Hovetrichosides C−G, Five New Glycosides of Two Auronols, Two Neolignans, and a Phenylpropanoid from the Bark of *Hovenia trichocarea*

Kazuko Yoshikawa,* Kimura Eiko, Noriko Mimura, Yuko Kondo, and Shigenobu Arihara

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

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Two 2-hydroxy-2-benzylcoumaranone glycosides, 2,4,6-trihydroxy-2-[(4′-hydroxyphenyl) methyl]-3(2*H*)-benzofuranone-4-yl-*β*-D-glucopyranoside (maesopsin 4-*O*-glucoside) (**1**) and 2,4,6-trihydroxy-2-[(4′-hydroxyphenyl) methyl]-3(2*H*)-benzofuranone-4-yl-*β*-D-glucopyranosido-4′-yl-α-L-rhamnopyranoside (maesopsin 4-*O*-glucosido 4′-*O*-rhamnoside) (**2**), two neolignan glycosides, 2*R*-(*E*)-2,3-dihydro-2-(4′-hydroxy-3′-methoxylphenyl)-5-(3″-hydroxy-1″-propenyl)-7-methoxy-3-benzofuranmethanol-4′-yl-*β*-D-glucopyranosyl-(1→3)-[*β*-D-glucopyranosyl-(l→2)]-*β*-D-glucopyranoside (**3**) and (*threo*) 1-(4′-hydroxy-3′-methoxy)-2-(4″-hydroxymethyl-2″,6″-dimethoxyphenoxy)-propane-1,3-diol-4′-yl-*β*-D-glucopynoside (**4**), and a phenylpropanoid glycoside, 3-methoxy-5-(2′-propenyl)-1,2-benzenediol-1-yl-*β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside (**5**) were isolated from the bark of *Hovenia trichocarea*. Compounds **1**−**5** were named hovetricosides C−G, respectively, and their structures were established by extensive NMR experiments and chemical methods. Also obtained in this investigation were the known compounds acanthoside B, kelampayoside A, shashenoside I, and 3,4,5-trimethoxyphenol-1-*O*-*β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside.

In a previous paper,[1] we reported the isolation and structure elucidation of two new 1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol 1-*O*-glucosides, designated as hovetrichosides A and B, from the EtOH extract of the bark of *Hovenia trichocarea* Chun et Tsiang (Rhamnaceae). Further purification of the resulting fractions by Si gel, and reversed-phase HPLC gave hovetrichosides C (**1**), D (**2**), E (**3**), F (**4**), and G (**5**), along with maesopsin (**6**) (Chart 1),[2,3] acanthoside B,[4] kelampayoside A,[5] shashenoside I,[6] and 3,4,5-trimethoxyphenol-1-*O*-*β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside.[7] The known compounds were identified and characterized from their spectroscopic data. We describe here the isolation and structure elucidation of hovetrichosides C−G (**1**−**5**) by various NMR techniques, including COSY, HMQC, HMBC, and ROESY experiments and by chemical degradation.

Results and Discussion

Hovetrichoside C (**1**) $[\alpha]^{25}_{D}$ −54.1° (*c* 1.9, MeOH) had the molecular formula $C_{21}H_{22}O_{11}$ (negative FABMS, *m/z* 449 $[M - H]^-$), that is, 162 mass units ($C_6H_{10}O_5$) higher than that of maesopsin (**6**). The ^1H and ^{13}C NMR spectra of **1** displayed two sets of signals due to a maesopsin and a hexosyl group. The ratio of the intensity of each pair of signals was 3:2. In contrast to **6**, which exists as enantiomeric pairs due to the reversible nature of the hemiketal at C-2, the attachment of a glucosyl moiety in **1** produces a pair of diastereoisomers thus giving rise to a double set of signals. Acid hydrolysis of **1** afforded **6** and D-glucose, which was confirmed by specific rotation using chiral detection in HPLC analysis.[8] In the ^1H NMR spectrum of **1** one anomeric proton signals appeared at *δ* 5.50 (0.6H, d, *J* = 8.0 Hz) and 5.60 (0.4H, d, *J* = 8.0 Hz), disclosing the glucose having *β*-configuration. The appearance of the lower shifted phenolic OH at *δ* 10.55 (1H, s) due to hydrogen bond between carbonyl group in the ^1H NMR spectrum (DMSO-d_6), from **1** to **6** indicated the probable point of glucosyl linkage in the aglycon as being at C-4. Further, the HMBC spectrum showed connectivities between the major H-1 (*δ* 5.50) of glucose and major C-4 (*δ* 158.51) of the aglycon. Thus, **1** was formulated as 2,4,6-trihydroxy-2-[(4′-hydroxyphenyl) methyl]-3(2*H*)-benzofuranone-4-yl-*β*-D-glucopyranoside (maesopsin 4-*O*-glucoside). Auronols (2-hydroxy-2-benzylcoumaranones) are rare in nature, and the only glycoside is maesopsin-6-*O*-glucoside, which was recently isolated from *Ceanothus americanus*.[3]

