ^{13}C-NMR spectrum of **1**, it was deduced that two hydroxyl groups are present at positions 3 and 24 on the A ring, as in soyasapogenol B (Tables I and II).

Two dimensional ^{1}H[^{1}H]-, ^{1}H[^{13}C]- and ^{1}H[^{13}C] long-range shift correlation (^{1}H–^{1}H correlation spectroscopy (COSY), ^{1}H–^{13}C COSY and ^{1}H–^{13}C long-range COSY) experiments were carried out to determine the positions of the carbonyl group and hydroxymethyl group on the D or E ring. In the ^{1}H–^{1}H COSY spectrum of wistariasapogenol

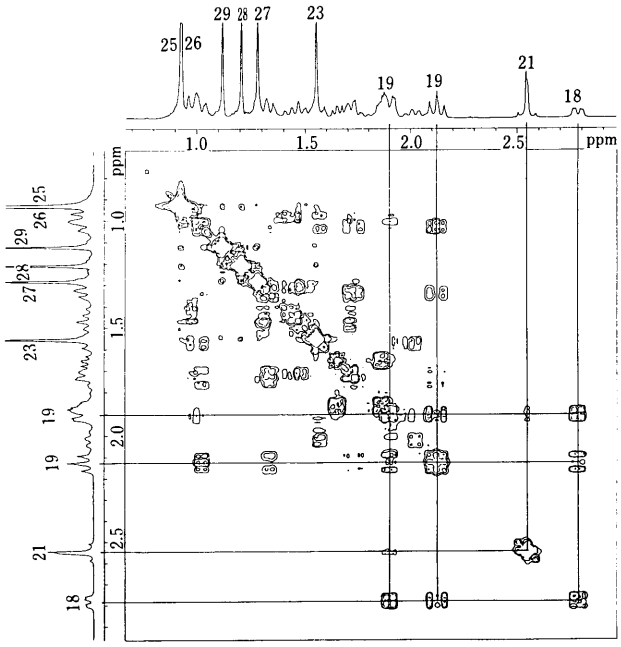


Fig. 1. A Part of the ^{1}H–^{1}H COSY Spectrum of **1** in Pyridine-d_5

TABLE I. ^{1}H-NMR Chemical Shift Values of the Acetates **4**, **5**, **9** and **10** (300 MHz in $CDCl_3$)

	3-αH	12-H	18-H	22-αH	24-H_2	30-H_2	–$COCH_3$	–CH_3
10	4.59 (dd, J=5.7, 10.1)	5.26 (t, J=3.5)	2.28 (dd, J=3.8, 13.5)	4.64 (t, J=3.6)	4.14, 4.37 (ABq, J=11.7)		2.03, 2.04, 2.07	0.81, 0.89, 0.97, 0.98, 1.00, 1.03, 1.14
4	4.59 (dd, J=5.9, 10.1)	5.31 (t, J=3.4)	2.41 (dd, J=4.2, 13.5)		4.14, 4.37 (ABq, J=11.7)	3.76, 3.92 (ABq, J=11.1)	2.05, 2.06, 2.07	0.96, 0.99, 2×1.01, 1.03, 1.20
5	4.59 (dd, J=5.9, 10.1)	5.28 (t, J=3.7)		3.37 (dd, J=1.9, 7.8)	4.14, 4.37 (ABq, J=11.7)	3.67, 3.69 (ABq, J=7.5)	2.04, 2.07	0.87, 0.95, 0.98, 1.02, 1.03, 1.14
9	4.60 (dd, J=5.8, 10.7)	5.26 (t, J=3.4)	2.20 (dd, J=3.7, 13.6)	4.66 (t, J=3.1)	4.14, 4.37 (ABq, J=11.8)	3.99, 4.12 (ABq, J=10.7)	2.00, 2.04, 2.05, 2.07	0.81, 0.94, 0.96, 0.98, 1.03, 1.15

Chemical shifts are shown in δ-values (ppm) with coupling constants (J) in Hz. The abbreviations t, dd and ABq refer to triplet, doublet of doublet and AB type quartet, respectively.

