Four Cycloartane Triterpenoids and Six Related Saponins from *Passiflora edulis*[1]

Kazuko Yoshikawa,* Susumu Katsuta, Junko Mizumori, and Shigenobu Arihara

Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Yamashiro-Cho, Tokushima 770-8514, Japan

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Four cycloartane triterpenes, cyclopassifloic acids A (**1**), B (**2**), C (**3**), and D (**4**), and six related saponins, cyclopassiflosides I (**5**), II (**6**), III (**7**), IV (**8**), V (**9**), and VI (**10**), were isolated from the leaves and stems of *Passiflora edulis*, and their structures were elucidated on the base of extensive NMR experiments and chemical methods. Cyclopassifloic acids A−D were assigned as 22(*R*),24(*S*)-1α,3*β*,22,24,31-pentahydroxy-24-methylcycloartan-28-oic acid; 24(*S*)-1α,3*β*,24,31-tetrahydroxy-24-methylcycloartan-28-oic acid; 20(*S*),24(*S*)-1α,3*β*,21,24,31-pentahydroxy-24-methylcycloartan-28-oic acid; and 22(*R*)-1α,3*β*,22-trihydroxy-24-oxocycloartan-28-oic acid, respectively. Cyclopassiflosides I−VI, in turn, were established as the 28-*O*-*β*-D-glucopyranosides of cyclopassifloic acids A−D. Finally, cyclopassiflosides III and V were demonstrated as the 28,31-bis-*O*-*β*-D-glucopyranosides of cyclopassifloic acids B and C, respectively. Also obtained in this investigation were the known compounds passiflorin (**11**) and passifloric acid (**12**).

Passion flowers (*Passiflora* spp.) (Passifloraceae) have been used as traditional folk medicines of Europe and North America owing to their sedative and anti-hypertensive properties.[2] A number of *Passiflora* species are present as official drugs in the pharmacopeias of several countries; *P. incarnata*, for example, used to be used as a herbal sedative in the 1980s in Britain.[3] Previous investigations have reported the isolation of passiflorin,[4,5] quadrangulo-side,[6] 9,19-cyclolanosta-22,25-epoxy-3*β*,21,22(*R*)-triol-3*β*-*O*-gentiobioside,[7,8] 9,19-cyclolanosta-21,24-epoxy-3*β*,25,26-triol-3*β*-*O*-gentiobioside,[7,8] and oleanolic acid 3-*O*-sophoroside from *Passiflora* species.[7,8] As part of our ongoing study on the saponin constituents of higher plants,[9,10] we have investigated *P. edulis* Sims cultivated in a greenhouse. The water extract of the leaves and stems of *P. edulis* gave four new cycloartane triterpenes, termed cyclopassifloic acids A (**1**), B (**2**), C (**3**), and D (**4**), and their related saponins, cyclopassiflosides I (**5**), II (**6**), III (**7**), IV (**8**), V (**9**), and VI (**10**), along with a known cycloartane saponin, passiflorin (**11**) and its aglycon, passifloric acid (**12**). This paper discribes experimental evidence that has led to the structural and stereochemical assignments of compounds **1**−**10**.

Results and Discussion

Cyclopassifloic acid A (**1**) was obtained as needles, and its IR spectrum showed hydroxy (3450 cm^{-1}) and carboxy (1710 cm^{-1}) absorptions. The molecular formula $C_{31}H_{52}O_7$ for **1**, obtained from the observation of a quasimolecular ion at *m*/*z* 535 $[M - H]^-$ in the negative-ion FABMS and DEPT ^{13}C NMR data, indicated six equivalents of unsaturation, one of which was accounted for by a carboxy group. This implied that **1** was a pentacyclic triterpene. The ^1H NMR spectrum of **1** exhibited three doublet methyl signals at *δ* 1.20, 1.23, and 1.27; three singlet methyl signals at *δ* 0.97, 1.06, and 1.75; two characteristic cyclopropane protons at *δ* 0.56 and 0.82 (each d, $J = 4.0$ Hz), for a hydroxymethylene group at *δ* 4.13 and 4.22 (each d, $J = 10.5$ Hz); and three hydroxymethine signals at *δ* 3.92 (dd, $J = 2.5, 2.5$ Hz), 4.58 (m), and 5.59 (dd, $J = 13.0, 4.0$ Hz). The ^{13}C NMR spectral comparison of **1** with **12**, showed that **1** differs structurally from **12** only in the side chain (C-20−C-27 and C-30), which is composed of one each oxymethylene and methine, one oxygenated quaternary carbon, one methylene, two methine, and three secondary methyl carbons for **1**. The regiochemistry of these side chain carbons was established from $^1H-^1H$ and $^{13}C-^1H$ COSY and HMBC experiments. The long-range correlations between H_3-21 and C-22, H-22 and C-24, H_2-31 and C-24, and H-25 and C-24 established the presence of a secondary hydroxy group at C-22 and a tertiary hydroxy and a hydroxymethyl group at the C-24 position. Thus, cyclopassifloic acid A was determined as **1** (except for the configuration at C-22 and C-24). The absolute configurations at C-22 and C-24 were elucidated by derivation of **1** and **12** to 22(*R*),24(*S*)-1α,3*β*,22 ,24,28,31-hexahydroxy-24-methylcycloartane (**13**). Hence, $NaBH_4$ reduction of the monomethyl ester obtained by methylation of **1** with CH_2N_2 gave **13**, which was also obtained by $NaBH_4$ treatment of the methyl ester of **12**. Thus, the structure and stereochemistry of cyclopassifloic acid A were determined as **1**.

Cyclopassifloic acid B (**2**), $C_{31}H_{52}O_6$, showed a $[M - H]^-$ ion peak at *m*/*z* 519, 16 mass units less than that of **1**. A ^{13}C NMR spectral comparison of **2** with **1** showed that **2** differed structurally from **1** only in the side chain. In the ^{13}C NMR spectrum of **2**, the C-20 (*δ* 37.4) and C-22 (*δ* 32.0) signals were shifted upfield by 6.0 and 38.3 ppm, respectively, while that of C-21 (*δ* 19.8) was shifted downfield by 7.1 ppm, compared with those of **1**, indicating the absence of the secondary hydroxy group at the C-22. Thus, cyclopassifloic acid B was determined as **2** (except for the configuration at C-24). The absolute configuration at C-24 was determined to be *S* through the application of the benzoate rule[11] for the 1,3,31,glc(Ac)$_4$-heptaacetate and its 24-benzoate (**14**) of **6**, which, on alkaline hydrolysis, gave **2**. Thus, the structure and stereochemistry of cyclopassifloic acid B were determined as **2**.

