Dammarane-Type Glycosides from *Gynostemma pentaphyllum*

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Fifteen new dammarane glycosides (**1**−**15**), together with four known compounds, gypenosides IV, VIII, LXXI, and XLIX, were isolated from the MeOH extract of the aerial parts of *Gynostemma pentaphyllum*. Their structures were elucidated by 1D and 2D NMR spectra interpretation as well as by chemical degradation.

Gynostemma pentaphyllum (Thunb.) Makino (Cucurbitaceae), a perennial creeping herb distributed in Japan, Korea, the People's Republic of China, and Southeast Asia, was once used as a sweetener in Japan and has been used as a folk medicine in the People's Republic of China.[1] Previous investigations of this plant have shown the occurrence of dammarane-type glycosides called the gypenosides that are structurally related to ginseng saponins.[2] Because ginsenosides are well-known biologically active principles in Korean ginseng[2] and have been regarded as the principal bioactive ingredients of *Panax ginseng* C. A. Meyer (Araliaceae),[3] *G. pentaphyllum* has received much attention. *G. pentaphyllum* may prevent cardiac myocytes from ischemic damage by inhibiting the "calcium overload"[4] and exhibits weak activity in preventing Ha-ras cancer gene mutation in rats.[5] Recently, certain gypenosides were reported to inhibit the proliferation of Hep-3B and HA22T cells, by affecting calcium and sodium currents in a dose-dependent manner.[6]

In the present study, we have isolated 19 dammarane-type glycosides from the title plant, comprising 15 new compounds (**1**−**15**) and four known compounds. The structure elucidation of **1**−**15** was accomplished mainly on the basis of the interrelation of 2D NMR spectral data, including ^{1}H−^{1}H and ^{1}H−^{13}C chemical shift correlation spectroscopy. None of these new compounds were found to be sweeter than sucrose.

Results and Discussion

The known compounds gypenosides (Gyp) IV,[2b] VIII,[2b] XLIX,[2i] and LXXI[2l] were identified by comparison of their spectral data with those described in the literature.

Compound **1** was obtained as an amorphous powder. The molecular weight was determined from the positive HRESIMS at *m*/*z* 1105.6152 for the $[M + H]^+$ ion (calcd for $C_{55}H_{93}O_{22}$, 1105.6158 $[M + H]^+$). The ^{13}C and DEPT NMR spectra gave 55 signals, of which 25 were assigned to the sugar moiety and 30 to a triterpene moiety. The ^{1}H NMR spectrum of **1** showed seven singlets assignable to the aglycon methyls at δ 0.79−1.71, two of which were diagnostic for methyls linked to an sp^2 carbon (δ 1.71 and 1.67). The ^{1}H NMR spectrum of **1** also showed one acetyl methyl singlet at δ 2.06 and an olefinic proton at δ 5.30 (1H, t, J = 6.6 Hz). A 3β-hydroxyl substitution was evident from the chemical shift, and the J values of the proton were ascribable to H-3α at δ 3.30 (1H, dd, J = 11.6, 3.8 Hz). On the basis of its ^{1}H and ^{13}C NMR data, the aglycon of **1** was identified as 3β,20*S*,21-trihydroxydammar-24-ene.[9] Glycosidation of the alcoholic function at C-3 and C-21 was indicated by the significant downfield shift observed for these carbon signals in **1**, compared with the corresponding signals in a model compound reported in the literature.[9]

Acid hydrolysis of **1** yielded D-glucose, D-xylose, and L-rhamnose in a ratio of 2:1:1 by GC analysis of the acetate derivatives of the component monosaccharides compared with the acetate derivatives of the standard sugars. The chemical shifts, the signal multiplicities, the absolute values of the coupling constants, and their magnitude in the ^{1}H NMR spectrum, as well as the ^{13}C NMR data, indicated a β-configuration for the glucosyl units [δ 4.78 (1H, d, J = 8.2 Hz, H-1 of glc); δ 105.1 (C-1 of glc)], a β-configuration for the xylosyl unit [δ 4.96 (1H, d, J = 7.6 Hz, H-1 of xyl); δ 105.1 (C-1 of xyl)], and an α-configuration for the rhamnosyl unit [δ 6.42 (1H, br s, H-1 of rha); δ 101.9 (C-1 of rha)]. The ^{13}C NMR data allowed the assignment of the pyranose forms of D-glucose, D-xylose, and L-rhamnose. All ^{1}H and ^{13}C NMR signals of the four sugar units in **1** were assigned using ^{1}H−^{1}H COSY, HMQC, and HMBC spectra. The linkage sites and sequences of the four saccharides, of the acetyl group, and of the aglycon were deduced from an HMBC experiment. Correlations were observed between H-1 of one glucose (glc-1) and C-3 of the aglycon, H-1 of the rhamnose and C-2 of glc-1, H-1 of the xylose and C-3 of glc-3, H-1 of glc-2 and C-21 of the aglycon, and H-6 of glc-1 and the carbonyl carbon of the acetyl group (Figure S1, Supporting Information). Thus, the structure of **1** was elucidated as 3β,20*S*,21-trihydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][β-D-xylopyranosyl-(1→3)]-β-D-[6-*O*-acetylglucopyranosyl]}-21-*O*-β-D-glucopyranoside.

Compound **2** was isolated as an amorphous powder. Its molecular formula was established as $C_{54}H_{92}O_{22}$ from the negative HRESIMS quasi-molecular ion at *m*/*z* 1091.6008 (calcd for $C_{54}H_{91}O_{22}$, 1091.6001 $[M - H]^-$). Comparison of the ^{1}H and ^{13}C NMR spectra of **1** and **2** indicated that they had an identical aglycon moiety. Hydrolysis of compound **2** yielded L-rhamnose and D-glucose. By GC analysis of the acetate derivatives of the component monosaccharides, it was clear that **2** contained three units of D-glucose and one of L-rhamnose. The linkage sites and sequences of the four saccharides and of the aglycon were also determined by an HMBC experiment (Figure S2, Supporting Information). On the basis of the above results, the structure of **2** was elucidated as 3β,20*S*,21-trihydroxydammar-24-ene 3-*O*-

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{[α-L-rhamnopyranosyl(1→2)][β-D-glucopyranosyl(1→3)]-β-D-glucopyranosyl}-21-*O*-β-D-glucopyranoside.

The positive HRESIMS quasi-molecular ion of **3** at *m/z* 1063.6059 established its formula as $C_{53}H_{90}O_{21}$ (calcd for $C_{53}H_{91}O_{21}$, 1063.6052 $[M + H]^+$). Comparison of the ^1H and ^{13}C NMR spectra of **2** and **3** indicated they had the same aglycon moiety. Hydrolysis of compound **3** yielded L-rhamnose, D-xylose, and D-glucose in a ratio of 1:1:2. The only difference between **2** and **3** was that one of the glucosyl groups in **2** was replaced by a xylosyl group. The β-xylosyl linkage was defined on the basis of the *J* value of its anomeric proton ($J = 7.7$ Hz).[2b] The linkage sites and sequences of the four saccharides and of the aglycon were also determined by an HMBC experiment (Figure S2, Supporting Information). Thus, the structure of **3** was determined as 3β,20*S*,21-trihydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucopyranosyl}-21-*O*-β-D-glucopyranoside.

Compound **4** was purified as an amorphous powder. It contained four monosaccharide units from its ^1H and ^{13}C NMR spectra. Hydrolysis of **4** yielded L-arabinose, L-rhamnose, D-xylose, and D-glucose in a ratio of 1:1:1:1. The positive HRESIMS quasi-molecular ion at *m/z* 1049.5896 suggested a molecular formula of $C_{52}H_{88}O_{21}$ (calcd for $C_{52}H_{89}O_{21}$, 1049.5891 $[M + H]^+$), indicating the presence of two more hydrogen atoms than in Gyp-XLIX.[2i] The ^{13}C NMR data were very similar to those of Gyp-XLIX except for a hydroxymethyl group (δ 61.8) instead of an aldehyde function (δ 205.6). In the HMBC spectrum, cross-peaks were found between the signal at δ 61.8 and H-5 (δ 1.04, m), supporting the location of the hydroxymethyl group at C-19. Assignments of the ^1H and ^{13}C NMR signals of all four sugar units were made from the $^1H-^1H$ COSY, HMQC, and HMBC spectra. The linkage sites and sequences of the saccharides and of the aglycon were also determined using an HMBC experiment (Figure S3, Supporting Information). Thus, the structure of compound **4** was established as 3β,19,20*S*,21-tetrahydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-α-L-arabinopyranosyl}-21-*O*-β-D-glucopyranoside.

