[Chem. Pharm. Bull. 36(5)1646—1663(1988)]

Tannins and Related Compounds. LXVII.[1] Isolation and Characterization of Castanopsinins A—H, Novel Ellagitannins Containing a Triterpenoid Glycoside Core, from *Castanopsis cuspidata* var. *sieboldii* NAKAI. (3)

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(Received September 26, 1987)

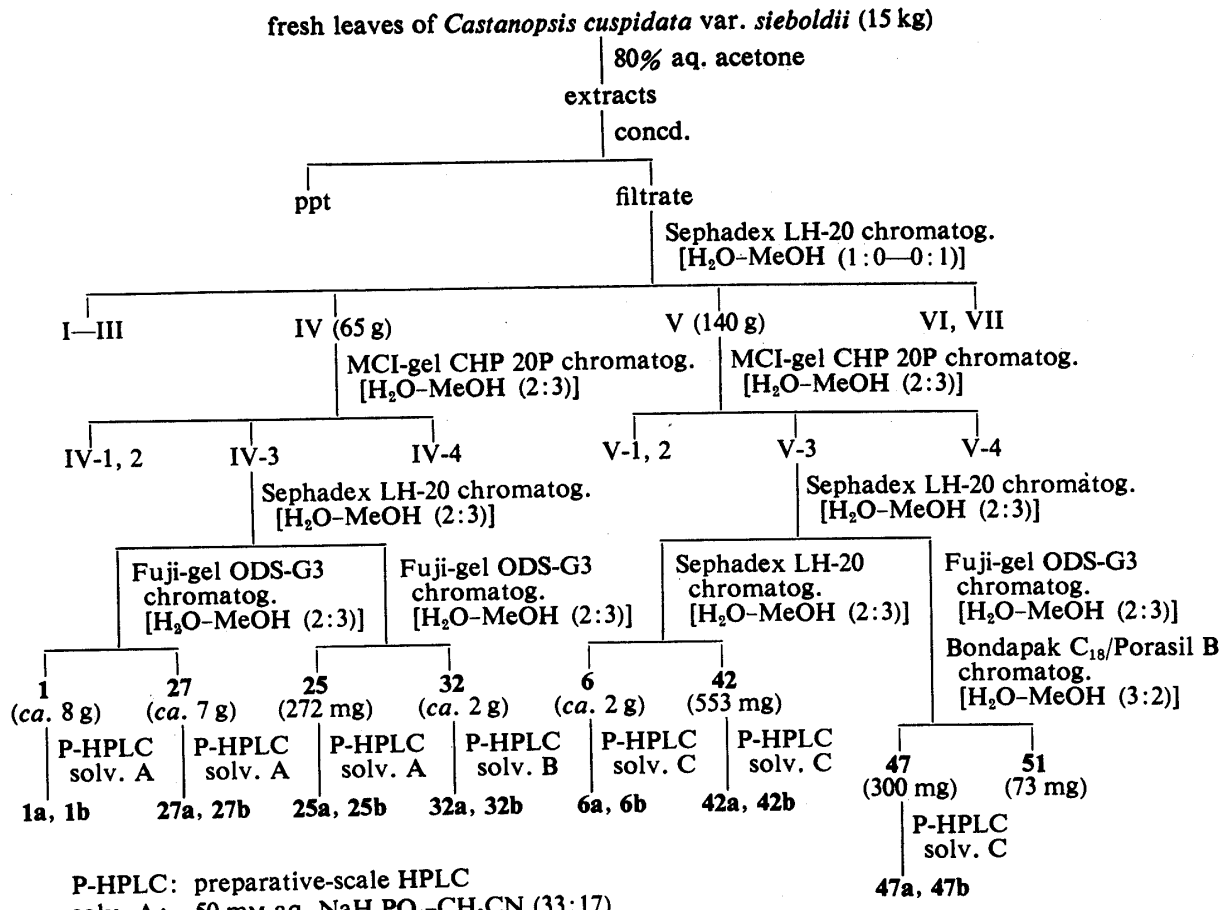
A new class of ellagitannins, castanopsinins A—H (**1**, **6**, **25**, **27**, **32**, **42**, **47** and **51**), containing a triterpenoid glycoside core, have been isolated from the leaves of *Castanopsis cuspidata* var. *sieboldii* NAKAI (Fagaceae). On the basis of spectroscopic and chemical data these compounds have been characterized as 3,23-(*R*)- (**1**), 24-*O*-galloyl-3,23-(*R*)- (**6**), 2,3-(*R*)- (**25**), 3,23-(*S*)- (**27**), 3,24-(*S*)- (**32**), 24-*O*-galloyl-3,23-(*S*)- (**42**), 3′-*O*-galloyl-23,24-(*R*)- (**47**) and 24,3′-di-*O*-galloyl-3,23-(*R*)-hexahydroxydiphenoyl (**51**) 2α,3β,23,24-tetrahydroxyolean(urs)-12-en-28-oic acid 28-*O*-β-D-glucopyranosides. In addition, separation of structural isomers consisting of a mixture of oleanane- and ursane-type triterpenoids was successfully achieved.

Keywords——*Castanopsis cuspidata* var. *sieboldii*; Fagaceae; castanopsinin A—H; ellagitannin; triterpenoid 28-*O*-β-D-glucopyranoside; 2α,3β,23,24-tetrahydroxyolean(urs)-12-en-28-oic acid; castanopsigenin A, B; (*R*)- and (*S*)-hexahydroxydiphenic acid; atropisomerism

In previous papers, we reported on the isolation and characterization of a variety of ellagitannins based on the cores of *proto*-quercitol,[2] *scyllo*-quercitol,[3] salidroside,[4] gluconic acid[5] and D-glucose (pyranose[6a] and open-chain[7] forms). In continuing our chemical studies on tannin and related compounds, we have now isolated a series of novel ellagitannins named castanopsinins A—H (**1**, **6**, **25**, **27**, **32**, **42**, **47** and **51**), which contain a triterpenoid glucoside core in their molecules, from *Castanopsis cuspidata* var. *sieboldii* NAKAI (Fagaceae) (Japanese name: sudazii). This paper describes the isolation and structure determination of these tannins.

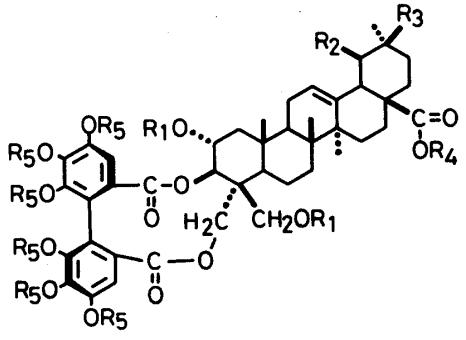
The fresh leaves were extracted with 80% aqueous acetone, and the extract was subjected to a combination of Sephadex LH-20, MCI-gel CHP 20P, Fuji-gel ODS-G3 and Bondapak C_{18}/Porasil B chromatographies with various solvent systems to yield thin-layer chromatographically homogeneous compounds, castanopsinins A—H (**1**, **6**, **25**, **27**, **32**, **42**, **47** and **51**). Examination of the ^{1}H- and ^{13}C-nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra of these compounds showed that they each consist of a mixture of two structural isomers. Subsequent separation of a part of each mixture (except for **51**) by preparative-scale high-performance liquid chromatography (HPLC) gave pure compounds (**1a**, **b**, **6a**, **b**, **25a**, **b**, **27a**, **b**, **32a**, **b**, **42a**, **b** and **47a**, **b**). However, owing to the difficulties in isolating large amounts of pure samples, only the physical and spectroscopic data were obtained by using these pure samples, and each mixture consisting of two structural isomers was used for the following structural elucidation.

Castanopsinins A (**1**) and B (**6**) showed a dark blue coloration with ferric chloride reagent, and were also positive to the Liebermann–Burchard reaction, giving a purple color. The ^{1}H- and ^{13}C-NMR spectra of **1** exhibited signals due to a hexahydroxydiphenoyl (HHDP) ester group [δ 7.18 and 7.28 (each 1H, s)] and a sugar moiety (δ 62.2, 71.2, 74.1, 78.8,

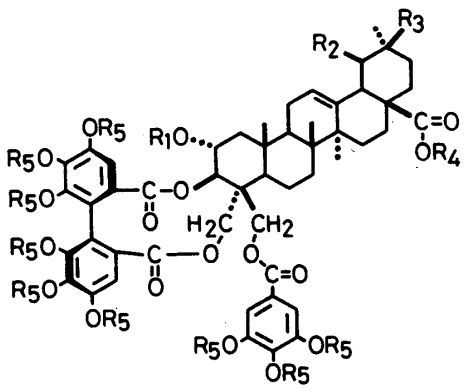


P-HPLC: preparative-scale HPLC
solv. A: 50 mM aq. NaH_2PO_4–CH_3CN (33:17)
solv. B: 50 mM aq. NaH_2PO_4–CH_3CN (16:9)
solv. C: 50 mM aq. NaH_2PO_4–CH_3CN (27:23)

Chart 1



	R_1	R_2	R_3	R_4	R_5
1	H	H	Me	Glc	H
	H	Me	H	Glc	H
2a	H	H	Me	Glc	Me
2b	H	Me	H	Glc	Me
3	H	H	Me	H	H
	H	Me	H	H	H
4	H	H	Me	Me	Me
	H	Me	H	Me	Me
5	Ac	H	Me	Me	Me
	Ac	Me	H	Me	Me



	R_1	R_2	R_3	R_4	R_5
6	H	H	Me	Glc	H
	H	Me	H	Glc	H
7	H	H	Me	Glc	Me
	H	Me	H	Glc	Me
8	H	H	Me	H	H
	H	Me	H	H	H
9	H	H	Me	Me	Me
	H	Me	H	Me	Me
10	Ac	H	Me	Me	Me
	Ac	Me	H	Me	Me

Chart 2

79.1 and 95.7), while the spectra of **6** showed the presence of a galloyl group [δ 8.01 (2H, s)], in addition to an HHDP group [δ 7.08 and 7.54 (each 1H, s)] and a similar sugar moiety (δ 62.1, 71.0, 74.1, 78.8, 79.3 and 95.9). Methylation of **1** with dimethyl sulfate and anhydrous potassium carbonate in dry acetone, followed by careful silica gel chromatography, yielded two hexamethyl ethers (**2a** and **2b**). On alkaline methanolysis with 2% methanolic sodium methoxide, **2a** and **2b** furnished the respective hydrolysates (**11a** and **11b**), together with dimethyl hexamethoxydiphenoate (**14**) and D-glucose as common products. The ^{13}C-NMR spectra (Table I) of **11a** and **11b** showed the presence of thirty carbons including five methyls, a tri-substituted double bond, a carboxylic acid and four carbons carrying an oxygen function, thus suggesting that **11a** and **11b** are triterpenoid derivatives. In addition, the differences in the chemical shifts of the double bond carbons (δ 123.3 and 145.5 in **11a**; δ 125.4 and 139.0 in **11b**), assignable to the triterpenoid C(12) and C(13), indicated them to be

TABLE I. ^{13}C-NMR Spectral Data for Compounds **11a**, **11b**, **13a**, **13b**, **19** and **20**

Carbon No.	**11a**[a]	**11b**[a]	**13a**[b]	**13b**[b]	**19**[b]		**20**[b]
C-1	43.4	43.4	44.1	44.1	41.8	41.8	41.8
C-2	69.9	69.9	69.2	69.2	69.3	69.3	69.3
C-3	79.6	79.6	74.4	74.4	71.8	71.8	71.9
C-4	46.2	46.2	45.3	45.3	43.6	43.6	43.7
C-5	48.5	48.5	48.1	48.2	47.9	47.9	47.6
C-6	19.7	21.6	19.1	21.3	19.1	21.1	19.1
C-7	33.2[c]	33.9	32.6[c]	33.0	33.8	33.8	33.8
C-8	40.6	40.5	39.3	39.5	39.6	39.4	39.9
C-9	47.8	47.5	47.5	47.9	48.0	48.0	47.9
C-10	38.1	38.1	37.5	37.7	36.6	36.7	36.7
C-11	24.2[d]	24.9	23.4[d]	23.5	23.5	23.5	23.6
C-12	123.3	125.4	122.1	124.9	121.9	125.0	123.4
C-13	145.4	139.8	143.6	138.3	143.9	138.3	142.4
C-14	42.8	42.8	41.7	42.0	41.7	41.8	39.7
C-15	28.8	29.2	27.7	27.9	27.8	27.5	32.2
C-16	24.1[d]	26.5	23.0[d]	24.2	22.9	24.1	76.2
C-17	47.1	48.5	46.7	48.1	46.7	48.5	47.7
C-18	42.5	54.4	41.3	52.9	41.2	52.8	40.6
C-19	46.2	40.8	45.9	39.1	45.7	39.0	46.2
C-20	31.6	38.8	30.7	38.8	30.7	38.8	30.5
C-21	35.0	31.2	33.9	30.7	33.8	30.7	35.2
C-22	33.6[c]	42.8	32.4[c]	36.5	32.3	36.6	31.0
C-23	62.9	62.9	62.6	62.6	62.9	62.9	62.9
C-24	64.5	64.5	63.5	63.5	63.9	63.9	63.9
C-25	17.5[e]	17.5[c]	16.5[e]	16.7	16.4	16.6	16.4
C-26	17.7[e]	17.7[c]	17.2[e]	16.5	17.0	16.8	16.9
C-27	26.5	24.9	26.0	23.4	25.7	23.5	26.4
C-28	177.6	177.0	177.9	177.8	178.1	177.9	176.0
C-29	33.9	18.5	33.1	17.0	33.1	16.8	33.2
C-30	24.7	21.6	23.6	21.1	23.5	21.2	24.3
COOMe			51.4	51.4	51.5	51.5	52.1
OCOMe			20.7	20.7	20.7	20.7	
			20.9	20.9	20.9	20.9	
			(3C)	(3C)	(3C)	(3C)	
–COO–			169.9	169.9	169.9	169.9	
			170.0	170.0	170.1	170.1	
			170.2	170.2	170.4	170.4	
			170.6	170.6	170.7	170.7	

a) Measured in CD_3OD. *b*) Measured in $CDCl_3$. *c*—*e*) Assignments may be interchanged.

