Tannins and Related Polyphenols of Melastomataceous Plants. III.[1] Nobotanins G, H and I, Dimeric Hydrolyzable Tannins from *Heterocentron roseum*

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Three new hydrolyzable tannin dimers, nobotanins G (6), H (12) and I (13), have been isolated from the leaves of *Heterocentron roseum* (Melastomataceae), and their structures were elucidated on the basis of chemical degradations and nuclear magnetic resonance spectral analyses. Nobotanin I (13) is a novel dimer possessing a depsidone-forming valoneoyl group in the molecule. Five known tannins, casuarictin (1), strictinin (2), geraniin (3), and nobotanins B (4) and F (5), were also isolated.

Keywords *Heterocentron roseum*; Melastomataceae; tannin; ellagitannin dimer; nobotanin G; nobotanin H; nobotanin I; depsidone; valoneoyl group

We previously reported the isolation and structure elucidation of novel hydrolyzable tannin oligomers [nobotanins A, B (**4**), C, E and F (**5**)] from *Tibouchina semidecandra* COGN (Melastomataceae).[1,2] As a part of our continuing studies on the tannins of Melastomataceous plants, we have investigated *Heterocentron roseum* A. BR. *et* BOUCH., which is a shrub native to Mexico and was found to be rich in tannins by a chromatographic survey, and isolated eight hydrolyzable tannins including three new dimers which are structurally related to nobotanin B and hence were designated as nobotanins G, H and I.[3]

The 1-butanol extract obtained from the aqueous acetone homogenate of the leaves was fractionated by column chromatography over Diaion HP-20, and subsequently over Toyopearl HW-40, to yield nobotanins G (**6**), H (**12**) and I (**13**). Five known tannins were also isolated and