Cyclopassifloic acid C (**3**) showed the same quasimolecular ion peak (negative FABMS, *m*/*z* 535 $[M - H]^-$) as **1**. The ^1H NMR spectrum of **3** exhibited two doublet methyl signals at *δ* 1.19 and 1.21 and four singlet methyl signals at *δ* 1.06, 1.55, 1.55, and 1.74. In the ^{13}C NMR spectrum of **3**, the C-17 (*δ* 55.1), C-20 (*δ* 74.7), C-21 (*δ* 26.1), and C-22 (*δ* 38.1) signals were shifted downfield by 2.3, 37.3, 6.3, and 6.1 ppm, respectively, while those of C-16 (*δ* 23.0)

* To whom correspondence should be addressed. Tel.: 88-622-9611. Fax: 88-655-3057. E-mail: yosikawa@ph.bunri-u.ac.jp.

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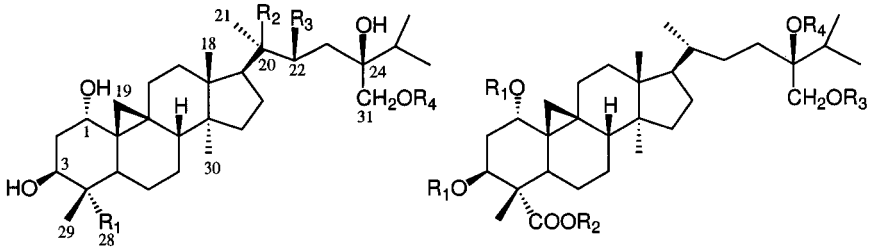
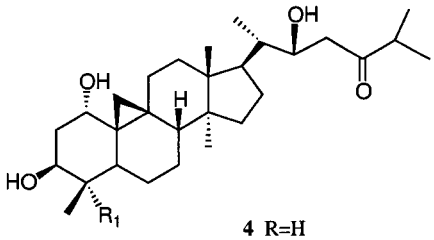
Chart 1

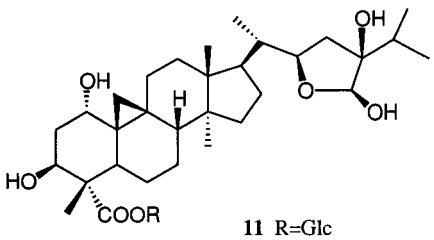


1 R_1=COOH, R_2=R_4=H, R_3=OH
3 R_1=COOH, R_2=OH, R_3=R_4=H
5 R_1=COOGlc, R_2=R_4=H, R_3=OH
8 R_1=COOGlc, R_2=OH, R_3=R_4=H
9 R_1=COOGlc, R_2=OH, R_3=H, R_4=Glc
13 R_1=CH_2OH, R_2=R_4=H, R_3=OH

2 R_1=R_2=R_3=R_4=H
6 R_1=R_3=R_4=H, R_2=Glc
7 R_1=R_4=H, R_2=R_3=Glc
14 R_1=R_3=Ac, R_2=(Glc)Ac_4, R_4=Bz



4 R=H
10 R=Glc



11 R=Glc
12 R=H

and C-23 (δ 29.2) were shifted upfield by 5.5 and 2.5 ppm. However, the C-24−C-27 signals were not shifted when compared with those of **2**, indicating the hydroxy group to be at the C-20 position. The absolute configuration at C-24 was assumed to be the same as that of **2** because the carbon signals due to C-23−C-25, and C-31 of **3** were superimposable on those of **2**. From these data and by biogenetic considerations, the structure of cyclopassifloic acid C was determined as **3**.

Cyclopassifloic acid D (**4**), $C_{30}H_{48}O_6$, showed a $[M - H]^-$ ion peak at *m/z* 503. A ^{13}C NMR spectral comparison of **4** with **1** showed that **4** differs structurally from **1** only in the side chain, which was composed of one secondary hydroxy group and two methine, one methylene, three secondary methyl, and one carbonyl carbons for **4**. The $^1H-^1H$ COSY and HMBC experiments corroborated the connectivities between these carbons. The hydroxylated tertiary carbon (δ 69.7) was defined at C-22 from long-range couplings between H_3-21/C-22 and H_2-23/C-22. Also, the long-range couplings between H-22 and C-24, H_3-26 and C-24, and H_3-27 and C-24 established the carbonyl at the C-24 position. The stereochemistry of **4** was confirmed by derivation from **1** with $NaIO_4$ to **4**. Hence, the structure of cyclopassifloic acid D was determined as **4**.

Cyclopassifloside I (**5**) was obtained as an amorphous solid. The molecular formula was deduced as $C_{37}H_{62}O_{12}$ from a $[M - H]^-$ peak observed at *m/z* 697 in the negative-ion FABMS and from its DEPT experiment. The IR spectrum showed hydroxy (3400 cm^{-1}) and ester (1730 cm^{-1}) absorptions. The ^1H and ^{13}C NMR spectra of **5** showed the presence of **1** and an ester-linked glucose from the characteristic chemical shifts of the anomeric proton (δ 6.53) and carbon (δ 96.5). On alkaline hydrolysis, **5** afforded **1** as the aglycon, while acid treatment of **5** gave D-glucose, which was confirmed by specific rotation using chiral detection by HPLC analysis.[12,13] The coupling constant (J = 8.0 Hz) of the anomeric proton in the ^1H NMR spectrum of **5** indicated that the glucose unit has a β configuration. A ^{13}C NMR spectral comparison of **5** with **1** showed glycosylation shifts of −3.5 ppm at the C-28 signal and +0.6 ppm at the C-4 signal, demonstrating the sugar linkage to be located at C-28.[14,15] Furthermore, in the HMBC experiment on **5**, the anomeric proton signal at δ 6.53 gave a cross-peak with the ester carbon signal at δ 176.6 (C-28). Thus, the structure of **5** was formulated as cyclopassifloic acid A 28-*O*-β-D-glucopyranoside.