The negative HRESIMS quasi-molecular ion at *m/z* 1077.5847 of **5** established its molecular formula as $C_{53}H_{90}O_{22}$ (calcd for $C_{53}H_{89}O_{22}$, 1077.5845 $[M - H]^-$). Hydrolysis of compound **5** yielded L-rhamnose, D-xylose, and D-glucose in a ratio of 1:1:2. Its ^{13}C NMR data were very similar to those of compound **3**. The only difference was that a methyl group in **3** was replaced by a hydroxymethyl group at C-19 in **5**. The linkage sites and sequences of the saccharides and of the aglycon were also determined using an HMBC experiment (Figure S3, Supporting Information). Thus, the structure of compound **5** was elucidated as 3β,19,20*S*,21-tetrahydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-β-D-glucopyranosyl}-21-*O*-β-D-glucopyranoside.

Compound **6** was isolated as an amorphous powder. It gave a positive reaction to KI-starch test paper, indicating the presence of a hydroperoxyl function.[7] The negative HRESIMS molecular ion of **6** displayed a quasi-molecular ion peak at *m/z* 1077.5483, corresponding an elemental formula of $C_{52}H_{86}O_{23}$ (calcd 1077.5481 $[M - H]^-$). Comparison of the molecular formula of **6** and Gyp-XLIX[2i] revealed that two more oxygen atoms in compound **6** were present. Hydrolysis of compound **6** revealed that it contained four monosaccharide units, L-rhamnose, D-xylose, L-arabinose, and D-glucose, in a ratio of 1:1:1:1. Its ^{13}C NMR data were very similar to those of Gyp-XLIX, except for the chain from the C-22 to C-27 positions. Moreover, it had two methine olefinic carbons instead of one methine olefinic carbon and one quaternary olefinic carbon as in Gyp-XLIX. From its HMBC spectrum, one oxygen-bearing quaternary carbon signal at δ 81.4 was correlated with the hydrogens at δ 1.52 (3H, s) and 6.20 (1H, m). According to the literature,[8] it could be judged that the olefinic function was at C-23 and C-24, and the hydroperoxyl function was at C-25, which was confirmed by HMBC cross-peaks. Thus, compound **6** was determined as 19-oxo-3β,20*S*,21-trihydroxy-25-hydroperoxydammar-23-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][β-D-xylopyranosyl(1→3)]-α-L-arabinopyranosyl}-21-*O*-β-D-glucopyranoside.

The positive HRESIMS of **7** showed a quasi-molecular ion peak at *m/z* 1111.5897, establishing the molecular formula as $C_{53}H_{90}O_{24}$ (calcd for $C_{53}H_{91}O_{24}$, 1111.5893 $[M + H]^+$). It also had a positive reaction to KI-starch test paper, which indicated there was a hydroperoxyl group in compound **7**.[7] Comparison of the ^1H and ^{13}C NMR spectra of **7** and **6** indicated that **7** had a 4-hydroperoxyl-4-methylpent-2-enyl chain moiety at C-20. Moreover, comparison of the ^1H and ^{13}C NMR spectra between **7** and Gyp-IV[2b] revealed that the only difference was that the 4-methylpent-3-enyl chain moiety at C-20 in Gyp-IV was replaced by a 4-hydroperoxyl-4-methylpent-2-enyl chain moiety in **7**. Therefore, **7** was identified as 3β,12,20*S*-trihydroxy-25-hydroperoxydammar-23-ene 3-*O*-{[β-D-glucopyranosyl(1→2)-β-D-glucopyranosyl]-20-*O*-[β-D-xylopyranosyl(1→6)]-β-D-glucopyranoside. The structure was confirmed by $^1H-^1H$ COSY, HMQC, and HMBC NMR experiments.

Compound **8** was obtained as an amorphous powder. The positive HRESIMS displayed a quasi-molecular ion peak at *m/z* 1063.5688, indicating a molecular formula of $C_{52}H_{86}O_{22}$ (calcd for $C_{52}H_{87}O_{22}$ 1063.5689 $[M + H]^+$). Comparison of the ^1H and ^{13}C NMR spectra of **8** and Gyp-LXXI[2l] indicated that **8** had a 3-hydroxyl-4-methylpent-4-enyl chain moiety at C-20. Moreover, comparison of the ^1H and ^{13}C NMR spectra of **8** and Gyp-XLIX[2i] revealed that the only difference was that a 4-methylpent-3-enyl chain moiety at C-20 in Gyp-XLIX was replaced by a 3-hydroxyl-4-methylpent-4-enyl chain moiety in **8**. Thus, the structure of compound **8** was identified as 19-oxo-3β,20*S*,21,24*S*-tetrahydroxydammar-25-ene 3-*O*-{[α-L-rhamnopyranosyl-(1→2)][β-D-xylopyranosyl(1→3)]-α-L-arabinopyranosyl}-21-*O*-β-D-glucopyranoside, which was confirmed by $^1H-^1H$ COSY, HMQC, and HMBC NMR experiments.

Compound **9** was obtained as an amorphous powder. The molecular weight was determined by the positive HRESIMS at *m/z* 919.5262 for the $[M + H]^+$ ion (calcd for $C_{46}H_{79}O_{18}$, 919.5266 $[M + H]^+$). The ^{13}C and DEPT ^{13}C NMR spectra gave 46 signals, of which 16 were assigned to the saccharide portion and 30 to a triterpene moiety. The ^1H NMR spectrum of **9** showed eight singlets assignable to tertiary methyls at δ 0.92−1.81. Substitution with a 3β-hydroxyl group was evident from the chemical shift and the *J* values of H-3α at δ 3.34 (1H, dd, $J = 11.6$ Hz, 4.3 Hz). By comparison of its ^1H and ^{13}C NMR spectra with those of known dammarane-type saponins,[2] it was evident that compound **9** was devoid of any olefinic group signals. From biogenetic considerations and its NMR data, the aglycon of **9** was identified as 3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane.[9] Hydrolysis of **9** yielded D-glucose and D-xylose by GC analysis of the acetate derivatives of the component monosaccharides, in a ratio of 1:2. The chemical shifts, the multiplicity of the signals, the absolute values of the coupling constants, and their magnitude in the ^1H NMR spectrum, as well as the ^{13}C

NMR data, indicated a β-configuration at the anomeric position for the glucosyl unit [δ 4.94 (1H, d, J = 7.7 Hz, H-1 of glc); δ 105.1 (C-1 of glc)] and β-configurations for the xylosyl units [δ 5.27 (1H, d, J = 7.2 Hz, H-1 of xyl); δ 107.1 (C-1 of xyl) and δ 5.02 (1H, d, J = 7.4 Hz, H-1 of xyl′); δ 106.0 (C-1 of xyl′)]. ^{13}C NMR data and GC analysis allowed assignment of the pyranose form to D-glucose and D-xylose. All ^{1}H and ^{13}C NMR signals of the three sugar units were assigned from the ^{1}H−^{1}H COSY, HMQC, HMBC, and TOCSY spectra. The linkage sites and sequences of the three saccharides and of the aglycon were deduced from an HMBC experiment (Figure S4, Supporting Information). Correlations were observed between H-1 of the glucose and C-3 of the aglycon, H-1 of one xylose and C-2 of the glucose, and H-1 of the second xylose and C-6 of the glucose. Thus, the structure of **9** was elucidated as 3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-xylopyranosyl(1→2)][β-D-xylopyranosyl(1→6)]-β-D-glucopyranoside.

The molecular formula of **10** was established as $C_{47}H_{80}O_{19}$ from the negative HRESIMS quasi-molecular ion at m/z 947.5212 (calcd for $C_{47}H_{79}O_{19}$, 947.5215 [M − H]$^-$). Comparison of the ^{1}H and ^{13}C NMR spectra between **9** and **10** indicated they had an identical aglycon moiety. The major difference between **9** and **10** was that the xylosyl group in **9** was replaced by a hexosyl group in **10**. Hydrolysis of compound **10** yielded D-xylose and D-glucose in a ratio of 1:2. Thus, one xylosyl group in **9** was deduced to be replaced by a glucosyl group. The β-glucosyl linkage of this site was defined on the basis of the J value of its anomeric proton (J = 7.6 Hz). The linkage sites and sequences of the three saccharides and of the aglycon were also determined by an HMBC experiment (Figure S4, Supporting Information). Thus, the structure of **10** was determined as 3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-glucopyranosyl(1→2)][β-D-xylopyranosyl(1→6)]-β-D-glucopyranoside.