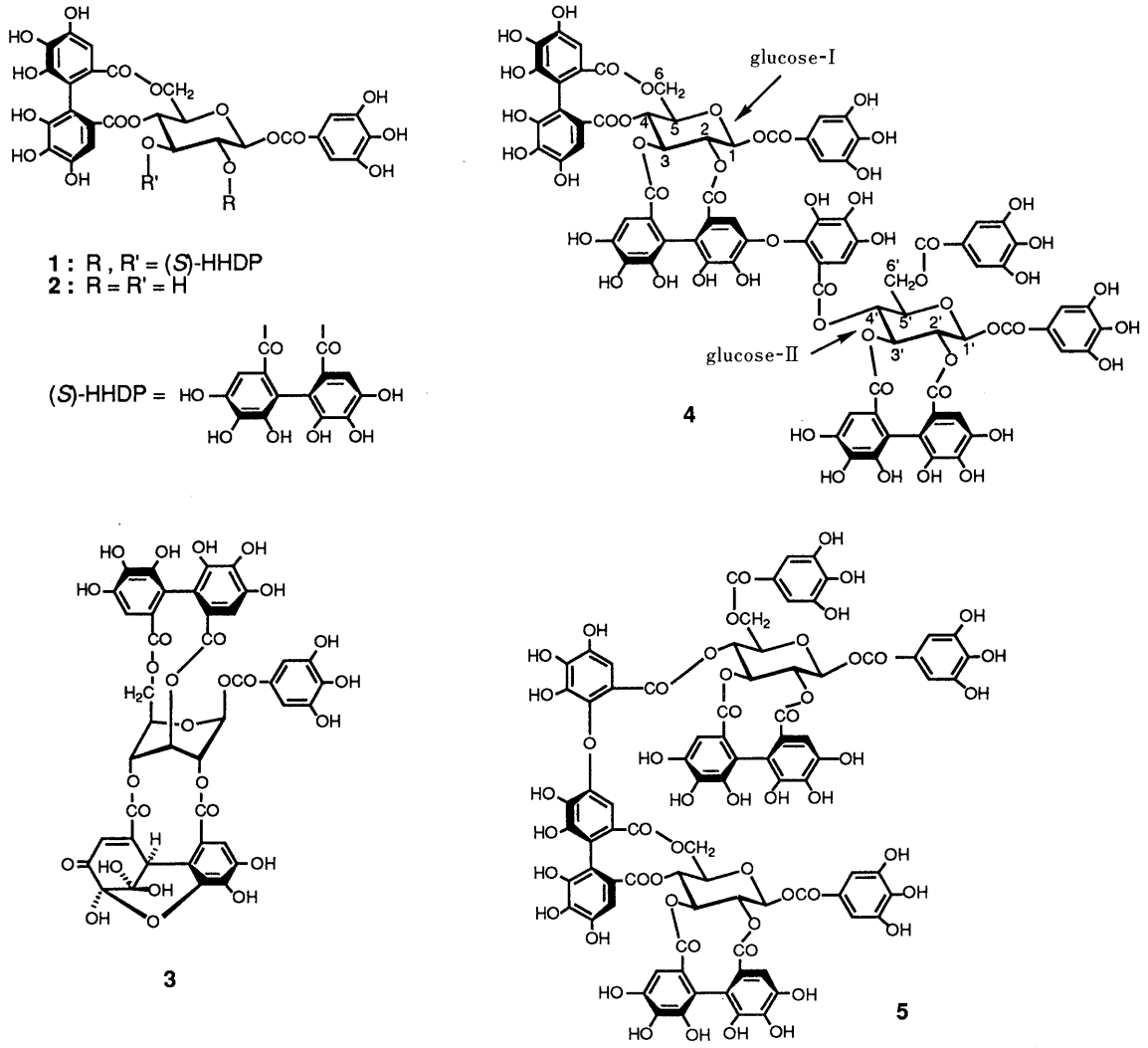


Chart 1

characterized as casuarictin (**1**),[4] strictinin (**2**),[4] geraniin (**3**),[5] and nobotanins B (**4**)[1] (the main tannin, 0.015% of the fresh leaves) and nobotanin F (**5**).[2]

Nobotanin G (**6**) was obtained as an off-white amorphous powder. Its molecular formula $C_{68}H_{50}O_{44}$ was deduced from the fast-atom bombardment mass spectrum (FAB-MS) [*m/z* 1593 $(M+Na)^+$] and the proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra as described below. Acid hydrolysis of **6** gave glucose, gallic acid (**7**), ellagic acid (**8**) and valoneic acid dilactone (**9**). The ^{1}H-NMR spectrum of **6** exhibited three 2H singlets (δ 7.24, 7.14, 7.00) and five 1H singlets (δ 7.08, 6.62, 6.54, 6.37, 6.14) in the aromatic region, which are consistent with the presence of three galloyl groups, a hexahydroxydiphenoyl (HHDP) group and a valoneoyl group in the molecule. The dimeric nature of **6** is apparent from two anomeric proton signals at δ 6.12 (d, $J=8.5$ Hz) and δ 5.70 ($J=8.0$ Hz). In addition to these anomeric proton signals, the coupling patterns of the other glucose protons, which were assigned from the ^{1}H–^{1}H shift correlation spectrum (COSY) (Table I), are consistent with those of $^4C_1$ glucopyranose residues. The signals due to one (glucose-I) of the glucose cores showed a close resemblance to those of glucose-I of nobotanin B (**4**), indicating that **6** has the HHDP group and the HHDP part of the valoneoyl group at O-4/O-6 and O-2/O-3. Since the presence of hydroxyl groups at O-2′ and O-3′ of the other glucose core (glucose-II) was indicated by remarkable upfield shifts of H-2′ [δ 3.64 (dd, $J=8.0$, 10.0 Hz)] and H-3′ [δ 3.79 (t, $J=10.0$ Hz)] relative to those of glucose-I, three galloyl groups and a galloyl part of valoneoyl group in **6** should be at O-1, O-1′, O-4′ and O-6′. The H-5′ signal of glucose-II was observed at considerably high field [δ 3.40 (br d, $J=10.0$ Hz)], as found for H-5′ [δ 3.45 (br d, $J=10.0$ Hz)] of nobotanin B (**4**).[1] These findings indicate that nobotanin G (**6**) is an analog of **4** lacking an HHDP group at O-2′/O-3′.

Partial hydrolysis of **6** in hot water yielded three hydrolyzates, one of which was identified as strictinin (**2**).[4] The ^{1}H-NMR spectrum of the second hydrolyzate (**10**) [*m/z* 959 $(M+Na)^+$] indicated the presence of two galloyl groups [δ 6.81, 7.08 (each 2H, s)] and a dilactonized valoneoyl group [δ 7.19, 7.20, 7.49 (each 1H, s)]. These data and the chemical shifts of the glucose signals (see Experimental) are in agreement with those of one of the partial hydrolyzates having the structure **10**, obtained previously upon similar hydrolysis of nobotanins B (**4**) and F (**5**),[1,2] and their identity was confirmed by direct comparison. The ^{1}H-NMR spectrum of the third hydrolyzate (**11**) exhibited the proton signals due to a valoneoyl [δ 6.09, 6.70, 7.06 (each 1H, s)] and three galloyl groups [δ 6.93, 7.09, 7.20 (each 2H, s)] and two anomeric protons [δ 6.14, 5.65 (each d, $J=8.5$ Hz)], indicating that **11** is a dimer. The large upfield shifts of the H-4 (δ 3.82) and H-6 (δ3.88, 3.95) protons in **11**, relative to those of **6**, indicated that the HHDP group at O-4/O-6 in **6** was eliminated by the hydrolysis. The structure of this third hydrolyzate was therefore formulated as **11**, taking the structures of **2** and **10** into consideration.

