New Cycloartane Triterpenoids from *Passiflora edulis*[1]

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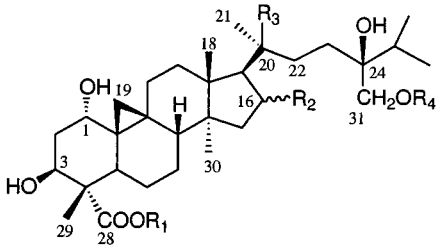
Three cycloartane triterpenes, cyclopassifloic acids E (**1**), F (**2**), and G (**3**), and their saponins, cyclopassiflosides VII (**4**), VIII (**5**), IX (**6**), X (**7**), and XI (**8**), were isolated from the leaf and stem parts of *Passiflora edulis*. The structures of **1**−**8** were elucidated on the basis of extensive NMR experiments and by chemical methods.

The genus *Passiflora* (Passifloraceae) comprises about 400 species of herbaceous vines or trees distributed mainly in tropical America, with a smaller number of species occurring in southeast Asia, India, Malaysia, and Australia.[2] In a previous paper, we reported the isolation and structure elucidation of four cycloartane triterpenes, cyclopassifloic acids A−D, and their saponins, cyclopassiflosides I−VI, from the leaves and stems of *P. edulis* Sims.[3] Further purification of the resulting fractions by Si gel afforded cyclopassifloic acids E−G (**1**−**3**), and their saponins, cyclopassiflosides VII−XI (**4**−**8**), respectively. This paper summarizes the experimental evidence that led to the structural and stereochemical assignments of compounds **1**−**8**.

Results and Discussion

Cyclopassifloic acid E (**1**) was obtained as needless and gave a FABMS quasi-molecular ion at *m/z* 551 $[M - H]^-$, 16 mass units greater than that of cyclopassifloic acid C (**9**) by an oxygen atom.[3] Its IR spectrum showed hydroxy (3450 cm^{-1}) and carboxy (1710 cm^{-1}) absorptions. The ^1H NMR spectrum of **1** exhibited two doublet methyl signals at δ 1.18 and 1.21; four singlet methyl signals at δ 0.98, 1.55, 1.74, and 1.92; two characteristic cyclopropane protons at δ 0.58 and 0.87 (each d, $J = 4.0$ Hz); an oxygenated methylene group at δ 4.01 and 4.06 (each d, $J = 11.0$ Hz); and three oxygenated methine signals at δ 3.94 (br s), 5.05 (dt, $J = 6.0$, 8.0 Hz), and 5.58 (dd, $J = 12.0$, 4.0 Hz). In the ^{13}C NMR spectrum of **1**, the C-15 (δ 49.6), C-16 (δ 73.6), and C-20 (δ 76.9) signals were shifted downfield by 14.2, 50.6, and 2.2 ppm, respectively, while that of C-14 (δ 47.4) was shifted upfield by 1.9 ppm. However, the C-22−C-27 and C-31 signals were not shifted when compared with analogous data for **9**, indicating the hydroxy group to be at the C-16 position. In the ^1H NMR spectrum of **1**, the C-16 proton appeared as a double triplet ($J = 6.0$, 8.0 Hz) at δ 5.05, but its shape did not provide any information about the configuration of the hydroxy group. However, a β-OH group at C-16 could be assigned from the downfield shift of H-18 (δ 1.92) owing to the syn-parallel disposition of C-18 methyl and C-16-OH, compared with that (δ 1.55) of **9**[3] and by the observation of NOE effects between H-16, H_3-30, and H-17. The absolute configuration at C-24 was assumed to be the same as that of **9** because the carbon signals due to C-22−C-25 and C-31 of **1** were superimposable with those of **9**. From the analysis of all of these data and from biogenetic considerations, the structure of cyclopassifloic acid E was determined as 20(*S*),24(*S*)-1α,3*β*,16*β*,-20,24,31-hexahydroxy-24-methylcycloartan 28-oic acid.