The positive HRESIMS quasi-molecular ion of **11** was observed at m/z 787.4848. Accordingly compound **11** was determined to have the elemental composition $C_{41}H_{70}O_{14}$ (calcd for $C_{41}H_{71}O_{14}$, 787.4843 [M + H]$^+$). The aglycon of **11** was the same as that of **9** from comparison of their ^{1}H and ^{13}C NMR spectra. Hydrolysis of **11** yielded D-glucose and D-xylose in a ratio of 1:1. From the HMBC spectrum, correlations were observed between H-1 of the xylose and C-3 of the aglycon, and H-1 of the glucose and C-2 of the xylose. Thus, compound **11** was identified as 3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-glucopyranosyl(1→2)]-β-D-xylopyranoside.

The ^{1}H and ^{13}C NMR data of **12** were very similar to those of **11** except for the sugar moiety. The positive HRESIMS quasi-molecular ion appeared at m/z 787.4848. Thus, compound **12** was determined to have the elemental composition $C_{41}H_{70}O_{14}$ (calcd 787.4843 [M + H]$^+$), which was the same as that of **11**. Hydrolysis of **12** also yielded D-glucose and D-xylose in a ratio of 1:1. From the HMBC spectrum, correlations were observed between H-1 of the glucose and C-3 of the aglycon, and H-1 of the xylose and C-2 of the glucose. Thus, compound **12** was elucidated as 3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-xylopyranosyl(1→2)]-β-D-glucopyranoside.

The negative HRESIMS quasi-molecular ion at m/z 797.4685 of **13** established the molecular formula as $C_{42}H_{70}O_{14}$ (calcd for $C_{42}H_{69}O_{14}$, 797.4687 [M − H]$^-$). The ^{13}C NMR spectrum of **13** suggested a 20,25-epoxydammarane-type triterpene skeleton with an acetyl function. By comparison of the ^{13}C NMR spectrum with those of **9**−**12**, an additional quaternary carbonyl carbon signal (δ 171.1) and an additional methyl carbon signal (δ 21.4) were observed. The acetyl function was located at the C-23 position from connectivity of the quaternary carbonyl signal (δ 171.1) with H-23 (δ 5.80, 1H, dt, J = 10.5, 4.0 Hz) in the HMBC experiment. Hydrolysis of **13** yielded D-xylose. According to its ^{1}H and ^{13}C NMR spectra, **13** contained two units of D-xylose. The linkage sites and sequences of the two saccharides and of the aglycon were determined using an HMBC experiment (Figure S5, Supporting Information). Thus, **13** was deduced as 23-*O*-acetyl-3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-xylopyranosyl(1→2)]-β-D-xylopyranoside.

Compound **14** was obtained as an amorphous powder. The positive HRESIMS molecular ion of **14** displayed a quasi-molecular ion peak at m/z 829.4943 (calcd for $C_{43}H_{73}O_{15}$, 829.4949 [M + H]$^+$). Moreover, from its ^{13}C NMR spectrum, **14** could be assigned the same aglycon as that of **13**. By acid hydrolysis analysis, it was found that the only difference between **14** and **13** was that one xylosyl unit in **13** was replaced by one glucosyl unit. By an HMBC experiment, the linkage sites of the two sugars and of the aglycon were determined (Figure S5, Supporting Information). Therefore, **14** was determined as 23-*O*-acetyl-3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-xylopyranosyl(1→2)]-β-D-glucopyranoside.

The positive HRESIMS of **15** showed a quasi-molecular ion peak at m/z 961.5376, establishing the molecular formula was $C_{48}H_{80}O_{19}$ (calcd 961.5372 [M + H]$^+$). From the ^{1}H and ^{13}C NMR spectra, **15** had the same aglycon and the saccharide chain as that of **9**. Comparison of the ^{1}H and ^{13}C NMR data of **9** and **15** revealed that the only difference between **15** and **9** was that **15** had one more acetyl group. The acetyl group was located at the C-23 position from its HMBC cross-peak between the quaternary carbonyl signal (δ 171.1) and H-23 (δ 5.73, 1H, dt, J = 10.8, 4.0 Hz). On the basis of the above results, the structure of **15** was elucidated as 23-*O*-acetyl-3β,12β,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[β-D-xylopyranosyl-(1→2)][β-D-xylopyranosyl(1→6)]-β-D-glucopyranoside. The structure was confirmed by ^{1}H−^{1}H COSY, HMQC, and HMBC NMR experiments.

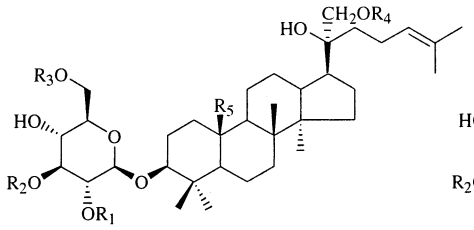
Accordingly, as a result of this investigation, the structures of 15 new compounds from *G. pentaphyllum* were identified, and among these, saponins based on the aglycon 20*S*,25-epoxydammarane (**9**−**15**) were isolated from this plant for the first time.

Experimental Section

General Experimental Procedures. Optical rotations were measured in MeOH with a Perkin-Elmer model 341 polarimeter. NMR spectra were obtained on a Bruker AMX-500 spectrometer in C_5D_5N solution. Chemical shifts are reported in ppm. ^{1}H NMR chemical shifts were referenced to the center peak of the residual solvent signal (δ 7.58). ^{13}C NMR spectra were referenced to the center peak of the solvent at δ 135.9. ESIMS were run on a Bruker Esquire 3000 plus spectrometer in MeOH and HRESIMS were run on a Bruker Atex III spectrometer in MeOH, respectively. GC: Shimadzu GC-14BPF column, 5% OV-225/AW-DMCS-Chromosorb W (80−100 mesh), 3 mm i.d. × 2.5 m; column temperature, 210 °C; injection temperature, 250 °C; carrier gas, N_2 at a flow rate of 25 mL/min; detector, FID.

Plant Material. *Gynostemma pentaphyllum* was collected in Hunan Province, People's Republic of China, in May 2002. A voucher specimen of the plant (No. 2002003) was identified by Mr. Jin-Gui Shen and deposited at the herbarium of Chinese National Center for Drug Screening, Shanghai, People's Republic of China.

Chart 1

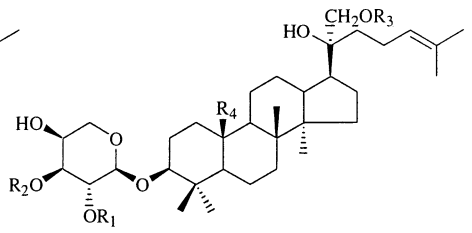


1 R_1 = Rha, R_2 = Xyl, R_3 = CH_3CO, R_4 = Glc′, R_5 = CH_3

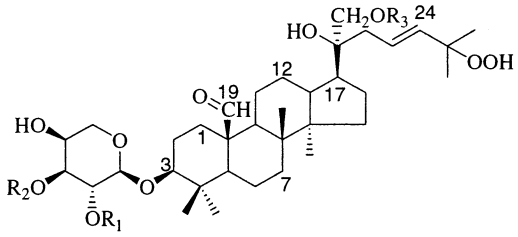
2 R_1 = Rha, R_2 = Glc′, R_3=H, R_4 = Glc″, R_5 = CH_3

3 R_1 = Rha, R_2 = Xyl, R_3 = H, R_4 = Glc′, R_5 = CH_3

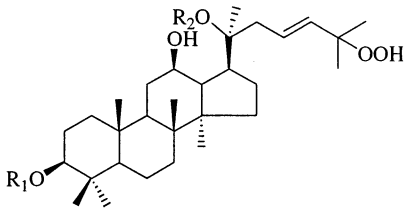
5 R_1 = Rha, R_2 = Xyl, R_3 = H, R_4 = Glc′, R_5 = CH_2OH



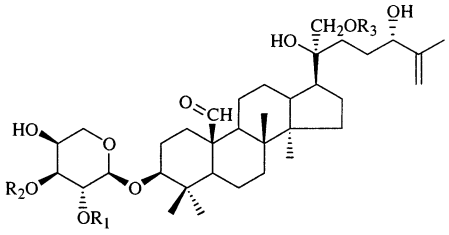
4 R_1 = Rha, R_2 = Xyl, R_3 = Glc, R_4 = CH_2OH