After the positions of the acyl groups in **6** had been established in this way, the orientation of the valoneoyl group was determined with the aid of the ^{1}H–^{13}C long-range COSY as follows. Among the HHDP and valoneoyl protons, the singlets at δ 6.54 and 6.62 were assigned to the HHDP protons, based on the correlations *via* three-bond coupling with the ester carbonyl carbons

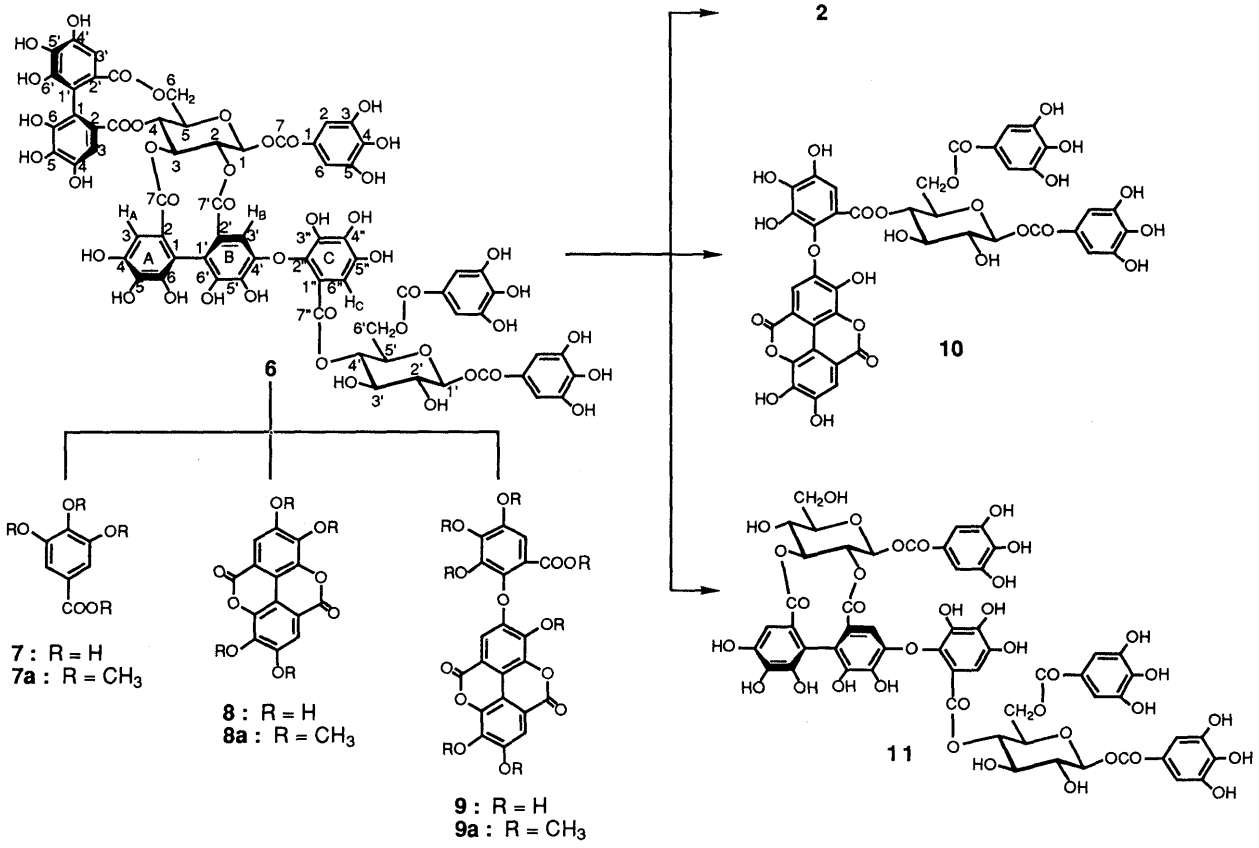


Chart 2

TABLE I. ^{1}H-NMR Data[a] for the Glucose Moieties of **4**, **6**, **12** and **13** (400 MHz, Acetone-d_6, J in Hz)

