Characterization of New Sweet Triterpene Saponins from *Albizia myriophylla*[1]

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Received May 17, 2002

Five new oleanane-type triterpene saponins, albiziasaponins A−E (**1**−**5**), were isolated from the stems of *Albizia myriophylla* collected in Thailand, together with two known triterpene saponins, licorice-saponin F3 and yunganoside B_1. The structures of the new compounds were elucidated on the basis of chemical and physicochemical evidence. In addition, when sensory tests were performed on sweetness, albiziasaponin B (**2**), with a carbonyl group at the C-30 position, was found to show a potent sweetness intensity relative to sucrose (600 times).

Albizia myriophylla Benth. (Leguminosae) is widely distributed in southeastern Asian countries such as Thailand (local name "Cha Em Thai") and Vietnam ("Cay Song Ran"). In the Thai and Vietnamese systems of traditional medicine, the stems of *A. myriophylla* are used to substitute for licorice due to their sweet taste. In chemical studies on *A. myriophylla*, several lignan glycosides and alkaloids were isolated from the bark of Vietnamese *A. myriophylla*.[2] However, the sweet-tasting constituents of this natural medicine were left undetermined.

In the course of our characterization studies on bioactive saponins and glycosides,[3] five new oleanane-type triterpene saponins, albiziasaponins A−E (**1**−**5**), were isolated from the stems of *A. myriophylla* collected in Thailand. In addition, the two principal saponins, albiziasaponins A (**1**) and B (**2**), were examined for relative sweetness compared with sucrose. This paper deals with the isolation, structural elucidation, and sensory evaluation of the new saponin constituents of *A. myriophylla*.

Results and Discussion

The stems of *A. myriophylla* (collected in Kanchanaburi Province, Thailand) were cut and extracted with methanol under reflux. The methanolic extract was partitioned with a mixture of EtOAc and water to furnish the EtOAc-soluble and H_2O-soluble fractions. The H_2O-soluble fraction was separated by silica gel and octadecyl silica gel (ODS) column chromatography and finally HPLC to give albiziasaponins A [**1**, 1.49% (w/w) from the natural medicine], B (**2**, 0.13%), C (**3**, 0.007%), D (**4**, 0.021%), and E (**5**, 0.016%) together with albiziasaponin A monomethyl ester (**1a**, 0.012%), licorice-saponin F3[4] (0.008%), and yunganoside B_1[5] (0.003%). Albiziasaponin A (**1**), $[\alpha]_D^{24}$ −28.2° (MeOH), was obtained as colorless fine crystals from $CHCl_3$−MeOH with mp 226−229 °C. The IR spectrum of **1** showed absorption bands at 1760 and 1640 cm^{-1} ascribable to γ-lactone and olefin functions and broad bands at 3453 and 1047 cm^{-1} suggestive of an oligoglycoside structure. In the positive- and negative-ion FABMS of **1**, quasimolecular ion peaks were observed at *m/z* 969 $[M + H]^+$, 991 $[M + Na]^+$, and 967 $[M - H]^-$, and HRFABMS analysis revealed the molecular formula of **1** to be $C_{48}H_{72}O_{20}$. Furthermore, fragment ion peaks at *m/z* 821 $[M - C_6H_{11}O_4]^-$ and 645 $[M - C_{12}H_{19}O_{10}]^-$ derived by cleavage of the glycosidic linkages at the C-2″ and C-2′ positions, respectively, were observed in the negative-ion FABMS of **1**. On enzymatic hydrolysis of **1** with glycyrrhizic acid hydrolase, 24-hydroxy-11-deoxoglabrolide (**6**)[6] was obtained as the aglycon. Acid hydrolysis with 5% aqueous sulfuric acid (H_2SO_4)−1,4-dioxane (1:1) of **1** liberated D-glucuronic acid and L-rhamnose, which were identified by GLC analysis of their trimethylsilyl thiazolidine derivatives.[7] The ^1H and ^{13}C NMR (pyridine-d_5, Table 1) spectra of **1**, which were assigned by various NMR experiments,[8] showed signals assignable to two glucuronopyranosyl moieties [δ 5.06 (d, J = 7.6 Hz, H-1′) and 5.87 (d, J = 7.6 Hz, H-1″)] and a rhamnopyranosyl moiety [δ 1.81 (d, J = 6.4 Hz, H-6‴) and 6.27 (br s, H-1‴)], together with an aglycon moiety [δ 0.71, 0.82, 0.98, 1.20, 1.22, 1.51 (all s, H_3-25, 26, 28, 29, 27, and 23), 2.13 (dd, J = 6.4, 13.3 Hz, H-18), 3.45 (dd, J = 4.3, 11.6 Hz, H-3), 3.48, 4.40 (both d, J = 11.6 Hz, H_2-24), 4.20 (br d, J = ca. 6 Hz, H-22), 5.13 (br s, H-12)]. The oligoglycoside structure and its connectivity to the aglycon in **1** were confirmed by a HMBC experiment. Thus, long-range correlations were observed between the signals of H-1′ and C-3, H-1″ and C-2′, and H-1‴ and C-2″. On the basis of this evidence, the structure of albiziasaponin A (**1**) was elucidated as shown. The 6′-methyl ester of **1**, albiziasaponin A monomethyl ester (**1a**), was also isolated. The position of the methyl ester of **1a** was determined from the HMBC correlation between the methyl ester proton [δ 3.77 (s, $-OCH_3$)] and C-6′ (δ_C 169.6).