The negative-ion FABMS of cyclopassifloside II (**6**), $C_{37}H_{62}O_{11}$, gave a quasimolecular ion at *m/z* 681 $[M - H]^-$, 16 mass units less than that of **5**. The ^1H and ^{13}C NMR spectra of **6** showed that it was composed of **2** and an ester-linked glucose (δ 6.52, 96.6). The alkaline hydrolysis of **6** afforded **2** as the aglycon. The ^{13}C NMR shifts for C-4 (δ 56.5) and C-28 (δ 176.6) and the sugar moiety at C-28 of **6** were also in good agreement with those of **5**. Hence, the structure of **6** was formulated as cyclopassifloic acid B 28-*O*-β-D-glucopyranoside.

Cyclopassifloside III (**7**) gave a quasimolecular ion at *m/z* 843 $[M - H]^-$, 162 mass units greater than that of **6**. The ^1H and ^{13}C NMR spectra of **7** showed the presence of **2**, a β-glucopyranosyl group (δ 4.96, d, J = 8.0 Hz), and an ester-linked β-glucosyl group (δ 6.49, d, J = 8.0 Hz). Enzymatic hydrolysis of **7** gave **6**. The ^{13}C NMR spectral comparison of **7** with **6** disclosed C-31 (+9.0 ppm) as the glycosylation site in the former. Therefore, the structure of **7** was established as cyclopassifloic acid B 28,31-bis-*O*-β-D-glucopyranoside. Recently, Kasai and co-workers reported cyclotricuspidoside A from the leaves and stems of *Trichosanthes tricuspidata*, but the absolute configuration at C-24 remained unclear.[16] Compound **7** seems to be identical with cyclotricuspidoside A because of the good agreement of both sets of NMR data.

Cyclopassifloside IV (**8**) had the same molecular formula, $C_{37}H_{62}O_{12}$, as **5**. The ^1H and ^{13}C NMR spectra of **8** showed the presence of **3** and an ester-linked β-glucosyl group (δ 6.40, d, J = 8.0 Hz). On alkaline hydrolysis, **8** afforded **3** as the aglycon. The ^1H and ^{13}C NMR shifts for the aglycon and the sugar moiety at C-28 of **8** were in good agreement

with those of **5**. Hence, the structure of **8** was formulated as cyclopassifloic acid C 28-*O*-*β*-D-glucopyranoside.

Cyclopassifloside V (**9**) gave a quasimolecular ion at *m/z* 859 $[M - H]^-$, 162 mass units larger than that of **8**. The ^{13}C NMR spectral comparison of **9** with **8** showed that these two compounds differed structurally only in the side chain, though a sugar unit is affixed to the C-28 position in both cases. Enzymatic hydrolysis of **9** gave **8**. In the ^{13}C NMR spectrum of **9**, the C-31 (δ 75.0) signal was shifted downfield by 8.9 ppm compared with that of **8**, indicating a second glucosyl moiety to be at the C-31 position. Thus, the structure of **9** was formulated as cyclopassifloic acid C 28,31-bis-*O*-*β*-D-glucopyranoside.

Cyclopassifloside VI (**10**) was obtained as an amorphous solid. The molecular formula was deduced as $C_{36}H_{58}O_{11}$ from a $[M - H]^-$ peak observed at *m/z* 665 in the negative-ion FABMS and from its DEPT ^{13}C NMR data. The IR spectrum showed hydroxy (3450 cm^{-1}), ester (1735 cm^{-1}), and ketone (1710) absorptions.The ^1H and ^{13}C NMR spectra of **10** demonstrated the presence of **4** and an ester-linked *β*-glucosyl group (δ 6.48, d, J = 8.0 Hz). Alkaline hydrolysis of **10** afforded **4** as the aglycon. The ^1H and ^{13}C NMR shifts for the aglycon and the sugar moiety at C-28 of **10** were in good agreement with those of **5**. Hence, the structure of **10** was formulated as cyclopassifloic acid D 28-*O*-*β*-D-glucopyranoside.

Experimental Section

General Experimental Procedures. Melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were obtained on a JASCO DIP-360 polarimeter. IR spectra were recorded on a Hitachi IR-27G, and NMR spectra were run on Varian UNITY 600 and/or a JEOL GSX-400 spectrometer in C_5D_5N solution, using TMS as internal standard. NMR experiments included the $^1H-^1H$ COSY, HMQC, HMBC, DEPT, and ROESY pulse sequences. Coupling constants (J values) are given in Hz. FABMS (Xe gun, 10 kV, triethylene glycol as the matrix) were measured on a JEOL JMS−HX-100 mass spectrometer. Kieselgel 60 (230−400 mesh, Merck) and Si gel $60F_{254}$ (Merck) were used for column chromatography and TLC, respectively. For HPLC analysis, samples were injected into a Hitachi HPLC system (L-6200 pump) equipped with an RI detector (Waters 410) and chiral detector (Shodex OR-1).

Plant Material. *P. edulis* was cultivated at the botanical garden of Tokushima Bunri University, and collected in March 1982. A specimen (TB 5425) is deposited at the herbarium of the Department of Pharmacognosy, Tokushima Bunri University, Tokushima, Japan.

Extraction and Isolation. The air-dried leaves and stems (1.8 kg) of *P. edulis* were extracted with hot water. The water extract was passed through an Amberlite XAD-2 column. The column was washed with H_2O, then eluted with 20, 40, and 100% MeOH, successively. The MeOH eluate (42 g) was purified by repeated column chromatography over Si gel, eluting with $CHCl_3$−MeOH−H_2O (25:4:0.1−25:8:0.5), $CHCl_3$−MeOH−EtOAc−H_2O (4:2:6:1, lower layer), and $CHCl_3$−MeOH−EtOAc−H_2O (2:2:4:1, lower layer) to afford cyclopassifloic acids A (**1**, 35 mg), B (**2**, 10 mg), C (**3**, 8 mg), and D (**4**, 6 mg), cyclopassiflosides I (**5**, 170 mg), II (**6**, 130 mg), III (**7**, 1.30 g), IV (**8**, 90 mg), V (**9**, 340 mg), and VI (**10**, 100 mg); passiflorin (**11**, 4.50 g); and passifloric acid (**12**, 20 mg).