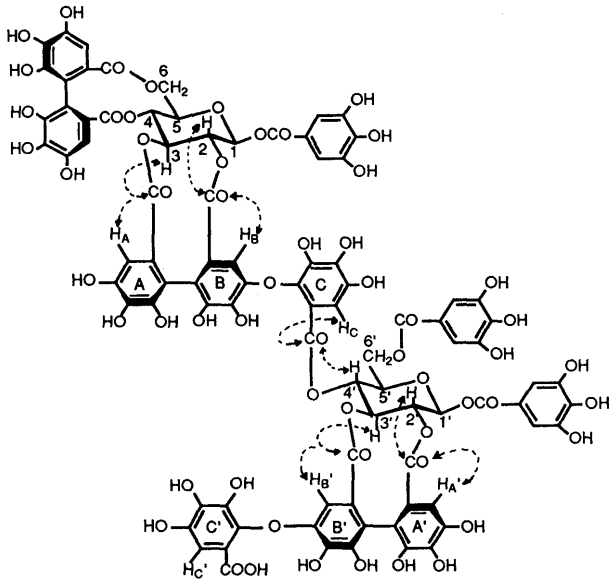
	4	**6**[b]	**12**	**13**
Glucose-I				
H-1	6.20 (d, J=8.5)	6.12 (d, J=8.5)	6.21 (d, J=9.0)	6.20 (d, J=8.5)
H-2	5.10 (dd, J=8.5, 9.0)	5.08 (t, J=8.5)	5.08 (t, J=9.0)	5.10 (dd, J=8.5, 9.0)
H-3	5.82 (dd, J=9.0, 10.0)	5.70 (dd, J=8.5, 10.0)	5.81 (dd, J=9.0, 10.0)	5.82 (dd, J=9.0, 10.0)
H-4	5.17 (t, J=10.0)	5.12 (t, J=10.0)	5.16 (t, J=10.0)	5.17 (t, J=10.0)
H-5	4.67 (dd, J=6.0, 10.0)	4.56 (dd, J=6.0, 10.0)	4.62 (br dd, J=10.0, 6.0)	4.65 (dd, J=6.0, 10.0)
H-6	5.33 (dd, J=6.0, 13.5)	5.28 (dd, J=6.0, 13.0)	5.32 (dd, J=6.0, 13.0)	5.32 (dd, J=6.0, 13.5)
	3.92 (d, J=13.5)	3.86 (d, J=13.0)	3.89 (dd, J=2.0, 13.0)	3.92 (dd, J=13.5)
Glucose-II				
H-1′	6.02 (d, J=8.5)	5.70 (d, J=8.0)	6.00 (d, J=8.5)	6.03 (d, J=8.5)
H-2′	5.18 (dd, J=8.5, 10.0)	3.64 (dd, J=8.0, 10.0)	5.13 (dd, J=8.5, 10.0)	5.17 (dd, J=8.5, 10.0)
H-3′	5.41 (t, J=10.0)	3.79 (t, J=10.0)	5.31 (t, J=10.0)	5.44 (t, J=10.0)
H-4′	5.83 (t, J=10.0)	5.43 (t, J=10.0)	5.68 (t, J=10.0)	5.83 (t, J=10.0)
H-5′	3.45 (br d, J=10.0)	3.40 (br d, J=10.0)	3.40 (br d, J=10.0)	3.41 (br d, J=10.0)
H-6′	4.92 (br d, J=13.0)	4.75 (br d, J=13.0)	4.83 (br d, J=13.0)	4.91 (br d, J=13.0)
	3.91 (dd, J=2.0, 13.0)	3.83 (dd, J=2.0, 13.0)	3.90 (dd, J=2.0, 13.0)	3.86 (br d, J=13.0)

a) Assigned by ^{1}H–^{1}H COSY. b) Measured at 500 MHz.

TABLE II. ^{1}H–^{13}C Long-Range Shift Correlation Data for Nobotanin G (**6**) (J_{CH}=6 Hz)

	Correlated *via* two or three bonds with	
δ_C 169.52 (ester)	δ_H 6.37 (Val H-3)	
δ_C 168.63 (ester)	δ_H 6.14 (Val H-3′),	δ_H 5.08 (Gluc H-2)
δ_C 165.12 (ester)	δ_H 7.08 (Val H-6″),	δ_H 5.43 (Gluc H-4′)
δ_C 167.95 (ester)	δ_H 6.54 (HHDP H-3),	δ_H 5.12 (Gluc H-4)
δ_C 168.25 (ester)	δ_H 6.62 (HHDP H-3′),	δ_H 5.28 (Gluc H-6)[a]
		δ_H 3.86 (Gluc H-6)[a]
δ_C 164.60 (ester)	δ_H 7.00 (Gal H-2, 6),	δ_H 6.12 (Gluc H-1)
δ_C 165.55 (ester)	δ_H 7.14 (Gal H-2, 6),	δ_H 4.75 (Gluc H-6′)
		δ_H 3.83 (Gluc H-6′)
δ_H 6.37 (Val H-3)	δ_C 114.85 (Val C-1),	δ_C 136.00 (Val C-5)
δ_H 6.14 (Val H-3′)	δ_C 116.64 (Val C-1′),	δ_C 147.05 (Val C-4′)
	δ_C 136.13 (Val C-5′)	
δ_H 7.08 (Val H-6″)	δ_C 135.56 (Val C-2″),	δ_C 140.21 (Val C-3″)
	δ_C 144.39 (Val C-4″)	
δ_H 6.54 (HHDP H-3)	δ_C 116.16 (HHDP C-1),	δ_C 136.53 (HHDP C-5)
δ_H 6.62 (HHDP H-3′)	δ_C 115.72 (HHDP C-1′),	δ_C 136.24 (HHDP C-5′)