TABLE II. ^{13}C-NMR Chemical Shift Values of **1**, **2**, **3** and **8** (75 MHz, in Pyridine-d_5)

	1	2	3	8
C-1	38.91	38.90	38.98	38.98
C-2	28.43	28.41	28.48	28.47
C-3	80.11	80.10	80.16	80.18
C-4	43.20	43.18	43.24	43.24
C-5	56.34	56.36	56.40	56.42
C-6	19.11	19.13	19.17	19.17
C-7	33.39	33.60	33.58	33.55
C-8	39.90	39.81	40.08	40.10
C-9	48.01	48.06	48.18	48.16
C-10	37.05	37.08	37.07	37.07
C-11	24.05	24.08	24.13	24.09
C-12	123.97	123.66	122.46	122.77
C-13	142.22	142.78	144.87	144.68
C-14	42.10	42.83	42.41	42.39
C-15	25.51	25.67	26.47	26.47
C-16	27.35	26.48	28.71	28.73
C-17	47.80	38.56	38.06	38.10
C-18	47.45	45.18	45.38	45.21
C-19	42.95	46.06	46.86	42.16
C-20	38.88	39.97	30.94	35.90
C-21	47.03	39.28	42.35	38.79
C-22	216.01	85.75	75.58	75.23
C-23	23.60	23.59	23.63	23.60
C-24	64.57	64.56	64.63	64.61
C-25	16.21	16.23	16.31	16.28
C-26	16.91	16.95	17.12	17.10
C-27	25.41	25.12	25.76	25.86
C-28	21.31	23.53	28.71	21.28
C-29	26.99	22.55	33.30	28.57
C-30	68.26	76.41	21.23	70.32

A (**1**), the relationship of the 18-H proton (at δ 2.78) to the 19-H_2 methylene protons (at δ 1.90 and 2.14) (ABX system) was elucidated as shown in Fig. 1. In addition, a cross peak due to the W type ^{1}H–^{1}H long range coupling between one of the 19-H_2 at δ1.90 and the methylene proton signal at δ 2.55 assigned to the α-position to the carbonyl group was also observed.

Further, we measured the ^{1}H–^{13}C long range COSY of **1** in order to confirm the connectivities of the partial structure and substituent groups. As shown in formula A, the olefinic proton at δ 5.40 (12-H) is correlated with the carbons at δ 42.95 (C-19), 42.10 (C-14) and 47.45 (C-18), and the carbon at δ 42.95 (C-19) is correlated with protons at δ 2.55 (α-position to carbonyl), 2.78 (18-H) and 1.14 (CH_3). Similarly, the methyl carbon at δ 26.99 (it showed a cross peak with the protons at δ 1.14 in the ^{1}H–^{13}C COSY spectrum, as shown in Fig. 2) is also correlated with the proton signals at δ 2.14 (19-H), 2.55 and 3.68 (–CH_2OH), and the methylene carbon signals at δ 47.03 (it showed a cross peak with the proton signals at δ 2.55 in the ^{1}H–^{13}C COSY spectrum) is correlated with the protons at δ 1.14 (C-29-H_3) and 1.90 (19-H). The carbonyl carbon signal at δ216.01 is correlated with the proton signals at δ 2.55 and 1.23 (CH_3). Some other significant long-range ^{1}H–^{13}C correlations are indicated by arrows in formula A (Fig. 3). From these results, the position of the carbonyl group was concluded to be at C-22, and the methyl and hydroxymethyl groups are assigned at C-29 or C-30, respectively.

The relative stereochemistry and position of the hydroxymethyl group of **1** were determined on the basis of the results of difference nuclear Overhauser effect (difference