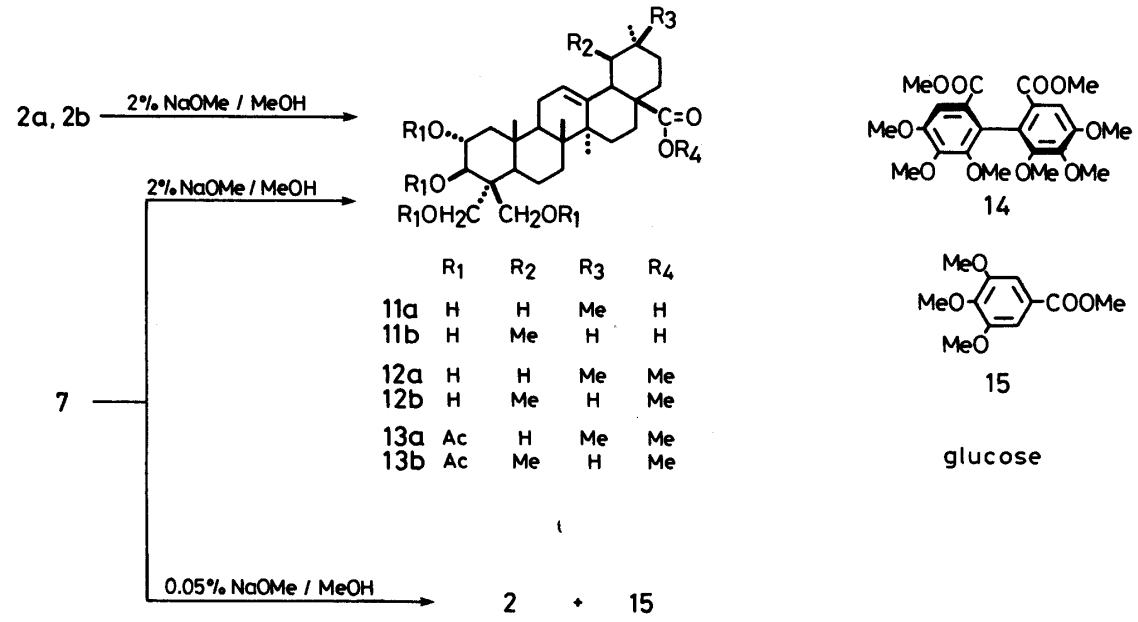


Chart 3

oleanene and ursene types, respectively.[8]

On the other hand, similar methylation of **6** afforded the nonamethyl ether (**7**, in fact, composed of **7a** and **7b**), which showed an overlapped spot on thin-layer chromatography (TLC) in every solvent system tested, and therefore could not be separated. The ^{1}H- and ^{13}C-NMR spectra of **7** were similar to those of **2a** and **2b**, except for the presence of a trimethoxybenzoyl group (δ 7.37) and the lowfield shifts [δ 3.78 and 4.75 (each 1H, J= 11.7 Hz)] of a pair of geminally coupled doublets due to an isolated methylene. Alkaline methanolysis of **7** with 2% methanolic sodium methoxide yielded methyl trimethoxybenzoate (**15**), dimethyl hexamethoxydiphenoate (**14**), D-glucose and a hydrolysate, whose ^{1}H-NMR spectrum was identical with that of **11a** plus **11b**, while mild methanolysis with 0.05% methanolic sodium methoxide selectively cleaved only the benzoyl ester linkage to yield the methanolysate, which was found to be identical with **2** (**2a** plus **2b**). From these findings, it has become clear that compounds **1** and **6** are ellagitannins possessing a mixture of tetrahydroxy oleanene- and ursene-type triterpenoid glucoside cores in each molecule.

The structures of the triterpenoid moieties were further examined as follows. On treatment with diazomethane, the triterpenoids (**11a** and **11b**) afforded the methyl esters (**12a** and **12b**, respectively). The electron impact mass spectra (EI-MS) of these compounds showed the same $[M]^{+}$ peak at m/z 518, with significant peaks at m/z 262 and 203 which were presumed to be formed by the retro-Diels–Alder-type fission of the C-ring (Chart 4), and which are characteristic to an olean- or an urs-12-en-28-oic acid methyl ester. In addition, the observation of these prominent peaks suggested the absence of a hydroxyl group on the C, D and E rings. Actually, another prominent peak at m/z 256, which was considered to be a fragment derived from the remaining part, was consistent with tetrahydroxy substitution of the A- and/or B-rings. The ^{1}H-NMR spectra of the tetraacetates (**13a** and **13b**), prepared from **12a** and **12b** by usual acetylation, showed, together with four acetyl singlets (δ 1.98, 2.01, 2.05 and 2.10), lowfield shifts of two geminally coupled doublets [δ 3.87 and 4.15 (each 1H, J= 12 Hz)] and of a two-proton singlet (δ 4.29), which were assignable to isolated methylenes, namely to the C(23)- and C(24)-protons, respectively. Furthermore, the spectra showed lowfield shifts of a one-proton doublet [δ 5.18 (J= 10 Hz)] and a one-proton multiplet (δ 5.20), whose coupling patterns were consistent with those observed in 2α,3β-hydroxy triterpenoid derivatives. On the basis of these findings, **11a** and **11b** were presumed to be 2α,3β,23,24-

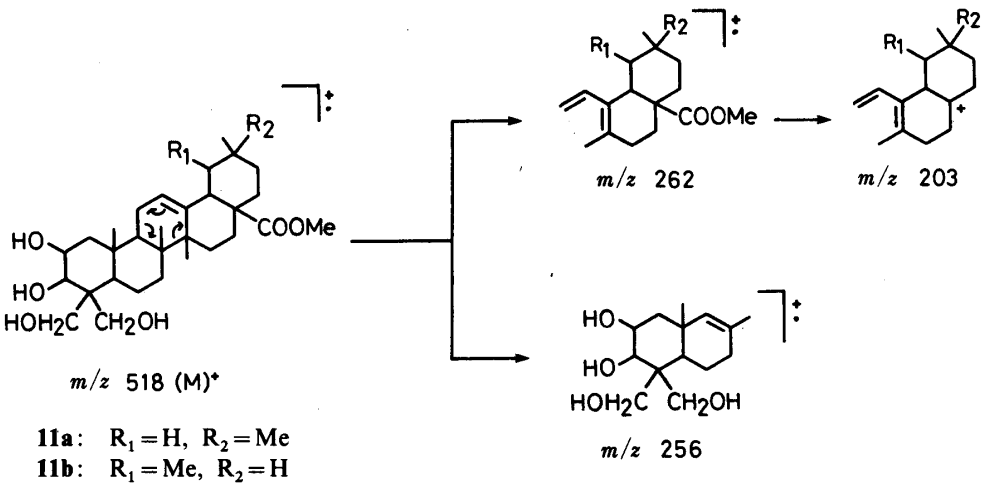


Chart 4. EI-MS Fragmentation of **11a** and **11b**

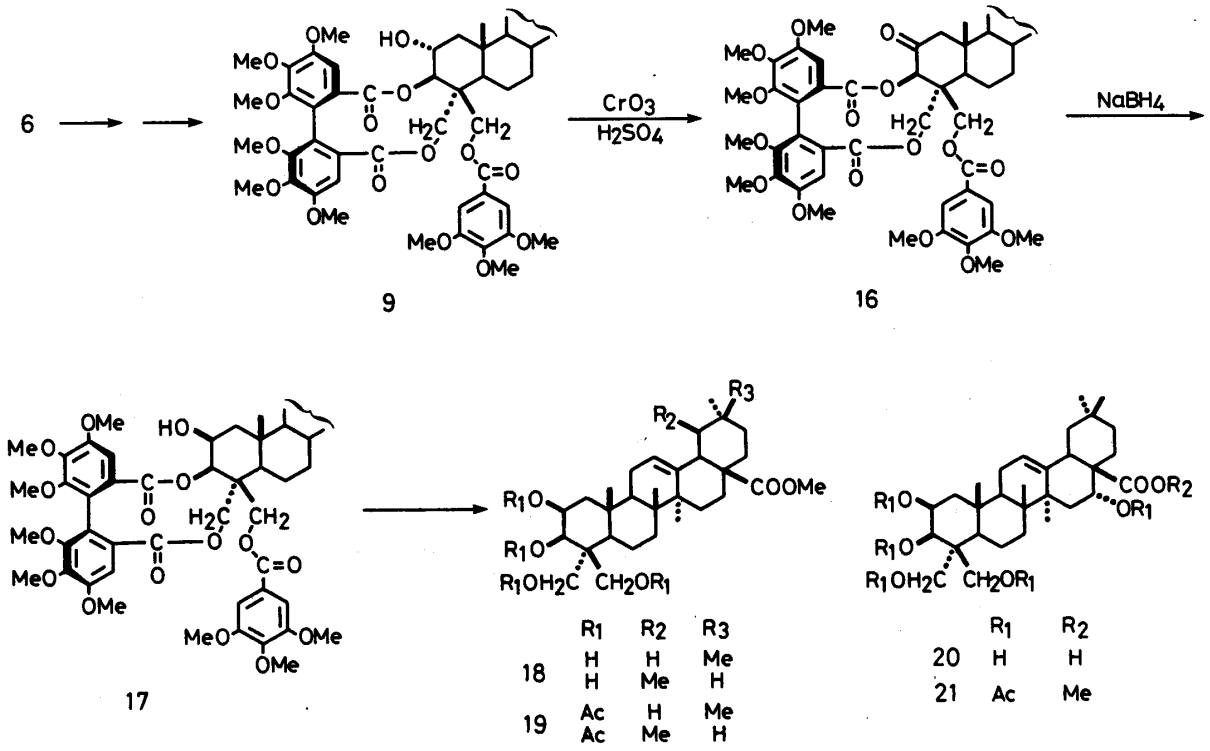


Chart 5

tetrahydroxyolean- and urs-12-en-28-oic acids, respectively.

In order to establish definitively the locations and configurations of the hydroxyl groups in the triterpenoid skeleton, an attempt was made to convert **6** to the structurally related compound, platycodigenin (**20**),[9] which possesses a 2β,3β,23,24-tetrahydroxy-substitution system and differs only in the configuration at the C(2)-position. Selective hydrolysis of the sugar linkage in **6** with 2 N sulfuric acid yielded D-glucose and compound (**8**) [fast atom bombardment mass spectrum (FAB-MS) *m/z*: 959 $[M+H]^+$], which was methylated with dimethyl sulfate and potassium carbonate in dry acetone to give the decamethyl derivative (**9**) [field desorption mass spectrum (FD-MS) *m/z*: 1098 $(M)^+$]. On oxidation with chromium trioxide, **9** afforded a ketone (**16**) [FD-MS *m/z*: 1096 $(M)^+$; ^{13}C-NMR: δ 217.7 (C=O)], which was reduced with sodium borohydride to yield the alcohol (**17**) almost quantitatively [FD-MS

m/z: 1098 $(M)^+$]. The ^{1}H-NMR spectrum of **17** exhibited a well-separated doublet due to the C(3)-proton at δ 5.03, and the smaller coupling constant (J=4 Hz) of this signal than that found in **9** clearly indicated that **17** possesses 2β-configuration. Subsequent alkaline methanolysis of **17** with 2% methanolic sodium methoxide gave, together with dimethyl hexamethoxydiphenoate (**14**) and methyl trimethoxybenzoate (**15**), a tetrahydroxy derivative (**18**) [EI-MS *m/z*: 518 $(M)^+$], which formed the tetraacetate (**19**) on acetylation. Comparison of the ^{13}C-NMR data of the acetate (**19**) with those of the platycodigenin methyl ester pentaacetate (**21**)[9] showed that the chemical shifts of the signals arising from the A- and B-rings were almost identical (Table I), thus confirming the 2α,3β,23,24-tetrahydroxy substitution of the triterpenoid moiety. Accordingly, **11a** and **11b** were concluded to be 2α,3β,23,24-tetrahydroxyolean- and urs-12-en-28-oic acids, and were named castanopsigenins A and B, respectively.