Hovetrichoside D (**2**), $C_{27}H_{32}O_{15}$ showed an ion peak at *m/z* 595 $[M - H]^-$ in the FABMS, 146 mass units ($C_6H_{10}O_4$) more than that of **1**. On acid hydrolysis, **2** gave **6**, and D-glucose and L-rhamnose in the ratio of 1:1. The ^1H and ^{13}C NMR spectra of **2** also exhibited two sets of signals. The intensity of each pair of signals was in the ratio 3:2. The coupling constant (*J* = 7.5 Hz) of the anomeric proton signal of the D-glucosyl moiety as well as the chemical shifts (*δ* 5.89 and 5.87 in pyridine-d_5) of the anomeric protons of the L-rhamnosyl moiety indicated a glucosyl moiety having the *β* configuration, with a rhamnose moiety having the α configuration. The position of sugar linkages to the aglycon was determined by the HMBC experiment. The HMBC spectrum of **2** showed long-range correlations between the major H-1 (*δ* 5.54) of the glucose and major C-4 (*δ* 158.52) of aglycon, and the major H-1 (*δ* 5.89) of rhamnose and major C-4′ (*δ* 156.38), indicating a glucosyl unit to be located at C-4 and a rhamnosyl unit at C-4′. Accordingly, **2** was formulated as 2,4,6-trihydroxy-2-[(4′-hydroxyphenyl)-methyl]-3(2*H*)-benzofura-

* To whom correspondence should be addressed. Tel.: (81) 886-22-9611. Fax: (81) 886-55-3051.

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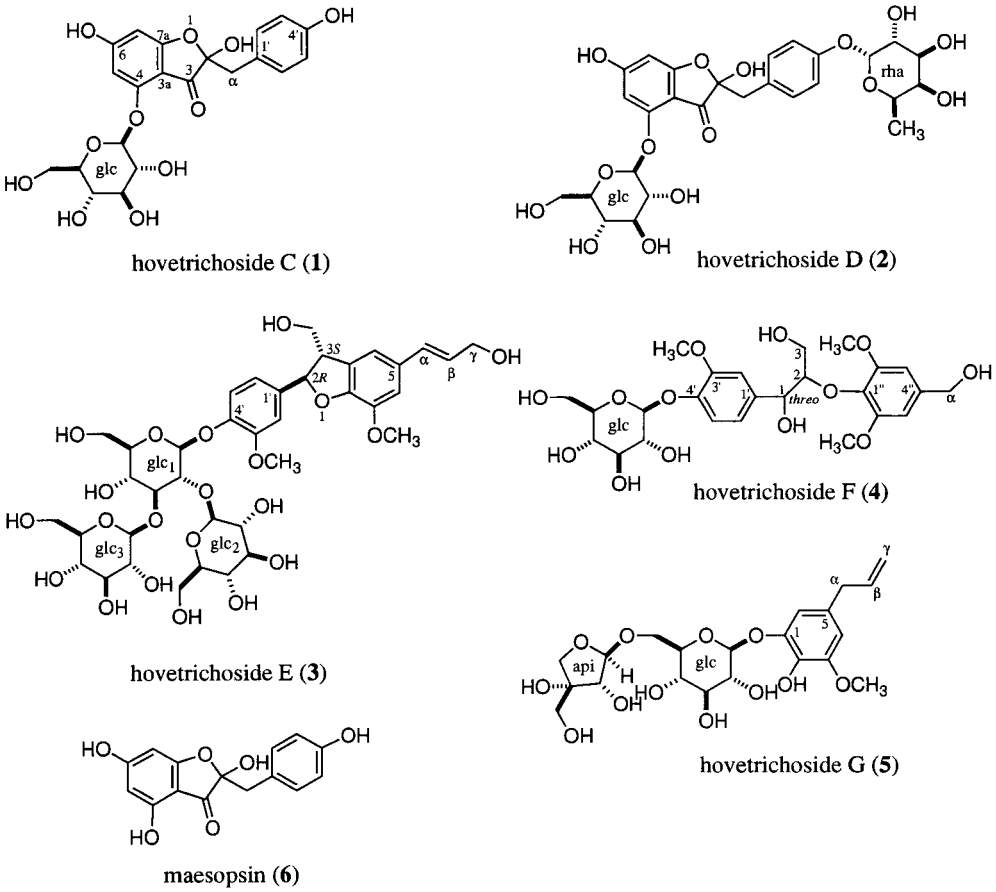
Chart 1