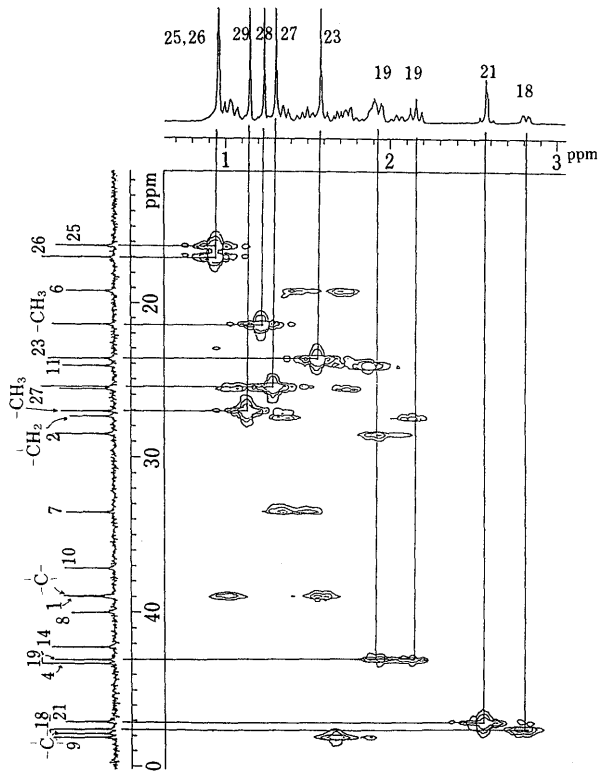


Fig. 2. A Part of ^{1}H–^{13}C COSY Spectrum of **1** in Pyridine-d_5

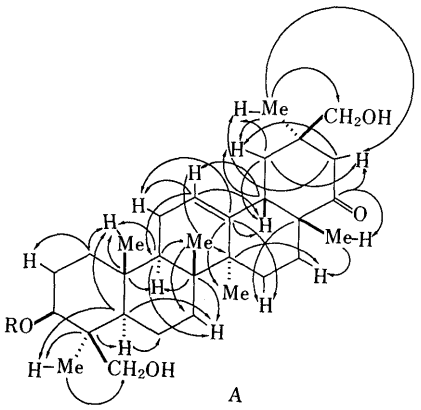


Fig. 3. Correlations in ^{1}H–^{13}C Long-Range COSY of **1**

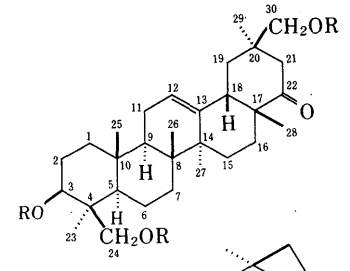
NOE) experiments. Irradiation at 18-H (at δ 2.78) enhanced the signal intensity of the methyl protons (δ 1.23, C-28-H_3), one of the methylene protons (δ 1.90, 19-β-H), an olefinic proton (δ5.40, 12-H) and methylene protons (δ3.68) of hydroxymethyl, and irradiation at the methyl proton signals [δ 1.29 (C-27-H_3) and 1.14 (C-29-H_3), respectively] enhanced the signal intensity of the methylene proton at δ 2.14 (19-α-H). Some other significant NOE enhancements observed are also shown by arrows in formula B (Fig. 4). Therefore, 18-H, 19-H (at δ 1.90), the hydroxymethyl group and the methyl group (at δ 1.23) are oriented at the β-side of the E ring, and C-27-H_3, 19-H (at δ 2.14) and the methyl group (at δ 1.14) are located at the α-side of the E ring. From these data, **1** was characterized as 22-oxo-3β, 24,30-trihydroxyolean-12-ene.

The other sapogenol (**2**), $C_{30}H_{48}O_3$, was obtained from fraction IV by acid hydrolysis with 20% H_2SO_4 in ethanol as colorless prisms, and the acetylation of **2** afforded a di-

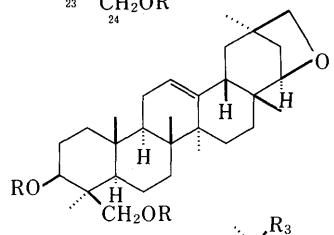
acetate (**5**). In the MS of **2** and **5**, retro Diels–Alder type fragment ion peaks (at *m/z* 224 and 308 due to the A, B rings and at *m/z* 232 and 232 due to the D, E rings, respectively) were observed, suggesting the presence of two hydroxy groups on the A, B rings and one ether group on the D, E rings. From the 2D-NMR spectra of **2** as well as **1**, **2** was characterized as 22β,30-oxido-3β,24-dihydroxyolean-12-ene. However, the major saponin of fraction IV was permethylated with dimsyl carbanion and methyl iodide[9] followed by acid hydrolysis to yield a trimethylether (**6**). The dimethylether of **2** was not obtained by this method, and the acetylation of **6** afforded a monoacetyl trimethylether (**7**). From these experiments, it was deduced that **2** was an artifact formed from tetrahydroxysapogenol by dehydroxylation. Hydrolysis of fraction IV with 1 N H_2SO_4 in ethanol afforded a tetrahydroxysapogenol, $C_{30}H_{50}O_4$, (wistariasapogenol B, **8**) together with the ethereal compound (**2**). Acetylation of **8** with pyridine and acetic anhydride afforded the tetraacetate (**9**) as a colorless amorphous solid. From a comparison of the ^{13}C-NMR spectrum of **8** and the ^{1}H-NMR spectrum of **9** with those of soyasapogenol B and related compounds,[6] it was deduced that the genuine sapogenol **8** was 3β,22β,24,30-tetrahydroxyolean-12-ene. All ^{13}C-NMR signals of **8** were reasonably assigned as listed in Table II by the methods of distortionless enhancement by polarization transfer and ^{1}H–^{13}C COSY.