The locations of the HHDP and galloyl groups in **1** and **6** were determined in the following ways. Acid hydrolysis of **1** with 2 N sulfuric acid selectively cleaved the sugar linkage to yield a hydrolysate (**3**) and D-glucose. The hydrolysate (**3**) formed the heptamethyl derivative (**4**) on methylation as described above. The ^{1}H-NMR spectrum of **4** showed the presence of a hexamethoxydiphenoyl (HMDP) group [δ 6.70 and 6.76 (each 1H, s)]. This fact indicated that the HHDP group in **1** is located at the hydroxyls in the triterpenoid skeleton, and not in the sugar moiety. Furthermore, in the spectrum of **4**, the lowfield shifts of a doublet [δ 5.10 (J= 10.7 Hz)] and a pair of geminally coupled doublets [δ 4.03 and 5.12 (J= 11.7 Hz)] suggested the location of the HHDP group at the C(3)- and C(23)- or C(24)-positions. Further methylation of **4** by the Kuhn method yielded the nonamethyl derivative (**22**), which, on alkaline methanolysis, gave a methanolysate (**23**) and dimethyl hexamethoxydiphenoate (**14**). When treated with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid, the methanolysate (**23**) readily formed the isopropylidene derivative (**24**). Since the formation of a 3,23-*O*-isopropylidene derivative was reported to be much easier than in the case of a 3,24-isopropylidene,[10] this finding indicated that the HHDP group is situated at the C(3)- and C(23)-positions in **1**.

In the case of **6**, the formation of the above-mentioned decamethyl derivative (**9**) and the decamethyl monoacetate (**10**) [FD-MS *m/z*: 1140 $(M)^+$] from **8** confirmed that the galloyl group is also located in the triterpenoid moiety. The ^{1}H-NMR spectrum of **10** exhibited a double-triplet signal [δ 5.57 (J=4.4, 10.3 Hz)], which was shifted downfield by acetylation.

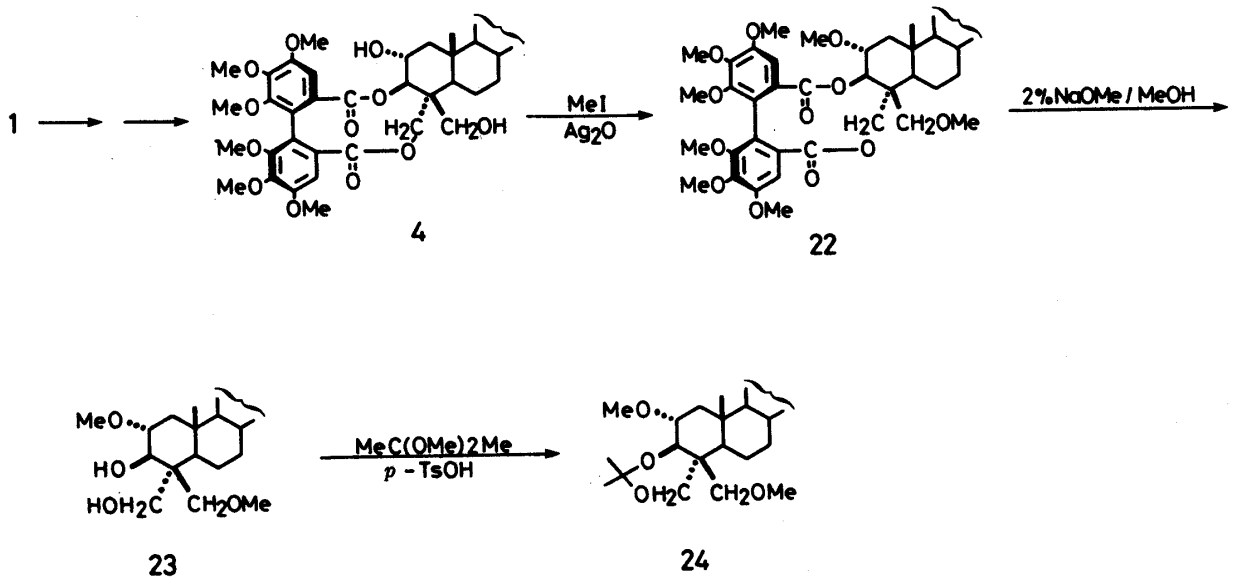
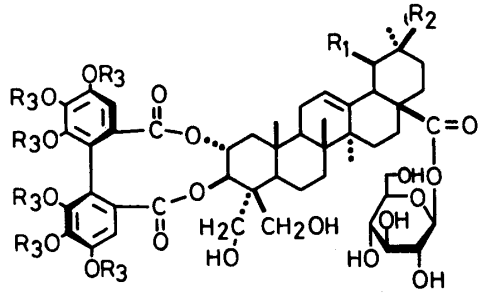


Chart 6

This methine signal could be assigned to the C(2)-proton on the basis of the coupling with the above-mentioned C(3)-methine doublet. From these chemical and spectral findings, the location of the galloyl group was determined to be at the C(24)-position.

The atropisomerism of the HHDP group was established to be in the *R*-series on the basis of the positive sign of the specific optical rotation [+26.4° ($CHCl_3$)] of the dimethyl hexamethoxydiphenoate (**14**),[6b] while the location of the sugar moiety at the C(28)-position, as well as the β-configuration of the anomeric center, was determined from the chemical shifts (δ 5.43 and δ 95.7 in **1**; δ 5.45 and δ 95.9 in **6**) and the coupling constant (J=8 Hz) of the anomeric signals in the ^{1}H- and ^{13}C-NMR spectra.

From the chemical and spectral evidence described above, the structures of castanopsinins A and B were characterized as 3,23-(*R*)- and 24-*O*-galloyl-3,23-(*R*)-hexahydroxydiphenoyl 2α,3β,23,24-tetrahydroxyolean(urs)-12-en-28-oic acid 28-*O*-β-D-glucopyranoside, respectively.



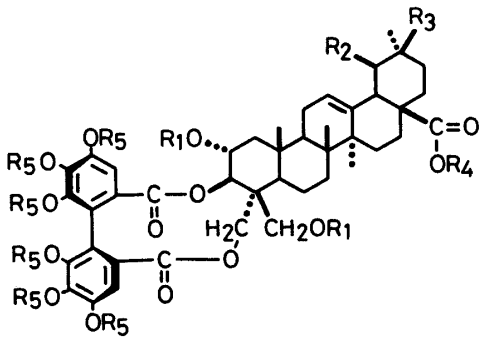
	R_1	R_2	R_3
25	H	Me	H
	Me	H	H
26	H	Me	Me
	Me	H	Me

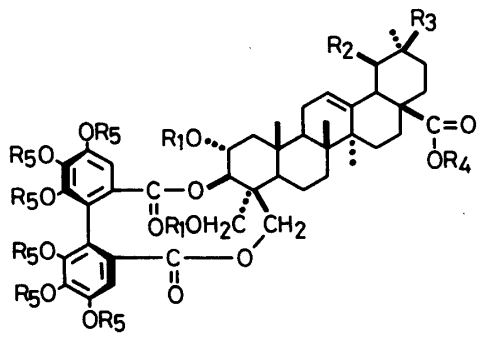
Chart 7

Castanopsinin C (**25**) was shown to have the same constitution as that of **1** by negative FAB-MS [*m/z*: 967 $[M-H]^-$] and also by the ^{1}H-NMR spectrum which exhibited signals due to an HHDP group [δ 7.12 and 7.78 (each 1H, s)], and a sugar and a triterpenoid moiety. On methylation with dimethyl sulfate and anhydrous potassium carbonate in dry acetone, **25** yielded the hexamethyl derivative (**26**). Subsequent alkaline methanolysis of **26** furnished, together with D-glucose and (*R*)-dimethyl hexamethoxydiphenoate (**14**), a methanolysate whose ^{1}H-NMR spectrum was identical with those of **11a** plus **11b**. Since in the ^{1}H-NMR spectrum of **26** a one-proton multiplet (δ 4.20) and a doublet [δ 4.85 (J=9.8 Hz)], assignable to the C(2)- and C(3)-protons, respectively, were shifted downfield by acylation, the HHDP group was concluded to be located at these positions. In addition, the relatively lowfield resonance (δ 5.49) with a large coupling constant (J=8 Hz) of the sugar anomeric signal confirmed the location of the sugar moiety at the C(28)-position and the β-mode of the anomeric linkage. Thus, castanopsinin C was characterized as **25**.

Castanopsinins D (**27**) and E (**32**) were also found to consist of a triterpenoid, a sugar and an HHDP group as revealed by ^{1}H- and ^{13}C-NMR spectroscopy. On methylation, **27** and **32** formed the respective hexamethyl ethers (**28** and **33**), which were methanolyzed with 2% methanolic sodium methoxide to yield D-glucose, dimethyl hexamethoxydiphenoate (**37**) and a triterpenoid identical with **11a** plus **11b**. Although these findings were closely related to those of **1** and **25**, the sign of the specific optical rotation [−25.3° ($CHCl_3$)] of dimethyl hexamethoxydiphenoate obtained here was opposite, indicating the chirality to be in the *S*-series.

On acid hydrolysis, followed by methylation, **27** and **32** gave the heptamethyl derivatives (**30** and **35**, respectively). The ^{1}H-NMR spectra of these methylates were similar, showing in each case the lowfield shifts of a doublet [δ 5.10 (J=10 Hz) in **30**; δ 4.93 (J=9.3 Hz) in **35**] and of a pair of geminally coupled doublets [δ 4.02 and 5.10 (J=12 Hz) in **30**; δ 3.81 and 5.01 (J=11.7 Hz) in **35**], thus suggesting that the HHDP group is attached to the C(3)- and C(23)- or





	R_1	R_2	R_3	R_4	R_5
27	H	H	Me	Glc	H
	H	Me	H	Glc	H
28	H	H	Me	Glc	Me
	H	Me	H	Glc	Me
29	H	H	Me	H	H
	H	Me	H	H	H
30	H	H	Me	Me	Me
	H	Me	H	Me	Me
31	Ac	H	Me	Me	Me
	Ac	Me	H	Me	Me

	R_1	R_2	R_3	R_4	R_5
32	H	H	Me	Glc	H
	H	Me	H	Glc	H
33	H	H	Me	Glc	Me
	H	Me	H	Glc	Me
34	H	H	Me	H	H
	H	Me	H	H	H
35	H	H	Me	Me	Me
	H	Me	H	Me	Me
36	Ac	H	Me	Me	Me
	Ac	Me	H	Me	Me

Chart 8

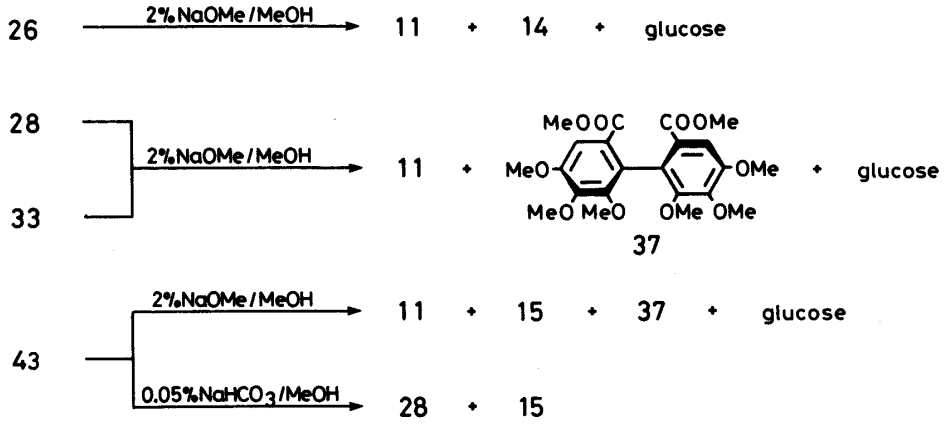


Chart 9

C(24)-positions. Permethylation of **30** and **35** by the Kuhn method gave the respective octamethyl derivatives (**38** and **40**), which on alkaline methanolysis yielded the methanolysates (**39** and **41**). The ^{1}H-NMR spectrum and physical constants of **39** were identical with those of **23** derived from **1**. Accordingly, castanopsinin D was concluded to be 3,23-(*S*)-hexahydroxydiphenoyl 2α,3β,23,24-tetrahydroxyolean(urs)-12-en-28-oic acid 28-*O*-β-D-glucopyranoside (**27**). On the other hand, **41** gave many decomposition products in an attempt to prepare an isopropylidene derivative, and therefore the location of the HHDP group was concluded to be at the C(3)- and C(24)-positions. Thus, castanopsinin E was characterized as 3,24-(*S*)-hexahydroxydiphenoyl 2α,3β,23,24-tetrahydroxyolean(urs)-12-en-28 oic acid 28-*O*-β-D-glucopyranoside (**32**).