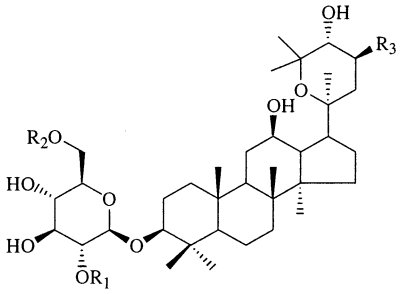
6 R_1 = Rha, R_2 = Xyl, R_3 = Glc



7 R_1 = Glc(2→1)Glc′, R_2 = Glc″(6→1)Xyl



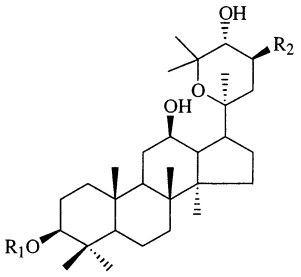
8 R_1 = Rha, R_2 = Xyl, R_3 = Glc



9 R_1 = Xyl, R_2 = Xyl′, R_3 = OH

10 R_1 = Glc′, R_2 = Xyl, R_3 = OH

15 R_1 = Xyl, R_2 = Xyl′, R_3 = OAc



11 R_1 = Xyl(2→1)Glc, R_2 = OH

12 R_1 = Glc(2→1)Xyl, R_2 = OH

13 R_1 = Xyl(2→1)Xyl′, R_2 = OAc

14 R_1 = Glc(2→1)Xyl, R_2 = OAc

Extraction and Isolation. The dried and powdered aerial parts of *G. pentaphyllum* (2.0 kg) were extracted successively with petroleum ether (5 L) and MeOH (3 × 5 L) at room temperature. Removal of MeOH under reduced pressure left a dark residue (70 g). The residue was subjected to silica gel column chromatography, eluted with chloroform−methanol (100:10, 100:20, 100:30, 100:50), to yield four fractions (A−D). Fraction B (15 g) was passed through a Sephadex LH-20 (25−100 μm, Merck, Darmstadt, Germany) column, eluted with methanol to remove flavonoids. Then, the fraction was subjected to MCI gel CHP 20P (75−150 μm, Mitsubishi Kasei Industry Co., Ltd., Tokyo, Japan) column chromatography, eluted with water−acetone (9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1) to yield eight subfractions (B-1−8). Subfraction B-1 (190 mg) was subjected to RP-18 (20−45 μm, Fuji Silysia Chemical Ltd., Fuji, Japan) flash column chromatography, eluted with methanol−water (60:40), to give **11** (20 mg) and **12** (20 mg). Subfraction B-2 (1 g) was purified by a RP-18 flash column, eluted with methanol−water (65:35), to give **13** (54 mg). Subfraction B-3 (1 g) was chromatographed by RP-18 flash column chromatography, eluted with methanol−water (65:35), to afford a mixture. This mixture was then subjected to silica gel column chromatography, eluted with chloroform−methanol−water (6:1:0.1), to afford **14** (70 mg). Fraction C (10 g) was passed over a Sephadex LH-20 column, eluted with methanol to remove flavonoids, and then was subjected to MCI gel CHP

Table 1. ^{1}H NMR Data of Compounds **1**−**4** in C_5D_5N[a]

	1	2	3	4
1	1.60 m, 0.92 m	1.51 m, 0.92 m	1.69 m, 0.95 m	2.61 d (11.7), 0.95 m
2	2.20 m	2.20 m	2.26 m	2.30 m, 2.22 m
3	3.30 dd (11.6, 3.8)	3.40 m	3.30 dd (11.3, 3.9)	3.48 br d (11.3)
5	0.74 m	0.74 m	0.73 br d (11.5)	1.04 m
6	1.50 m	1.50 m	1.52 m	1.50 m
7	1.50 m, 1.22 m	1.50 m, 1.30m	1.49 m, 1.22 m	1.70 m, 1.42 m
9	1.34 m	1.32 m	1.25 m	1.56 m
11	1.41 m	1.41 m	1.49 m	2.20 m, 2.02 m
12	1.93 m	2.00 m	1.90 m	2.30 m, 2.22 m
13	2.10 m	2.10 m	2.09 m	2.21 m
15	1.61 m, 1.11 m	1.71 m, 1.19 m	1.67 m, 1.11 m	1.77 m, 1.23 m
16	1.87 m	1.85 m	1.88 m	2.21 m
17	2.21 m	2.20 m	2.20 m	2.30 m
18	0.96 s	1.02 s	0.94 s	1.38 s
19	0.79 s	0.86 s	0.74 s	4.31 m, 4.22 m
21	4.38 m, 4.00 m	4.40 m, 4.10 m	4.39 d (10.2), 4.05 d (10.2)	4.41 m, 4.06 d (9.8)
22	2.09 m, 1.90 m	2.08 m, 2.00 m	2.10 m, 1.90 m	2.15 m, 1.98 m
23	2.45 m, 2.32 m	2.52 m, 2.40 m	2.47 m, 2.32 m	2.49 m, 2.39 m
24	5.30 t (6.6)	5.28 t (6.0)	5.46 t (6.6)	5.30 t (6.3)
26	1.71 s	1.77 s	1.70 s	1.72 s
27	1.67 s	1.72 s	1.65 s	1.70 s
28	1.28 s	1.32 s	1.27 s	1.31 s
29	1.15 s	1.18 s	1.18 s	1.29 s
30	0.97 s	1.02 s	0.94 s	1.12 s
	C-3-Glc	C-3-Glc	C-3-Glc	C-3-Ara
1	4.78 d (8.2)	4.91 d (6.6)	4.90 d (7.4)	5.01 d (6.0)
2	4.15 m	4.15 m	4.22 m	4.70 t (6.0)
3	4.12 m	4.28 m	4.18 m	4.34 m
4	3.80 t (9.0)	4.11 m	4.00 m	4.52 m
5	3.93 m	4.02 m	3.92 m	4.38 m, 3.90 m
6	4.80 m, 4.70 m	4.53 m, 4.38 m	4.50 m, 4.38 m	
$-COCH_3$	2.06 s			
Rha				
1	6.42 br s	6.50 br s	6.70 br s	6.19 br s
2	4.55 m	4.64 m	4.58 m	4.62 m
3	4.66 m	4.88 m	4.78 m	4.77 br s
4	4.18 m	4.35 m	4.29 m	4.31 m
5	4.70 m	4.79 m	4.66 m	4.62 m
6	1.67 d (7.0)	1.60 d (6.3)	1.68 d (6.2)	1.68 d (5.8)
	Xyl	Glc′	Xyl	Xyl
1	4.96 d (7.6)	5.17 d (7.5)	5.00 d (7.7)	5.03 d (7.7)
2	3.93 m	4.05 m	3.96 m	3.98 m
3	4.07 m	4.12 m	4.08 m	4.17 m
4	4.11 m	4.16 m	4.11 m	4.16 m
5	4.28 m, 3.70 t (10.5)	3.96 m	4.26 m, 3.70 t (10.0)	4.37 m, 3.72 t (10.0)
6		4.43 m, 4.30 m		
	C-21-Glc′	C-21-Glc″	C-21-Glc′	C-21-Glc
1	5.02 d (7.7)	5.08 d (8.1)	5.05 d (7.6)	5.03 d (7.7)
2	4.06 m	4.12 m	4.08 m	4.11 m
3	4.20 m	4.28 m	4.22 m	4.25 m
4	4.18 m	4.17 m	4.22 m	4.25 m
5	3.96 m	3.98 m	3.98 m	3.99 m
6	4.54 m, 4.33 m	4.57 m, 4.38 m	4.57 m, 4.39 m	4.58 m, 4.40 m

[a] 500 MHz; referenced to δ 7.58 (C_5D_5N); *J* values (Hz) in parentheses.