Albiziasaponin B (**2**), $[\alpha]_D^{24}$ +4.6° (MeOH), was also obtained as colorless fine crystals from $CHCl_3$−MeOH with mp 220−223 °C. The IR spectrum of **2** showed absorption bands at 3453, 1730, 1645, and 1047 cm^{-1}, ascribable to hydroxyl, carboxyl, olefin, and ether functions. The molecular formula, $C_{48}H_{74}O_{20}$, of **2** was determined from the positive- and negative-ion FABMS (*m/z* 993 $[M + Na]^+$ and 969 $[M - H]^-$) and by HRFABMS. Furthermore, fragment ion peaks at *m/z* 823 $[M - C_6H_{11}O_4]^-$, 647 $[M - C_{12}H_{19}O_{10}]^-$, and 471 $[M - C_{18}H_{27}O_{16}]^-$, which were derived by cleavage of the glycosidic linkage at the C-2″, C-2′, and C-3 positions, were observed in the negative-ion FABMS of **2**. Enzymatic hydrolysis of **2** with glycyrrhizic acid hydrolase afforded azukisapogenol (**7**),[9] while acid hydrolysis of **2** with 5% aqueous H_2SO_4−1,4-dioxane (1:1) liberated D-glucuronic acid and L-rhamnose.[7] The ^1H and ^{13}C NMR (pyridine-d_5, Table 1) spectra of **2** showed signals assignable to an azukisapogenol moiety [δ 0.72, 0.88, 0.90, 1.31, 1.37, 1.52 (all s, H_3-25, 28, 26, 27, 29, and 23), 2.39 (dd, J = 3.1, 12.8 Hz, H-18), 3.45 (dd, J = 4.0, 12.8 Hz, H-3), 3.49, 4.39 (both d, J = 11.6 Hz, H_2-24), 5.44 (br s, H-12)], two glucurono-

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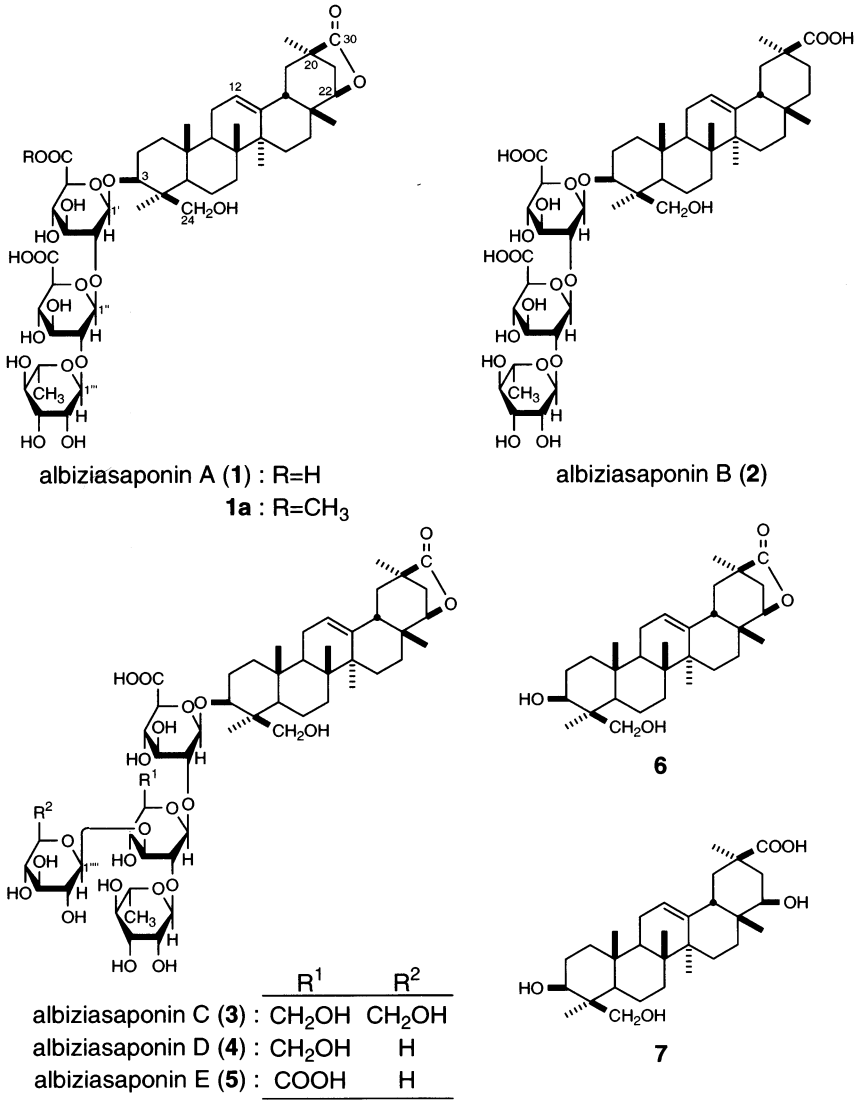
10.1021/np020220l CCC: $22.00
Published on Web 09/28/2002