Cyclopassifloic acid A (1): colorless needles, mp 229−231 °C; $[\alpha]^{25}_D$ +56.6 ° (*c* 1.5, MeOH); IR (KBr) ν_{max} 3450 (OH), 1710 (COOH), 1050 cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.56, 0.82 (1H each, d, J = 4.0 Hz, H_2-19), 0.97 (3H, s, H_3-30), 1.06 (3H, s, H_3-18), 1.20, 1.27 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.23 (3H, d, J = 7.0 Hz, H_3-21), 1.75 (3H, s, H_3-29), 2.03 (2H, m, H_2-23), 2.31 (1H, ddd, J = 13.0, 13.0, 2.5 Hz, H-2*β*), 2.40 (1H, qq, J = 7.0 Hz, H-25), 2.52 (1H, ddd, J = 13.0, 4.0, 2.5 Hz, H-2α), 2.77 (1H, m, H-11α), 3.44 (1H, dd, J = 12.0, 4.5 Hz, H-5α), 3.92 (1H, dd, J = 2.5, 2.5 Hz, H-1), 4.13, 4.22 (1H each, d, J = 10.5 Hz, H_2-31), 4.58 (1H, m, H-22), 5.59 (1H, dd, J = 13.0, 4.0 Hz, H-3); ^{13}C NMR data, see Table 1; HMBC (H/C) 1/3, 1/5, 2/3, 2/10, 6/5, 6/8, 6/10, 11/9, 11/10, 11/12, 17/13, 17/14, 17/16, 17/20, 18/12, 18/12, 18/13, 18/14, 18/17, 19/1, 19/11, 21/17/, 21/22, 23/20, 23/22, 23/24, 23/25, 23/31, 25/23, 25/24, 25/26, 25/27, 26/24, 26/25, 27/24, 27/25, 29/3, 29/4, 29/5, 30/8, 30/13, 30/14, 30/15, 31/23, 31/24, 31/25; FABMS *m/z* $[M - H]^-$ 535; *anal.* C 67.00%, H 9.95%, calcd for $C_{31}H_{52}O_7 \cdot H_2O$, C 67.12%, H 9.81%.

Cyclopassifloic acid B (2): amorphous powder; $[\alpha]^{25}_D$ +48.7° (*c* 2.2, MeOH); IR (KBr) ν_{max} 3450 (OH), 1700 (COOH), 1040 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.53, 0.84 (1H each, d, J = 4.0 Hz, H_2-19), 0.99 (3H, s, H_3-30), 1.03 (3H, s, H_3-18), 1.00, 1.22 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.22 (3H, d, J = 7.0 Hz, H_3-21), 1.73 (3H, s, H_3-29), 2.28 (1H, m, H-2*β*), 2.28 (1H, m, H-25), 2.56 (1H, ddd, J = 13.0, 4.0, 2.5 Hz, H-2α), 2.75 (1H, m, H-11α), 3.41 (1H, dd, J = 12.0, 4.0 Hz, H-5α), 3.92 (1H, br s, H-1), 3.99, 4.05 (1H each, d, J = 11.0 Hz, H2−31), 5.56 (1H, dd, J = 12.0, 4.0 Hz, H-3); ^{13}C NMR data, see Table 1; FABMS *m/z* $[M - H]^-$ 519; *anal.* C 68.92%, H 10.34%, calcd for $C_{31}H_{52}O_6 \cdot H_2O$, C 69.11%, H 10.10%.

Cyclopassifloic acid C (3): amorphous powder; $[\alpha]^{25}_D$ +23.8° (*c* 2.1, MeOH); IR (KBr) ν_{max} 3450 (OH), 1710 (COOH), 1050 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.56, 0.85 (1H each, d, J = 4.0 Hz, H_2-19), 1.06 (3H, s, H-30), 1.19, 1.21 (3H each, d, J = 7.0 Hz, H_3-26 and 27), 1.55 (3H, s, H_3-18), 1.55 (3H, s, H3-21), 1.74 (3H, s, H_3-29), 2.45 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.75 (1H, m, H-11α), 3.45 (1H, dd, J = 11.0, 3.0 Hz, H-5α), 3.92 (1H, br s, H-1), 5.53 (1H, dd, J = 12.0, 4.0 Hz, H-3); ^{13}C NMR data, see Table 1; FABMS *m/z* $[M - H]^-$ 535; *anal.* C 67.10%, H 9.90%, calcd for $C_{31}H_{52}O_7 \cdot H_2O$, C 67.12%, H 9.81%.

Cyclopassifloic acid D (4): colorless needles, mp 202−203 °C; $[\alpha]^{25}_D$ +48.3° (*c* 0.4, MeOH); IR (KBr) ν_{max} 3450 (OH), 1705 (CO, COOH), 1090, 1030 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.51, 0.71 (1H each, d, J = 4.0 Hz, H_2-19), 0.90 (3H, s, H_3-30), 0.99 (3H, s, H_3-18), 1.14, 1.17 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.16 (3H, d, J = 6.0 Hz, H_3-21), 1.66 (3H, s, H_3-29), 2.25 (1H, ddd, J = 13.0, 13.0, 2.5 Hz, H-2*β*), 2.48 (1H, ddd, J = 13.0, 4.0, 2.5 Hz, H-2α), 2.54 (1H, d, J = 12.0 Hz, Hb-23), 2.74 (1H, m, H-11α), 2.80 (1H, qq, J = 7.0 Hz, H-25), 2.89 (1H, dd, J = 12.0, 5.0 Hz, Ha-23), 3.33 (1H, dd, J = 12.0, 3.5, H-5α), 3.87 (1H, br s, H-1), 4.67 (1H, dd, J = 10.0, 2.0 Hz, H-22), 5.55 (1H, dd, J = 13.0, 4.0 Hz, H-3); ^{13}C NMR data, see Table 1; FABMS *m/z* $[M - H]^-$ 503; *anal.* C 68.85%, H 9.80%, calcd for $C_{30}H_{48}O_6 \cdot H_2O$, C 68.93%, H 9.64%.