Cyclopassifloic acid F (**2**) showed a FABMS $[M - H]^-$ ion peak at *m/z* 535, 16 mass units less than that of **1**. A ^{13}C NMR spectral comparison of **2** with **1** showed that these compounds differed structurally only at C-20 in the side chain. Thus, in the ^{13}C NMR spectrum of **2**, the C-20 (δ 33.5), C-21 (δ 19.5), and C-22 (δ 32.1) signals were shifted upfield by 43.4, 6.6, and 6.2 ppm, respectively, compared to those of **1**, indicating the absence of a tertiary hydroxy group at C-20. The chemical shift value of δ 1.44 for H_3-18, owing to the syn-parallel disposition of C-18 methyl and C-16-OH, and compared with that (δ 1.03) of cyclopassifloic acid B (**10**),[3] suggested that the hydroxy group at C-16 should be β. From these data, the structure of cyclopassifloic acid F was determined as 24(*S*)-1α,3*β*,16*β*,24,31-pentahydroxy-24-methylcycloartan 28-oic acid.



1 R_1=R_4=H, R_2=β-OH, R_3=OH
2 R_1=R_3=R_4=H, R_2=β-OH
3 R_1=R_3=R_4=H, R_2=α-OH
4 R_1=Glc, R_2=β-OH, R_3=OH, R_4=H
5 R_1=Glc, R_2=β-OH, R_3=R_4=H
6 R_1=R_4=Glc, R_2=β-OH, R_3=H
7 R_1=Glc, R_2=α-OH, R_3=R_4=H
8 R_1=R_4=Glc, R_2=α-OH, R_3=H
9 R_1=R_2=R_4=H, R_3=OH
10 R_1=R_2=R_3=R_4=H

Cyclopassifloic acid G (**3**) has the same molecular ion peak (FABMS, *m/z* 535 $[M - H]^-$) as **2**. The ^{13}C NMR spectral comparison of **3** with **2** showed that **3** is the C-16 epimer of **2**. In the ^1H NMR spectrum of **3**, the C-16 appeared as a double doublet (dd, $J = 6.5$, 6.0 Hz) at δ 4.30. A downfield shift of H_3-30 (δ 1.42), owing to the syn-parallel disposition of C-30 methyl and C-16-OH, compared with that (δ 0.99) of **10**,[3] supported an α-OH group at C-16. From those data, the structure of cyclopassifloic acid G was determined as 24(*S*)-1α,3*β*,16α,24,31-pentahydroxy-24-methylcycloartan 28-oic acid.

Cyclopassifloside VII (**4**) had a molecular formula of $C_{37}H_{62}O_{13}$ as established by the $[M - H]^-$ peak observed at *m/z* 713 in the negative-ion FABMS and in a DEPT NMR experiment. The IR spectrum showed hydroxy (3400 cm^{-1})

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and ester (1735 cm^{-1}) absorptions. The ^1H and ^{13}C NMR spectra of **4** 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). The alkaline hydrolysis of **4** afforded **1** as the aglycon, while the acid treatment of **4** gave D-glucose, which was confirmed by specific rotation using chiral detection by HPLC analysis.[4,5] In the ^1H NMR spectrum of **4**, the coupling constant (J = 8.0 Hz) of the anomeric proton indicated the glucose to have the β configuration. The ^{13}C NMR spectral data comparison of **4** with **1** showed glycosylation shifts of −3.9 ppm at the C-28 signal and +0.8 ppm at the C-4 signal, demonstrating the sugar linkage to be located at the C-28 COOH group.[6,7] Furthermore, in a HMBC experiment on **4**, 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 **4** was formulated as cyclopassifloic acid E 28-*O*-β-D-glucopyranoside.

The negative-ion FABMS of cyclopassifloside VIII (**5**) gave a quasi-molecular ion at *m/z* 697 $[M - H]^-$, 16 mass units less than that of **4**. The ^1H and ^{13}C NMR spectra of **5** showed that **5** was composed of **2** and an ester-linked glucose (δ_H 6.50, δ_C 96.5; H-1′ and C-1′, respectively). The alkaline hydrolysis of **5** afforded **2** as the aglycon. The ^{13}C NMR shifts for C-4 (δ 56.4) and C-28 (δ 176.7) and the sugar moiety at C-28 of **5** were also in good agreement with those of **4**. Hence, the structure of **5** was formulated as cyclopassifloic acid F 28-*O*-β-D-glucopyranoside.