none-4-yl-β-D-glucopyranosido-4′-yl-α-L-rhamnopyranoside (maesopsin 4-*O*-glucosido-4′-*O*-rhamnoside).

The molecular formula $C_{38}H_{52}O_{21}$ of hovetrichoside E (**3**) was derived from the quasi-molecular ion peak at *m*/*z* 843 $[M - H]^-$ in the FABMS and the ^{13}C NMR spectrum. The λ_{max} at 210, 233, and 278 nm in the UV spectrum of **3** indicated a conjugated system similar to that of coniferyl alcohol. The ^1H NMR spectrum showed the presence of a guaiacyl group at δ 7.28, 7.27, 7.05, and 3.70, of a 5-substitued coniferyl group at δ 7.29, 7.13, 6.91, 6.58, and 4.59, of a 2,3-dihydro-3-hydroxymethylfuranyl group at δ 6.01, 4.24, 4.18, and 3.84, and of three hexosyl groups at δ 5.63, 5.60, and 5.34 (each anomeric H, d, J = 8.0 Hz). HMBC correlations between H-2 and C-3, CH_2OH, C-1′, C-2′, C-6′, C-3a and C-7a, H-3 and C-2, CH_2OH, C-1′ and C-4, H−α and C-4, C-5, C-6 and C−γ, and anomeric H and C-4′ led to the planar structure of **3**. The NOE interactions between OMe/H-2′ and OMe/H-6 allowed the locations of the methoxy at C-3′ and C-7. These results suggested that compound **3** was dehydrodiconiferyl alcohol 4-*O* triglycoside. Indeed, in the ^{13}C NMR spectrum of **3**, the chemical shifts due to the aglycon moiety were in good agreement with those of 2,3-dihydro-2-(3′-methoxy-4′-hydroxylphenyl)-5-(3″-hydroxy-1″-propenyl)-7-methoxy-3-benzofuranmethanol-4′-yl-β-D-glucopyranoside.[9,10] The relative stereochemistry of the dihydrofuran ring was elucidated by a ROESY experiment. The strong NOEs between H-2/H-2′, H-2/H-6′, H-3/H-2′, and H-3/H-6′, and the very weak NOE between H-2/H-3 indicated trans 2/3 configuration. The absolute configuration of the dihydrofuran ring was determined using CD spectroscopic evidence. The CD spectrum of **3** showed a positive Cotton effect at 220 nm ($\Delta\epsilon$ = +1.00) and a negative Cotton effect at 232 nm ($\Delta\epsilon$ = − 8.98). Lemiere *et al.* reported that the configuration at C-2 and C-3 of the dihydrobenzofuran skeleton can be clearly distinguished in the 240−220 nm region.[11] Hence, the absolute configurations of the dihydrofuran ring in **3** were determined to be 2*R*,3*S*.

Acid hydrolysis of **3** afforded D-glucose confirmed by specific rotation using chiral detection in HPLC analysis. In the ^1H NMR spectrum of **3**, three anomeric proton signals appeared at δ 5.63, 5.60, and d 5.34, indicating that each glucose has a β-configuration. The corresponding three anomeric carbons were observed at δ 99.8, 104.9, and 105.2. Also, the downfield shifted ^{13}C NMR resonances among the sugar units were observed at δ 87.8 and 81.1, indicating the probable point of glycosidic linkage in the oligosaccharide to be at C-4′. $^1H-^1H$ COSY and HMQC experiments revealed the glycosdic attachments at C-2 (δ 81.1) and C-3 (87.8) for glucose (glc_1). Further, the HMBC spectrum showed connectivities between the H-1 proton of glc_1 and C-4′, the H-1′ proton of glc_2 and C-2′ of glc_1, and the H-1″ proton of glc_3 and C-3′ of glc_1. Thus, **3** was formulated as (2*R*-*trans*)-2,3-dihydro-2-(4′-hydroxy-3′-methoxylphenyl)-5-(3″-hydroxy-1″-propenyl)-7-methoxy-3-benzofuranmethanol-4′-yl-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(l→2)]-β-D-glucopyranoside.