Furthermore, the stereochemistry of **8** was confirmed by difference NOE experiments, as in the case of **1**. Irradiation at 18-H (δ 2.62), enhanced the signal intensities of the olefinic proton (δ5.35), hydroxymethyl protons (δ3.91) and one of the C-19 methylene protons (δ 1.68), and irradiation at the methyl signal (δ 1.16) enhanced the signal intensities of the hydroxymethyl protons (δ 3.91), one each of the methylene protons at C-19 and C-21 (δ1.90 and 1.73, respectively) and the proton at C-22 (δ3.78). Irradiation at the methyl proton signal (δ 1.28) which was assigned to C-27 also enhanced the signal intensity of one of the methylene protons at C-19 (δ 1.90). Some other significant NOE results are indicated by arrows in formula C (Fig. 4). It was concluded that the structure of the genuine sapogenol is as shown by the formula **8**.[10]

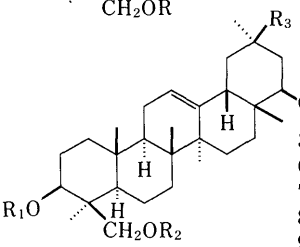
The structure elucidation of glycosides of **1** and **8**, and examination of the anti-tumor promoting activities of these compounds are in progress.



1 : R=-H
4 : R=-Ac



2 : R=-H
5 : R=-Ac



3 : R_1=R_2=-H, R_3=-Me
6 : R_1=-H, R_2=-Me, R_3=-CH_2OMe
7 : R_1=-Ac, R_2=-Me, R_3=-CH_2OMe
8 : R_1=R_2=-H, R_3=-CH_2OH
9 : R_1=R_2=-Ac, R_3=-CH_2OAc
10 : R_1=R_2=-Ac, R_3=-Me

Chart 1

Experimental

Melting points were taken on a Yanagimoto micro melting point apparatus, and are uncorrected. IR spectra were recorded on a Shimadzu IR-408 spectrometer. MS were determined on a Hitachi M-80 mass spectrometer. ^{1}H-and ^{13}C-NMR spectra were recorded on a Varian XL-300 using tetramethylsilane as an internal standard. 2D-NMR and difference NOE spectra were recorded on a JEOL JNM GX-400 spectrometer. Optical rotations were measured on a JASCO DIP-181 digital polarimeter. Preparative high performance liquid chromatography (HPLC) was carried out on a Nihon Bunseki Kogyo LC-09 using a gel permeation chromatography column (300 mm × 2) with an refractive index (RI) detector.

Plant Materials and Extraction The knots of *W. brachybotrys* were collected at Shikoku, Japan, in 1986. Herbarium specimens have been deposited in the herbarium of Kyoto Pharmaceutical University. The chopped-up knots of *W. brachybotrys* (2.5 kg) were exhaustively extracted with 80% hot MeOH. The solvent was removed *in vacuo*, leaving a dark