a) Observed upon separate measurement with J_{CH}=8 Hz.



12

Chart 3

at δ 167.95 and 168.25, which showed cross peaks with the H-4 and H-6 signals of glucose-I, respectively. The remaining 1H singlets at δ 6.14, 6.37, 7.08 are thus due to the valoneoyl protons. The former two signals were assigned to H_B and H_A, respectively, based on a comparison of their chemical shifts with the reported data,[1] and also on their correlations through three-bond couplings with the valoneoyl C-1′ and C-1 signals at δ 116.64 and 114.85. The H_B (δ 6.14) and H_C (δ 7.08) signals showed cross peaks with the carbonyl carbon resonances at δ 168.63 and 165.12, *via* three-bond couplings. These ester carbonyl carbons were also correlated with the H-2 and H-4′ signals of the glucose residues, to establish the orientation of the valoneoyl group in **6**, which is the same as that of nobotanin B (**4**). The position of the other acyl groups have thus been confirmed, leading to the structure (**6**) for nobotanin G (Table II).

Nobotanin H (**12**) was obtained as an off-white amorphous powder with the molecular formula $C_{89}H_{60}O_{57}$ [FAB-MS m/z 2063 $(M+Na)^+$]. Acid hydrolysis of **12** with 5% sulfuric acid yielded **7**, **8**, **9** and glucose. The ^{1}H-NMR spectrum of **12** exhibited in the aromatic region three 2H singlets [δ 7.27, 7.12, 6.98] and eight 1H singlets [δ 7.19, 7.14, 6.65, 6.54, 6.48, 6.40, 6.21, 6.07], which indicated the presence of three galloyl, an HHDP and two valoneoyl groups. The glucose proton signals are closely similar to those of nobotanin B (**4**), as summarized in Table I. The structural similarity between **4** and **12** was also shown by their glucose carbon resonances in the ^{13}C-NMR spectra (Table III).

Therefore, nobotanin H (**12**) is presumed to be an analog of **4** having a valoneoyl group in place of one of the HHDP groups of **4**. The location of the valoneoyl groups at O-2/O-3 and O-2′/O-3′ of the glucose cores in **12** was determined by partial hydrolysis of **12** in hot water, yielding strictinin (**2**) and nobotanin G (**6**). The absolute configurations of the HHDP and valoneoyl groups in **12** were all *S*, as evidenced by the circular dichroism (CD) spectrum, which exhibited a strong positive Cotton effect at 225 ($[\theta]+39\times10^4$).[6]

The reversed orientation of the valoneoyl group at O-2′/O-3′ from that at O-2/O-3 as in the formula **12** was revealed by the ^{1}H–^{13}C long-range shift correlation coherence spectroscopy (COLOC) of **12**. The valoneoyl H_B and $H_{B'}$ protons were assigned to the signals at δ 6.07 and 6.21, based on their chemical shifts[1] and two-bond long-range couplings with the ethereal aromatic carbons at δ 146.70 and 146.87. The signal at δ 6.07 was correlated through three-bond long-range coupling with an ester carbonyl carbon signal at δ 168.33, which was also correlated with the glucose H-2 signal at δ 5.08, in an analogous way to that of the nobotanin G moiety. The proton signal at δ 6.21 (valoneoyl $H_{B'}$) was clearly correlated with the glucose H-3′ signal (δ 5.31) through an ester carbonyl carbon at δ 169.32. The connectivities among the valoneoyl H_A and $H_{A'}$ signals (δ 6.40, 6.54), and glucose H-3 and H-2′ were similarly shown by their correlations through the signals at δ 169.57 and 168.56. The locations of the remaining acyl groups in **12**, established by the chemical degradation as mentioned above, were also consistent with the evidence from this NMR technic as shown in Fig. 1.