Chart 1



pyranosyl moieties [δ 5.07 (d, J = 7.6 Hz, H-1′) and 5.90 (d, J = 7.9 Hz, H-1″)], and a rhamnopyranosyl moiety [δ 1.80 (d, J = 6.1 Hz, H-6‴) and 6.31 (br s, H-1‴)]. The proton and carbon signals assignable to the oligoglycoside moiety of **2** were superimposable on those of **1**. The oligoglycoside structure and its connectivity were confirmed by HMBC experiment, which showed long-range correlations between the signals of H-1′ and C-3, H-1″ and C-2′, and H-1‴ and C-2″. Consequently, the structure of albiziasaponin B (**2**) was determined as shown.

Albiziasaponin C (**3**), $[\alpha]_D^{24}$ −12.6° (MeOH), was also obtained as colorless fine crystals from $CHCl_3$−MeOH with mp 269−272 °C. The positive- and negative-ion FABMS of **3** showed quasimolecular and fragment ion peaks at m/z 1139 $[M + Na]^+$, 1115 $[M - H]^-$, 969 $[M - C_6H_{11}O_4]^-$, 953 $[M - C_6H_{11}O_5]^-$, and m/z 645 $[M - C_{18}H_{31}O_{14}]^-$. The HRFABMS revealed the molecular formula of **3** to be $C_{54}H_{84}O_{24}$, and the IR spectrum showed absorption bands at 3453, 1765, 1632, 1078, and 1048 cm^{-1}, ascribable to hydroxyl, γ-lactone, olefin, and ether functions. On acid hydrolysis of **3** with 5% aqueous H_2SO_4−1,4-dioxane (1:1) D-glucuronic acid, D-glucose, and L-rhamnose were detected.[7] On enzymatic hydrolysis of **3** with glycyrrhizic acid hydrolase, the aglycon **6** was obtained. The ^1H and ^{13}C NMR (pyridine-d_5, Table 1) spectra of **3** showed signals assignable to an aglycon moiety [δ 0.68, 0.82, 0.98, 1.18, 1.19, 1.46 (all s, H_3-25, 26, 28, 29, 27, and 23), 2.13 (dd, J = 6.7, 12.8 Hz, H-18), 3.33, 4.28 (both d-like, H_2-24), 3.42 (dd, J = 4.6, 11.9 Hz, H-3), 4.15 (br d, J = ca. 6 Hz, H-22), 5.12 (br s, H-12)], a glucuronopyranosyl moiety [δ 4.97 (d, J = 7.6 Hz, H-1′)], two glucopyranosyl moieties [δ 5.01 (d, J = 7.6 Hz, H-1⁗) and 5.75 (d, J = 7.6 Hz, H-1″)], and a rhamnopyranosyl moiety [δ 1.75 (d, J = 6.4 Hz, H-6‴) and 6.33 (br s, H-1‴)]. In the HMBC experiment on **3**, long-range correlations were observed between the following proton and carbon signals: H-1′ and C-3, H-1″ and C-2′, H-1‴ and C-2″, and H-1⁗ and C-3″. These findings led to the elucidation the structure of albiziasaponin C (**3**) as shown.

Albiziasaponins D (**4**) and E (**5**) were isolated as colorless fine crystals from $CHCl_3$−MeOH (**4**: mp 238−240 °C; **5**: mp 240−242 °C). Their IR spectra showed absorption bands assignable to hydroxyl, γ-lactone, olefin, and ether functions (**4**: 3445, 1765, 1655, and 1043 cm^{-1}; **5**: 3445, 1752, 1655, 1078, and 1047 cm^{-1}), which were similar to those of **1** and **3**. The positive- and negative-ion FABMS of **4** showed quasimolecular ion peaks at m/z 1087 $[M + H]^+$, 1109 $[M + Na]^+$, and 1085 $[M - H]^-$, in addition to fragment ion peaks at m/z 953 $[M - C_5H_9O_4]^-$, 939 $[M - C_6H_{11}O_4]^-$, and 645 $[M - C_{17}H_{29}O_{13}]^-$. In turn, quasimolecular ion peaks at m/z 1101 $[M + H]^+$, 1123 $[M + Na]^+$, and 1099 $[M - H]^-$ and fragment ion peaks at m/z 967

Table 1. ^{13}C NMR Data for Albiziasaponins A−E (**1**−**5**) and Albiziasaponin A Monomethyl Ester (**1a**)[a]