Hovetrichoside F (**4**) was obtained as an amorphous powder. The UV spectrum showed absorption maxima at 230 and 280 nm, suggesting the presence of an aromatic ring. The ^1H NMR spectrum showed the

Table 1. ^{1}H and ^{13}C NMR Data (600 and 150 MHz) for Hovetrichosides C (**1**) and D (**2**) and Maesopsin (**6**) in Pyridine-d_5

	1				**2**					
carbon	major		minor		major		minor		**6**	
no	^{13}C	^{1}H, mult (*J*)	^{13}C	^{1}H, mult (*J*)	^{13}C	^{1}H, mult (*J*)	^{13}C	^{1}H, mult (*J*)	^{13}C	^{1}H, mult (*J*)
2	107.52		107.47		107.08		107.05		107.40	
3	195.50		195.54		194.83		194.87		195.41	
3a	103.25		103.25		103.15		103.19		103.14	
4	158.51		158.43		158.52		158.48		159.92	
5	97.13	6.59 d (1.5)	97.35	6.67 d (1.5)	96.96	6.57 d (2.0)	97.20	6.69 d (1.5)	97.45	6.42 d (1.5)
6	170.95		170.89		170.55		170.55		170.21	
7	93.21	6.41 d (1.5)	93.28	6.47 d(1.5)	93.17	6.39 d (2.0)	93.24	6.44 d (1.5)	91.15	6.23 d (1.5)
7a	173.79		173.70		173.40		173.34		173.46	
1′	125.65		125.57		128.73		128.77		125.75	
2′, 6′	132.70	7.54 d (8.5)	132.70	7.55 d (8.5)	132.50	7.57 d (9.0)	132.50	7.55 d (8.5)	132.60	7.58 d (1.5)
3′, 5′	115.95	7.02 d (8.5)	115.87	7.08 d (8.5)	116.52	7.16 d (8.0)	116.47	7.16 d (8.5)	115.82	7.04 d (1.5)
4′	157.90		157.89		156.38		156.30		157.74	
α	41.90	3.69 s (2H)	42.08	3.62 d (14.0)	41.70	3.67 d (14.0)	41.85	3.59 d (14.0)	42.25	3.87 d (14.0)
				3.52 d (14.0)		3.60 d (14.0)		3.44 d (14.0)		3.90 d (14.0)
glc 1	102.05	5.50 d (8.0)	101.72	5.60 d (8.0)	101.83	5.54 d (7.5)	101.66	5.68 d (7.5)		
2	74.26	4.35 dd (8.0, 8.0)	74.39	4.35 dd (8.0, 8.0)	74.21	ca. 4.30 m	74.37	ca. 4.30 m		
3	78.24	4.29 dd (8.0, 8.0)	78.34	4.30 dd (8.0, 8.0)	78.51	ca. 4.28 m	78.41	ca. 4.28 m		
4	70.99	4.22 dd (8.0, 8.0)	70.94	4.28 dd (8.0, 8.0)	70.73	ca. 4.25 m	70.67	ca. 4.25 m		
5	79.15	3.92 m	79.02	3.92 m	79.11	3.88 m	79.05	3.88 m		
6	62.22	4.36 dd (11.0, 2.5)	62.22	4.36 dd (11.0, 2.5)	62.18	ca. 4.30 m	62.11	ca. 4.30 m		
		4.27 dd (11.0, 5.5)		4.27 dd (11.0, 5.5)		ca. 4.30 m		ca. 4.30 m		
rha 1					99.98	5.89 s	99.92	5.87s		
2					72.47	ca. 4.56 m	72.50	ca. 4.56 m		
3					71.95	ca. 4.56 m	71.95	ca. 4.56 m		
4					73.70	ca. 4.25 m	73.77	ca. 4.25 m		
5					70.78	4.09 m	70.78	4.18 m		
6					18.48	1.45 d (6.5)	18.57	1.51 d (6.5)		