Castanopsinin F (**42**) exhibited, in the negative FAB-MS, the same $[M-H]^-$ peak at *m/z* 1119 as that of **6**. The ^{1}H-NMR spectrum clearly indicated the presence of an HHDP group [δ 6.87 and 7.14 (each 1H, s)] and a galloyl group [δ 7.92 (2H, s)]. Methylation of **42** with

TABLE II. ^{13}C-NMR Spectral Data[a)]

	1a	1b	6a	6b	25a	25b	27a	27b	32a	32b	42a	42b	47a	47b	51	
Triterpenoid																
C-1	47.7	46.2	48.6	48.4	48.2	48.6	47.6	48.0	47.9	47.8	47.9	48.4	47.6	47.6	47.6	47.6
C-2	68.3	68.3	66.6	66.6	67.3	67.3	67.7	67.7	67.6	67.6	65.3	65.3	68.3	68.3	66.5	66.5
C-3	78.8	78.8	78.9	78.9	79.1	79.1	84.8	84.8	77.2	77.2	84.8	84.8	78.9	78.9	79.0	79.0
C-4	48.8	48.8	48.6	48.6	48.5	48.4	48.6	48.6	48.6	48.7	47.9	47.9	48.6	48.6	48.6	48.6
C-5	57.4	57.3	57.4	57.4	56.4	56.4	57.6	57.7	57.6	57.6	50.8	50.8	57.4	57.4	57.3	57.3
C-6	20.0	20.0	19.9	19.9	20.0	19.9	20.0	20.3	20.1	20.3	20.8	20.8	19.8	19.9	20.0	20.1
C-7	33.8	33.8	30.8	33.0	30.9	33.6	33.0	33.5	30.8	33.5	30.8	33.7	30.9	33.3	30.8	33.1
C-8	39.7	40.2	39.2	39.7	39.7	40.1	39.2	40.0	40.1	40.1	40.0	40.2	39.7	40.0	39.4	39.7
C-9	47.6	47.6	47.6	47.6	47.9	48.5	48.0	48.1	48.0	48.6	48.6	48.6	47.6	47.6	47.6	47.6
C-10	38.1	38.1	38.2	38.1	38.1	38.2	38.6	38.5	38.6	38.6	38.9	38.8	38.1	38.2	38.1	38.1
C-12	122.8	125.7	122.9	125.6	123.1	125.6	122.8	125.3	123.1	126.1	123.0	125.6	123.1	125.6	123.0	125.7
C-13	144.1	138.5	144.3	138.7	144.1	139.0	144.9	139.3	144.1	138.4	144.2	138.5	144.5	140.5	144.0	140.0
C-23	71.2	71.3	69.9	69.8	67.1	67.1	71.6	71.6	64.5	64.5	69.6	69.8	71.5	71.5	71.1	71.1
C-24	62.2	62.2	61.8	61.8	61.1	61.1	63.6	63.6	65.0	65.0	63.0	63.1	61.8	61.8	61.7	61.7
C-28	176.4	176.2	176.6	176.3	176.6	176.5	176.4	176.1	176.3	176.1	176.6	176.4	176.5	176.4	176.3	176.0
Glucose																
C-1	95.7	95.7	95.9	95.9	95.7	95.8	95.7	95.7	95.6	95.6	95.8	95.8	95.4	95.4	95.4	95.4
C-2	74.1	74.1	74.1	74.1	74.3	74.0	74.2	74.2	74.1	74.1	74.1	74.0	72.3	72.3	72.2	72.2
C-3	78.8[b)]	78.8[b)]	79.3[b)]	79.3[b)]	79.3[b)]	79.3[b)]	78.9[b)]	78.9[b)]	78.9[b)]	78.9[b)]	79.3[b)]	79.2[b)]	80.0	80.0	80.1	80.1
C-4	71.2	71.2	71.0	71.0	71.1	71.4	71.1	71.1	71.2	71.1	71.1	71.3	69.0	69.0	68.9	68.9
C-5	79.1[b)]	79.1[b)]	78.8[b)]	78.8[b)]	78.9[b)]	78.9[b)]	79.1[b)]	79.1[b)]	78.9[b)]	78.9[b)]	78.9[b)]	78.8[b)]	78.9	78.9	79.0	79.0
C-6	62.2	62.2	62.1	62.1	62.4	62.4	62.3	62.3	62.3	62.4	62.3	62.4	62.6	62.6	62.5	62.5

HHDP																
C-1	116.4 (2C)	116.3 (2C)	116.7 (2C)	116.7 (2C)	118.2	118.1	116.8 (2C)	116.5 (2C)	115.2	115.4	116.2	116.4	116.5 (2C)	116.5 (2C)	116.7 (2C)	116.8 (2C)
					118.4	118.6			116.5	116.4	116.7	116.8				
C-2	127.4	127.5	126.8	126.9	126.7	127.1	127.5 (2C)	127.1 (2C)	126.8	126.5	126.7	126.8	127.5	127.5	126.7	126.7
	127.6	127.6	127.4	127.4	127.1	127.3			128.2	128.3	127.1	127.1	127.6	127.6	127.4	127.4
C-3	107.3	107.5	107.5	107.5	106.6	106.6	107.5	107.5	108.1 (2C)	107.9 (2C)	106.9	106.9	107.3	107.3	107.6	107.7
	108.3	108.4	108.6	108.6	108.0	108.0	108.2	108.2			108.1	108.2	108.3	108.3	108.6	108.6
C-4,6	146.0 (2C)	146.0 (2C)	145.9[c] (2C)	145.9[c] (2C)	146.0 (2C)	145.9 (2C)	146.4 (2C)	146.4 146.7	146.3 (2C)	146.2 (2C)	145.9[c] (2C)	146.0[c] (2C)	146.0[c] (2C)	146.0[c] (2C)	145.9[c] (2C)	146.0[c] (2C)
	146.4	146.4	146.5[c]	146.4[c]	146.5	146.4	146.5	146.5	146.5	146.5	146.5[c]	146.5[c]	146.5[c]	146.5[c]	146.5[c]	146.4[c]
	146.6	146.6	146.7[c]	146.8[c]	146.7	146.7	146.7	146.8	147.0	147.1	146.7[c]	146.7[c]	146.8[c]	146.7[c]	146.8[c]	146.8[c]
C-5	137.6 (2C)	137.7 (2C)	137.8 (2C)	137.8 (2C)	137.8 (2C)	137.8 (2C)	137.7 (2C)	137.5 (2C)	137.2	137.2	137.0	137.0	137.8	137.7	137.7	137.8
									137.7	137.7	137.8	137.8	138.3	138.3	137.9	137.9
Galloyl																
C-1			121.3	121.3							121.4	121.4	121.7	121.7	121.3 121.6	
C-2,6			111.9	111.9							110.5	110.5	110.5	110.5	110.5 111.9	
C-3,5			146.7[c]	146.7[c]							147.4[c]	147.4[c]	147.4[c]	147.4[c]	147.1[c] 147.4[c]	
C-4			141.6	141.6							140.7	140.7	140.7	140.7	140.7 141.5	
–COO–																
	169.4	169.4	167.4	167.5	168.8	168.8	169.4	169.3	169.3 (2C)	169.3 (2C)	168.0	168.0	167.3	167.5	167.2	167.3
	169.6	169.0	169.0	169.4	170.7	168.8	169.6	169.6			169.9 (2C)	169.7	169.7	169.8	169.0	169.5
			169.7	169.7												

a) Spectra were measured in pyridine-d_5 at 25.05 MHz. *b, c*) Assignments may be interchanged in each column.

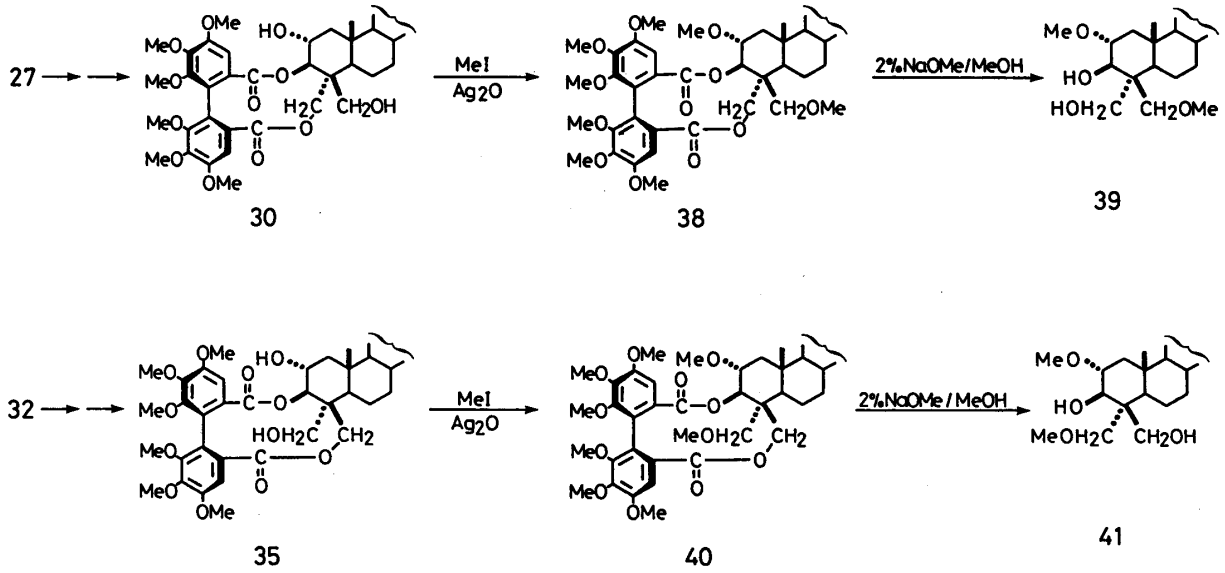
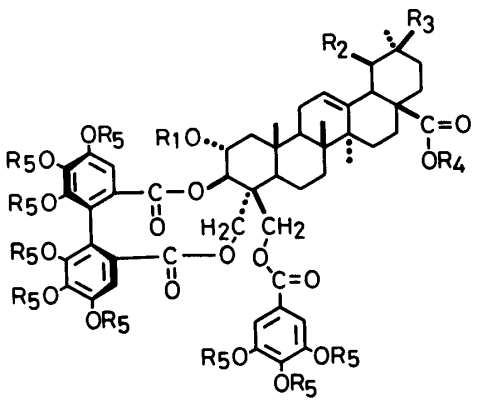


Chart 10



	R_1	R_2	R_3	R_4	R_5
42	H	H	Me	Glc	H
	H	Me	H	Glc	H
43	H	H	Me	Glc	Me
	H	Me	H	Glc	Me
44	H	H	Me	H	H
	H	Me	H	H	H
45	H	H	Me	Me	Me
	H	Me	H	Me	Me
46	Ac	H	Me	Me	Me
	Ac	Me	H	Me	Me

Chart 11

dimethyl sulfate and potassium carbonate in dry acetone yielded the nonamethyl ether (**43**), and alkaline methanolysis of **42** with 2% sodium methoxide in methanol liberated methyl trimethoxybenzoate (**15**), dimethyl (*S*)-hexamethoxydiphenoate (**37**) and the triterpenoid (**11a** plus **11b**). However, when methanolyzed in a weakly alkaline medium (0.05% methanolic sodium bicarbonate), **43** gave **15** and a hydrolysate, which was found to be identical with **28** by comparison of the ^{1}H-NMR data. These findings indicated that **42** contains one galloyl group attached to **28**. The ^{1}H-NMR spectrum of **43** was closely related to that of **2**, showing similar lowfield shifts of a doublet [δ 5.16 (J = 10.7 Hz)] and two pairs of geminally coupled methylene signals [δ 4.19 and 5.60 (each 1H, d, J = 11.7 Hz), δ 3.78 and 4.99 (each 1H, d, J = 11.2 Hz)], assignable to the C(3)-, C(23)- and C(24)-protons. Thus, the location of the galloyl group was concluded to be at the C(24)-position, and the structure of castanopsinin F is represented by formula **42**.