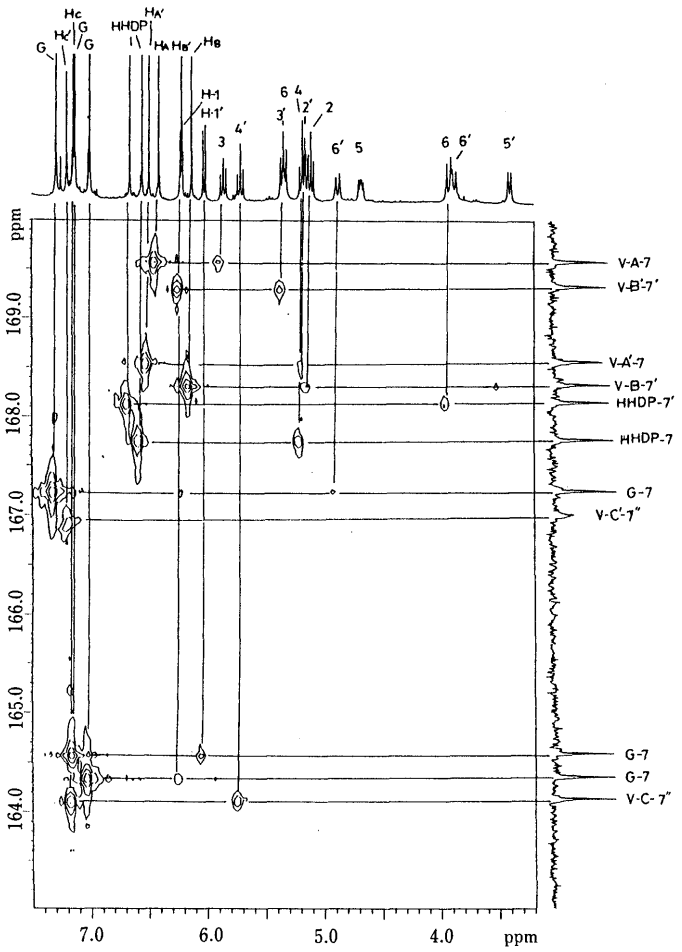


Fig. 1. COLOC Spectrum of **12**

An average J_{CH} value for two- and three-bond coupling was set at 7 Hz. V-A (A′)-7, V-B (B′)-7′, V-C (C′)-7″, HHDP-7 (7′) and G-7 mean the ester carbonyl carbon resonances of the valoneoyl A (A′)-, B (B′)- and C (C′)-rings, and of the HHDP and galloyl groups, respectively.

Nobotanin I (**13**) was also shown to be a dimer related to nobotanin H (**12**), by acid hydrolysis giving the same products (**7**, **8**, **9** and glucose) as those from **12**, and by the ^{1}H-NMR spectrum, which indicated the identity in the numbers of galloyl, HHDP and valoneoyl groups in **13** with those of **12**, as revealed by three 2H singlets [δ 7.30, 7.10,

Table III. ^{13}C-NMR Data[a] for the Glucose Moieties of **4**, **6**, **12** and **13** (100 MHz, Acetone-d_6)

	4	**6**	**12**	**13**
Glucose-I				
C-1	92.34	92.31	92.37	92.37
C-2	76.77	76.58	76.77	76.78
C-3	76.98	76.96	76.99	76.99
C-4	69.61	69.49	69.66	69.62
C-5	73.37	73.29	73.38	73.49
C-6	63.37	63.24	63.40	63.38
Glucose-II				
C-1′	92.34	92.59	92.37	92.29
C-2′	75.38	74.24	75.27	75.16
C-3′	78.07	75.20	78.02	78.53
C-4′	66.89	70.86	66.72	66.85
C-5′	73.92	73.18	73.89	73.95
C-6′	63.57	63.24	63.55	63.38

a) Assigned by ^{1}H–^{13}C COSY.