	1	2	3	4	5	1a		1	2	3	4	5	1a
C-1	38.8	38.8	38.5	38.5	38.5	38.9	C-1′	104.9	104.9	105.2	105.2	104.9	104.7
C-2	26.5	26.7	26.5	26.5	26.5	26.5	C-2′	78.2	78.3	78.4	78.4	78.0	78.2
C-3	90.4	90.5	91.8	91.8	90.4	90.3	C-3′	77.5	77.6	78.5	78.4	78.3	76.5
C-4	44.1	44.1	43.8	43.8	44.2	44.3	C-4′	73.7	73.7	73.7	73.7	73.7	73.5
C-5	56.3	56.3	56.3	56.3	56.3	56.3	C-5′	78.2	78.3	77.4	77.4	77.7	78.3
C-6	18.7	18.8	18.6	19.0	19.0	18.9	C-6′	172.4	172.3	172.2	172.3	172.2	169.6
C-7	33.4	33.1	33.3	33.3	33.5	33.5	$COOCH_3$						51.9
C-8	42.9	41.9	42.9	42.8	42.9	42.8	C-1″	102.1	102.1	101.8	101.8	101.9	102.1
C-9	47.6	47.8	47.6	47.6	47.7	47.6	C-2″	78.6	78.7	77.3	77.6	78.6	78.6
C-10	36.6	36.6	36.5	36.5	36.6	36.6	C-3″	77.1	77.2	88.9	87.6	85.9	76.5
C-11	23.9	24.0	24.0	24.0	24.0	23.9	C-4″	73.0	73.1	67.9	70.7	71.0	72.6
C-12	125.1	122.8	125.2	125.1	125.2	125.0	C-5″	78.4	78.3	77.6	77.7	77.1	78.4
C-13	140.9	145.1	140.8	140.8	140.8	140.6	C-6″	171.8	171.5	61.3	61.3	170.9	183.5
C-14	39.7	40.1	39.7	39.7	39.7	39.7	C-1″	102.2	102.2	102.3	102.4	100.6	102.3
C-15	25.1	27.3	25.2	25.2	25.2	25.1	C-2″	72.3	72.2	72.3	72.2	72.3	72.2
C-16	26.6	26.6	26.6	26.6	26.7	26.6	C-3″	72.6	72.6	72.8	72.7	72.8	72.6
C-17	36.1	32.4	36.1	36.1	36.1	36.0	C-4″	74.4	74.4	74.4	74.3	74.4	74.2
C-18	45.2	48.7	45.2	45.2	45.2	45.2	C-5″	69.5	69.5	69.5	69.5	69.7	69.5
C-19	42.6	43.5	42.7	42.7	42.7	42.6	C-6″	18.9	18.9	19.0	19.0	18.9	18.9
C-20	42.3	44.3	42.3	42.3	42.3	42.2	C-1‴			104.5	105.2	105.1	
C-21	38.5	31.9	38.5	38.5	38.8	38.4	C-2‴			75.0	74.7	72.3	
C-22	84.7	39.1	84.5	84.5	84.5	84.3	C-3‴			78.6	78.4	74.3	
C-23	23.1	23.1	22.9	22.8	23.2	23.3	C-4‴			71.6	67.8	69.3	
C-24	63.2	63.3	63.5	63.4	63.3	63.1	C-5‴			78.6	67.1	67.5	
C-25	15.5	15.5	15.6	15.6	15.6	15.5	C-6‴			62.5			
C-26	16.8	16.9	16.8	16.8	16.8	16.8							
C-27	24.9	26.2	25.0	24.9	25.0	24.9							
C-28	23.5	28.5	23.6	23.5	23.6	23.5							
C-29	20.5	29.1	20.6	20.6	20.6	20.5							
C-30	180.6	179.6	180.2	180.2	180.2	179.9							

[a] Measured in pyridine-d_5 at 125 MHz.

$[M - C_5H_9O_4]^-$ and 953 $[M - C_6H_{11}O_4]^-$ were observed for **5**. HRFABMS analysis revealed the molecular formulas of **4** and **5** to be $C_{53}H_{82}O_{23}$ and $C_{53}H_{80}O_{24}$, respectively. Enzymatic hydrolysis of **4** and **5** with glycyrrhizic acid hydrolase furnished **6** as their common aglycon. Acid hydrolysis of **4** with 5% aqueous H_2SO_4−1,4-dioxane (1:1) liberated D-glucuronic acid, D-glucose, L-rhamnose, and D-xylose, while D-glucuronic acid, L-rhamnose, and D-xylose were obtained by acid hydrolysis of **5**.[7] The ^1H and ^{13}C NMR (pyridine-d_5, Table 1) spectra of **4** showed signals due to a xylopyranosyl moiety [δ 4.86 (d, J = 7.3 Hz, H-1‴)], a glucuronopyranosyl moiety [δ 4.97 (d, J = 8.0 Hz, H-1′)], a glucopyranosyl moiety [δ 5.74 (d, J = 7.6 Hz, H-1″)], and a rhamnopyranosyl moiety [δ 1.74 (d, J = 6.1 Hz, H-6‴) and 6.24 (br s, H-1‴)], which were similar to those of **3**, except for the C-3″ xylopyranosyl moiety. In turn, the ^1H and ^{13}C NMR (pyridine-d_5, Table 1) spectra of **5** showed signals assignable to a xylopyranosyl moiety [δ 4.89 (d, J = 7.3 Hz, H-1‴)], two glucuronopyranosyl moieties [δ 5.03 (d, J = 7.6 Hz, H-1′) and 5.89 (d, J = 7.6 Hz, H-1″)], and a rhamnopyranosyl moiety [δ 1.75 (d, J = 6.4 Hz, H-6‴) and 6.15 (br s, H-1‴)], which were similar to those of **1**, except for the C-3″ xylopyranosyl moiety. Finally, the oligoglycoside structures of **4** and **5** were characterized by HMBC experiments on **4** and **5**, in which long-range correlations were observed between the following proton and carbon signals: H-1′ and C-3, H-1″ and C-2′, H-1‴ and C-2″, and H-1⁗ and C-3‴, respectively. Consequently, the structures of albiziasaponins D (**4**) and E (**5**) were elucidated as shown.