presence of a guaiacyl group at δ 7.60, 7.54, 7.29, and 3.70; a syringyl group at δ 6.96, 4.95, and 3.70; a glycerol group at δ 5.68, 4.81, 4.58, and 4.15; and a hexosyl group at δ 5.68. The ^{1}H−^{13}C long-range coupling of H-1 to C-2, C-3, C-1′, C-2′, and C-6′; H-2 to C-1, C-3, C-1′, and C-4″; H−α to C-1″, C-2″, and C-6″, and anomeric H to C-4′ led to the planar structure of **4**. The NOE interaction between OMe/H-2′, OMe/H-2″, and OMe/H-6″ showed the methoxy groups at C-3′, C-3″, and C-6″. Furthermore, an NOE was detected between the anomeric H at δ 5.68 and the H-5′ at δ 7.60. These results suggested that compound **4** was 1-(4′-hydroxy-3′-methoxyphenyl)-2-(4″-hydroxymethyl-2″,6″-dimethoxyphenoxy)-propane-1,3-diol-4′-yl-monosaccharide. The chemical shift of C-2 at δ 87.9 in the ^{13}C NMR spectrum (in pyridine-d_5) of **4** indicated that **4** was a pure *threo* isomer: the *erythro* isomer has the C-2 at δ 86.5.[12] Acid hydrolysis of **4** afforded D-glucose confirmed by specific rotation using chiral detection in HPLC analysis. Hence, **4** was formulated as (*threo*) 1-(4′-hydroxy-3′-methoxy)-2-(4″-hydroxymethyl-2″,6″-dimethoxyphenoxy)-propane-1,3-diol-4′-yl-β-D-glucopynoside.

The last compound, hovetrichoside G (**5**), showed phenolic properties and the molecular formula $C_{21}H_{30}O_{12}$ from the quasi-molecular ion peak at *m*/*z* 473 $[M - H]^-$ in FABMS. The ^{1}H NMR spectrum indicated a 1,2,3,5-tetrasubstituted benzene ring at δ 7.16 and 6.73 and one methoxy group at δ 3.90, an allyl group at δ 6.12, 5.23, 5.16, and 3.46, and two anomeric protons at δ 5.28 and 5.71. On acid hydrolysis, **5** gave D-glucose and D-apiose confirmed by specific rotation using chiral detection in HPLC analysis. The ^{1}H−^{13}C long-range correlations between H-α and C-4, C-5, C-6, C-β, and C-γ; H-4/H-6 and C-5; methoxymethyl and C-3; and H-1 of glucose and C-1 indicated that **5** was 6-hydroxyeugenol 1-*O*-disaccharide.[6] The ^{13}C NMR chemical shifts for the sugar moieties of **5** were very similar to those of kelampayoside A,[5] indicating that both compounds had the same sugar sequences. Also, long-range correlations between C-6 of glucose and H-1 of apiose were all definitely observed. Furthermore, the coupling constant (J = 7.5 Hz) of the anomeric proton signal of the D-glucosyl moiety, as well as the chemical shift (δ 111.3 in pyridine-d_5) of the anomeric carbon of the D-apiosyl moiety, demonstrated that both sugar moieties have β-anomeric configurations.[5] Thus, the structure of **5** was determined to be 3-methoxy-5-(2′-propenyl)-1,2-benzenediol-1-yl-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside.

Compound **6** $[\alpha]^{25}_D \pm 0°$ (*c* 1.9, MeOH) was obtained as a pale yellow powder. The molecular formula was established as $C_{15}H_{12}O_6$, on the basis of HREIMS and corresponds to 10 degrees of unsaturation. Analysis of the various NMR data of **6** showed that **6** was 2,4,6-trihydroxy-2-[(4-hydroxyphenyl)-methyl]-3(2*H*)-benzofuranone (maesopsin), which was originally isolated from *Maesopsis eminii*.[2]

Experimental Section

General Experimental Procedures. Melting points were measured with a Yanagimoto micromelting point apparatus and were uncorrected. Optical rotations were determined on a JASCO DIP-360 polarimeter. IR spectra were recorded on a JASCO FT/IR-5300, NMR spectra on Varian UNITY 600, and/or JEOL GSX-400 spectrometer in pyridine-d_5 or DMSO-d_6 solution using TMS as internal standard. NMR experiments included ^{1}H−^{1}H COSY, HMQC, HMBC, TOCSY, and ROESY. Coupling constants (J values) are given in Hz. The FABMS (Xe gun, 10 kV, triethylene glycol as the matrix) was measured on a JEOL JMS−PX303 mass spectrometer. HPLC separations were performed with a Hitachi HPLC system (L-7100 Pump, L-4000 UV).