Cyclopassifloside I (5): amorphous solid; $[\alpha]^{25}_D$ +54.5° (*c* 0.2, MeOH); IR (KBr) ν_{max} 3400 (OH), 1730 (ester), 1070, 1040 cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.53, 0.73 (1H each, d, J = 4.0 Hz, H_2-19), 0.87 (3H, s, H_3-30), 1.03 (3H, s, H_3-18), 1.21, 1.27 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.22 (3H, d, J = 6.0 Hz, H_3-21), 1.68 (3H, s, H_3-29), 2.03 (2H, m, H_2-23), 2.24 (1H, ddd, J = 12.0, 12.0, 2.5 Hz, H-2*β*), 2.40 (1H, qq, J = 7.0 Hz, H-25), 2.43 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.76 (1H, m, H-11α), 3.36 (1H, dd, J = 12.0, 4.5 Hz, H-5α), 3.86 (1H, br s, H-1), 4.03 (1H, m, H-5′ of Glc), 4.13, 4.20 (1H each, d, J = 11.0 Hz, H_2-31), 4.18 (1H, dd, J = 8.0, 8.0 Hz, H-2′ of Glc), 4.29 (1H, dd, J = 8.0, 8.0 Hz, H-3′ of Glc), 4.38 (1H, dd, J = 8.0, 8.0 Hz, H-4′ of Glc), 4.40 (2H, m, H-6′ of Glc), 4.57 (1H, m, H-22), 5.59 (1H, dd, J = 12.0, 4.0 Hz, H-3), 6.53 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; FABMS *m/z* $[M - H]^-$ 697; *anal.* C, 61.89%, H 9.29%, calcd for $C_{37}H_{62}O_{12} \cdot H_2O$, C 61.99%, H 9.05%.

Cyclopassifloside II (6): amorphous solid; $[\alpha]^{25}_D$ +46.8° (*c* 6.8, MeOH); IR (KBr) ν_{max} 3450 (OH), 1730 (ester), 1070, 1060 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.53, 0.75 (1H each, d, J = 4.5 Hz, H_2-19), 0.88 (3H, s, H_3-30), 1.00 (3H, s, H_3-18), 1.00 (3H, d, J = 6.0 Hz, H_3-21), 1.20, 1.23 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.69 (3H, s, H_3-29), 2.75 (1H, m, H-11α), 3.35 (1H, dd, J = 11.0, 4.0 Hz, H-5α), 3.88 (1H, br s, H-1), 4.00, 4.03 (1H each, d, J = 11.0 Hz, H_2-31), 4.02 (1H, m, H-5′ of Glc), 4.17 (1H, dd, J = 8.0, 8.0 Hz, H-2′ of Glc), 4.29 (1H, dd, J = 8.0, 8.0 Hz, H-3′ of Glc), 4.36 (1H, dd, J = 8.0, 8.0 Hz, H-4′ of Glc), 4.40 (2H, m, H-6′ of Glc), 5.58 (1H, dd, J = 12.0,

Table 1. ^{13}C NMR Spectral Data for Compounds **1**−**10** and **13** in C_5D_5N

		(δ m)										
	C	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**13**
	1	72.5 d	72.4 d	72.4 d	72.3 d	72.4 d	72.7 d	72.5 d	72.4 d	72.6 d	72.4 d	72.9d
	2	38.3 t	38.4 t	38.3 t	38.2 t	38.2 t	38.3 t	38.3 t	38.3 t	38.3 t	38.3 t	38.5
	3	70.7 d	70.7 d	70.6 d	70.6 d	70.7 d	70.9 d	70.8 d	70.7 d	70.8 d	70.7 d	70.4 d
	4	55.7 s	55.6 s	56.4 s	56.3 s	56.3 s	56.5 s	56.5 s	56.3 s	56.5 s	56.3 s	46.1 s
	5	37.7 d	37.6 d	37.5 d	37.6 d	37.6 d	37.8 d	37.7 d	37.7 d	37.8 d	37.6 d	34.6 d
	6	23.4 t	23.4 t	23.3 t	23.4 t	23.1 t	23.2 t	23.1 t	23.0 t	23.1 t	23.0 t	21.5 t
	7	26.0 t	26.0 t	26.0 t	25.9 t	25.7 t	25.8 t	25.8 t	25.8 t	25.8 t	25.8 t	26.3 t
	8	48.3 d	48.0 d	47.9 d	48.1 d	48.3 d	48.4 d	48.3 d	47.8 d	48.0 d	48.2 d	48.9 d
	9	20.9 s	21.0 s	20.9 s	20.8 s	20.9 s	21.2 s	21.1 s	20.8 s	20.9 s	20.9 s	21.1 s
	10	30.3 s	30.3 s	30.2 s	30.1 s	30.1 s	30.3 s	30.3 s	30.3 s	30.4 s	30.2 s	30.4 s
	11	26.4 t	26.4 t	26.4 t	26.0 t	26.1 t	26.4 t	26.4 t	26.5 t	26.5 t	26.1 t	26.2 t
	12	33.0 t	33.4 t	33.5 t	33.1 t	33.1 t	33.3 t	33.5 t	33.7 t	33.4 t	33.1 t	33.5 t
	13	45.9 s	45.6 s	46.2 s	45.8 s	45.9 s	45.7 s	45.7 s	46.3 s	46.4 s	45.9 s	45.2 s
	14	48.7 s	49.2 s	49.3 s	48.6 s	48.7 s	49.3 s	49.2 s	49.4 s	49.5 s	48.6 s	48.9 s
	15	36.0 t	36.0 t	35.4 t	36.0 t	36.1 t	36.1 t	36.1 t	35.6 t	35.8 t	36.0 t	36.5 t
	16	27.6 t	28.5 t	23.0 t	27.4 t	27.6 t	28.6 t	28.5 t	22.9 t	23.1 t	27.4 t	27.9 t
	17	49.8 d	52.8 d	55.1 d	49.6 d	49.4 d	52.9 d	52.9 d	55.0 d	55.2 d	49.7 d	49.7 d
	18	18.3 q	18.4 q	19.8 q	18.3 q	18.3 q	18.6 q	18.5 q	19.8 q	19.9 q	18.3 q	18.7 q
	19	29.9 t	30.1 t	30.2 t	30.0 t	29.9 t	30.3 t	30.1 t	30.3 t	30.4 t	30.1 t	30.6 t
	20	43.4 d	37.4 d	74.7 s	42.8 d	43.4 d	37.4 d	37.3 d	74.8 s	74.8 s	42.9 d	43.5 d
	21	12.7 q	19.8 q	26.1 q	12.5 q	12.6 q	19.7 q	19.6 q	26.1 q	26.1 q	12.6 q	12.9 q
	22	70.3 d	32.0 t	38.1 t	69.7 d	70.3 d	32.0 t	31.9 t	38.1 t	38.5 t	69.7 d	69.6 d
	23	33.1 t	31.7 t	29.2 t	42.0 t	33.1 t	31.9 t	30.4 t	29.3 t	29.5 t	42.0 t	33.5 t
	24	76.5 s	76.1 s	76.0 s	214.6 s	76.5 s	76.0 s	75.8 s	76.0 s	75.6 s	214.7 s	76.7 s
	25	33.8 d	33.7 d	33.6 d	42.9 d	33.9 d	33.8 d	33.5 d	33.7 d	33.6 d	42.9 d	33.8 d
	26	17.3 q	17.7 q	17.4 q	18.1 q	17.2 q	17.7 q	17.6 q	17.5 q	17.4 q	18.1 q	17.4 q
	27	17.5 q	17.8 q	17.6 q	18.0 q	17.5 q	17.8 q	17.7 q	17.7 q	17.6 q	18.1 q	17.7 q
	28	180.1 s	180.1 s	180.0 s	180.1 s	176.6 s	176.6 s	176.6 s	176.7 s	176.6 s	176.7 s	67.7 t
	29	9.8 q	9.8 q	9.7 q	9.6 q	9.6 q	9.8 q	9.8 q	9.6 q	9.8 q	9.6 q	10.9 q
	30	19.6 q	18.7 q	20.3 q	19.5 q	19.7 q	18.8 q	18.8 q	20.2 q	20.4 q	19.6 q	20.0 q
	31	66.4 t	66.3 t	66.3 t		66.5 t	66.2 t	75.2 t	66.1 t	75.0 t	66.5 t	66.6 t
28-Glc	1′					96.5 d	96.6 d	96.6 d	96.5 d	96.5 d	96.5 d	
	2′					74.7 d	74.8 d	74.8 d	74.8 d	74.8 d	74.7 d	
	3′					78.4 d	78.5 d	78.5 d	78.4 d	78.5 d	78.4 d	
	4′					71.0 d	71.4 d	71.3 d	71.4 d	71.3 d	71.0 d	
	5′					79.5 d	79.5 d	79.5 d	79.5 d	79.4 d	79.6 d	
	6′					62.1 t	62.4 t	62.4 t	62.4 t	62.4 t	62.1 t	
31-Glc	1″							106.0 d		105.8 d		
	2″							75.4 d		75.4 d		
	3″							78.5 d		78.5 d		
	4″							72.0 d		71.9 d		
	5″							78.5 d		78.5 d		
	6″							63.0 t		62.9 t		