Since the stems of *A. myriophylla* have been used as a substitute for licorice and the methanolic extract showed sweetness, we examined the sweetness of the principal saponins (**1** and **2**). Compound **2**, with a carboxyl group at the C-30 position, showed potent sweetness, which was 600 times sweeter than that of sucrose, while the sweetness of **1**, which has a lactone group at the C-30 position, was only 5 times sweeter than sucrose. Accordingly, a free carboxyl group at the C-30 position seems to be essential for the potent sweetness with this compound class. Compound **2** was also the most abundant sweet-tasting constituent of this plant.

Experimental Section

General Experimental Procedures. 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; ^1H NMR spectra, JEOL LNM-500 (500 MHz) spectrometer; ^{13}C NMR spectra, JEOL LNM-500 (125 MHz) spectrometer with tetramethylsilane as an internal standard; FABMS and HRFABMS, JEOL JMS-SX 102A mass spectrometer; HPLC detector, Shimadzu RID-6A refractive index detector.

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

Plant Material. The stems of *A. myriophylla* were collected in Muang District, Kanchanaburi Province, Thailand, in July 2001. It was identified by one of the authors (Y.P.). A voucher of the plant is on file in our laboratory (T-02).

Extraction and Isolation. The dried stems of *A. myriophylla* (1.0 kg) were cut and extracted three times with MeOH under reflux. Evaporation of the solvent under reduced pressure provided the MeOH extract (151.5 g, 15.2%), and a part of it (121.2 g) was partitioned with EtOAc−H_2O (1:1). Removal of the solvents under reduced pressure yielded an EtOAc-soluble fraction (24.6 g, 3.1%) and a H_2O-soluble fraction (96.6 g, 12.1%). The H_2O-soluble fraction (83.0 g) was separated by reversed-phase silica gel column chromatography [2.0 kg, H_2O

→ MeOH−H_2O (60:40) → MeOH] to give six fractions [Fr. 1 (43.1 g), Fr. 2 (0.9 g), Fr. 3 (9.1 g), Fr. 4 (12.1 g), Fr. 5 (16.0 g), and Fr. 6 (1.8 g)]. Fraction 3 (9.1 g) was subjected to normal-phase silica gel column chromatography [30 g, $CHCl_3$−MeOH−H_2O (15:3:1, lower layer → 6:4:1) → MeOH] to give albiziasaponin A (**1**, 850 mg, 0.12%). Fraction 4 (200 mg) was purified by HPLC [YMC-Pack Ph, 250 × 20 mm i.d., MeOH−1% aqueous AcOH (70:30)] to furnish **1** (97 mg, 0.85%). Fraction 5 (16.0 g) was further separated by reversed-phase silica gel column chromatography [480 g, MeOH−H_2O (70:30) → MeOH] to afford four fractions [Fr. 5-1 (2.6 g), Fr. 5-2 (6.0 g), Fr. 5-3 (2.2 g), and Fr. 5-4 (5.2 g)]. Fraction 5-2 (3.0 g) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., MeOH−1% aqueous AcOH (70:30)] to give eight further fractions [Fr. 5-2-1 (213 mg), Fr. 5-2-2 (102 mg), Fr. 5-2-3 (24 mg), Fr. 5-2-4 (89 mg), Fr. 5-2-5 (=**1**, 1800 mg, 0.52%), Fr. 5-2-6 (339 mg), Fr. 5-2-7 (324 mg), and Fr. 5-2-8 (109 mg)]. Fraction 5-2-4 (89 mg) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., CH_3CN−1% aqueous AcOH (35:75)] to furnish albiziasaponin E (**5**, 56 mg, 0.016%). Fraction 5-2-6 (339 mg) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., CH_3CN−1% aqueous AcOH (35:75)] to afford albiziasaponins C (**3**, 24 mg, 0.007%) and D (**4**, 15 mg, 0.004%). Fraction 5-2-7 (324 mg) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., CH_3CN−1% aqueous AcOH (40:60)] to give albiziasaponin A monomethyl ester (**1a**, 40 mg, 0.012%) and **4** (59 mg, 0.017%). Fraction 5-2-8 (109 mg) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., CH_3CN−1% aqueous AcOH (40:60)] to give licorice-saponin F3 (29 mg, 0.008%). Fraction 5-3 (1.8 g) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., MeOH−1% aqueous AcOH (80:20)] to give Fr. 5-3-1 (134 mg), Fr. 5-3-2 (30 mg), Fr. 5-3-3 (79 mg), Fr. 5-3-4 [albiziasaponin B (**2**, 800 mg, 0.13%)], and Fr. 5-3-5 (757 mg). Finally, fraction 5-3-1 (134 mg) was purified by HPLC [YMC-Pack ODS-A, 250 × 20 mm i.d., MeOH−1% aqueous AcOH (75:35)] to give yunganoside B_1 (19 mg, 0.003%).