Castanopsinin G (**47**) afforded, on methylation and subsequent alkaline methanolysis, methyl trimethoxybenzoate (**15**), D-glucose, (*R*)-dimethyl hexamethoxydiphenoate (**14**) and a triterpenoid (**11**), while acid hydrolysis of **47** with 1 N methanolic sulfuric acid gave two hydrolysates (**49** and **50**). The ^{1}H-NMR spectrum of **49** showed, together with HHDP signals [δ 7.23 and 7.26 (each 1H, s)], the lowfield shifts of two pairs of doublets [δ 3.74 and 6.05 (each 1H, J = 11 Hz), δ 4.39 and 5.24 (each 1H, J = 11 Hz)], which were attributable to the

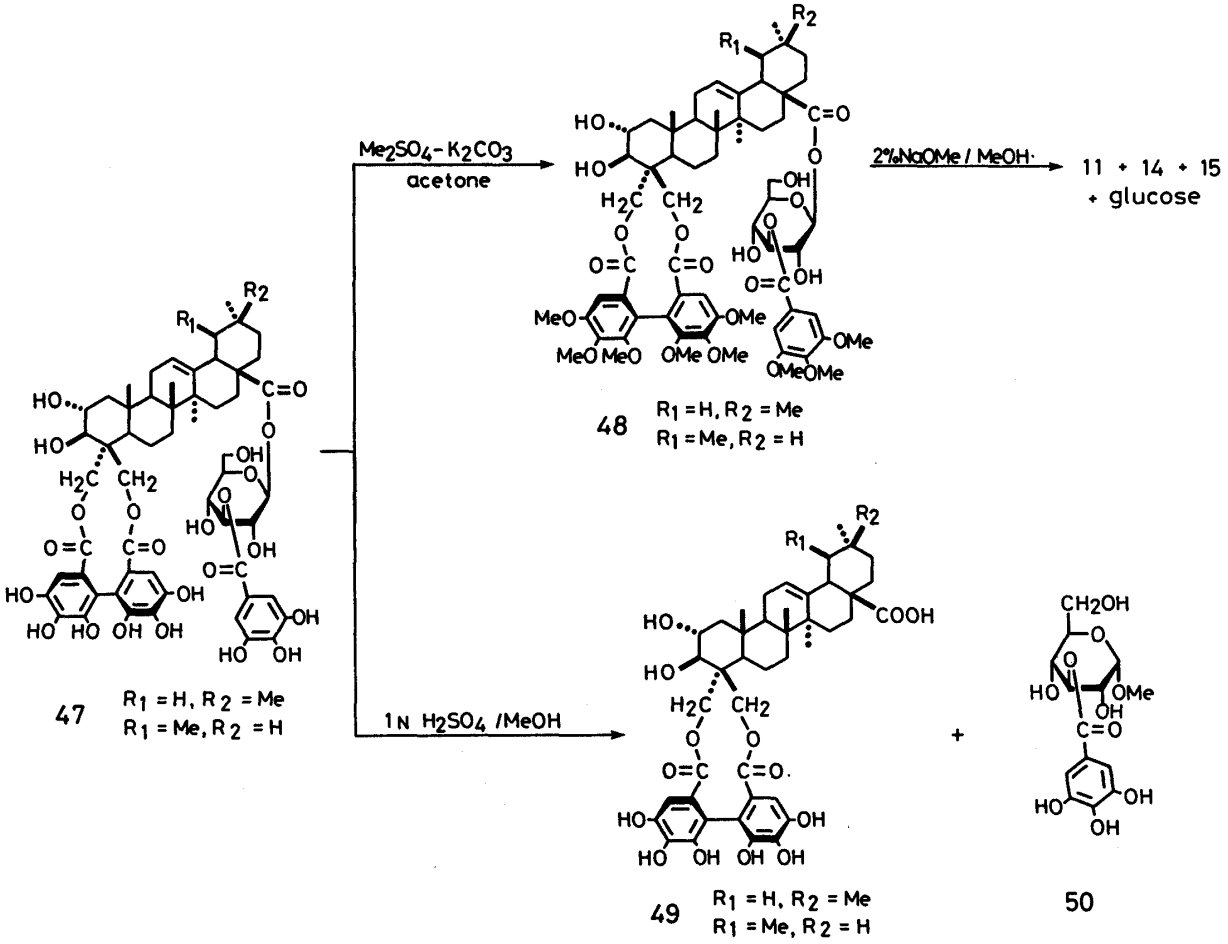


Chart 12

triterpenoid C(23)- and C(24)-methylene protons, indicating that the HHDP group is located at these positions. On the other hand, the ^{13}C-NMR spectrum of **50** exhibited, together with galloyl and methoxyl signals, six signals (δ 62.6, 69.0, 72.4, 78.8, 80.0 and 101.4) suggestive of the presence of a glucose moiety. Furthermore, since in the ^{1}H-NMR spectrum of **50** the anomeric proton signal appeared as a doublet with a small coupling constant at δ 4.78 (J= 4 Hz), **50** was considered to contain a methyl α-D-glucopyranoside moiety. The location of the galloyl group in **50** was determined to be at the C(3)-position by ^{13}C-NMR analysis, which showed the lowfield shift of the C(3)-signal by +1.1 ppm as compared with that of methyl α-D-glucopyranoside, and upfield shifts (−1.9 and −2.2 ppm, respectively) of the neighboring C(2)- and C(4)-carbons.

The position of the glucose moiety was determined to be at the C(28)-carboxyl group on the basis of the chemical shift (δ 95.4) of the anomeric carbon signal in **47**. From these chemical and spectroscopic data, castanopsinin G was characterized as **47**.

Castanopsinin H (**51**) contained one additional galloyl group as revealed by the negative FAB-MS [m/z: 1271 $[M-H]^-$] and ^{1}H-NMR examination [δ 7.86 and 8.02 (each 2H, s, 2 × galloyl-H); δ 7.08 and 7.53 (each 1H, s, HHDP)]. On acid hydrolysis with 2 N methanolic sulfuric acid, **51** furnished two hydrolysates, which were found to be identical with **8** and **50** by comparisons of the ^{1}H-NMR data, thus confirming the structure of castanopsinin H to be represented by the formula **51**.

Castanopsinins A—H (**1**, **6**, **25**, **27**, **32**, **42**, **47** and **51**) represent the first examples of ellagitannins based on a triterpenoid glucoside core, and this is also the first report of the isolation of ellagitannins (such as **1**, **27**, **6** and **42**) possessing both (*R*)- and (*S*)-HHDP groups

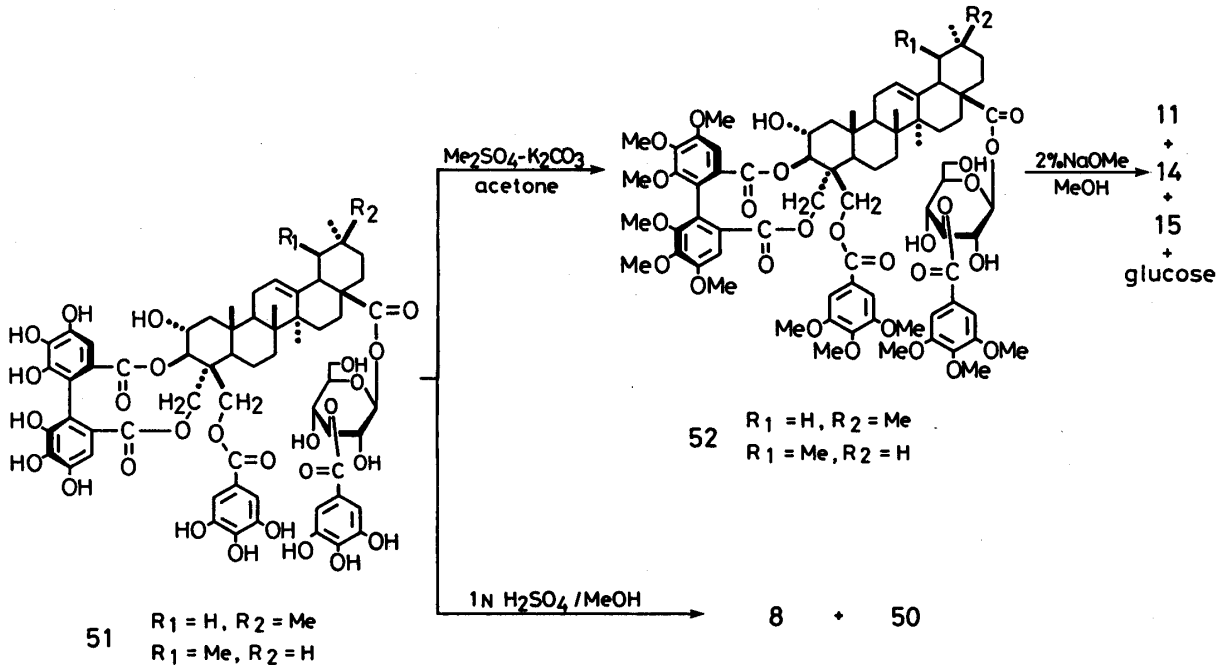


Chart 13

in the same positions of the polyalcohol moieties. Taking the specificity of the enzyme activity into account, it is rather unusual that compounds having *R*- and *S*-chiralities co-exist in one plant species.

Experimental

Optical rotations were measured with a JASCO DIP-4 digital polarimeter. ^{1}H (100 MHz)-, ^{13}C (25.05 MHz)- and ^{1}H(400 MHz)-NMR spectra were taken with JEOL PS-100, JEOL FX-100 and JEOL FX-400 spectrometers, respectively, with tetramethylsilane as an internal standard; chemical shifts are given on a δ (ppm) scale. FAB-, FD- and EI-MS were recorded on JEOL JMS DX-300 and D-300 spectrometers. Column chromatography was carried out with Sephadex LH-20 (25—100 μ, Pharmacia Fine Chemical Co., Ltd.), MCI-gel CHP 20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.), Fuji-gel ODS-G3 (43—65 μ, Fuji Gel Hanbai Co., Ltd.), Bondapak C_{18}/Porasil B (37—75 μ, Waters Associates, Inc.) and Kieselgel 60 (70—230 mesh, Merck). TLC was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm thick, Merck) with benzene–ethyl formate–formic acid (1 : 7 : 1 or 1 : 5 : 1.5) and precoated Cellulose F_{254} plates (0.1 mm, Merck) with 2% acetic acid, and the spots were detected by the use of ferric chloride, 10% sulfuric acid and aniline–hydrogen phthalate reagents. For preparative-scale HPLC, a Toyo Soda apparatus equipped with a CCPM solvent delivery system, a UV-8000 spectrometer, and an ODS-80T (4 mm i.d. × 300 mm) column was used [mobile phase : CH_3CN–50 mM aqueous NaH_2PO_4 (17 : 33, 9 : 16 or 23 : 27)].

Isolation——The fresh leaves (15 kg) of *Castanopsis cuspidata* var. *sieboldii* were extracted with 80% aqueous acetone at room temperature. The extract was concentrated under reduced pressure, and the resulting precipitates, consisting mainly of chlorophylls and waxes, were removed by filtration. The filtrate was applied to a column of Sephadex LH-20. Elution with H_2O containing increasing amounts of MeOH afforded seven fractions, I (500 g), II (150 g), III (150 g), IV (65 g), V (140 g), VI (21 g) and VII (24 g). Among these fractions, fractions IV and V were separately subjected to chromatography over MCI-gel CHP 20P with H_2O–MeOH (2 : 3) to give four fractions in each case. Fraction IV-3 was chromatographed over Sephadex LH-20 and Fuji-gel ODS-G3 to give castanopsinins A (**1**) (*ca.* 8 g), C (**25**) (272 mg), D (**27**) (*ca.* 7 g) and E (**32**) (*ca.* 2 g). Repeated chromatography of fraction V-3 over Sephadex LH-20, Fuji-gel ODS-G3 and Bondapak C_{18}/Porasil B with various solvent systems afforded castanopsinins B (**6**) (*ca.* 2 g), F (**42**) (553 mg), G (**47**) (300 mg) and H (**51**) (73 mg). Subsequent purification of a part of each castanopsinin (except for castanopsinin H) by preparative-scale HPLC yielded pure compounds (**1a, b, 6a, b, 25a, b, 27a, b, 32a, b, 42a, b** and **47a, b**).

General Procedure for Methylation——A mixture of the sample (50—450 mg), dimethyl sulfate (0.2—2 ml) and anhydrous potassium carbonate (0.3—3 g) in dry acetone (4—20 ml) was refluxed for 2—4 h with stirring. After removal of inorganic salts by filtration, the filtrate was concentrated under reduced pressure to give an oily residue, which was chromatographed over silica gel using $CHCl_3$–MeOH–H_2O (9 : 1 : 0.1) or benzene–acetone (8 : 1) to give

the methyl derivative.

General Procedure for Acid Hydrolysis——The sample (50—200 mg) in MeOH (2—5 ml) was hydrolyzed with 2 N aqueous sulfuric acid (2—5 ml) at 80 °C for 2—3 h. After concentration of the reaction mixture under reduced pressure, the aqueous solution furnished a white precipitate, which was collected by filtration. The precipitate was subjected to chromatography over MCI-gel CHP 20P [H_2O–MeOH (1 : 0—2 : 3)] to yield a hydrolysate. The aqueous layer was neutralized with barium carbonate, and the resulting inorganic salts were filtered off. The filtrate was chromatographed over Sephadex LH-20. Elution with H_2O afforded D-glucose [$[\alpha]_D^{20}$ +48.2° (H_2O)].