20P column chromatography, eluted with water−acetone (9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1), to yield eight subfractions (C-1−8). Subfraction C-2 (1.3 g) was further purified by silica gel H flash column chromatography, eluted with chloroform−methanol−water (8:1:0.1), to give a mixture. This mixture was purified on a RP-18 flash column, eluted with MeOH−H_2O (63:37), to yield compound **15** (70 mg). Fraction D (20 g) was passed through a Sephadex LH-20 column, eluted with methanol to remove flavonoids. Then, the fraction rich in saponin was subjected to MCI gel CHP 20P column chromatography, eluted with water−acetone (10:1, 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1), to yield nine subfractions (D-1−9). Subfraction D-1 (3 g) was further purified by RP-18 flash column chromatography, eluted with methanol−water (65:35), to give compound **3** (300 mg), and eluted with methanol−water (83:17) to afford compound **1** (100 mg). Subfraction D-2 (1 g) was further chromatographed on a RP-18 flash column, eluted with MeOH−H_2O (65:35), to yield compound **2** (110 mg), eluted with acetone−water (35:65), to yields compounds **9** (38 mg) and **10** (23 mg). Subfraction D-3 (1 g) was subjected to RP-18 flash column chromatography, eluted with methanol−water (60:40), to give Gyp-XLIX[2i] (100 mg). Subfraction D-4 (3 g) was chromatographed by RP-18 flash column chromatography, eluted with methanol−water (50:50), to afford **6** (28 mg), successively eluted with methanol−water (65:35) to give **4** (72 mg) and Gyp-IV[2b] (105 mg). Subfraction D-5 (1 g) was further purified by RP-18 flash column chromatography, eluted with methanol−water (65:35), to give **5** (30 mg). Subfraction D-6 (1 g) was separated on a RP-18 column, eluted with methanol−water (55:45), to afford **8** (30 mg). Subfraction D-7 (1 g) was purified on a RP-18 flash column, eluted with methanol−water (55:45), to afford **7** (29 mg). Subfraction D-8 (2 g) was subjected to RP-18 flash column chromatography to yield Gyp-VIII[2b] (81 mg). Subfraction D-9 (2 g) was purified by RP-18 flash column chromatography to give Gyp-LXXI[2l] (24 mg).

3*β*,20*S*,21-Trihydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-xylopyranosyl(1→3)]-*β*-D-[6-*O*-acetylglucopyranosyl]}-21-*O*-*β*-D-glucopyranoside (1): amorphous powder; $[\alpha]^{20}_D$ −2.6° (*c* 0.97, MeOH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; HRESIMS *m*/*z* 1105.6152 (calcd for

Table 2. ^{13}C NMR Data of Compounds **1**−**8** in C_5D_5N

carbon	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1	39.9	39.9	39.9	35.1	35.3	33.7	39.4	33.7
2	27.0	27.0	27.2	27.7	28.0	27.8	26.9	27.8
3	89.0	88.9	89.0	88.9	89.5	87.3	89.2	87.3
4	39.9	39.8	40.0	39.9	39.9	40.7	39.9	40.5
5	57.0	56.8	56.9	57.5	57.6	55.0	56.6	55.0
6	18.7	18.7	18.7	18.5	18.5	17.8	18.7	17.8
7	35.8	36.2	35.8	36.4	36.4	34.8	35.4	34.8
8	40.9	40.8	41.0	41.2	41.2	40.2	40.3	40.2
9	51.3	51.1	51.3	53.3	53.3	53.0	50.4	53.0
10	37.0	37.0	37.3	42.3	42.3	52.9	37.1	52.9
11	22.0	21.9	22.0	24.9	25.0	22.4	31.1	22.4
12	24.8	24.8	24.8	27.7	28.0	24.5	70.7	24.8
13	41.9	41.9	42.0	42.4	42.5	41.8	49.8	41.7
14	50.6	50.6	50.7	51.0	51.0	50.3	51.7	50.4
15	31.7	31.7	31.9	32.2	32.2	32.0	30.8	32.1
16	27.0	27.0	27.2	29.0	29.0	27.7	26.6	27.7
17	46.3	46.3	46.4	46.3	46.3	46.3	52.1	46.4
18	15.9	15.9	16.0	16.3	16.3	16.1	16.2	16.2
19	16.7	16.7	16.7	61.8	61.8	205.6	16.5	205.6
20	76.5	76.5	76.4	76.7	76.7	76.8	83.5	76.3
21	76.5	76.5	76.6	76.6	76.7	76.3	23.5	76.3
22	36.8	36.7	36.7	36.8	36.8	39.9	40.3	32.8
23	23.5	23.4	23.6	23.6	23.6	126.8	126.9	30.5
24	126.1	126.1	126.0	126.2	126.3	138.3	138.3	76.1
25	131.1	131.0	131.0	131.0	131.0	81.4	81.6	150.1
26	26.0	25.9	25.9	26.0	26.0	25.3	25.6	110.3
27	17.9	17.9	17.9	18.0	17.9	25.2	25.3	18.4
28	28.0	28.0	28.1	28.9	28.8	26.5	28.3	26.5
29	16.9	16.8	17.0	17.2	17.2	16.5	16.8	16.5
30	16.8	17.0	16.8	17.4	17.4	17.4	17.4	17.4
	C-3-Glc	C-3-Glc	C-3-Glc	C-3-Ara	C-3-Glc	C-3-Ara	C-3-Glc	C-3-Ara
1	105.1	105.1	105.1	104.9	105.2	104.8	105.3	104.9
2	76.8	77.0	77.0	74.8	77.1	74.7	83.5	74.7
3	87.9	89.6	88.0	81.6	88.4	81.7	78.3	81.8
4	70.0	70.0	69.9	68.3	69.9	68.4	71.9	68.5
5	74.5	78.3	78.1	64.9	78.1	65.1	78.1	65.2
6	64.3	62.4	62.0		62.2		63.0	
−O*C*OCH$_3$	170.9							
−OCO*C*H$_3$	20.9							
	Rha	Rha	Rha	Rha	Rha	Rha	Glc′	Rha
1	101.9	101.2	101.0	102.1	101.9	102.1	106.2	102.1
2	72.6	72.5	72.5	72.7	72.7	72.7	77.3	72.6
3	72.5	72.5	72.6	72.5	72.5	72.5	78.4	72.5
4	74.0	73.9	74.0	74.0	74.0	74.0	71.9	73.9
5	70.0	70.0	69.0	70.2	69.9	70.2	78.2	70.1
6	18.8	18.7	18.7	18.7	18.7	18.7	62.9	18.7
	Xyl	Glc′	Xyl	Xyl	Xyl	Xyl		Xyl
1	105.1	104.0	105.0	105.2	105.0	105.3		105.3
2	74.9	75.2	74.9	74.6	75.0	74.5		74.5
3	78.4	77.9	78.4	77.7	78.4	77.8		77.8
4	70.7	71.5	70.7	71.0	70.8	71.0		71.2
5	67.4	78.5	67.0	67.1	67.4	67.1		67.0
6		62.8						
							C-20-Glc″	
1							98.4	
2							75.0	
3							79.1	
4							71.7	
5							76.9	
6							70.1	
							C-20-Xyl	
1							105.7	
2							75.2	
3							78.1	
4							71.3	
5							67.2	
	C-21-Glc′	C-21-Glc″	C-21-Glc′	C-21-Glc	C-21-Glc′	C-21-Glc		C-21-Glc
1	106.3	106.1	106.0	106.2	106.3	106.2		106.1
2	75.5	75.5	75.6	75.6	75.6	75.6		75.5
3	78.7	78.6	78.7	78.6	78.8	78.6		78.6
4	71.9	71.8	71.9	71.8	71.8	71.8		71.8
5	78.6	78.6	78.6	78.7	78.7	78.7		78.6
6	63.0	62.9	63.0	63.0	62.9	62.9		62.9

Table 3. ^{1}H NMR Data of the Aglycon of Compounds **5**−**8** in C_5D_5N[a]