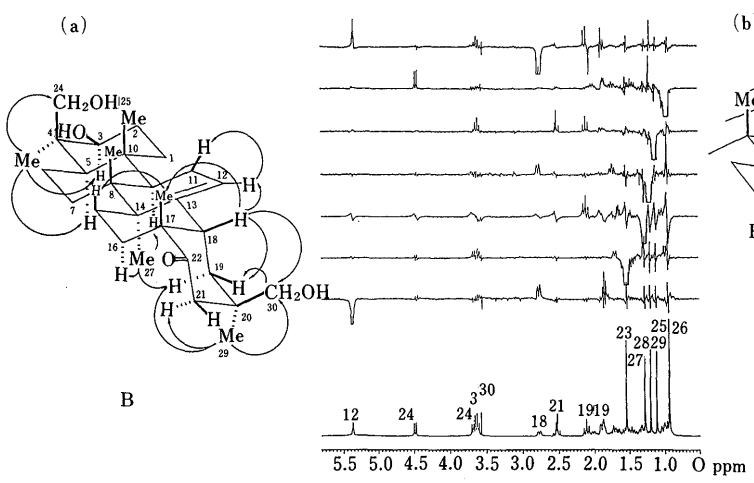


Fig. 4(a). Difference NOE Spectrum of **1**

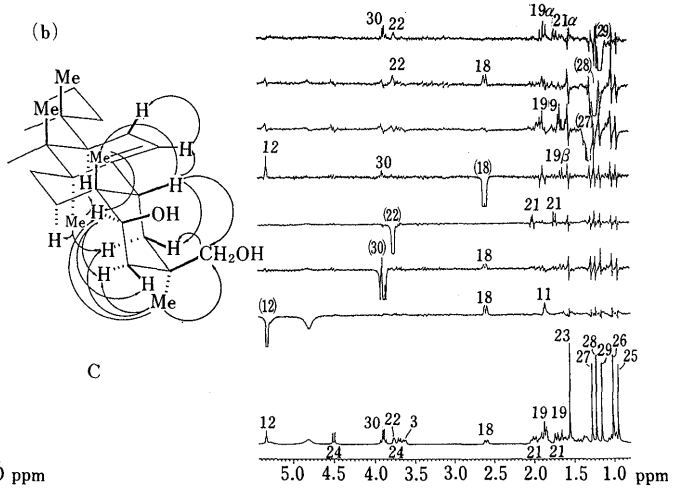


Fig. 4(b). Difference NOE Spectrum of **8**

brown syrup. The syrup was suspended in water and extracted with *n*-hexane, ether, AcOEt and *n*-BuOH saturated with water, in that order. The *n*-BuOH layer was evaporated *in vacuo* to give 42 g of a dark residue.

Isolation and Hydrolysis of Crude Saponin The *n*-BuOH extract (10 g) was fractionated by column chromatography on silica gel (solvent: MeOH–$CHCl_3$–H_2O (65 : 35 : 10)) to afford four fractions, I, II, III and IV. These fractions were methylated with diazomethane in MeOH. From the methylated crude saponin of fractions I and II, methyl esters of soyasaponin I (80 mg) and soyasaponin II (35 mg) were, respectively, isolated and shown to be identical with authentic samples in terms of HPLC and thin layer chromatography (TLC) behavior, and IR and ^{13}C-NMR spectra. Fraction III (200 mg) was refluxed with 20% H_2SO_4 (30 ml) in EtOH (30 ml) for 2.5 h, and concentrated to half the initial volume *in vacuo*. The mixture was extracted with EtOAc, and the extract was washed with water and evaporated *in vacuo*. The residue was chromatographed on silica gel, and purified by recrystallization from MeOH and water to yield soyasapogenol B (**3**, 30 mg) as colorless needles, and wistariasapogenol A (**1**, 22 mg) as colorless prisms. Soyasapogenol B was identical with an authentic sample (TLC behavior and IR spectrum). Properties of **1** are as follows: mp 265—267 °C, $[\alpha]_D^{27}$ +53.9° (c=0.17, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1696 (>C=O). HRMS *m/z*: 472.3572 (M^+, $C_{30}H_{48}O_4$, requires 472.3552), 248.1787 (base, $C_{16}H_{24}O_2$ due to D/E rings, requires 248.1775), 224.1803 ($C_{14}H_{24}O_2$ due to A/B rings, requires 224.1774). ^{13}C-NMR (Table II). Fraction IV (100 mg) was hydrolyzed with 20% H_2SO_4 by the same method as described above, and purified by recrystallization from MeOH–H_2O to yield **2** (25 mg) as colorless prisms. mp 243—244 °C, $[\alpha]_D^{27}$ +46.3° (c=0.20, MeOH), IR ν_{max}^{KBr} cm^{-1}: 3400—3500 (OH). HRMS *m/z*: 456.3629 (M^+, $C_{30}H_{48}O_3$, requires 456.3601), 232.1821 (base, $C_{16}H_{24}O_1$ due to D/E rings, requires 232.1825), 224.1764 ($C_{14}H_{24}O_2$ due to A/B rings, requires 224.1774). ^{13}C-NMR (Table II).

Fraction IV (150 mg) was refluxed with 1 N H_2SO_4 (10 ml) in EtOH (10 ml) for 1.5 h, and the reaction mixture was concentrated to half the initial volume *in vacuo*. The mixture was extracted with EtOAc, and the organic layer was evaporated *in vacuo*. The residue was fractionated by column chromatography on silica gel, and then purified by HPLC (recycled 13 times with MeOH) followed by recrystallization from MeOH to afford **2** (12 mg) and **8** (35 mg) as colorless prisms, mp 287—289 °C, $[\alpha]_D^{20}$ +133.2° (c=0.28, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400—3450 (OH). MS *m/z*: 474 (M^+), 456 (M−H_2O), 250 (D/E ring residue), 232 (250−H_2O). *Anal.* Calcd for $C_{30}H_{50}O_4 \cdot H_2O$: C, 73.12; H, 10.64. Found: C, 72.98; H, 10.82. ^{13}C-NMR (Table II).