General Procedure for Acetylation——The sample (12—40 mg) was acetylated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) overnight at room temperature. The reaction mixture was poured into ice-water, and the resulting white precipitate was collected by filtration. The precipitate was purified by chromatography over silica gel with benzene–acetone (6 : 1) to give the acetate.

Castanopsinin A (1a)——An off-white amorphous powder, $[\alpha]_D^{20}$ +70.8° (c=0.40, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 2H_2O$: C, 59.75; H, 6.82. Found: C, 59.67; H, 6.78. ^{1}H-NMR (pyridine-d_5) δ: 7.18, 7.28 (each 1H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

Castanopsinin A (1b)——An off-white amorphous powder, $[\alpha]_D^{20}$ +75.9° (c=0.45, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 2H_2O$: C, 59.75; H, 6.82. Found: C, 59.55; H, 6.97. ^{1}H-NMR (pyridine-d_5) δ: 7.18, 7.28 (each 1H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

The Hexamethyl Ether of 1 (2a)——A white amorphous powder, $[\alpha]_D^{18}$ +54.6° (c=1.01, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{76}O_{19}\cdot 2H_2O$; C, 61.75; H, 7.40. Found: C, 61.70; H, 7.26. ^{1}H-NMR ($CDCl_3$) δ: 4.02, 5.10 (each 1H, d, J= 11.7 Hz, 23-H), 5.10 (1H, d, J=10 Hz, 3-H), 5.31 (1H, br s, 12-H), 5.50 (1H, d, J=8 Hz, anomeric-H), 6.73, 6.79 (each 1H, s, HMDP-H). FD-MS m/z: 1052 $(M)^+$.

The Hexamethyl Ether of 1 (2b)——A white amorphous powder, $[\alpha]_D^{18}$ +50.1° (c=0.76, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{76}O_{19}\cdot 2H_2O$: C, 61.75; H, 7.40. Found: C, 61.35; H, 7.53. ^{1}H-NMR ($CDCl_3$) δ: 4.04, 5.13 (each 1H, d, J= 11.7 Hz, 23-H), 5.10 (1H, d, J=10 Hz, 3-H), 5.27 (1H, br s, 12-H), 5.47 (1H, d, J=8 Hz, anomeric-H), 6.73, 6.79 (each 1H, s, HMDP-H). FD-MS m/z: 1052 $(M)^+$.

Alkaline Methanolysis of 2a——**2a** (90 mg) was treated with 2% methanolic sodium methoxide (8 ml) at 70 °C for 4.5 h. The reaction mixture was neutralized with Amberlite IR-120B (H^+ form) resins, and the solvent was evaporated off under reduced pressure. The residue was chromatographed over silica gel using $CHCl_3$–MeOH–H_2O (19 : 1 : 0—9 : 1 : 0.1) to give dimethyl (*R*)-hexamethoxydiphenoate (**14**) as a syrup, $[\alpha]_D^{20}$ +26.4° (c=0.70, $CHCl_3$) and a hydrolysate (**11a**) (28 mg) as a white amorphous powder, $[\alpha]_D^{18}$ +47.4° (c=0.84, MeOH). ^{1}H-NMR (CD_3OD) δ: 3.46 (1H, d, J=10 Hz, 3-H), 3.51, 4.06 (each 1H, d, J=12 Hz, 23- or 24-H), 3.64, 4.06 (each 1H, d, J=12 Hz, 23- or 24-H), 3.70 (1H, m, 2-H), 5.26 (1H, br s, 12-H). Further elution with $CHCl_3$–MeOH–H_2O (7 : 3 : 0.3) gave a syrup [$[\alpha]_D^{20}$ +47.4° (c=0.35, H_2O)], which was shown to be identical with D-glucose by TLC examination [solvent : *n*-BuOH–pyridine–H_2O (6 : 4 : 3), Rf: 0.32].

Alkaline Methanolysis of 2b——**2b** (90 mg) was treated with 2% methanolic sodium methoxide (8 ml) at 70 °C for 4 h. The reaction mixture was worked up as described above to afford **14** [$[\alpha]_D^{18}$ +26.4° (c=0.87, $CHCl_3$)], glucose and a hydrolysate (**11b**) (30 mg) as a white amorphous powder, $[\alpha]_D^{20}$ +45.9° (c=0.44, MeOH). ^{1}H-NMR (CD_3OD) δ: 3.46 (1H, d, J=10 Hz, 3-H), 3.51, 4.06 (each 1H, d, J=12 Hz, 23- or 24-H), 3.64, 4.06 (each 1H, d, J=12 Hz, 23- or 24-H), 3.70 (1H, m, 2-H), 5.23 (1H, br s, 12-H).

Methylation of 11a with Diazomethane——A solution of **11a** (25 mg) in MeOH (2 ml) was treated with an ethereal solution of diazomethane under ice-cooling for 10 min. The solvent was evaporated off and the residue was chromatographed over silica gel using $CHCl_3$–MeOH–H_2O (10 : 1 : 0.1) to yield the methyl ester (**12a**) (22 mg) as a white amorphous powder, $[\alpha]_D^{19}$ +45.4° (c=0.61, $CHCl_3$). *Anal.* Calcd for $C_{31}H_{50}O_6\cdot 3/2H_2O$: C, 68.22; H, 9.79. Found: C, 68.54; H, 9.36. EI-MS m/z: 518 $(M)^+$, 262, 256, 203.

Methylation of 11b with Diazomethane——A solution of **11b** (23 mg) in MeOH (2 ml) was treated with an ethereal solution of diazomethane under ice-cooling for 10 min. Work-up as described for **11a** gave the methyl ester (**12a**) (20 mg) as a white amorphous powder, $[\alpha]_D^{19}$ +42.0° (c=0.45, $CHCl_3$). *Anal.* Calcd for $C_{31}H_{50}O_6\cdot 3/2H_2O$: C, 68.22; H, 9.79. Found: C, 68.01; H, 9.66. EI-MS m/z: 518 $(M)^+$, 262, 256, 203.

The Methyl Ester Tetraacetate of 12a (13a)——A white amorphous powder, $[\alpha]_D^{20}$ +68.5° (c=0.45, $CHCl_3$). *Anal.* Calcd for $C_{39}H_{58}O_{10}$: C, 68.19; H, 8.51. Found: C, 68.36; H, 8.76. ^{1}H-NMR ($CDCl_3$) δ: 1.98, 2.01, 2.05, 2.10 (each 3H, s, 4 × OCOMe), 3.60 (3H, s, COOMe), 3.87, 4.15 (each 1H, d, J=12 Hz, 23-H), 4.29 (2H, s, 24-H), 5.18 (1H, d, J=10 Hz, 3-H), 5.20 (1H, m, 2-H). EI-MS m/z: 686 $(M)^+$.

The Methyl Ester Tetraacetate of 12b (13b)——A white amorphous powder, $[\alpha]_D^{20}$ +54.6° (c=0.35, $CHCl_3$). *Anal.* Calcd for $C_{39}H_{58}O_{10}$: C, 68.19; H, 8.51. Found: C, 68.43; H, 8.44. ^{1}H-NMR ($CDCl_3$) δ: 1.98, 2.01, 2.05, 2.10 (each 3H, s, 4 × OCOMe), 3.62 (3H, s, COOMe), 3.87, 4.15 (each 1H, d, J=12 Hz, 23-H), 4.29 (2H, s, 24-H), 5.18 (1H, d, J=10 Hz, 3-H), 5.20 (1H, m, 2-H). EI-MS m/z: 686 $(M)^+$.

The Hydrolysate of 1 (3)——An off-white amorphous powder, $[\alpha]_D^{21}$ +58.3° (c=0.76, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 7.18, 7.25 (each 1H, s, HHDP-H). FAB-MS m/z: 807 $[M+H]^+$.

The Heptamethyl Derivative of 3 (4)——A white amorphous powder, $[\alpha]_D^{22}$ +101.4° (c=0.70, $CHCl_3$). *Anal.* Calcd for $C_{51}H_{68}O_{14}\cdot H_2O$: C, 66.36; H, 7.64. Found: C, 66.83; H, 7.50. ^{1}H-NMR ($CDCl_3$) δ: 4.03, 5.12 (each 1H, d,

$J=12$ Hz, 23-H), 5.10 (1H, d, $J=10.7$ Hz, 3-H), 5.26 (1H, br s, 12-H), 6.70, 6.76 (each 1H, s, HMDP-H). FD-MS *m/z*: 904 $(M)^+$.

The Heptamethyl Diacetate of 4 (5)——A white amorphous powder, $[\alpha]_D^{22}$ +95.5° ($c=0.65$, $CHCl_3$). *Anal.* Calcd for $C_{55}H_{76}O_{16}$: C, 66.78; H, 7.34. Found: C, 67.01; H, 7.44. ^{1}H-NMR ($CDCl_3$) δ: 1.99, 2.01 (each 3H, s, OCOMe), 3.98, 4.75 (each 1H, d, $J=12$ Hz, 23- or 24-H), 4.14, 4.75 (each 1H, d, $J=12$ Hz, 23- or 24-H), 4.76 (1H, d, $J=10$ Hz, 3-H), 5.20 (1H, m, 2-H), 6.72, 6.73 (each 1H, s, HMDP-H). FD-MS *m/z*: 988 $(M)^+$.

Permethylation of 4——**4** (100 mg) was methylated with silver oxide (0.4 g) and methyl iodide (0.7 ml) in dimethylformamide (DMF) (2 ml) at room temperature for 3 h. After removal of inorganic salts by filtration, the solvent was evaporated *in vacuo* to give an oily residue, which was passed through a silica gel column with benzene–acetone (8 : 1) to give the nonamethyl derivative (**22**) (70 mg) as a white amorphous powder, $[\alpha]_D^{19}$ +47.6° ($c=0.55$, $CHCl_3$). EI-MS *m/z*: 932 $(M)^+$.

Alkaline Hydrolysis of 22——**22** (60 mg) was treated with 2% methanolic sodium methoxide (3 ml) at 70 °C for 4 h. The reaction mixture was worked up in the same way as for **1** to yield **14** and the methanolysate (**23**) (25 mg) as a white amorphous powder, $[\alpha]_D^{19}$ +54.1° ($c=0.35$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 3.01 (1H, d, $J=9$ Hz, 3-H), 3.42, 3.60 (12H, s, 2 × OMe, COOMe), 4.00 (1H, m, 2-H), 5.22 (1H, br s, 12-H). EI-MS *m/z*: 546 $(M)^+$.

Acetonidation of 23——A solution of **23** (20 mg) in benzene (2 ml) was treated with 2,2-dimethoxypropane (0.1 ml) and *p*-toluenesulfonic acid (0.2 mg) at room temperature for 10 min. The solvent was evaporated off under reduced pressure, and the residue was chromatographed over silica gel with benzene–acetone (19 : 1) to give the 3,23-monoacetonide (**24**) (17 mg) as a white amorphous powder, $[\alpha]_D^{19}$ +42.1° ($c=0.50$, $CHCl_3$). *Anal.* Calcd for $C_{36}H_{58}O_6$: C, 73.68; H, 9.96. Found: C, 73.36; H, 9.82. ^{1}H-NMR ($CDCl_3$) δ: 1.40, 1.43 (each 3H, s, $C(Me)_2$), 3.79 (2H, s, 23-H). EI-MS *m/z*: 586 $(M)^+$.

Castanopsinin B (6a)——An off-white amorphous powder, $[\alpha]_D^{18}$ +35.1° ($c=0.49$, MeOH). *Anal.* Calcd for $C_{57}H_{68}O_{23}\cdot 5H_2O$: C, 56.52; H, 6.49. Found: C, 56.63; H, 6.17. ^{1}H-NMR (pyridine-d_5) δ: 7.08, 7.54 (each 1H, s, HHDP-H), 8.01 (2H, s, galloyl-H). Negative FAB-MS *m/z*: 1119 $[M-H]^-$.

Castanopsinin B (6b)——An off-white amorphous powder, $[\alpha]_D^{18}$ +99.0° ($c=0.60$, MeOH). *Anal.* Calcd for $C_{57}H_{68}O_{23}\cdot 6H_2O$: C, 55.69; H, 6.56. Found: C, 55.83; H, 6.33. ^{1}H-NMR (pyridine-d_5) δ: 7.08, 7.54 (each 1H, s, HHDP-H), 8.01 (2H, s, galloyl-H). Negative FAB-MS *m/z*: 1119 $[M-H]^-$.