Cyclopassifloside IX (**6**) gave a FABMS quasi-molecular ion at *m/z* 859 $[M - H]^-$, 162 mass units greater than that of **5**, corresponding to a hexosyl derivative $C_6H_{10}O_5$ of **5**. The ^1H and ^{13}C NMR spectra of **6** showed the presence of **2** and a β-glucopyranosyl group (δ 4.91, d, J = 8.0 Hz; H-1″) and an ester-linked β-glucosyl group (δ 6.41, d, J = 8.0 Hz; H-1′). Enzymatic hydrolysis of **6** gave **5**. The ^{13}C NMR spectral data comparison of **6** with **5** disclosed C-31 (+8.8 ppm) as an additional glycosylation site in the former compound. Therefore, the structure of **6** was established as cyclopassifloic acid F 28,31-bis-*O*-β-D-glucopyranoside.

Cyclopassifloside X (**7**) had the same molecular formula, $C_{37}H_{62}O_{12}$, as **5**. The ^1H and ^{13}C NMR spectra of **7** showed the presence of **3** and an ester-linked β-glucosyl group (δ 6.47, d, J = 8.0 Hz; H-1′). On alkaline hydrolysis, compound **7** afforded **3** as the aglycon. The ^1H and ^{13}C NMR shifts for the aglycon and the sugar moiety at C-28 of **7** were in good agreement with those of **5**. Hence, the structure of **7** was formulated as cyclopassifloic acid G 28-*O*-β-D-glucopyranoside.

Cyclopassifloside XI (**8**) gave a FABMS quasi-molecular ion at *m/z* 859 $[M - H]^-$, 162 mass units greater than that of **7**, corresponding to a hexosyl $C_6H_{10}O_5$ derivative of **7**. The ^1H and ^{13}C NMR spectra of **8** showed the presence of **3** and a β-glucopyranosyl group (δ 4.92, d, J = 8.0 Hz; H-1″) and an ester-linked β-glucosyl group (δ 6.50, d, J = 8.0 Hz; H-1′). The ^{13}C NMR spectral data comparison of **8** with **7** showed that the two compounds differed structurally only in the side chain. Enzymatic hydrolysis of **8** gave **7**. In the ^{13}C NMR spectrum of **8**, the C-31 (δ 75.2) signal was shifted downfield by 9.1 ppm compared to that of **7**, indicating a glucosyl moiety to be at the C-31 position. Thus, the structure of **8** was formulated as cyclopassifloic acid G 28,31-bis-*O*-β-D-glucopyranoside.

Recently, Kasai et al. reported cyclotricuspidosides B and C from the leaves and stems of *Trichosanthes tricuspidata*, but the absolute configuration at C-24 remained unclear.[8] Compounds **6** and **8** seem to be identical with cyclotricuspidosides B and C, respectively, because of the good agreement of their NMR data.

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 spectrometer, NMR spectra were run on Varian UNITY 600 and/or a JEOL GSX-400 spectrometer, and FABMS were measured on a JEOL JMS−HX-100 mass spectrometer.

Plant Material. *P. edulis* was cultivated at the botanical garden of Tokushima Bunri University, Tokushima, Japan, 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 MeOH eluate[3] (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 E (**1**, 25 mg), F (**2**, 40 mg), and G (**3**, 10 mg) and cyclopassiflosides VII (**4**, 40 mg), VIII (**5**, 240 mg), IX (**6**, 300 mg), X (**7**, 350 mg), and XI (**8**, 400 mg).