Licorice-saponin F3[4] and yunganoside B_1[5] were identified by comparison of their physical data ($[\alpha]_D$, IR, ^1H NMR, ^{13}C NMR, MS) with reported values.

Albiziasaponin A (1): colorless fine crystals from $CHCl_3$−MeOH, mp 226−229 °C; $[\alpha]_D^{24}$ −28.2° (*c* 0.10, MeOH); IR (KBr) ν_{max} 3453, 2940, 1760, 1640, 1047 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) δ 0.71, 0.82, 0.98, 1.20, 1.22, 1.51 (3H each, all s, H_3-25, 26, 28, 29, 27, and 23), 1.81 (3H, d, J = 6.4 Hz, H-6‴), 2.13 (1H, dd, J = 6.4, 13.3 Hz, H-18), 3.45 (1H, dd, J = 4.3, 11.6 Hz, H-3), 3.48, 4.40 (1H each, both d, J = 11.6 Hz, H_2-24), 4.20 (1H, br d, J = ca. 6 Hz, H-22), 5.06 (1H, d, J = 7.6 Hz, H-1′), 5.13 (1H, br s, H-12) 5.87 (1H, d, J = 7.6 Hz, H-1″), 6.27 (1H, br s, H-1‴); ^{13}C NMR data, see Table 1; positive-ion FABMS *m/z* 969 $[M + H]^+$, 991 $[M + Na]^+$; negative-ion FABMS *m/z* 967 $[M - H]^-$, 821 $[M - C_6H_{11}O_4]^-$, 645 $[M - C_{12}H_{19}O_{10}]^-$; HRFABMS *m/z* 969.4724 (calcd for $C_{48}H_{73}O_{20}$ $[M + H]^+$, 969.4695), 991.4543 (calcd for $C_{48}H_{72}O_{20}Na$ $[M + Na]^+$, 991.4515).

Albiziasaponin A monomethyl ester (1a): colorless fine crystals from $CHCl_3$−MeOH, mp 209−212 °C; $[\alpha]_D^{25}$ −16.6° (*c* 0.86, MeOH); ^1H NMR (pyridine-d_5, 500 MHz) δ 0.79, 0.84, 0.97, 1.19, 1.20, 1.54 (3H each, all s, H_3-25, 26, 28, 29, 27, and 23), 1.78 (3H, d, J = 6.1 Hz, H-6‴), 2.13 (1H, dd like, H-18), 3.45 (1H, dd, J = 4.8, 11.9 Hz, H-3), 3.54, 4.43 (1H each, both d like, H_2-24), 3.77 (3H, s, $-OCH_3$), 4.15 (1H, br d, J = ca. 6 Hz, H-22), 5.03 (1H, d, J = 7.4 Hz, H-1′), 5.13 (1H, br s, H-12) 5.87 (1H, d, J = 7.7 Hz, H-1″), 6.29 (1H, br s, H-1‴); ^{13}C NMR data, see Table 1; positive-ion FABMS *m/z* 983 $[M + H]^+$, 1005 $[M + Na]^+$; negative-ion FABMS *m/z* 981 $[M - H]^-$, 835 $[M - C_6H_{11}O_4]^-$.

Albiziasaponin B (2): colorless fine crystals from $CHCl_3$−MeOH, mp 220−223 °C; $[\alpha]_D^{24}$ +4.6° (*c* 0.10, MeOH); IR (KBr) ν_{max} 3453, 2930, 1730, 1645, 1047 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) δ 0.72, 0.88, 0.90, 1.31, 1.37, 1.52, (3H each, all s, H_3-25, 28, 26, 27, 29, and 23), 1.80 (3H, d, J = 6.1 Hz, H-6‴), 2.39 (1H, dd, J = 3.1, 12.8 Hz, H-18), 3.45 (1H, dd, J = 4.0, 12.8 Hz, H-3), 3.49, 4.39 (1H each, both d, J = 11.6 Hz, H_2-24), 5.07 (1H, d, J = 7.6 Hz, H-1′), 5.44 (1H, br s, H-12), 5.90 (1H, d, J = 7.9 Hz, H-1″), 6.31 (1H, br s, H-1‴); ^{13}C NMR data, see Table 1; positive-ion FABMS *m/z* 993 $[M + Na]^+$; negative-ion FABMS *m/z* 969 $[M - H]^-$, 823 $[M - C_6H_{11}O_4]^-$, 647 $[M - C_{12}H_{19}O_{10}]^-$, 471 $[M - C_{18}H_{27}O_{16}]^-$; HRFABMS *m/z* 993.4696 (calcd for $C_{48}H_{74}O_{20}Na$ $[M + Na]^+$, 993.4671).