The Nonamethyl Ether of 6 (7)——A white amorphous powder, $[\alpha]_D^{18}$ +104.3° ($c=0.42$, $CHCl_3$). *Anal.* Calcd for $C_{66}H_{86}O_{23}$: C, 63.55; H, 6.95. Found: C, 63.13; H, 7.11. ^{1}H-NMR ($CDCl_3$) δ: 4.13 (1H, m, 2-H), 3.78, 4.75 (each 1H, d, $J=11.7$ Hz, 24-H), 4.28, 4.89 (each 1H, d, $J=12$ Hz, 23-H), 4.75 (1H, d, $J=9$ Hz, 3-H), 5.28 (1H, br s, 12-H), 5.51 (1H, d, $J=8$ Hz, anomeric-H), 6.44, 6.69 (each 1H, s, HMDP-H), 7.37 (2H, s, trimethoxybenzoyl-H). FD-MS *m/z*: 1246 $(M)^+$.

Alkaline Methanolysis of 7——**7** (50 mg) was treated with 2% methanolic sodium methoxide (3 ml) at 70 °C for 4 h. Work-up in the same way as for **2a** gave **14**, $[\alpha]_D^{20}$ +27.4° ($c=1.30$, $CHCl_3$), methyl trimethoxybenzoate (**15**) and **11** (20 mg).

Partial Alkaline Methanolysis of 7——A solution of **7** (40 mg) in 0.05% sodium methoxide in dry methanol (2 ml) was left standing at room temperature for 70 h. After neutralization with Amberlite IR-120B (H^+ form) resin, the solution was concentrated to a syrup, which was chromatographed over silica gel with $CHCl_3$–MeOH–H_2O (10 : 1 : 0.1) to give **15** and **2** (10 mg).

The Hydrolysate of 6 (8)——An off-white amorphous powder, $[\alpha]_D^{17}$ +99.8° ($c=0.66$, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 7.17, 7.54 (each 1H, s, HHDP-H), 8.01 (2H, s, galloyl-H).

The Decamethyl Derivative of 8 (9)——A white amorphous powder, $[\alpha]_D^{19}$ +128.8° ($c=0.40$, $CHCl_3$). *Anal.* Calcd for $C_{61}H_{78}O_{18}$: C, 66.65; H, 7.15. Found: C, 66.58; H, 7.24. ^{1}H-NMR ($CDCl_3$) δ: 3.78, 4.76 (each 1H, d, $J=11.4$ Hz, 24-H), 4.10 (1H, m, 2-H), 4.50, 4.89 (each 1H, d, $J=11.7$ Hz, 23-H), 4.76 (1H, d, $J=9.8$ Hz, 3-H), 5.24 (1H, br s, 12-H), 6.44, 6.70 (each 1H, s, HMDP-H), 7.40 (2H, s, trimethoxybenzoyl-H). FD-MS *m/z*: 1098 $(M)^+$.

The Decamethyl Monoacetate of 9 (10)——A white amorphous powder, $[\alpha]_D^{19}$ +89.9° ($c=0.44$, $CHCl_3$). *Anal.* Calcd for $C_{63}H_{80}O_{19}$: C, 66.30; H, 7.07. Found: C, 66.63; H, 7.08. ^{1}H-NMR ($CDCl_3$) δ: 1.73 (3H, s, OCOMe), 3.78, 4.87 (each 1H, d, $J=11.4$ Hz, 24-H), 4.39, 4.76 (each 1H, d, $J=11.7$ Hz, 23-H), 4.92 (1H, d, $J=10.3$ Hz, 3-H), 5.26 (1H, br s, 12-H), 5.57 (1H, dt, $J=4.4$, 10.3 Hz, 2-H), 6.35, 6.69 (each 1H, s, HMDP-H), 7.32 (2H, s, trimethoxybenzoyl-H). FD-MS *m/z*: 1140 $(M)^+$.

Oxidation of 9——A solution of **9** (550 mg) in DMF (6 ml) was oxidized with chromium trioxide (240 mg) and concentrated sulfuric acid (0.1 ml) for 2 h with stirring and ice-cooling. The reaction mixture was poured into ice-water. The precipitate was collected and passed through a silica gel column with benzene–acetone (19 : 1—4 : 1) to yield the ketone (**16**) (472 mg) as a white amorphous powder, $[\alpha]_D^{20}$ +80.0° ($c=0.67$, $CHCl_3$). ^{13}C-NMR ($CDCl_3$) δ: 217.7 (C=O). FD-MS *m/z*: 1096 $(M)^+$.

Reduction of 16——**16** (300 mg) was reduced with sodium borohydride (30 mg) in tetrahydrofuran (6 ml) for 2 h under ice-cooling. The reaction mixture was diluted with water, acidified with acetic acid under ice-cooling, and concentrated to dryness under reduced pressure. The residue was chromatographed over silica gel with benzene–acetone (5 : 1) to give the alcohol (**17**) (260 mg) as a white amorphous powder, $[\alpha]_D^{25}$ +60.5° ($c=0.75$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 5.03 (1H, d, $J=4$ Hz, 3-H). FD-MS *m/z*: 1098 $(M)^+$.

Alkaline Methanolysis of 17——**17** (240 mg) was treated with 2% methanolic sodium methoxide (8 ml) at 70 °C for 4 h. The reaction mixture was worked up in the same way as described before to yield **14**, **15** and a hydrolysate (**18**) (70 mg) as a white amorphous powder, $[\alpha]_D^{25}$ +46.5° (c=0.56, $CHCl_3$). *Anal.* Calcd for $C_{31}H_{50}O_6$: C, 71.78; H, 9.72. Found: C, 71.66; H, 9.59. EI-MS m/z: 518 $(M)^+$.

The Methyl Ester Tetraacetate of 18 (19)——A white amorphous powder, $[\alpha]_D^{25}$ +78.5° (c=0.61, $CHCl_3$). *Anal.* Calcd for $C_{39}H_{58}O_{10}$: C, 68.36; H, 8.76. Found: C, 68.25; H, 8.47. ^{1}H-NMR ($CDCl_3$) δ: 2.00, 2.04, 2.09 (12H, s, 4 × OCOMe), 3.61 (3H, s, COOMe), 4.01, 4.26 (each 1H, d, J=12 Hz, 23-H), 4.56 (2H, s, 24-H), 5.04 (1H, d, J=4 Hz, 3-H), 5.10 (1H, m, 2-H), 5.20 (1H, br s, 12-H). EI-MS m/z: 686 $(M)^+$.

Castanopsinin C (25a)——An off-white amorphous powder, $[\alpha]_D^{18}$ +13.5° (c=0.85, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 2H_2O$: C, 59.75; H, 6.82. Found: C, 59.82; H, 7.01. ^{1}H-NMR (pyridine-d_5) δ: 7.12, 7.78 (each 1H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

Castanopsinin C (25b)——An off-white amorphous powder, $[\alpha]_D^{18}$ +10.5° (c=0.99, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 2H_2O$: C, 59.75; H, 6.82. Found: C, 59.61; H, 6.75. ^{1}H-NMR (pyridine-d_5) δ: 7.12, 7.78 (each 1H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

The Hexamethyl Ether of 25 (26)——A white amorphous powder, $[\alpha]_D^{18}$ +21.5° (c=0.75, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{76}O_{19}\cdot 2H_2O$: C, 62.79; H, 7.34. Found: C, 62.95; H, 7.37. ^{1}H-NMR ($CDCl_3$) δ: 4.20 (1H, m, 2-H), 4.85 (1H, d, J=9.8 Hz, 3-H), 5.28 (1H, br s, 12-H), 6.88, 7.47 (each 1H, s, HMDP-H). FD-MS m/z: 1052 $(M)^+$.

Alkaline Methanolysis of 26——**26** (30 mg) was treated with 2% methanolic sodium methoxide (2 ml) at 70 °C for 3 h. Work-up as described before gave glucose, **14**, $[\alpha]_D^{20}$ +26.0° (c=0.56, $CHCl_3$) and **11** (15 mg).

Castanopsinin D (27a)——An off-white amorphous powder, $[\alpha]_D^{20}$ +52.8° (c=0.48, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 3/2H_2O$: C, 60.29; H, 6.78. Found: C, 60.10; H, 6.67. ^{1}H-NMR (pyridine-d_5) δ: 7.18, 7.28 (each 1H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

Castanopsinin D (27b)——An off-white amorphous powder, $[\alpha]_D^{20}$ +50.6° (c=0.50, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 3H_2O$: C, 58.70; H, 6.90. Found: C, 58.80; H, 7.01. ^{1}H-NMR (pyridine-d_5) δ: 7.18, 7.28 (each 1H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

The Hexamethyl Ether of 27 (28)——A white amorphous powder, $[\alpha]_D^{20}$ +48.5° (c=0.77, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{76}O_{19}\cdot 2H_2O$: C, 61.75; H, 7.40. Found: C, 61.44; H, 7.23. ^{1}H-NMR ($CDCl_3$) δ: 4.03, 5.12 (each 1H, d, J=11.7 Hz, 23-H), 5.12 (1H, d, J=10.7 Hz, 3-H), 5.28 (1H, br s, 12-H), 6.73, 6.79 (each 1H, s, HMDP-H). FD-MS m/z: 1052 $(M)^+$.

Alkaline Methanolysis of 28——**28** (150 mg) was treated with 2% methanolic sodium methoxide (8 ml) at 70 °C for 4.5 h. The reaction mixture was worked up as described above to afford dimethyl (*S*)-hexahydroxydiphenoate (**37**) as a syrup, $[\alpha]_D^{22}$ −25.3° (c=0.81, $CHCl_3$) and **11** (30 mg).

The Hydrolysate of 27 (29)——An off-white amorphous powder, $[\alpha]_D^{19}$ +49.0° (c=0.55, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 7.20, 7.25 (each 1H, s, HHDP-H).

The Heptamethyl Derivative of 29 (30)——A white amorphous powder, $[\alpha]_D^{22}$ −22.6° (c=0.80, $CHCl_3$). *Anal.* Calcd for $C_{51}H_{68}O_{14}$: C, 66.36; H, 7.64. Found: C, 66.01; H, 7.23. ^{1}H-NMR ($CDCl_3$) δ: 4.02, 5.10 (each 1H, d, J=12 Hz, 23-H), 5.10 (1H, d, J=10 Hz, 3-H), 5.24 (1H, br s, 12-H), 6.70, 6.76 (each 1H, s, HMDP-H). FD-MS m/z: 904 $(M)^+$.

The Heptamethyl Diacetate of 30 (31)——A white amorphous powder, $[\alpha]_D^{22}$ −20.5° (c=0.75, $CHCl_3$). *Anal.* Calcd for $C_{55}H_{72}O_{16}$: C, 66.78; H, 7.34. Found: C, 67.04; H, 7.44. ^{1}H-NMR ($CDCl_3$) δ: 1.96, 1.98 (each 3H, s, OCOMe), 4.10, 5.14 (each 1H, d, J=12 Hz, 23-H), 4.90 (1H, d, J=10 Hz, 3-H), 5.02 (2H, s, 24-H), 5.00 (1H, m, 2-H), 5.20 (1H, br s, 12-H), 6.58, 6.70 (each 1H, s, HMDP-H). EI-MS m/z: 988 $(M)^+$.

Permethylation of 30——**30** (100 mg) was methylated with silver oxide (0.4 g) and methyl iodide (0.6 ml) in DMF (2 ml) at room temperature for 2 h. The reaction mixture was worked up as described for **4** to yield the nonamethyl derivative (**38**) (62 mg) as a white amorphous powder, $[\alpha]_D^{18}$ +86.2° (c=0.78, $CHCl_3$). EI-MS m/z: 932 $(M)^+$.

Alkaline Methanolysis of 38——**38** (55 mg) was treated with 2% methanolic sodium methoxide (1.5 ml) at 70 °C for 3 h. Work-up as described before furnished **37** and a hydrolysate (**39**) (18 mg), which was identified as **22** by comparison of the physical and spectral data.

Castanopsinin E (32a)——An off-white amorphous powder, $[\alpha]_D^{20}$ +6.5° (c=0.88, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 3/2H_2O$: C, 60.29; H, 6.78. Found: C, 60.04; H, 6.93. ^{1}H-NMR (pyridine-d_5) δ: 7.22 (2H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

Castanopsinin E (32b)——An off-white amorphous powder, $[\alpha]_D^{20}$ +10.3° (c=0.76, MeOH). *Anal.* Calcd for $C_{50}H_{64}O_{19}\cdot 2H_2O$: C, 59.75; H, 6.82. Found: C, 59.65; H, 6.99. ^{1}H-NMR (pyridine-d_5) δ: 7.22 (2H, s, HHDP-H). Negative FAB-MS m/z: 967 $[M-H]^-$.

The Hexamethyl Ether of 32 (33)——A white amorphous powder, $[\alpha]_D^{20}$ +10.8° (c=0.97, $CHCl_3$). *Anal.* Calcd for $C_{56}H_{76}O_{19}\cdot 3/2H_2O$: C, 62.26; H, 7.37. Found: C, 62.35; H, 7.32. ^{1}H-NMR ($CDCl_3$) δ: 4.05 (1H, m, 2-H), 4.51 (1H, d, J=12 Hz, 24-H), 4.90 (1H, d, J=9 Hz, 3-H), 5.28 (1H, br s, 12-H), 6.68, 6.80 (each 1H, HMDP-H). FD-MS m/z: 1052 $(M)^+$.