Table 2. ^{1}H and ^{13}C NMR Data (600 and 150 MHz) for Hovetrichosides E (**3**), F (**4**), and G (**5**) in Pyridine-d_5

	3		**5**			**4**	
carbon	^{13}C	^{1}H, mult (*J*)	^{13}C	^{1}H, mult (*J*)		^{13}C	^{1}H, mult (*J*)
1			146.8		1	73.3	5.68 d (7.0)
2	88.3	6.01 d (6.5)	135.7		2	87.9	4.81 ddd (7.5, 7.0, 4.5)
3	54.9	3.84 ddd (7.5, 6.5, 5.5)	149.6		3	61.1	4.58 dd (12.0, 4.5)
3a	130.4						4.15 dd (12.0, 7.5)
4	115.9	7.29 d (1.5)	108.6	6.73 d (1.5)	1′	137.5	
5	131.9		132.5		2′	112.1	7.54 d (2.0)
6	111.6	7.13 d (1.5)	111.8	7.16 d (1.5)	3′	149.7	
7	144.9				4′	147.0	
7a	148.8				5′	115.9	7.60 d (8.5)
1′	136.3				6′	120.2	7.29 dd (8.5, 2.0)
2′	150.2	7.28 d (1.5)			1″	139.5	
3′	147.0				2″	104.4	6.96 s
4′	114.6				3″	153.8	
5′	118.7	7.27 d (8.5)			4″	135.2	
6′	136.3	7.05 d (8.5, 1.5)			5″	153.8	
α	129.9	6.91 dt (16.0, 1.5)	46.8	3.62 d (2H, 6.5)	6″	104.4	6.96 s
β	129.1	6.58 dd (16.0, 5.5)	139.0	6.12 ddd (17.0, 10.0, 6.5)	α	64.3	4.95 s (2H)
γ	63.1	4.59 dt (2H, 5.5, 1.5)	116.0	5.23 d (17.0)			
				5.16 d (10.0)			
CH_2OH	64.1	4.24 dd (11.0, 5.5)					
		4.18 dd (11.0, 7.5)					
MeO 3 or 7	56.2	3.84 s	56.7	3.90 s	MeO 3′	55.9	3.70 s
MeO 3′	55.9	3.70 s			MeO 3″, 5″	56.1 × 2	3.70 s × 2
glc_1 1	99.8	5.63 d (8.0)	104.9	5.28 d (7.5)	glc 1	102.4	5.68 d (7.0)
2	81.1	4.56 dd (9.0, 8.0)	75.3	4.10 m	2	74.9	4.35 m
3	87.8	4.36 dd (9.0, 9.0)	78.2	4.08 m	3	78.6	4.35 m
4	69.3	4.17 dd (9.0, 9.0)	71.7	4.10 m	4	71.2	4.35 m
5	78.3	4.07 d d d (9.0, 5.0, 2.0)	77.6	3.98 m	5	78.8	4.10 m
6	62.5	4.58 dd (12.0, 2.0)	68.9	4.58 dd (11.0, 2.5)	6	62.3	4.50 dd (11.0, 12.5)
		4.30 dd (12.0, 5.0)		4.11 dd (11.0, 5.5)			4.40 dd (11.0, 5.5)
api or 1 (1′)	104.9	5.60 d (8.0)	111.3	5.71 d(2.0)			
(glc_2) 2 (2′)	76.2	4.08 dd (8.5, 8.0)	78.1	4.58 d (2.0)			
3 (3′)	78.7	4.28 dd (8.5, 8.5)	80.7				
4 (4′)	71.4	4.31 dd (9.5, 8.5)	75.1	4.47 (9.5), 4.25 (9.5)			
5 (5′)	77.7	3.84 d d d (9.0, 4.0, 2.5)	65.8	4.08 s (2H)			
6 (6′)	62.1	4.22 dd (12.0, 2.5)					
		3.95 dd (12.0, 4.0)					
glc_3 1″	105.2	5.34 d (8.0)					
2″	75.2	4.09 dd (8.0, 8.0)					
3″	78.6	4.23 dd (8.0, 8.0)					
4″	71.6	4.17 dd (8.0, 8.0)					
5″	78.1	3.95 d d d (8.0, 5.0, 2.5)					
6″	61.9	4.40 dd (12.0, 2.5)					
		41.8 dd (12.0, 5.0)					

Plant Material. The bark of *Hovenia trichocarea* was collected in April 1995. A voucher specimen is deposited in the Herbarium of Faculty of Pharmaceutical Sciences, Tokushima Bunri University, Tokushima, Japan.