Cyclopassifloic acid E (1): colorless needless, mp 227−228 °C; $[\alpha]^{25}_D$ +41.2° (*c* 0.9, MeOH); IR (KBr) ν_{max} 3450 (OH), 1710 (COOH), 1050 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.58, 0.87 (1H each, d, J = 4.0 Hz, H_2-19), 0.98 (3H, s, H_3-30), 1.18, 1.21 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.55 (3H, s, H_3-21), 1.74 (3H, s, H_3-29), 1.92 (3H, s, H_3-18), 2.19 (1H, d, J = 8.0 Hz, H-17), 2.83 (2H, m, H_2-22), 2.84 (1H, m, H-11α), 3.44 (1H, dd, J = 12.0, 4.0 Hz, H-5), 3.94 (1H, br s, H-1), 4.01, 4.06 (1H each, d, J = 11.0 Hz, H_2-31), 5.05 (1H, dt, J = 6.0, 8.0 Hz, H-16), 5.58 (1H, dd, J = 12.0, 4.0 Hz, H-3); ^{13}C NMR data, see Table 1; FABMS *m/z* $[M - H]^-$ 551; *anal.* C 65.24%, H 9.54%, calcd for $C_{31}H_{52}O_8 \cdot H_2O$, C 65.10%, H 9.68%.

Cyclopassifloic acid F (2): amorphous powder; $[\alpha]^{25}_D$ +48.2° (*c* 5.1, MeOH); IR (KBr) ν_{max} 3400 (OH), 1705 (COOH), 1040, 1015, 990 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.55, 0.84 (1H each, d, J = 4.0 Hz, H_2-19), 1.01 (3H, s, H_3-30), 1.10 (3H, d, J = 6.0 Hz, H_3-21), 1.17 (6H, d, J = 7.0 Hz, H_3-26 and -27), 1.44 (3H, s, H_3-18), 1.70 (3H, s, H_3-29), 2.48 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.77 (1H, m, H-11α), 3.37 (1H, dd, J = 12.0, 4.0 Hz, H-5), 3.91 (1H, br s, H-1), 3.98, 4.01 (1H each, d, J = 11.0 Hz, H_2-31), 4.67 (1H, dt, J = 6.0, 8.0 Hz, H-16), 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 67.12%, H 9.81%, calcd for $C_{31}H_{52}O_7 \cdot H_2O$, C, 67.10%, H 9.99%.

Cyclopassifloic acid F (3): amorphous powder; $[\alpha]^{25}_D$ +39.3° (*c* 3.0, MeOH); IR (KBr) ν_{max} 3450 (OH), 1700 (COOH), 1065, 1030 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.58, 0.84 (1H each, d, J = 4.0 Hz, H_2-19), 1.07 (3H, d, J = 6.0 Hz, H_3-21), 1.11 (3H, s, H_3-18), 1.20, 1.22 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.42 (3H, s, H_3-30), 1.74 (3H, s, H_3-29), 2.48 (1H, ddd, J = 12.0, 4.5, 2.5 Hz, H-2α), 2.55 (1H, m, H-11α), 3.44 (1H, dd, J = 12.0, 4.0 Hz, H-5), 3.93 (1H, br s, H-1), 3.97, 4.05 (1H each, d, J = 11.0 Hz, H_2-31), 4.30 (1H, dd, J = 6.5, 6.0 Hz, H-16), 5.58 (1H, dd, J = 12.0, 4.5 Hz, H-3); ^{13}C NMR data, see Table 1; FABMS *m/z* $[M - H]^-$ 535; *anal.* C 67.12%, H 9.81%, calcd for $C_{31}H_{52}O_7 \cdot H_2O$, C, 67.05%, H 9.95%.

Cyclopassifloside VII (4): colorless needless, mp 163−165 °C; $[\alpha]^{25}_D$ +35.6° (*c* 1.5, MeOH); IR (KBr) ν_{max} 3400 (OH), 1735 (ester), 1065, 1020 cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 0.54, 0.76 (1H each, d, J = 4.5 Hz, H_2-19), 0.87 (3H, s, H_3-30), 1.13 (3H, m, H-6β and H_2-7), 1.18, 1.20 (3H each, d, J = 7.0 Hz, H_3-26 and 27), 1.48 (1H, m, H-11β), 1.54 (3H, s, H_3-21), 1.68 (3H, s, H_3-29), 1.71 (1H, dd, J = 11.0, 5.0 Hz, H-8), 1.78 (1H, dd, J = 13.0, 8.0 Hz, H-15β), 1.78 (1H, m, H-12β), 1.83 (1H, m, H-6α), 1.87 (3H, s, H_3-18), 1.95 (1H, dd, J = 13.0, 6.0 Hz, H-15α), 1.98 (1H, m, H-12α), 2.07 (1H, dt, J = 12.0, 3.5 Hz, H-23b), 2.16 (1H, d, J = 8.0 Hz, H-17), 2.25 (1H, dt, J = 12.0, 2.5 Hz, H-2β), 2.28 (1H, qq, J = 7.0 Hz, H-25), 2.28 (1H, m, H-23a), 2.33 (1H, dt, J = 12.0, 3.5 Hz, H-22b), 2.44 (2H, m,