Albiziasaponin C (3): colorless fine crystals from $CHCl_3$−MeOH, mp 269−272 °C; $[\alpha]_D^{24}$ −12.6° (*c* 0.10, MeOH); IR (KBr) ν_{max} 3453, 2926, 1765, 1632, 1078, 1048 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) δ 0.68, 0.82, 0.98, 1.18, 1.19, 1.46 (3H each, all s, H_3-25, 26, 28, 29, 27, and 23), 1.75 (3H, d, J = 6.4 Hz, H-6‴), 2.13 (1H, dd, J = 6.7, 12.8 Hz, H-18), 3.42 (1H, dd, J = 4.6, 11.9 Hz, H-3), 3.33, 4.28 (1H each, both d-like, H_2-24), 4.15 (1H, br d, J = ca. 6 Hz, H-22), 4.97 (1H, d, J = 7.6 Hz, H-1′), 5.01 (1H, d, J = 7.6 Hz, H-1⁗), 5.12 (1H, br s, H-12), 5.75 (1H, d, J = 7.6 Hz, H-1″), 6.33 (1H, br s, H-1‴); ^{13}C NMR data, see Table 1; positive-ion FABMS *m/z* 1139 $[M + Na]^+$; negative-ion FABMS *m/z* 1115 $[M - H]^-$, 969 $[M - C_6H_{11}O_4]^-$, 953 $[M - C_6H_{11}O_5]^-$, 645 $[M - C_{18}H_{31}O_{14}]^-$; HRFABMS *m/z* 1139.5261 (calcd for $C_{54}H_{84}O_{24}Na$ $[M + Na]^+$, 1139.5250).

Albiziasaponin D (4): colorless fine crystals from $CHCl_3$−MeOH, mp 238−240 °C; $[\alpha]_D^{24}$ −13.3° (*c* 0.10, MeOH); IR (KBr) ν_{max} 3445, 2930, 1765, 1655, 1078, 1043 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) δ 0.68, 0.82, 0.98, 1.19, 1.24, 1.49 (3H each, all s, H_3-25, 26, 28, 29, 27, and 23), 1.74 (3H, d, J = 6.1 Hz, H-6‴), 2.13 (1H, dd, J = 6.4, 13.1 Hz, H-18), 3.42 (1H, dd, J = 4.3, 11.6 Hz, H-3), 3.33, 4.28 (1H each, both d-like, H_2-24), 4.16 (1H, br d, J = ca. 6 Hz, H-22), 4.86 (1H, d, J = 7.3 Hz, H-1⁗), 4.97 (1H, d, J = 8.0 Hz, H-1′), 5.12 (1H, br s, H-12), 5.74 (1H, d, J = 7.6 Hz, H-1″), 6.24 (1H, br s, H-1‴); ^{13}C NMR data, see Table 1; positive-ion FABMS *m/z* 1087 $[M + H]^+$, 1109 $[M + Na]^+$; negative-ion FABMS *m/z* 1085 $[M - H]^-$, 953 $[M - C_5H_9O_4]^-$, 939 $[M - C_6H_{11}O_4]^-$, 645 $[M - C_{17}H_{29}O_{13}]^-$; HRFABMS *m/z* 1109.5157 (calcd for $C_{53}H_{82}O_{23}Na$ $[M + Na]^+$, 1109.5145).

Albiziasaponin E (5): colorless fine crystals from $CHCl_3$−MeOH, mp 240−242 °C; $[\alpha]_D^{24}$ −11.4° (*c* 0.10, MeOH); IR (KBr) ν_{max} 3445, 2933, 1752, 1655, 1078, 1047 cm^{-1}; ^1H NMR (pyridine-d_5, 500 MHz) δ 0.73, 0.83, 0.97, 1.18, 1.21, 1.49 (3H each, all s, H_3-25, 26, 28, 29, 27, and 23), 1.75 (3H, d, J = 6.4 Hz, H-6‴), 2.13 (1H, dd, J = 6.4, 13.1 Hz, H-18), 3.43 (1H, dd, J = 4.3, 11.6 Hz, H-3), 3.53, 4.40 (1H each, both d-like, H_2-24), 4.15 (1H, br d, J = ca. 7 Hz, H-22), 4.89 (1H, d, J = 7.3 Hz, H-1⁗), 5.03 (1H, d, J = 7.6 Hz, H-1′), 5.12 (1H, br s, H-12), 5.89 (1H, d, J = 7.6 Hz, H-1″), 6.15 (1H, br s, H-1‴); ^{13}C NMR data, see Table 1; positive-ion FABMS *m/z* 1101 $[M + H]^+$, 1123 $[M + Na]^+$; negative-ion FABMS *m/z* 1099 $[M - H]^-$, 967 $[M - C_5H_9O_4]^-$, 953 $[M - C_6H_{11}O_4]^-$; HRFABMS *m/z* 1123.4954 (calcd for $C_{53}H_{80}O_{24}Na$ $[M + Na]^+$, 1123.4937).