Extraction and Isolation. The fresh bark (10 kg) of *Hovenia trichocarea* collected in Tokushima prefecture, in April 1995, were extracted with absolute EtOH at room temperature for 6 weeks. The EtOH extract (200 g) was partitioned between H_2O and EtOAc. An aliquot (11 g) of the EtOAc-soluble portion (44 g) was repeatedly subjected to Si gel column chromatography with CH_2Cl_2−MeOH (25:1−25:2) and then with a reversed-phase Si gel column (ODS) with chromatography eluting with 3% MeOH to afford maesopsin (**6**, 15 mg). The H_2O layer was passed through an Amberlite XAD-2 column. After the column was washed with H_2O, the adsorbed materials were eluted with 20% MeOH, 50% MeOH, and 100% MeOH. The 50% MeOH eluate (9 g) was chromatographed on Si gel with CH_2Cl_2−MeOH−EtOAc−H_2O (2:2:4:1, lower layer) to give five fractions (Fractions 1−5). Fraction 4 (22.5 g) was subjected to HPLC on ODS (20% MeOH) to give five fractions (fractions 1′−5′). Fractions 2′ and 3′ were purified by preparative HPLC (ODS, 5% CH_3CN) to afford hovetrichosides C (**1**, 45 mg) and G (**5**, 30 mg), kelampoyoside A (275 mg), shahenoside I (110 mg), and 3,4,5-trimethoxyphenol-1-*O*-*β*-D-xylopyranosyl-(1→6)-*β*-D-glucopyranoside (10 mg). Further, the residue of fraction 4′ was purified by preparative HPLC (ODS, 7−13% CH_3CN) to afford hovetrichosides D (**2**, 60 mg), E (**4**, 60 mg), and F (**3**, 15 mg) and acanthoside B (10 mg). The EtOAc-soluble portion (70 g) was repeatedly subjected to Si gel with CH_2Cl_2−MeOH−H_2O (25:8:0.1, 25:4:0.1), followed by reversed-phase HPLC (ODS, 3% CH_3CN) to give maesopsin (**6**, 45 mg).

Hovetrichoside C (1): an amorphous powder; $[\alpha]^{25}_D$ −54.1° (*c* 1.9, MeOH); UV (MeOH) λ_{max} (log ϵ) 210 (4.26), 228 (4.24), 280 (3.87); FT-IR (dry film) ν_{max} 3335 (OH), 1695 (C=O), 1620, 1510 (aromatic) cm^{-1}; ^{1}H NMR (DMSO-d_6, 600 MHz) δ 2.89 and 2.96 (each 1H, d, J = 14.0 Hz, Ha), 4.58 (0.6H, m, H-5 of glc), 4.67 (0.4H, m, H-5 of glc), 4.88 (0.6H, d, J = 8.0 Hz, H-1 of glc), 4.95 (0.4H, d, J = 8.0 Hz, H-1 of glc), 5.92 (1H, d J = 1.5 Hz, H-7), 5.98 (0.6H, d, J = 1.5 Hz, H-5), 6.02 (0.4H, d, J = 1.5 Hz, H-5), 6.55 (2H, d, J = 8.5 Hz, H-3′, 5′), 6.93 (2H, d, J = 8.5 Hz, H-2′, 6′), 7.61 (0.4H, br s, 4′-OH), 7.63 (0.6H, br s, 4′-OH), 9.25 (1H, br s, 6-OH); ^{1}H and ^{13}C

NMR (pyridine-d_5), see Table 1; FABMS *m/z* $[M - H]^-$ 449, $[M - H - glc]^-$ 287.

Hovetrichoside D (2): an amorphous powder; $[\alpha]^{25}_D$ −39.6° (*c* 2.1, pyridine); UV (MeOH) λ_{max} (log ϵ) 208 (4.01), 230 (3.86), 256 (3.45), 261 (3.39), 280 (3.46); FT-IR (dry film) ν_{max} 3335 (OH), 1695 (C=O), 1615, 1510 (aromatic) cm^{-1}; ^1H and ^{13}C NMR (600 MHz), see Table 1; FABMS *m/z* $[M - H]^-$ 595.