	5	**6**	**7**	**8**
1	2.49 m, 0.79 t (11.5)	2.60 m, 0.67 m	1.61 m, 0.85 m	2.58 m, 0.68 m
2	2.35 m, 2.20 m	2.09 m	2.22 m, 1.90 m	2.11 m
3	3.50 br d (10.0)	3.31 br d (10.0)	3.40 dd (11.6, 4.2)	3.38 br d (10.0)
5	0.96 m	1.15 m	0.75 d 9.6	1.21 m
6	1.55 m	1.55 m	1.53 m	1.55 m
7	1.60 m, 1.33 m	1.62 m, 1.32 m	1.51 m, 1.23 m	1.70 m, 1.41 m
9	1.48 m	1.63 m	1.41 m	1.71 m
11	2.14 m, 1.96 m	1.67 m	2.10 m	1.62 m
12	2.36 m, 2.20 m	1.91 m	4.11 m	1.91 m
13	2.15 m	2.00 m	2.10 m	2.08 m
15	1.71 m, 1.19 m	1.60 m, 1.11 m	1.62 m, 1.08 m	1.65 m, 1.20 m
16	2.20 m	2.09 m	1.89 m	2.12 m
17	2.23 m	2.21 m	2.52 m	2.30 m
18	1.30 s	0.90 s	1.09 s	1.12 s
19	4.25 m, 4.15 m	10.3 s	0.92 s	10.2 s
21	4.35 d (9.3), 4.00 d (9.3)	4.36 m, 3.97 m	1.68 s	4.40 m, 4.02 m
22	2.08 m, 1.90 m	2.86 m, 2.61 m	3.19 m, 2.90 m	2.05 m, 1.90 m
23	2.45 m, 2.32 m	6.20 m	6.25 m	2.00 m
24	5.49 m	6.08 d (14.8)	6.20 m	4.45 m
26	1.66 s	1.59 s	1.72 s	5.30 br s, 4.99 br s
27	1.59 s	1.52 s	1.65 s	1.97 s
28	1.30 s	1.28 s	1.33 s	1.31 s
29	1.30 s	0.92 s	1.20 s	1.00 s
30	1.00 s	0.89 s	0.99 s	0.92 s

[a] 500 MHz; referenced to δ 7.58 (C_5D_5N); *J* values (Hz) in parentheses.

Table 4. ^{1}H NMR Data of the Sugar Moieties of Compounds **5**−**8** in C_5D_5N[a]

	5	**6**	**7**	**8**
	C-3-Glc	C-3-Ara	C-3-Glc	C-3-Ara
1	4.00 d (7.0)	4.90 d (5.4)	4.98 d (7.4)	4.94 d (5.7)
2	4.20 m	3.91 m	4.10 m	4.67 m
3	4.18 d (8.5)	4.27 d (9.4)	4.10 m	4.31 m
4	3.99 m	4.47 br s	4.39 m	4.51 m
5	4.20 m	4.28 m, 3.80 d (10.2)	4.20 m	4.33 m, 3.88 d (10.1)
6	4.34 d (9.4), 4.30 t (9.2)		4.61 d (11.1), 4.41 m	
	Rha	Rha	Glc′	Rha
1	6.40 br s	6.10 br s	5.42 d (7.4)	6.16 br s
2	4.59 d (9.0)	4.56 m	4.21 m	4.61 m
3	4.80 m	4.72 br s	4.32 m	4.76 br s
4	4.28 m	4.26 m	4.38 m	4.30 m
5	4.72 m	4.54 m	4.00 m	4.60 m
6	1.62 d (6.2)	1.60 d (5.8)	4.53 m, 4.12 m	1.66 d (5.4)
Xyl				
1	4.72 d (7.0)	5.00 d (7.3)		5.03 d (6.9)
2	3.97 m	3.92 m		3.98 m
3	4.20 m	4.09 m		4.13 m
4	4.21 m	4.11 m		4.17 m
5	4.26 m, 3.70 t (10.1)	4.30 m, 3.65 t (9.9)		4.35 m, 3.71 m
			C-20-Glc″	
1			5.20 d (7.5)	
2			4.00 m	
3			4.24 m	
4			4.20 m	
5			4.19 m	
6			4.78 m	
			4.37 m	
			Xyl	
1			5.02 d (7.3)	
2			4.10 m	
3			4.22 m	
4			4.38 m	
5			3.78 m	
	C-21-Glc′	C-21-Glc		C-21-Glc
1	5.00 d (7.3)	5.03 d (7.4)		5.03 d (6.9)
2	4.08 m	4.09 m		4.10 m
3	4.21 m	4.21 m		4.26 m
4	4.21 m	4.21 m		4.22 m
5	3.94 m	3.95 m		4.01 m
6	4.50 m, 4.33 d (9.4)	4.52 m, 4.35 m		4.58 m, 4.40 m

[a] 500 MHz; referenced to δ 7.58 (C_5D_5N); *J* values (Hz) in parentheses.

$C_{55}H_{93}O_{22}$ $[M + H]^+$, 1105.6158); GC analysis of sugar components, t_R 7.56, 4.84, and 17.35 min.

3*β*,20*S*,21-Trihydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-glucopyranosyl(1→3)]-*β*-D-glucopy-

Table 5. ^{1}H NMR Data of Compounds **9**−**12** in C_5D_5N[a]

	9	10	11	12
1	1.72 m, 1.00 m	1.70 m, 0.96 m	1.72 m, 0.96 m	1.53 m, 0.86 m
2	2.40 m, 1.90 m	2.30 m, 1.90 m	2.19 m, 1.96 m	2.30 m, 1.80 m
3	3.34dd (11.6, 4.3)	3.20 br d (11.5)	3.34dd (11.7, 4.3)	3.30 dd (11.4, 4.0)
5	0.73 d (9.4)	0.77 d (10.3)	0.80 d (11.0)	0.74 d (10.0)
6	1.60 m, 1.45 m	1.57 m, 1.42 m	1.58 m, 1.46 m	1.58 m, 1.45 m
7	1.46 m, 1.25 m	1.34 m, 1.18 m	1.48 m, 1.29 m	1.41 m, 1.20 m
9	1.50 m	1.40 m	1.53 m	1.41 m
11	2.14 m, 1.40 m	2.10 m, 1.30 m	2.13 m, 1.45 m	2.02 m, 1.45 m
12	3.82 m	3.72 m	3.83 m	3.78 m
13	2.01 t (10.2)	1.95 t (10.0)	2.02 t (10.0)	1.99 t (10.0)
15	1.52 m, 1.04 m	1.43 m, 0.95 m	1.52 m, 1.03 m	1.45 m, 0.98 m
16	1.90 m, 1.43 m	1.90 m, 1.41 m	1.91 m, 1.43 m	1.90 m, 1.43 m
17	2.30 m	2.21 m	2.31 m	2.24 m
18	0.96 s	0.85 s	0.96 s	0.89 s
19	0.92 s	0.79 s	0.91 s	0.83 s
21	1.52 s	1.43 s	1.52 s	1.46 s
22	2.32 m, 2.23 m	2.24 m, 2.18 m	2.31 m, 2.23 m	2.27 m, 2.18 m
23	4.52 m	4.50 m	4.52 m	4.45 m
24	3.92 d (9.3)	3.85 d (9.2)	3.91 d (9.3)	3.85 d (9.3)
26	1.69 s	1.60 s	1.67 s	1.61 s
27	1.81 s	1.74 s	1.80 s	1.74 s
28	1.32 s	1.26 s	1.31 s	1.32 s
29	1.20 s	1.09 s	1.17 s	1.12 s
30	0.99 s	0.89 s	1.00 s	0.97 s
	C-3-Glc	C-3-Glc	C-3-Xyl	C-3-Glc
1	4.94 d (7.7)	4.88 d (7.4)	4.91 d (6.6)	4.93 d (7.6)
2	4.12 m	4.12 m	4.27 m	4.14 m
3	4.21 m	4.21 m	4.30 m	4.30 m
4	4.20 m	4.20 m	4.23 m	4.17 m
5	4.31 m	4.21 m	4.38 m, 3.77 t (10.4)	4.25 m
6	4.86 d (10.4), 4.38 m	4.80 d (10.9), 4.28 m		4.56 d (11.3), 4.37 m
	Xyl	Glc′	Glc	Xyl
1	5.27 d (7.2)	5.03 d (7.6)	5.42 d (7.6)	5.25 d (7.0)
2	4.14 m	4.15 m	4.30 m	4.12 m
3	4.21 m	3.90 m	4.18 m	4.15 m
4	4.30 m	4.29 m	4.40 m	4.22 m
5	4.44 m	4.21 m	4.00 m	4.40 m, 3.70 t (10.6)
6		4.45 m	4.53 m	
	Xyl′	Xyl		
1	5.02 d (7.4)	4.95 d (7.3)		
2	4.10 m	4.03 m		
3	4.11 m	4.12 m		
4	4.30 m	4.07 m		
5	4.40 m	4.33 m		
	3.75 t (11.5)	3.69 t (11.0)		

[a] 500 MHz; referenced to δ 7.58 (C_5D_5N); *J* values (Hz) in parentheses.

ranosyl}-21-*O*-*β*-D-glucopyranoside (2): amorphous powder; $[\alpha]^{20}_D$ −1.9° (*c* 1.29, MeOH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; HRESIMS *m*/*z* 1091.6008 (calcd for $C_{54}H_{91}O_{22}$ [M − H]$^-$, 1091.6001); GC analysis of sugar components, t_R 4.84 and 17.40 min.