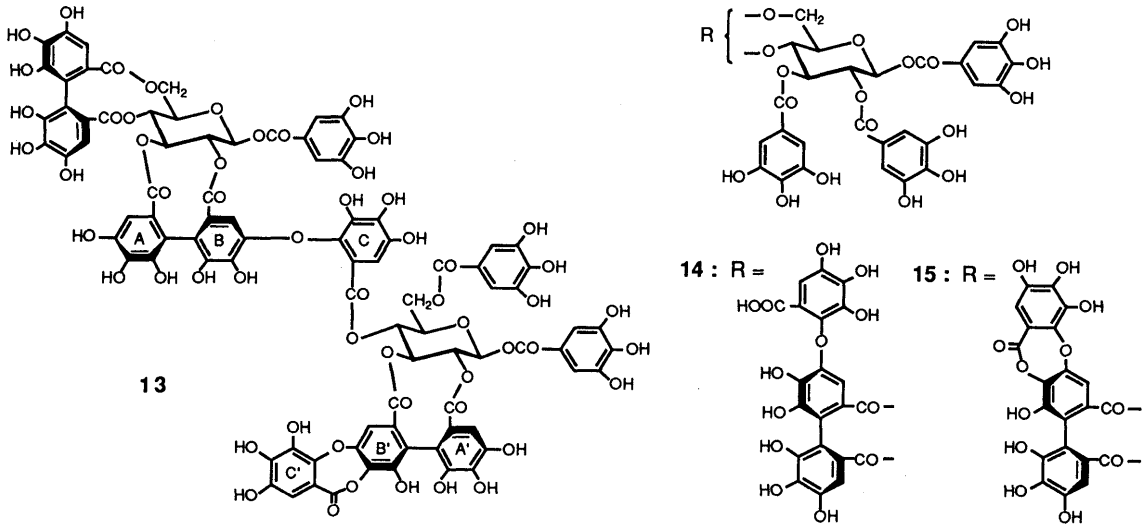


Chart 4

TABLE IV. ^{13}C Resonances for the Valoneoyl Groups of **12**, **13**, **14** and **15** (100 MHz, Acetone-d_6)

	12[a]		**13**		**14**[b]	**15**[b]
	Ring-A	Ring-A′	Ring-A	Ring-A′	Ring-A	Ring-A
C-1	114.42	116.02	114.33	114.25	115.9	114.2
C-2	126.56[c]	126.28[c]	126.58[c]	126.32[c]	125.5[c]	125.1
C-3	106.61	107.66	106.85	106.94	107.7	107.5
C-4	144.99	144.87	145.12	145.15	145.2	145.8
C-5	136.13	136.44	136.19	135.71	136.7	136.6
C-6	144.58[d]	144.42[d]	144.58[d]	144.42[d]	144.7	145.2
C-7	169.57	168.56	169.55	168.24	167.6	167.6
	Ring-B	Ring-B′	Ring-B	Ring-B′	Ring-B	Ring-B
C-1′	116.63	116.07	116.85	122.00	117.8	122.1
C-2′	126.06[c]	125.74[c]	126.09[c]	132.21	126.1[c]	132.8
C-3′	102.64	106.07	102.58	111.19	106.1	111.2
C-4′	146.70	146.87	146.84	151.65	146.8	151.7
C-5′	135,36	137.35	135.62	135.62	137.4	135.7
C-6′	145.07	144.87	145.03	148.78	144.7	148.6
C-7′	168.33	169.32	168.22	168.37	167.8	167.0
	Ring-C	Ring-C′	Ring-C	Ring-C′	Ring-C	Ring-C
C-1″	111.51	114.35	111.42	113.14	115.3	111.7
C-2″	135.50	137.63	135.65	141.37	137.5	141.3
C-3″	140.65	140.20	140.64	137.14	140.4	137.1
C-4″	139.90	140.02	140.27	143.42	139.8	143.4
C-5″	143.04	142.71	143.35	143.77	143.3	143.8
C-6″	110.29	110.50	110.05	110.52	110.1	109.9
C-7″	164.14	167.01	164.26	163.15	166.3	163.0

a) Assignments were confirmed by COLOC spectrum. *b*) Data from ref. 9 (measured at 126 MHz). *c, d*) These values are interchangeable.

7.00] and eight 1H singlets [δ 7.14, 7.03, 6.94, 6.64, 6.54, 6.49, 6.40, 6.11] in the aromatic region. The signals due to glucose residues in the ^1H- and ^{13}C-NMR spectra are also in agreement with those of nobotanin H (**12**) (Tables I and III). In an aqueous solution at 37 °C, nobotanin I (**13**) was converted almost quantitatively into nobotanin H (**12**). These data, coupled with the $(M+Na)^+$ peak at m/z 2045 (18 mass units lower than that of **12**) in FAB-MS, suggest that nobotanin I (**13**) is a lactonized form (depsidone) of **12**.

The chemical shifts of the valoneoyl proton signals of **12** differ from those of **13**, which were assigned by comparison with the HHDP and valoneoyl protons of **4**, **6** and **12**. The valoneoyl H-3′ signal, which is at δ 6.21 in **12**, shows a remarkable downfield shift to δ 7.03 (or 6.94) in **13**, while the H-6″ signal, which is at δ 7.19 in **12**, is shifted upfield [δ 6.94 (or 7.03)] in **13**. These differences are comparable to those between rugosin A (**14**)[7] and prostratin C (**15**)[8,9] [δ 6.32→7.12 (H-3′); δ 7.14→6.99 (H-6″)] or between rugosin C (**16**)[7] and its depsidone form, praecoxin C (**17**)[8] [δ 6.23→7.20 (H-3′); δ 7.09→6.95 (H-6″)].