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

	C	**1** (δ m)	**2** (δ m)	**3** (δ m)	**4** (δ m)	**5** (δ m)	**6** (δ m)	**7**(δ m)	**8** (δ m)	**9** (δ m)	**10** (δ m)
	1	72.4 d	72.6 d	72.6 d	72.1 d	72.3 d	72.3 d	72.4 d	72.3 d	72.4 d	72.4 d
	2	38.6 t	38.7 t	38.9 t	38.5 t	38.4 t	38.3 t	38.3 t	38.4 t	38.3 t	38.4 t
	3	70.7 d	70.9 d	70.8 d	70.8 d	70.8 d	70.9 d	70.8 d	70.8 d	70.6 d	70.7 d
	4	55.6 s	55.7 s	55.8 s	56.4 s	56.4 s	56.5 s	56.4 s	56.5 s	56.4 s	55.6 s
	5	37.8 d	37.8 d	37.9 d	37.8 d	37.7 d	37.8 d	37.7 d	37.8 d	37.5 d	37.6 d
	6	23.3 t	23.3 t	23.5 t	23.0 t	23.1 t	23.1 t	23.2 t	23.2 t	23.3 t	23.4 t
	7	26.1 t	26.1 t	26.4 t	26.0 t	25.9 t	26.0 t	26.0 t	26.0 t	26.0 t	26.0 t
	8	48.0 d	48.4 d	48.5 d	48.0 d	48.4 d	48.4 d	48.5 d	48.5 d	47.9 d	48.0 d
	9	20.8 s	20.9 s	20.5 s	20.5 s	20.9 s	21.1 s	20.5 s	20.5 s	20.9 s	21.0 s
	10	30.4 s	30.4 s	30.5 s	30.3 s	30.2 s	30.4 s	30.2 s	30.3 s	30.2 s	30.3 s
	11	26.1 t	26.1 t	26.4 t	25.9 t	26.0 t	26.0 t	26.0 t	26.3 t	26.4 t	26.4 t
	12	33.8 t	33.5 t	33.3 t	33.7 t	32.1 t	31.9 t	33.2 t	33.3 t	33.5 t	33.4 t
	13	46.7 s	45.7 s	48.0 s	46.7 s	45.6 s	45.8 s	47.9 s	47.9 s	46.2 s	45.6 s
	14	47.4 s	47.2 s	47.2 s	47.4 s	47.2 s	47.2 s	47.1 s	47.0 s	49.3 s	49.2 s
	15	49.6 t	49.1 t	48.5 t	49.4 t	49.1 t	49.1 t	48.5 t	48.5 t	35.4 t	36.0 t
	16	73.6 d	71.8 d	77.2 d	73.5 d	71.0 d	72.1 d	77.2 d	77.1 d	23.0 t	28.5 t
	17	55.3 d	57.4 d	61.0 d	55.2 d	57.3 d	57.4 d	60.9 d	61.8 d	55.1 d	52.8 d
	18	21.9 q	18.7 q	19.2 q	21.3 q	18.7 q	18.7 q	19.2 q	18.6 q	19.8 q	18.4 q
	19	29.9 t	30.2 t	29.2 t	30.5 t	30.3 t	30.4 t	29.2 t	29.6 t	30.2 t	30.1 t
	20	76.9 s	33.5 d	35.3 d	76.9 s	33.6 d	33.5 d	35.3 d	36.1 d	74.7 s	37.4 d
	21	26.1 q	19.5 q	19.5 q	26.3 q	19.6 q	19.6 q	19.6 q	19.3 q	26.1 q	19.8 q
	22	38.3 t	32.1 t	30.5 t	38.4 t	32.0 t	32.3 t	30.6 t	32.3 t	38.1 t	32.0 t
	23	29.9 t	30.4 t	30.0 t	30.1 t	30.5 t	30.7 t	30.4 t	30.6 t	29.2 t	31.7 t
	24	75.9 s	76.6 s	76.0 s	75.7 s	76.4 s	76.1 s	76.1 s	76.1 s	76.0 s	76.1 s
	25	33.5 d	33.5 d	34.1 d	33.6 d	33.3 d	33.5 d	34.1 d	34.3 d	33.6 d	33.7 d
	26	17.5 q	17.4 q	17.7 q	17.6 q	17.5 q	17.4 q	17.7 q	17.5 q	17.4 q	17.7 q
	27	17.6 q	17.8 q	17.8 q	17.7 q	17.8 q	17.6 q	17.8 q	17.5 q	17.6 q	17.8 q
	28	180.6 s	180.7 s	180.1 s	176.7 s	176.7 s	176.6 s	176.7 s	176.8 s	180.0 s	180.1 s
	29	9.7 q	9.8 q	9.9 q	9.7 q	9.7 q	9.8 q	9.8 q	9.8 q	9.7 q	9.8 q
	30	20.5 q	20.3 q	20.5 q	20.7 q	20.3 q	20.4 q	20.5 q	20.5 q	20.3 q	18.7 q
	31	66.0 t	66.2 t	66.1 t	66.0 t	66.3 t	75.1 t	66.1 t	75.2 t	66.3 t	66.3 t
Glc-28	1′				96.5 d	96.5 d	96.5 d	96.5 d	96.5 d		
	2′				74.8 d	74.7 d	74.8 d	74.7 d	74.7 d		
	3′				78.5 d	78.5 d	78.5 d	78.5 d	78.5 d		
	4′				70.9 d	71.7 d	71.7 d	71.1 d	71.7 d		
	5′				79.7 d	79.6 d	79.5 d	79.5 d	79.6 d		
	6′				62.0 t	62.1 t	62.4 t	62.4 t	62.1 t		
Glc-31	1″						105.5 d		105.7 d		
	2″						75.5 d		75.5 d		
	3″						78.5 d		78.5 d		
	4″						71.7 d		71.7 d		
	5″						78.5 d		78.5 d		
	6″						62.8 t		62.8 t		