3*β*,20*S*,21-Trihydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-xylopyranosyl(1→3)]-*β*-D-glucopyranosyl}-21-*O*-*β*-D-glucopyranoside (3): amorphous powder; $[\alpha]^{20}_D$ −6.6° (*c* 0.69, MeOH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; HRESIMS *m*/*z* 1063.6059 (calcd for $C_{53}H_{91}O_{21}$ [M + H]$^+$, 1063.6052); GC analysis of sugar components, t_R 7.51, 4.84, and 17.36 min.

3*β*,19,20*S*,21-Tetrahydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-xylopyranosyl(1→3)]-α-L-arabinopyranosyl}-21-*O*-*β*-D-glucopyranoside (4): amorphous powder; $[\alpha]^{20}_D$ −12.2° (*c* 1.14, MeOH); ^{1}H and ^{13}C NMR, see Tables 1 and 2; HRESIMS *m*/*z* 1049.5896 (calcd for $C_{52}H_{89}O_{21}$ [M + H]$^+$, 1049.5891); GC analysis of sugar components, t_R 7.50, 4.83, 17.37, and 6.13 min.

3*β*,19,20*S*,21-Tetrahydroxydammar-24-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-xylopyranosyl(1→3)]-*β*-D-glucopyranosyl}-21-*O*-*β*-D-glucopyranoside (5): amorphous powder; $[\alpha]^{20}_D$ −6.0° (*c* 1.00, MeOH); ^{1}H and ^{13}C NMR, see Tables 2−4; HRESIMS *m*/*z* 1077.5847 (calcd for $C_{53}H_{89}O_{22}$ [M − H]$^-$, 1077.5845); GC analysis of sugar components, t_R 7.52, 4.82, and 17.37 min.

19-Oxo-3*β*,20*S*,21-trihydroxy-25-hydroperoxydammar-23-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-xylopyranosyl(1→3)]-α-L-arabinopyranosyl}-21-*O*-*β*-D-glucopyranoside (6): amorphous powder; $[\alpha]^{20}_D$ −3.6° (*c* 0.91, MeOH); ^{1}H and ^{13}C NMR, see Tables 2−4; HRESIMS *m*/*z* 1077.5483 (calcd for $C_{52}H_{85}O_{23}$ [M − H]$^-$, 1077.5481); GC analysis of sugar components, t_R 7.50, 4.84, 17.39, and 6.13 min.

3*β*,12,20*S*-Trihydroxy-25-hydroperoxydammar-23-ene 3-*O*-{[*β*-D-glucopyranosyl(1→2)-*β*-D-glucopyranosyl]-20-*O*-[*β*-D-xylopyranosyl(1→6)]-*β*-D-glucopyranoside (7): amorphous powder; $[\alpha]^{20}_D$ +20.3° (*c* 0.83, MeOH); ^{1}H and ^{13}C NMR, see Tables 2−4; HRESIMS *m*/*z* 1111.5897 (calcd for $C_{53}H_{91}O_{24}$ [M + H]$^+$, 1111.5893); GC analysis of sugar components, t_R 7.50 and 17.38 min.

19-Oxo-3*β*,20*S*,21,24*S*-tetrahydroxydammar-25-ene 3-*O*-{[α-L-rhamnopyranosyl(1→2)][*β*-D-xylopyranosyl(1→3)]-α-L-arabinopyranosyl}-21-*O*-*β*-D-glucopyranoside (8): amorphous powder; $[\alpha]^{20}_D$ 0° (*c* 0.63, MeOH); ^{1}H and ^{13}C NMR, see Tables 2−4; HRESIMS *m*/*z* 1063.5688 (calcd for $C_{52}H_{87}O_{22}$ [M + H]$^+$, 1063.5689); GC analysis of sugar components, t_R 7.51, 4.81, 17.39, and 6.13 min.

3*β*,12*β*,23*S*,24*R*-Tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-xylopyranosyl(1→2)][*β*-D-xylopyranosyl-(1→6)]-*β*-D-glucopyranoside (9): amorphous powder; $[\alpha]^{20}_D$ 0° (*c* 0.34, MeOH); ^{1}H and ^{13}C NMR, see Tables 5 and 6;

Table 6. ^{13}C NMR Data of Compounds **9**−**15** in C_5D_5N[a]

carbon	9	10	11	12	13	14	15
1	39.5	39.3	39.5	39.6	39.5	39.4	39.4
2	27.1	26.9	27.1	27.1	27.1	26.9	27.0
3	89.3	89.3	89.0	89.2	89.1	89.3	89.3
4	39.9	39.8	40.1	40.1	40.1	39.9	39.9
5	56.7	56.5	56.8	56.8	56.8	56.6	56.6
6	18.7	18.6	18.8	18.7	18.7	18.6	18.6
7	35.3	35.2	35.4	35.4	35.3	35.2	35.2
8	40.2	40.2	40.3	40.3	40.3	40.2	40.2
9	50.6	50.5	50.6	50.7	50.5	50.4	50.4
10	37.2	37.1	37.3	37.2	37.3	37.0	37.1
11	32.2	31.9	32.4	32.1	32.1	32.0	31.8
12	70.8	70.6	70.8	70.8	70.8	70.7	70.7
13	49.5	49.5	49.7	49.3	49.8	49.7	49.7
14	52.5	52.4	52.5	52.2	52.5	52.3	52.3
15	32.0	32.2	32.0	32.4	31.8	31.7	31.7
16	27.1	27.9	28.0	27.1	27.8	27.6	27.7
17	52.7	52.6	52.7	52.7	52.8	52.6	52.7
18	15.9	15.8	15.9	15.9	16.0	15.8	15.9
19	16.4	16.6	16.8	16.5	16.8	16.6	16.6
20	79.6	79.5	79.7	79.7	79.5	79.4	79.4
21	27.7	27.7	27.8	28.0	27.3	27.9	27.0
22	37.5	37.4	37.6	37.6	34.6	34.5	34.5
23	67.3	67.3	67.4	67.4	71.8	71.8	71.7
24	81.0	81.1	81.0	81.0	77.1	77.1	77.0
25	79.4	79.3	79.5	79.5	79.7	79.5	79.6
26	24.8	24.8	24.7	24.9	24.9	24.7	24.8
27	30.6	30.5	30.7	30.7	30.6	30.4	30.4
28	28.0	28.2	28.3	27.8	28.0	27.9	27.9
29	16.7	16.7	16.8	16.8	16.4	16.3	16.3
30	18.1	18.0	18.1	18.2	18.0	17.9	17.9
$-OCOCH_3$					171.1	171.1	171.1
$-OCOCH_3$					21.4	21.3	21.3
	C-3-Glc	C-3-Glc	C-3-Xyl	C-3-Glc	C-3-Xyl	C-3-Glc	C-3-Glc
1	105.1	105.1	106.0	105.1	105.9	105.3	105.2
2	83.9	83.4	83.4	84.1	84.2	84.3	84.0
3	78.3	78.3	78.2	78.7	78.4	78.5	78.4
4	71.5	71.2	71.2	71.8	71.3	71.7	71.5
5	78.3	78.3	66.9	78.5	67.0	78.3	78.4
6	70.1	70.1		63.1		63.1	70.1
	Xyl	Glc′	Glc	Xyl	Xyl′	Xyl	Xyl
1	107.1	106.1	106.3	107.1	107.3	107.2	107.2
2	76.6	76.7	78.2	76.8	76.8	76.7	76.7
3	78.3	78.1	77.3	78.4	78.5	78.2	78.4
4	71.3	71.9	71.8	71.4	71.2	71.2	71.2
5	67.7	78.2	78.5	67.8	67.8	67.7	67.6
6		62.9	62.9				
	Xyl′	Xyl					Xyl′
X_1	106.0	106.0					106.1
X_2	74.9	74.9					75.0
X_3	76.7	77.1					76.7
X_4	71.3	71.5					71.2
X_5	67.2	67.2					67.2

[a] 125 MHz; referenced to δ 135.9 (C_5D_5N).

HRESIMS *m*/*z* 919.5262 (calcd for $C_{46}H_{79}O_{18}$ $[M + H]^+$, 919.5266); GC analysis of sugar components, t_R 7.52 and 17.36 min.