4.0 Hz, H-3), 6.52 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 681; *anal*. C 62.44%, H 9.47%, calcd for $C_{37}H_{62}O_{11}$·3/2 H_2O, C 62.60%, H 9.23%.

Cyclopassifloside III (7): amorphous solid; $[\alpha]^{25}_D$ +25.7° (*c* 3.5, MeOH); IR (KBr) ν_{max} 3450 (OH), 1730 (ester), 1070, 995 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.53, 0.75 (1H each, d, J = 4.5 Hz, H_2-19), 0.87 (3H, s, H_3-30), 0.97 (3H, d, J = 6.0 Hz, H_3-21), 0.99 (3H, s, H_3-18), 1.12, 1.14 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.68 (3H, s, H_3-29), 2.23 (1H, ddd, J = 12.0, 12.0, 3.0 Hz, H-2β), 2.42 (1H, ddd, J = 12.0, 4.0, 3.0 Hz, H-2α), 2.75 (1H, m, H-11α), 3.35 (1H, dd, J = 11.0, 4.0 Hz, H-5α), 3.87 (1H, br s, H-1), 3.96, 4.32 (1H each, d, J = 11.0 Hz, H2−31), 3.98 (1H, m, H-5″ of Glc), 4.07 (1H, dd, J = 8.0, 8.0 Hz, H-3″), 4.07 (1H, m, H-5′ of Glc), 4.15 (1H, dd, J = 8.0, 8.0 Hz, H-2′ of Glc), 4.22 (2H, m, H-2″ and 4″ of Glc, 4.26 (1H, dd, J = 8.0, 8.0 Hz, H-3′ of Glc), 4.35 (1H, dd, J = 8.0, 8.0 Hz, H-4′ of Glc), 4.38 (3H, m, H_2-6′ of Glc, H-6″ of Glc), 4.55, (1H, dd, J = 12.0, 2.5 Hz, H-6″ of Glc), 4.96 (1H, d, J = 8.0 Hz, H-1″ of Glc), 5.57 (1H, dd, J = 12.0, 4.0 Hz, H-3), 6.49 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 843; *anal*. C 59.37%, H 8.89%, calcd for $C_{43}H_{72}O_{16}$·3/2 H_2O, C 59.22%, H 8.67%.

Cyclopassifloside IV (8): amorphous solid; $[\alpha]^{25}_D$ +33.1° (*c* 6.3, MeOH); IR (KBr) ν_{max} 3400 (OH), 1730 (ester), 1070, 1040 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.49, 0.70 (1H each, d, J = 4.0 Hz, H_2-19), 0.92 (3H, s, H-30), 1.16, 1.18 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.48 (3H, s, H_3-18), 1.53 (3H, s, H_3-21), 1.64 (3H, s, H_3-29), 2.45 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.75 (1H, m, H-11α), 3.32 (1H, dd, J = 12.0, 4.5 Hz, H-5α), 3.87 (1H, br s, H-1), 3.97, 4.04 (1H each, d, J = 11.5 Hz, H_2-31), 4.00 (1H, m, H-5′ of Glc), 4.15 (1H, dd, J = 8.0, 8.0, H-2′ of Glc), 4.25 (1H, dd, J = 8.0, 8.0, H-3′ of Glc), 4.38 (1H, dd, J = 8.0, 8.0, H-4′ of Glc), 4.40 (2H, m, H_2-6′ of Glc), 5.53 (1H, dd, J = 12.0, 4.0 Hz, H-3), 6.40 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 697; *anal*. C 59.19%, H 8.94%, calcd for $C_{37}H_{62}O_{12}$·3 H_2O, C 59.02%, H 9.10%.