Acid Hydrolysis of Albiziasaponins A (1), B (2), C (3), D (4), and E (5). A solution of **1**−**5** (5 mg each) in 5% aqueous H_2SO_4−1,4-dioxane (1:1, 2 mL) was heated under reflux for 1 h. After cooling, the reaction mixture was neutralized with Amberlite IRA-400 (OH^- form) and the resin was removed by filtration. After removal of the solvent from the filtrate under reduced pressure, the residue was transferred to a Sep-Pak C_{18} cartridge with H_2O and MeOH. The H_2O eluate was concentrated in vacuo to give a residue, which was treated with L-cysteine methyl ester hydrochloride (4 mg) in pyridine (0.5 mL) at 60 °C for 1 h. After the reaction, the solution was treated with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.2 mL) at 60 °C for 1 h. The supernatant of the reaction mixture was then subjected to GLC analysis to identify the derivatives of D-glucuronic acid (**i**) and L-rhamnose (**ii**) from **1**−**5**; D-glucose (**iii**) from **3** and **4**; and D-xylose (**iv**) from **4** and **5**. GLC conditions: Supelco STB-1, 30 m × 0.25 mm (i.d.) capillary column; injector temperature, 230 °C; detector temperature, 230 °C; column temperature, 230 °C; He flow rate, 15 mL/min; t_R: (**i**) 26.4 min, (**ii**) 15.4 min, (**iii**) 24.2 min, and (**iv**) 13.8 min.

Enzymatic Hydrolysis of Albiziasaponins A (1) and C−E (3−5) To Afford 6. A solution of **1** (20.0 mg) in 0.1 M acetate buffer (pH 4.4, 2.0 mL) was treated with glycyrrhizinic acid hydrolase (Maruzen Pharmaceutical Co., Ltd., Hiroshima, Japan, 1.0 mL), and the mixture was stirred at 44 °C for 3 h. After treatment of the reaction mixture with EtOH, the solvent was evaporated to dryness under reduced pressure and the

residue was purified by silica gel column chromatography [1.0 g, *n*-hexanes−EtOAc (1:1)] to give **6** (7.0 mg, 72%). Using a similar procedure, a solution of **3** (10.0 mg), **4** (8.5 mg), or **5** (10.0 mg) in 0.1 M acetate buffer (pH 4.4, 1.0 mL) was treated with glycyrrhizinic acid hydrolase (0.5 mL each), and the mixture was stirred at 44 °C for 3 h. After EtOH was added to the reaction mixture, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography [1.0 g, *n*-hexane−EtOAc (1:1)] to furnish **6** (from **3**: 3.0 mg, 71%; from **4**: 2.1 mg, 57%; from **5**: 3.0 mg, 70%), which was identified by comparison of physical data ($[\alpha]_D$, IR, ^{1}H NMR, ^{13}C NMR) with reported values.[6]

Enzymatic Hydrolysis of Albiziasaponin B (2) Giving Azukisapogenol (7). A solution of **2** (20.0 mg) in 0.1 M acetate buffer (pH 4.4, 0.5 mL) was treated with glycyrrhizinic acid hydrolase (1.0 mL), and the mixture was stirred at 44 °C for 3 h. After the addition of EtOH to the reaction mixture, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography [1.0 g, *n*-hexane−EtOAc (1:1)] to give azukisapogenol (**7**, 9.2 mg, 97%), which was identified by a comparison of physical data ($[\alpha]_D$, IR, ^{1}H NMR, ^{13}C NMR) with reported values.[9]

Bioassay. Sensory Testing. Sweetness relative to sucrose was evaluated by a human sensory panel. Albiziasaponin A (**1**) was dissolved in water−ethanol (100:1) to make a 0.1% (w/v) solution, and sucrose solutions were prepared at graduated concentrations from 0.2 to 0.8% (w/v). Albiziasaponin B (**2**) was dissolved in water−ethanol (400:1) to make a 0.006% (w/v) solution, and sucrose solutions were prepared at graduated concentrations from 3.2 to 4.0% (w/v). Both samples were evaluated by a panel of five trained tasters in the manner described previously.[10] The panelists were asked to taste a sample solution and to estimate its sweetness intensity relative to that of the sucrose solution of appropriate concentration. Panelists were asked to taste samples in this way four times.

Acknowledgment. We are grateful to Dr. K. Mizutani and Ms. M. Yamana, Research Laboratories (Maruzen Pharmaceutical Co., Ltd., Hiroshima, Japan), for the sensory testing.

References and Notes

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NP020220L