H-2α and H-22a), 2.80 (1H, m, H-11α), 3.36 (1H, dd, J = 12.0, 4.5 Hz, H-5), 3.88 (1H, br s, H-1), 4.00, 4.06 (1H each, d, J = 11.0 Hz, H_2-31), 4.03 (1H, m, H-5′ of Glc), 4.17 (1H, dd, J = 8.5, 8.0 Hz, H-2′ of Glc), 4.29 (1H, t, J = 8.5 Hz, H-3′ of Glc), 4.39 (1H, t, J = 8.5 Hz, H-4′ of Glc), 4.40 (2H, m, H-6′ of Glc), 5.02 (1H, dt, J = 6.0, 8.0 Hz, H-16), 5.59 (1H, dd, J = 12.0, 4.5 Hz, H-3), 6.53 (1H, d, J = 8.0 Hz, H-1′ of Glc); ^{13}C NMR data, see Table 1; HMBC (H/C) 1/3, 1/5, 1/10, 3/29, 16/13, 17/12, 17/13, 17/16, 17/18, 17/20, 18/12, 18/13, 18/14, 18/17, 19/1, 19/9, 19/11, 21/17/, 21/20, 21/22, 22/20, 26/24, 26/25, 26/27, 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]$^-$ 713; *anal*. C, 59.18%, H 8.86%, calcd for $C_{37}H_{62}O_{13}\cdot 2H_2O$, C 59.00%, H 8.95%.