Hovetrichoside E (3): colorless needles, mp 227−229 °C; $[\alpha]^{25}_D$ −18.3° (*c* 0.9, pyridine); UV (MeOH) λ_{max} (log ϵ) 210 (4.49), 233 (4.46), 278 (4.17); ^1H and ^{13}C NMR (600 MHz), see Table 2; FABMS *m/z* $[M - H]^-$ 843, $[M - H - 162]^-$ 681; CD $\Delta\epsilon$ 289 (+3.56), 265 (+2.37), 232 (−8.98), 220 (+1.00).

Hovetrichoside F (4): an amorphous powder; $[\alpha]^{25}_D$ −28.2° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.10), 280 (3.60); ^1H and ^{13}C NMR (600 MHz), see Table 2; FABMS *m/z* $[M + K]^+$ 581.

Hovetrichoside G (5): an amorphous powder; $[\alpha]^{25}_D$ −75.7° (*c* 1.0, MeOH); UV (MeOH) λ_{max} (log ϵ) 228 (4.10), 280 (3.50); FT-IR (dry film) ν_{max} 3450 (OH), 1600, 1510 (aromatic) cm^{-1}; ^1H and ^{13}C NMR (600 MHz), see Table 2; FABMS *m/z* $[M - H]^-$ 473.

Maesopsin (6): an amorphous powder; $[\alpha]^{25}_D \pm 0°$ (*c* 1.9, MeOH); UV (MeOH) λ_{max} (log ϵ) 230 (4.10), 280 (3.60); FT-IR (dry film) ν_{max} 3410 (OH), 1685 (C=O), 1615, 1515 (aromatic) cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz) δ 2.86 and 2.92 (each 1H, d, J = 14.0 Hz, Hα), 5.71 (1H, d, J = 1.5 Hz, H-7), 5.77 (1H, d, J = 1.5 Hz, H-5), 6.54 (2H, d, J = 8.0 Hz, H-3′, 5′), 6.91 (2H, d, J = 8.0 Hz, H-2′, 6′), 7.42 (H, br s, 4′-OH), 9.16 (1H, br s, 6-OH), 10.55 (1H, br s, 4-OH); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 39.4 (C-α), 92.5 (C-7), 95.5 (C-5), 105.3 (C-2, C-3a), 114.3 (C-3′, 5′), 124.1 (C-1′), 131.0 (C-2′, 6′), 155.6 (C-4′), 157.7 (C-4), 167.8 (C-6), 171.5 (C-7a), 192.6 (C-3); ^1H and ^{13}C NMR (pyridine-d_6), see Table 1; HREIMS *m/z* 288.0625, calcd for $C_{16}H_{24}O_5$ 288.0634.

Acid Hydrolysis of Hovetrichosides C (1) and D (2). A solution of each compound **1** (10 mg) and **2** (13 mg) in 5% H_2SO_4−dioxane (1:1) was heated at 80° for 1.5 h. The reaction mixture was diluted with H_2O and extracted with EtOAc. The EtOAc layer was purified by passing through a Si gel column by elution with CH_2Cl_2−MeOH (30:1). Compounds **1** and **2** gave maesopsin (**6**, 2 mg), which was confirmed by ^1H NMR data and by co-HPLC with an authentic sample.

The aqueous layer was neutralized with Amberlite IRA-35 and evaporated in vacuo to dryness. The identification and the D or L configuration of sugar was determined by using RI detection (Waters 410) and chiral detection (Shodex OR-1) by HPLC {Shodex RSpak NH_2P-50 4E, $CH_3CN-H_2O-H_3PO_4$ (95:5:1), 1 mL/min, 47 °C} by comparison with an authentic sugar (10 mmol each of D-glc, L-glc and L-rha). The sugar portion from compound **1** gave the peak of D-(+)-glc at 20.7 min, and that from compound **2** gave the peak of L-(−)-rha at 6.40 min and D-(+)-glc at 20.7 min.

Identification of Component Sugars of Hovetrichosides E (3), F (4), and G (5): A solution of **3**, **4**, and **5** (each 2 mg) was carried out in the same way as described for **1** and **2**. The identification and the D or L configuration of sugar was determined by the same way as described for **1** and **2** with an authentic sugar (10 mmol each of D-glc, L-glc and D-apiose). The sugar portions from compounds **3** and **4** gave the peak of D-(+)-glc at 20.7 min, and that from compound **5** gave the peak of D-(+)-api at 8.30 min and D-(+)-glc at 20.7 min.

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