Alkaline Methanolysis of 33——**33** (80 mg) was treated with 2% methanolic sodium methoxide (4 ml) at 70 °C for 3 h. The reaction mixture was worked up in the same way as described for **28** to give **37**, $[\alpha]_D^{19}$ −25.3° (c=0.85,

$CHCl_3$) and **11** (23 mg).

The Hydrolysate of 32 (34)——An off-white amorphous powder, $[\alpha]_D^{19}$ +60.2° (c=0.98, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 7.21, 7.24 (each 1H, s, HHDP-H).

The Heptamethyl Derivative of 34 (35)——A white amorphous powder, $[\alpha]_D^{19}$ +3.9° (c=0.58, $CHCl_3$). *Anal.* Calcd for $C_{51}H_{68}O_{14}\cdot 1/2H_2O$: C, 67.01; H, 7.61. Found: C, 67.20; H, 7.38. ^{1}H-NMR ($CDCl_3$) δ: 3.81, 5.01 (each 1H, d, J=11.7 Hz, 24-H), 4.06 (1H, m, 2-H), 4.93 (1H, d, J=9.3 Hz, 3-H), 5.27 (1H, br s, 12-H), 6.68, 6.80 (each 1H, s, HMDP-H). FD-MS m/z: 904 $(M)^+$.

The Heptamethyl Diacetate of 35 (36)——A white amorphous powder, $[\alpha]_D^{20}$ +4.8° (c=0.63, $CHCl_3$). *Anal.* Calcd for $C_{55}H_{72}O_{16}$: C, 66.78; H, 7.34. Found: C, 66.72; H, 7.31. ^{1}H-NMR ($CDCl_3$) δ: 2.06, 2.10 (each 3H, s, 2×OCOMe), 3.98, 4.95 (each 1H, d, J=11.2 Hz, 24-H), 3.99, 4.57 (each 1H, d, J=11.7 Hz, 23-H), 5.12 (1H, d, J=8 Hz, 3-H), 5.20 (1H, m, 2-H), 5.24 (1H, br s, 12-H), 6.51, 6.81 (each 1H, s, HMDP-H). EI-MS m/z: 988 $(M)^+$.

Permethylation of 35——**35** (60 mg) was methylated with silver oxide (0.3 g) and methyl iodide (0.5 ml) in DMF (1 ml) at room temperature for 2.5 h. Work-up in the same way as described before gave the nonamethyl derivative (**40**) (47 mg) as a white amorphous powder, $[\alpha]_D^{18}$ +67.1° (c=0.44, $CHCl_3$). EI-MS m/z: 932 $(M)^+$.

Alkaline Methanolysis of 40——**40** (43 mg) was methanolyzed with 2% sodium methoxide in methanol to afford **37** and a hydrolysate (**41**) (15 mg) as a white amorphous powder. EI-MS m/z: 546 $(M)^+$.

Castanopsinin F (42a)——An off-white amorphous powder, $[\alpha]_D^{22}$ +102.5° (c=0.33, MeOH). *Anal.* Calcd for $C_{57}H_{68}O_{23}\cdot 6H_2O$: C, 55.69; H, 6.56. Found: C, 55.72; H, 6.30. ^{1}H-NMR (pyridine-d_5) δ: 6.87, 7.14 (each 1H, s, HHDP-H), 7.92 (2H, s, galloyl-H). Negative FAB-MS m/z: 1119 $[M-H]^-$.

Castanopsinin F (42b)——An off-white amorphous powder, $[\alpha]_D^{22}$ +82.3° (c=0.44, MeOH). *Anal.* Calcd for $C_{57}H_{68}O_{23}\cdot 5H_2O$: C, 56.52; H, 6.49. Found: C, 56.54; H, 6.23. ^{1}H-NMR (pyridine-d_5) δ: 6.87, 7.14 (each 1H, s, HHDP-H), 7.92 (2H, s, galloyl-H). Negative FAB-MS m/z: 1119 $[M-H]^-$.

The Nonamethyl Ether of 42 (43)——A white amorphous powder, $[\alpha]_D^{18}$ +91.6° (c=0.71, $CHCl_3$). *Anal.* Calcd for $C_{66}H_{86}O_{23}\cdot 2H_2O$: C, 61.76; H, 7.07. Found: C, 61.53; H, 7.09. ^{1}H-NMR ($CDCl_3$) δ: 3.78, 4.99 (each 1H, d, J=11.2 Hz, 24-H), 4.19, 5.60 (each 1H, d, J=11.7 Hz, 23-H), 5.16 (1H, d, J=10.7 Hz, 3-H), 5.30 (1H, br s, 12-H), 5.95, 6.79 (each 1H, s, HMDP-H), 7.23 (2H, s, trimethoxybenzoyl-H). FD-MS m/z: 1246 $(M)^+$.

Alkaline Methanolysis of 43——A solution of **43** (30 mg) in methanolic sodium methoxide (2% solution) (2 ml) was heated at 70 °C for 3.5 h to yield **15**, **37** [$[\alpha]_D^{20}$ −25.6° (c=0.95, $CHCl_3$)] and **11** (10 mg).

Partial Alkaline Methanolysis of 43——A solution of **42** (30 mg) in 0.05% methanolic sodium bicarbonate (1 ml) was kept standing at room temperature for 68 h. The reaction mixture was worked up as described before to give **37** and **28** (8 mg).

The Hydrolysate of 42 (44)——An off-white amorphous powder, $[\alpha]_D^{19}$ +110.8° (c=0.85, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 6.89, 7.16 (each 1H, s, HHDP-H), 7.92 (2H, s, galloyl-H).

The Decamethyl Derivative of 44 (45)——A white amorphous powder, $[\alpha]_D^{22}$ +75.8° (c=0.54, $CHCl_3$). *Anal.* Calcd for $C_{61}H_{78}O_{18}\cdot 1/2H_2O$: C, 66.10; H, 7.18. Found: C, 65.92; H, 7.24. ^{1}H-NMR ($CDCl_3$) δ: 4.20 (1H, d, J=11.2 Hz, 24-H), 5.00, 5.60 (each 1H, d, J=11.7 Hz, 23-H), 5.20 (1H, d, J=10.7 Hz, 3-H), 5.23 (1H, br s, 12-H), 5.96, 6.79 (each 1H, s, HMDP-H), 7.24 (2H, s, trimethoxybenzoyl-H). FD-MS m/z: 1098 $(M)^+$.

The Decamethyl Monoacetate of 45 (46)——A white amorphous powder, $[\alpha]_D^{24}$ +110.4° (c=0.80, $CHCl_3$). *Anal.* Calcd for $C_{63}H_{80}O_{19}$: C, 66.30; H, 7.07. Found: C, 66.01; H, 7.16. ^{1}H-NMR ($CDCl_3$) δ: 1.88 (3H, s, OCOMe), 4.23, 5.52 (each 1H, d, J=12 Hz, 23-H), 4.98 (1H, d, J=12 Hz, 24-H), 5.32 (1H, d, J=10 Hz, 3-H), 5.10 (1H, m, 2-H), 5.96, 6.78 (each 1H, s, HMDP-H), 7.19 (2H, s, trimethoxybenzoyl-H). FD-MS m/z: 1140 $(M)^+$.

Castanopsinin G (47a)——An off-white amorphous powder, $[\alpha]_D^{20}$ +43.2° (c=0.56, MeOH). *Anal.* Calcd for $C_{57}H_{68}O_{23}\cdot 6H_2O$: C, 55.69; H, 6.57. Found: C, 55.90; H, 6.31. ^{1}H-NMR (pyridine-d_5) δ: 7.15, 7.27 (each 1H, s, HHDP-H), 7.85 (2H, s, galloyl-H). Negative FAB-MS m/z: 1119 $[M-H]^-$.

Castanopsinin G (47b)——An off-white amorphous powder, $[\alpha]_D^{20}$ +39.8° (c=0.66, MeOH). *Anal.* Calcd for $C_{57}H_{68}O_{23}\cdot 4H_2O$: C, 57.37; H, 6.42. Found: C, 57.13; H, 6.20. ^{1}H-NMR (pyridine-d_5) δ: 7.15, 7.27 (each 1H, s, HHDP-H), 7.85 (2H, s, galloyl-H), Negative FAB-MS m/z: 1119 $[M-H]^-$.

The Nonamethyl Ether of 47 (48)——A white amorphous powder, $[\alpha]_D^{24}$ +56.2° (c=1.21, $CHCl_3$). *Anal.* Calcd for $C_{66}H_{86}O_{23}\cdot H_2O$: C, 62.64; H, 7.01. Found: C, 62.83; H, 7.15. ^{1}H-NMR ($CDCl_3$) δ: 3.56 (1H, d, J=10 Hz, 3-H), 4.10, 4.72 (each 1H, d, J=12 Hz, 23-H), 5.20 (1H, d, J=11 Hz, 24-H), 6.68, 6.70 (each 1H, s, HMDP-H), 7.28 (2H, s, trimethoxybenzoyl-H). FD-MS m/z: 1246 $(M)^+$.

Alkaline Methanolysis of 48——**48** (15 mg) was methanolyzed with methanolic sodium methoxide (2% solution) (2 ml) to give **14** [$[\alpha]_D^{19}$ +26.5° (c=0.47, $CHCl_3$)], **15**, glucose and **11** (8 mg).

Acid Methanolysis of 47——A solution of **47** (60 mg) in 1 N methanolic sulfuric acid (3 ml) was heated at 60 °C for 1 h. The reaction mixture was neutralized with barium carbonate, and the resulting inorganic salts were filtered off. The filtrate was concentrated to dryness under reduced pressure, and the residue was subjected to chromatography over Sephadex LH-20. Elution with H_2O afforded crude **50**, which was purified by chromatography over Bondapak C_{18}/Porasil B with H_2O–MeOH (9:1) to furnish **50** as a colorless syrup (14 mg), $[\alpha]_D^{20}$ +39.8° (c=0.55, H_2O). ^{1}H-NMR (acetone-d_6 + D_2O) δ: 3.44 (3H, s, OMe), 4.78 (1H, d, J=4 Hz, anomeric-H), 5.32 (1H, t, J=8 Hz, glc 3-H), 7.14 (2H, s, galloyl-H). Further elution with H_2O–MeOH (2:3) afforded crude **49**, which was subsequently

chromatographed over MCI-gel CHP 20P with 80% aqueous MeOH to yield **49** as an off-white amorphous powder (35 mg), $[\alpha]_D^{20}$ +42.3° (c=0.88, MeOH). ^{1}H-NMR (pyridine-d_5) δ: 3.43 (1H, d, J=9 Hz, 3-H), 3.75, 6.05 (each 1H, d, J=11 Hz, 23- or 24-H), 4.10 (1H, m, 2-H), 4.39, 5.24 (each 1H, d, J=11 Hz, 23- or 24-H), 5.21 (1H, br s, 12-H), 7.23, 7.26 (each 1H, s, HHDP-H). FD-MS m/z: 821 $[M+H]^+$.

Castanopsinin H (51)——An off-white amorphous powder, $[\alpha]_D^{20}$ +30.0° (c=0.60, MeOH). *Anal.* Calcd for $C_{64}H_{72}O_{27}\cdot 4H_2O$: C, 56.46; H, 5.92. Found: C, 56.11; H, 6.03. ^{1}H-NMR (pyridine-d_5) δ: 7.08, 7.53 (each 1H, s, HHDP-H), 7.86, 8.02 (each 2H, s, 2×galloyl-H). Negative FAB-MS m/z: 1359 $[M-H]^-$.

The Dodecamethyl Ether of 51 (52)——A white amorphous powder, $[\alpha]_D^{20}$ +82.5° (c=0.80, $CHCl_3$). *Anal.* Calcd for $C_{76}H_{96}O_{27}\cdot H_2O$: C, 62.54; H, 6.77. Found: C, 62.43; H, 6.35. FD-MS m/z: 1440 $(M)^+$.

Alkaline Methanolysis of 52——**52** (20 mg) was treated with 2% methanolic sodium methoxide (1 ml) at 70 °C for 3.5 h. The reaction mixture was worked up in the same way as described before to give glucose, **14** [$[\alpha]_D^{20}$ +25.9° (c=0.12, $CHCl_3$)], **15** and **11** (7 mg).

Acid Methanolysis of 51——A solution of **51** (15 mg) in 1 N methanolic sulfuric acid (0.5 ml) was heated at 60 °C for 1 h. Work-up as described for **47** yielded **8** (7 mg) and **50** (4 mg).

Acknowledgements The authors are grateful to Assoc. Prof. K. Mihashi of the Faculty of Pharmaceutical Sciences, Fukuoka University, for high-resolution ^{1}H-NMR measurement, and to Mr. Y. Tanaka, Miss K. Soeda and Mr. R. Isobe for the measurements of ^{1}H- and ^{13}C-NMR spectra and negative FAB-, FD- and EI-MS.

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