Cyclopassifloside V (9): amorphous solid; $[\alpha]^{25}_D$ +16.5° (*c* 6.8, MeOH); IR (KBr) ν_{max} 3450 (OH), 1735 (ester), 1070, 1035 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.49, 0.70 (1H each, d, J = 4.0 Hz, H_2-19), 0.93 (3H, s, H-30), 1.07, 1.11 (3H each, d, J = 7.0 Hz, H_3-26 and 27), 1.49 (3H, s, H_3-18), 1.50 (3H, s, H_3-21), 1.65 (3H, s, H_3-29), 2.24 (1H, ddd, J = 12.0, 12.0, 2.5 Hz, H-2β), 2.44 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.75 (1H, m, H-11α), 3.32 (1H, dd, J = 12.0, 4.5 Hz, H-5α), 3.87 (1H, br s, H-1), 3.87, 4.30 (1H each, d, J = 11.0 Hz, H_2-31), 3.95 (1H, m, H-5″ of Glc), 4.00 (1H, m, H-5′ of Glc), 4.02 (1H, dd, J = 8.0, 8.0 Hz, H-3″ of Glc), 4.12 (1H, dd, J = 8.0, 8.0 Hz, H-2′ of Glc), 4.20 (2H, m, H-2″ and H-4″ of Glc), 4.26 (1H, dd, J = 8.0, 8.0, H-3′ of Glc), 4.30 (1H, dd, J = 8.0, 8.0, H-4′ of Glc), 4.35 (3H, m, H_2-6′ and H-6″ of Glc), 4.52 (1H, dd, J = 12.0, 2.5, H-6″ of Glc), 4.91 (1H, d, J = 8.0 Hz, H-1″ of Glc), 5.54 (1H, dd, J = 12.0, 4.0 Hz, H-3), 6.41 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 859; *anal*. C 58.78%, H 8.43%, calcd for $C_{43}H_{72}O_{17}$·H_2O, C 58.75%, H 8.49%.

Cyclopassifloside VI (10): amorphous solid; $[\alpha]^{25}_D$ +36.2° (*c* 2.6, MeOH); IR (KBr) ν_{max} 3450 (OH), 1735 (ester), 1710 (CO), 1075, 1040 cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 0.53, 0.74 (1H each, d, J = 4.0 Hz, H_2-19), 0.87 (3H, s, H_3-30), 1.01 (3H, s, H_3-18), 1.13, 1.17 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.14 (3H, d, J = 6.0 Hz, H_3-21), 1.67 (3H, s, H_3-29), 2.24 (1H, ddd, J = 11.0, 11.0, 2.5 Hz, H-2β), 2.44 (1H, ddd, J = 11.0, 4.0, 2.5 Hz, H-2α), 2.54 (1H, d, J = 12.0 Hz, Hb-23), 2.75 (1H, m, H-11α), 2.82 (1H, qq, J = 7.0 Hz, H-25), 2.85 (1H, dd, J = 12.0, 5.0 Hz, Ha-23), 3.35 (1H, dd, J = 10.0, 5.0, H-5α), 3.87 (1H, br s, H-1), 4.00 (1H, m, H-5′ of Glc), 4.15 (1H, dd, J = 8.0, 8.0 Hz, H-2′ of Glc), 4.26 (1H, dd, J = 8.0, 8.0 Hz, H-3′ of Glc), 4.34 (1H, dd, J = 8.0, 8.0 Hz, H-4′ of Glc), 4.38 (2H, m, H-6′ of Glc), 4.66 (1H, dd, J = 11.0, 2.0 Hz, H-22), 5.56 (1H, dd, J = 11.0, 4.0 Hz, H-3), 6.48 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 665; *anal*. C 60.10%, H 8.88%, calcd for $C_{36}H_{58}O_{11}\cdot 3\,H_2O$, C 59.98%, H, 8.95%.

Identification of Component Sugars of Cyclopassiflosides I−VI (5−10). A solution of each compound (2−3 mg) in 5% H_2SO_4−dioxane (1:1) was heated at 100 °C for 3 h. The reaction mixture was diluted with H_2O, neutralized with Amberlite IRA-35, and evaporated *in vacuo* to dryness. The sugar was determined by HPLC using refractive index and chiral detection (Shodex RSpak DC-613, 80% CH_3CN, 0.8 mL/min, 70 °C) by comparison with authentic sugars (10 mM each of D-glc and L-glc). Each hydrolyzed sugar gave a positive peak at 13.40 min (D-glc; 13.38 min).

Methylation of Cyclopassifloic Acid A (1) and $NaBH_4$ Reduction of Methylation Product. A solution of **1** (30 mg) in MeOH (2 mL) was treated with CH_2N_2 for 24 h at 4 °C. The residue, after solvent removal, was purified by column chromatography on Si gel with EtOAc−MeOH (5:1) to give the methyl ester of **1**: mp 244−246 °C; $[\alpha]^{25}_D$ +46.8° (*c* 0.7, MeOH); FT−IR (KBr) ν_{max} 3400 (OH), 1710 (C=O), 1255, 1080, 1040 cm^{-1}; FABMS m/z [M − H]$^-$ 549. To a stirred solution of the methyl ester of **1** (20 mg) in MeOH (2 mL) was added $NaBH_4$ (40 mg), and the solution was kept for 2 h at room temperature. Workup as usual gave the reduction product (15 mg), which was purified by column chromatography on Si gel with EtOAc−MeOH (4:1) to afford **13**.