Cyclopassifloside VIII (5): amorphous solid; $[\alpha]^{25}_D$ +38.6° (*c* 1.3, MeOH); IR (KBr) ν_{max} 3400 (OH), 1735 (ester), 1065, 1030 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.53, 0.75 (1H each, d, J = 4.0 Hz, H_2-19), 0.91 (3H, s, H_3-30), 1.10 (3H, d, J = 6.0 Hz, H_3-21), 1.18 (6H, d, J = 7.0 Hz, H_3-26 and -27), 1.41 (3H, s, H_3-18), 1.67 (3H, s, H_3-29), 2.46 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.75 (1H, m, H-11α), 3.35 (1H, dd, J = 12.0, 4.0 Hz, H-5), 3.88 (1H, br s, H-1), 3.99, 4.02 (1H each, d, J = 11.0 Hz, H_2-31) 3.99 (1H, m, H-5′ of Glc), 4.15 (1H, t, J = 8.0 Hz, H-2′ of Glc), 4.27 (1H, t, J = 8.0 Hz, H-3′ of Glc), 4.37 (1H, t, J = 8.0 Hz, H-4′ of Glc), 4.40 (2H, m, H_2-6′ of Glc), 4.65 (1H, dt, J = 6.0, 8.0 Hz H-16), 5.55 (1H, dd, J = 12.0, 4.0 Hz, H-3), 6.50 (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 61.99%, H 9.00%, calcd for $C_{37}H_{62}O_{12}\cdot H_2O$, C 61.80%, H 9.28%.

Cyclopassifloside IX (6): amorphous solid; $[\alpha]^{25}_D$ +19.0° (*c* 1.3, MeOH); IR (KBr) ν_{max} 3450 (OH), 1730 (ester), 1070, 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), 0.87 (3H, s, H_3-30), 1.04 (3H, d, J = 6.0 Hz, H_3-21), 1.12 (6H, d, J = 7.0 Hz, H_3-26 and -27), 1.35 (3H, s, H_3-18), 1.66 (3H, s, H_3-29), 2.48 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.74 (1H, m, H-11α), 3.34 (1H, dd, J = 12.0, 4.0 Hz, H-5), 3.87 (1H, br s, H-1), 3.98, 4.01 (1H each, d, J = 11.0 Hz, H_2-31), 3.99 (1H, m, H-5″ of Glc), 4.04 (1H, m, H-5′ of Glc), 4.06 (1H, t, J = 8.0 Hz, H-2″ of Glc), 4.18 (1H, t, J = 8.0 Hz, H-2′ of Glc), 4.20 (1H, t, J = 8.0 Hz, H-4″ of Glc), 4.23 (1H, t, J = 8.0 Hz, H-3″ of Glc), 4.25 (1H, t, J = 8.0, H-3′ of Glc), 4.29 (1H, t, J = 8.0, H-4′ of Glc), 4.33 (2H, m, H-6′a and H-6″a of Glc), 4.42 (1H, dd, J = 12.5, 2.5, H-6′b of Glc), 4.53 (1H, dd, J = 12.0, 2.5, H-6″b of Glc), 4.67 (1H, dt, J = 6.0, 8.5 Hz, H-16), 4.91 (1H, d, J = 8.0 Hz, H-1″ of 31-Glc), 5.54 (1H, dd, J = 12.0, 4.0 Hz, H-3), 6.41 (1H, d, J = 8.0 Hz, H-1′ of 28-Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 859; *anal*. C 56.44%, H 8.59%, calcd for $C_{43}H_{72}O_{17}\cdot 3H_2O$, C 56.22%, H 8.72%.

Cyclopassifloside X (7): colorless needless, mp 167−169 °C; $[\alpha]^{25}_D$ +36.8° (*c* 2.1, MeOH); IR (KBr) ν_{max} 3400 (OH), 1740 (ester), 1065, 1030 cm^{-1}; ^1H NMR (400 MHz, C_5D_5N) δ 0.54, 0.73 (1H each, d, J = 4.0 Hz, H_2-19), 1.05 (3H, d, J = 6.0 Hz, H_3-21), 1.06 (3H, s, H_3-18), 1.19, 1.21 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.27 (3H, s, H_3-30), 1.59 (3H, s, H_3-29), 2.43 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.87 (1H, m, H-11α), 3.35 (1H, dd, J = 12.0, 4.5 Hz, H-5), 3.87 (1H, br s, H-1), 3.97, 4.04 (1H each, d, J = 11.5 Hz, H_2-31), 4.01 (1H, m, H-5′ of Glc), 4.14 (1H, t, J = 8.0 Hz, H-2′ of Glc), 4.26 (1H, t, J = 8.0, H-3′ of Glc), 4.28 (1H, m, H-16), 4.34 (1H, t, J = 8.0 Hz, H-4′ of Glc), 4.37 (2H, m, H_2-6′ of Glc), 5.56 (1H, dd, J = 12.0, 4.5

Hz, H-3), 6.47 (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 61.99%, H 9.00%, calcd for $C_{37}H_{62}O_{12}\cdot H_2O$, C 61.85%, H 9.15%.