Methylation and Methanolysis of Crude Saponin Fraction IV Dimsyl carbanion solution (10 ml, prepared from 1 g of NaH and 50 ml of dimethyl sulfoxide (DMSO)) was added to a solution of the crude saponin fraction IV (180 mg) in DMSO. The mixture was stirred for 1 h at room temperature under an N_2 stream. After addition of CH_3I (15 ml), the reaction mixture was stirred for 3 h at room temperature under an N_2 stream. The mixture was poured into ice-water, and extracted with Et_2O. The Et_2O extract was methanolyzed in anhydrous HCl–MeOH for 3 h. The reaction mixture was neutralized with Ag_2CO_3, and evaporated to afford a yellowish residue. The residue was chromatographed on silica gel to yield **6** (28 mg) as a colorless powder, mp 109—111 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1100 (R-O-R). ^{1}H-NMR (δ) $CDCl_3$: 5.20 (1H, t, J=3.7 Hz, C-12-H), 3.33, 3.31, 3.30 (3H, each s, O-CH_3), 1.22, 1.12 (3H, each s, C-CH_3), 0.94 (6H, s, 2×C-CH_3), 0.92, 0.85 (3H, each s, C-CH_3). MS *m/z*: 516 (M^+), 278 (D/E ring residue), 238 (A/B ring residue), 233.

General Procedure for Acetylation The acetates described below were prepared by acetylation of compounds **1**, **2**, **6** and **8** in Ac_2O in pyridine at room temperature for 18 h, followed by usual work up and purification by flash column chromatography[11] (silica gel: Merck Kieselgel 60, 230 mesh; solvent: benzene–acetone (9 : 1)) followed by recrystallization from MeOH to yield pure compounds.

The triacetate (**4**) (7 mg) was prepared from **1** (10 mg) as colorless prisms: mp 194—196 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735 (ROCOCH_3), 1705 (>C=O). MS *m/z*: 598 (M^+), 538 (M−AcOH), 478 (M−2×AcOH), 308 (A/B ring residue), 290 (D/E ring residue), 275 (290−CH_3), 248 (308−AcOH), 188 (248−AcOH). ^{1}H-NMR (Table I).

The diacetate (**5**) (8 mg) was prepared from **2** (13 mg) as a colorless powder: mp 198—199 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730 (ROCOCH_3), 1040 (C-O-C). MS *m/z*: 540 (M^+), 525 (M−15), 480 (M−AcOH), 308 (A/B ring residue), 248 (308−AcOH), 232 (D/E ring residue), 188 (248−AcOH). ^{1}H-NMR (Table I).

The monoacetate (**7**) (5 mg) was prepared from **6** (10 mg) as a colorless amorphous solid: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730 (ROCOCH_3), 1100 (C-O-C). MS *m/z*: 558 (M^+), 527 (M−OCH_3), 280 (A/B ring residue), 278 (D/E ring residue), 233 (278−OCH_3+H^+), 220 (280−AcOH). ^{1}H-NMR, $CDCl_3$ (δ): 5.21 (1H, t, J=3.3 Hz, C-12-H), 4.55 (1H, dd, J=11.2, 5.2 Hz, C_3-αH), 3.34, 3.30, 3.29 (3H, each s, OCH_3), 2.05 (3H, s, $OCOCH_3$), 1.11 (3H, s, C-CH_3), 1.01 (6H, s, 2×C-CH_3), 0.96, 0.94, 0.85 (3H, each s, C-CH_3).

The tetraacetate (**9**) (7 mg) was prepared from **8** (16 mg) as a colorless amorphous solid: IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730 (ROCOCH_3). MS *m/z*: 642 (M^+), 582 (M−AcOH), 522 (M−AcOH×2), 334 (D/E ring residue), 308 (A/B ring residue), 274 (334−AcOH), 248 (308−AcOH), 214 (334−AcOH×2), 188 (308−AcOH×2). ^{1}H-NMR (Table I).

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References and Notes

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