Compound 13: amorphous solid; $[\alpha]^{25}_D$ +64.4° (*c* 0.7, MeOH); IR (KBr) ν_{max} 3400 (OH), 1045, 1020 cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 0.52, 0.76 (1H each, d, J = 3.5 Hz, H_2-19), 0.97 (3H, s, H_3-30), 1.01 (3H, s, H_3-18), 1.22, 1.27 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.24 (3H, d, J = 6.5 Hz, H_3-21), 1.34 (3H, s, H_3-29), 2.03 (2H, m, H_2-23), 2.28 (1H, br dd, J = 12.0, 12.0 Hz, H-2β), 2.41 (1H, qq, J = 7.0 Hz, H-25), 2.45 (1H, m, H-2α), 3.85 (1H, br s, H-1), 3.89, 4.28 (1H each, d, J = 11.0 Hz, H_2-28), 4.13, 4.22 (1H each, d, J = 11.0 Hz, H_2-31), 4.58 (1H, m, H-22), 5.08 (1H, dd, J = 12.0, 4.0 Hz, H-3); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 521.

Methylation of Passifloric Acid (12) and $NaBH_4$ Reduction of Methylation Product. Compound **12** (20 mg) was treated in the same way as described for **1**. It, too, gave **13** (15 mg) by ^{1}H NMR and co-TLC.

Acetylation of Cyclopassifloside II (6) and Benzoylation of the Acetate of 6. A solution of **6** (20 mg) in Ac_2O−C_5H_5N (1:2, 2 mL) was kept at room-temperature overnight. Workup as usual afford a crude solid, which was purified by column chromatography on Si gel with EtOAc−MeOH (20:1) to afford the corresponding acetate: $[\alpha]^{25}_D$ +30.7° (*c* 1.5, MeOH); IR (KBr) ν_{max} 3500 (OH), 1765 (C=O), 1750 (C=O), 1235, 1070, 1040 cm^{-1}; FABMS m/z [M − H]$^-$ 891. To a stirred solution of the acetate of **2** (20 mg) in C_5H_5N (2 mL) was added C_6H_5COCl (20 mg), and the solution was kept for 24 h at room temperature. Workup as usual gave a benzoate (15 mg), which was purified by column chromatography on Si gel with EtOAc to afford the corresponding acetyl benzoate (**14**): $[\alpha]^{25}_D$ +33.5° (*c* 0.7, MeOH); IR (KBr) ν_{max} 1765 (C=O), 1755 (C=O), 1235, 1070, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05, 0.38 (^{1}H each, d, J = 4.5 Hz, H_2-19), 0.88 (3H, d, J = 6.0 Hz, H_3-21), 0.90 (3H, s, H_3-30), 0.92 (3H, s, H_3-18), 1.03, 1.05 (3H each, d, J = 7.0 Hz, H_3-26 and H_3-27), 1.18 (3H, s, H_3-29), 1.94, 2.01, 2.15 (3H each, s, Ac), 2.04, 2.05 (6H each, s, Ac), 2.70 (1H, dd, J = 12.0, 4.0 Hz, H-5), 3.82 (1H, m, H-5′ of Glc), 4.13 (1H, dd, J = 12.0, 2.5 Hz, H-6′ of Glc), 4.22 (1H, dd, J = 12.0, 4.5 Hz, H-6′ of Glc), 4.49, 4.57 (1H each, d, J = 12.0 Hz, H_2-31), 4.63 (1H, m, H-1), 5.15 (1H, dd, J = 8.0, 8.0 Hz, H-4′ of Glc), 5.25 (2H, m, H-2′ and H-3′ of Glc), 5.36 (1H, dd, J = 12.0, 4.0 Hz, H-3), 5.60 (1H, d, J = 8.0 Hz, H-1′ of Glc), 7.43 (2H, t, J = 7.5 Hz, H-3 and -5 of Bz), 7.55 (1H, t, J = 7.5 Hz, H-4 of Bz), 7.98 (2H, d, J = 7.5 Hz, H-2 and -6 of Bz); FABMS m/z [M − H]$^-$ 1079; *anal*. C 64.30%, H 7.50%, calcd for $C_{58}H_{80}O_{19}$, C 64.43%, H 7.46%.

Alkaline Hydrolysis of Cyclopassifloside I (5). A solution of **5** (30 mg) in 3% NaOH was kept under N_2 atmosphere at room temperature overnight. The reaction mixture was acidified with dilute HCl and then extracted with EtOAc. The EtOAc extract was purified by column chromatography on Si gel with EtOAc−MeOH (5:1) to give a sapogenin, which was confirmed by comparison of ^{1}H NMR data and by co-TLC as compound **1**.

Enzymatic Hydrolysis of Cyclopassifloside III (7). A solution of **7** (20 mg) in EtOH (0.2 mL) and 0.01 M NaH_2PO_4 buffer (pH 4.0, 1.8 mL) was incubated with crude cellulase (20 mg, Sigma) for one week at 37 °C. The reaction mixture was passed through a column of Amberlite XAD-2 and washed with H_2O, then eluted with MeOH. From the water eluate, D-(+)-glucose was detected in the same way as described for **5**. The crude hydrolysate (12 mg) obtained from the methanol eluate was purified by column chromatography on Si gel with EtOAc−MeOH (5:1) to give a prosapogenin, which was confirmed by comparison of ^{1}H NMR data and by co-TLC with compound **6**.

Enzymatic Hydrolysis of Cyclopassifloside V (9). Enzymatic hydrolysis of **9** (20 mg) was carried out in the same way as described for **7** to give a prosapogenin (13 mg), which was confirmed by comparison of ^{1}H NMR data and by co-TLC as being compound **8**.

Alkaline Hydrolysis of Cyclopassifloside II (6). Alkaline hydrolysis of **6** (15 mg) was carried out in the same way as described for **5** to give **2** (9 mg).

Alkaline Hydrolysis of Cyclopassifloside IV (8). Alkaline hydrolysis of **8** (15 mg) was carried out in the same way as described for **5** to give **3** (8 mg).

Alkaline Hydrolysis of Cyclopassifloside VI (10). Alkaline hydrolysis of **10** (15 mg) was carried out in the same way as described for **5** to give **4** (9 mg).

$NaIO_4$ Cleavage of Cyclopassifloic Acid A (1). To a stirred solution of **1** (20 mg) in MeOH (2 mL) was added $NaIO_4$ (20 mg) in water, and the solution was kept under N_2 atmosphere at room temperature for 2 h and extracted with EtOAc. The EtOAc extract was purified by column chromatography on Si gel with EtOAc−MeOH (5:1) to give an oxidation product, which was confirmed by comparison of ^{1}H NMR data and by co-TLC as being compound **4**.

References and Notes

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