Cyclopassifloside XI (8): colorless needless, mp 171−173 °C; $[\alpha]^{25}_D$ +13.6° (*c* 2.7, MeOH); IR (KBr) ν_{max} 3450 (OH), 1735 (ester), 1045, 1030 cm^{-1}; ^{1}H NMR (400 MHz, C_5D_5N) δ 0.54, 0.74 (1H each, d, J = 4.0 Hz, H_2-19), 1.03 (3H, d, J = 6.0 Hz, H_3-21), 1.03 (3H, s, H_3-18), 1.09, 1.14 (3H each, d, J = 7.0 Hz, H_3-26 and -27), 1.31 (3H, s, H_3-30), 1.68 (3H, s, H_3-29), 2.43 (1H, ddd, J = 12.0, 4.0, 2.5 Hz, H-2α), 2.83 (1H, m, H-11α), 3.36 (1H, dd, J = 12.0, 4.5 Hz, H-5), 3.87 (1H, br s, H-1), 3.94, 3.99 (1H each, d, J = 11.0 Hz, H_2-31), 3.95 (1H, m, H-5″ of Glc), 4.03 (1H, m, H-5′ of Glc), 4.05 (1H, t, J = 8.0 Hz, H-2″ of Glc), 4.15 (1H, t, J = 8.0 Hz, H-2′ of Glc), 4.20 (2H, t, J = 8.0 Hz, H-3“ and H-4” of Glc), 4.27 (1H, dd, J = 8.0, 8.0 Hz, H-3′ of Glc), 4.28 (1H, m, H-16), 4.35 (1H, t, J = 8.0 Hz, H-4′ of Glc), 4.38 (3H, m, H_2-6′a and H-6″a of Glc), 4.55 (1H, dd, J = 12.0, 2.5 Hz, H-6″b of Glc), 4.92 (1H, d, J = 8.0 Hz, H-1″ of 31-Glc), 5.58 (1H, dd, J = 12.0, 4.5 Hz, H-3), 6.50 (1H, d, J = 8.0 Hz, H-1′ of 28-Glc); ^{13}C NMR data, see Table 1; FABMS m/z [M − H]$^-$ 859; *anal*. C 56.44%, H 8.59%, calcd for $C_{43}H_{72}O_{17}\cdot H_2O$, C 56.33%, H 8.72%.

Identification of Sugar Components of Cyclopassiflosides VII−XI (4−8). 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 using RI and chiral detection, respectively, by HPLC (Shodex RSpak DC-613 column, 80% CH_3-CN, 0.8 mL/min, 70 °C). Each sugar unit gave a positive peak at 13.40 min (D-Glc; 13.38 min).

Alkaline Hydrolysis of Cyclopassifloside VII (4). A solution of **4** (20 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 (**1**, 12 mg).

Enzymatic Hydrolysis of Cyclopassifloside IX (6). A solution of **6** (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, glucose was detected by TLC [*n*-BuOH−HOAc−H_2O (3:1:1). 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 (**5**, 6 mg).

Enzymatic Hydrolysis of Cyclopassifloside XI (8). Enzymatic hydrolysis of **8** (20 mg) was carried out in the same way as described for **6** to give a prosapogenin (**7**, 13 mg).

Alkaline Hydrolysis of Cyclopassiflosides VIII (5) and X (7). Alkaline hydrolysis was carried out in the same way as described for **4** to give **2** (9 mg) from **5** (15 mg), and **3** (8 mg) from **7** (15 mg), respectively.

References and Notes

(1) These studies have been presented orally at the 104th Annual Meeting of the Japanese Society of Pharmacognosy, Sendai, April 1984, and at the 31th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, October 1984.
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