3*β*,12*β*,23*S*,24*R*-Tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-glucopyranosyl(1→2)][*β*-D-xylopyranosyl-(1→6)]-*β*-D-glucopyranoside (10): amorphous powder; $[\alpha]^{20}_D$ 0° (*c* 0.54, MeOH); ^1H and ^{13}C NMR, see Tables 5 and 6; HRESIMS *m*/*z* 947.5212 (calcd for $C_{47}H_{79}O_{19}$ $[M - H]^-$, 947.5215); GC analysis of sugar components, t_R 7.51 and 17.38 min.

3*β*,12*β*,23*S*,24*R*-Tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-glucopyranosyl(1→2)]-*β*-D-xylopyranoside (11): amorphous powder; $[\alpha]^{20}_D$ +17.8° (*c* 0.30, MeOH); ^1H and ^{13}C NMR, see Tables 5 and 6; HRESIMS *m*/*z* 787.4848 (calcd for $C_{41}H_{71}O_{14}$ $[M + H]^+$, 787.4843); GC analysis of sugar components, t_R 7.51 and 17.38 min.

3*β*,12*β*,23*S*,24*R*-Tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-xylopyranosyl(1→2)]-*β*-D-glucopyranoside (12): amorphous powder; $[\alpha]^{20}_D$ +18.1° (*c* 0.48, MeOH); ^1H and ^{13}C NMR, see Tables 5 and 6; HRESIMS *m*/*z* 787.4848 (calcd for $C_{41}H_{71}O_{14}$ $[M + H]^+$, 787.4843); GC analysis of sugar components, t_R 7.52 and 17.38 min.

23-*O*-Acetyl-3*β*,12*β*,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-xylopyranosyl(1→2)]-*β*-D-xylopyranoside (13): amorphous powder; $[\alpha]^{20}_D$ +36.8° (*c* 0.98, MeOH); ^1H and ^{13}C NMR, see Tables 6 and 7; HRESIMS *m*/*z* 797.4685 (calcd for $C_{42}H_{69}O_{14}$ $[M - H]^-$, 797.4687); GC analysis of sugar components, t_R 7.50 min.

23-*O*-Acetyl-3*β*,12*β*,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-xylopyranosyl(1→2)]-*β*-D-glucopyranoside (14): amorphous powder; $[\alpha]^{20}_D$ +39.5° (*c* 0.83, MeOH); ^1H and ^{13}C NMR, see Tables 6 and 7; HRESIMS *m*/*z* 829.4943 (calcd for $C_{43}H_{73}O_{15}$ $[M + H]^+$, 829.4949); GC analysis of sugar components, t_R 7.51 and 17.39 min.

23-*O*-Acetyl-3*β*,12*β*,23*S*,24*R*-tetrahydroxy-20*S*,25-epoxydammarane 3-*O*-[*β*-D-xylopyranosyl(1→2)][*β*-D-xylopyranosyl(1→6)]-*β*-D-glucopyranoside (15): amorphous powder; $[\alpha]^{20}_D$ +17.6° (*c* 1.03, MeOH); ^1H and ^{13}C NMR, see Tables 6 and 7; HRESIMS *m*/*z* 961.5376 (calcd for $C_{48}H_{81}O_{19}$ $[M +$

Table 7. ^{1}H NMR Data of Compounds **13**−**15**, in C_5D_5N[a]

	13	14	15
1	1.72 m, 0.99 m	1.53 m, 0.81 m	1.65 m, 0.90 m
2	2.40 m, 1.95 m	2.40 m, 1.83 m	2.60 m, 1.86 m
3	3.35 dd (11.6, 4.0)	3.31 dd (11.6, 4.2)	3.28 dd (11.3, 3.5)
5	0.84 d (10.6), 1.61 m	0.73 d (10.5), 1.55 m	0.67 d (9.0), 1.50 m
6	1.49 m	1.40 m	1.37 m
7	1.50 m, 1.30 m	1.41 m, 1.20 br d (10.4)	1.39 m, 1.18 m
9	1.53 m	1.40 m	1.40 m
11	2.16 m, 1.50 m	2.02 m, 1.43 m	2.07 m, 1.42 m
12	3.83 m	3.79 m	3.73 m
13	2.00 m	1.91 t (10.1)	1.90 t (10.5)
15	1.50 m, 1.04 m	1.42 m, 0.97 m	1.42 m, 0.95 m
16	1.90 m, 1.38 m	1.81 m, 1.48 m	1.81 m, 1.42 m
17	2.31 m	2.24 m	2.20 m
18	1.01 s	0.96 s	0.91 s
19	0.94 s	0.83 s	0.83 s
21	1.57 s	1.31 s	1.48 s
22	2.38 m, 2.20 m	2.29 m, 2.10 m	2.28 m, 2.10 m
23	5.80 dt (10.5, 4.0)	5.70 dt (10.5, 4.0)	5.73 dt (10.8, 4.0)
24	4.10 d (9.9)	4.00 d (9.8)	4.02 m
26	1.64 s	1.62 s	1.61 s
27	1.80 s	1.74 s	1.73 s
28	1.37 s	1.32 s	1.26 s
29	1.18 s	1.11 s	1.10 s
30	1.02 s	0.97 s	0.91 s
$OCOCH_3$	2.08 s	2.01 s	2.00 s
	C-3-Xyl	C-3-Glc	C-3-Glc
1	4.90 d (7.3)	4.93 d (7.7)	4.86 d (7.6)
2	4.18 m	4.12 m	4.02 m
3	4.25 m	4.30 m	4.22 m
4	4.30 m	4.15 m	4.10 m
5	4.39 dd (11.2, 4.7), 3.78 m	4.12 m	4.22 m
6		4.56 d (10.2), 4.33 m	4.80 d (10.7), 4.27 m
	Xyl′	Xyl	Xyl
1	5.30 d (7.2)	5.25 d (6.9)	5.23 d (7.2)
2	4.19 m	4.10 m	4.08 m
3	4.21 m	3.90 m	4.12 m
4	4.22 m	4.20 m	4.20 m
5	4.46 dd (11.2, 5.1), 3.78 m	4.40 m, 3.72 t (10.6)	4.31 m
			Xyl′
1			4.98 d (7.2)
2			4.02 m
3			4.02 m
4			4.20 m
5			4.35 m, 3.67 t (9.7)

[a] 500 MHz; referenced to δ 7.58 (C_5D_5N); *J* values (Hz) in parentheses.

H]$^+$, 961.5372); GC analysis of sugar components, t_R 7.50 and 17.37 min.

Acid Hydrolysis of Compounds 1−15.[10] Compounds **1**−**15** (4 mg each) in 10% HCl−dioxane (1:1, 1 mL) were each heated at 80 °C for 4 h in a water bath. The reaction mixtures were neutralized with Ag_2CO_3, filtered, and then extracted with $CHCl_3$ (1 mL × 3). After concentration, each H_2O layer (monosaccharide portion) was examined by TLC with $CHCl_3$−MeOH−H_2O (55:45:10) and compared with authentic samples.

Determination of Sugar Components. The monosaccharide subunits were obtained by hydrochloric acid hydrolysis as described above. The sugar residue was then dissolved in 2 mL of H_2O, 15 mg of $NaBH_4$ was added, and the mixture was left to stand for 2 h at ambient temperature. Several drops of 25% HOAc were added until the pH value was 4−5. After co-distillation with CH_3OH to remove the extra boracic acid and water, the resulting products were put into a vacuum-desiccator overnight and then heated at 110 °C for 15 min to further remove the water. Next, 3 mL of acetic anhydride was added and the solution was kept at 100 °C for 1 h. Then the solution was cooled and co-distillated with toluene several times. The acetate derivatives were dissolved in $CHCl_3$ and washed with distilled water and then sodium sulfate anhydrous, filtered, and then concentrated to 0.1 mL. The acetate derivatives were subjected to GC analysis to identify the sugars. Column temperature 210 °C; injection temperature 250 °C; carrier gas N_2 at a flow rate of 25 mL/min; D-glucose, D-xylose, L-arabinose, and L-rhamnose 17.38, 7.52, 6.13, and 4.85 min, respectively.

Bioassay. Sensory Testing. Sweetness relative to sucrose was evaluated by a human sensory panel.[11] None of the compounds were sweeter than sucrose.

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Supporting Information Available: Figures of HMBC interrelations of new compounds **1**−**5**, **9**, **10**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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