The ^{13}C-NMR spectrum of **13** was also consistent with its structure possessing the depsidone-forming valoneoyl group. The aromatic carbon resonances of **13** were assigned by comparison with those of **12**, which were unequivocally assigned by COLOC as described above, and with those of **14** and **15**.[9] The assignments of the valoneoyl carbons are summarized in Table IV. A remarkable upfield shift of the ring-C′ carbonyl carbons in **13** relative to the corresponding signal in **12** (δ 167.01→163.15), which is analogous to that observed in **14** and **15** [δ166.3→163.0 (C-7″)],[8] was observed. The lowfield shifts of the C-4′ and C-6′ signals of the valoneoyl B′-ring [δ 146.87→151.65 (C-4′); δ 144.87→148.78 (C-5′)] are also characteristic features of the formation of the depsidone. The other carbon resonances of **13** are also similar to those of **15** (Table IV), in accord with the presence of the depsidone-forming valoneoyl group in **13**.

The absolute configurations of the HHDP and the valoneoyl groups in **13** are the same as those of **12**, since these tannins have been chemically correlated with each other as mentioned above. The structure of nobotanin I is therefore represented by the formula **13**.[10]

Nobotanin I is the first dimer possessing the depsidone-forming valoneoyl group in the molecule.

Experimental

General Instruments (ultraviolet (UV), $[\alpha]_D$, NMR and mass spectrum (MS)) and chromatographic conditions (high-performance liquid chromatography (HPLC) and column chromatography) used in this work were the same as those described in the preceding paper. ^1H–^{13}C Long-range COSY were taken on Varian VXR 500 and Bruker AM-400 instruments with an average J_{CH} value of 6, 7 or 8 Hz for two- or three-bond coupling.

Isolation of Tannins Fresh leaves (2.1 kg) of *H. roseum*, provided by the Hiroshima Botanical Garden, in August, 1985, were homogenized in 70% acetone. The filtered homogenate was concentrated and extracted with ether, EtOAc and 1-butanol, successively. The 1-butanol extract (8.1 g) was chromatographed over Diaion HP-20 with H_2O containing increasing amounts of MeOH. The 40% MeOH eluate (3.6 g) was further chromatographed on Toyopearl HW-40 (coarse grade) developing with 70% MeOH→80% MeOH→MeOH–H_2O–acetone (7:2:1→6:2:2) to yield casuarictin (**1**) (30 mg), strictinin (**2**) (16 mg), nobotanin G (**6**) (36 mg), nobotanin H (**12**) (135 mg) and nobotanin B (**4**) (301 mg). The 60% MeOH eluate was similarly subjected to rechromatography over Toyopearl HW-40 using the same solvent system as described above to afford geraniin (**3**) (11 mg), **4** (11 mg), nobotanin F (**5**) (31 mg) and nobotanin I (**13**) (11 mg). Known tannins were identified by direct comparisons of their spectral data with those of authentic samples.

Nobotanin G (6) An off-white amorphous powder, $[\alpha]_D$ +56° (c=1.0, MeOH). UV λ_{max} (MeOH) nm (log ε): 218 (5.01), 273 (4.66). FAB-MS m/z: 1593 $(M+Na)^+$. *Anal.* Calcd for $C_{68}H_{50}O_{44}\cdot 9H_2O$: C, 47.11; H, 3.92. Found: C, 47.36; H, 3.89. ^1H-NMR (500 MHz, acetone-d_6+D_2O), aromatic protons, see text; glucose protons, see Table I. ^{13}C-NMR (126 MHz, acetone-d_6+D_2O) δ: 103.00 [valoneoyl (Val) C-3′], 106.69, 107.53, 107.76 [Val C-3, HHDP C-3, C-3′], 109.97 (2C), 110.14 (4C) [galloyl (Gal) C-2, C-6], 110.47 (Val C-6″), 114.18 (Val C-1″), 114.85 (Val C-1), 116.64 (Val C-1′), 115.72 (HHDP C-1′), 116.16 (HHDP C-1), 119.63, 120.32, 121.31 (Gal C-1), 125.41, 125.64, 125.88, 126.23 (HHDP C-2, C-2′), 135.56 (Val C-2″), 136.00 (Val C-5), 136.13 (Val C-5′), 136.24 (HHDP C-5′), 136.53 (HHDP C-5), 138.90, 139.41, 139.72 (Gal C-4), 140.17, 140.21 (Val C-3″, C-4″), 143.16 (Val C-5″), 144.39, 144.54, 144.88 (2C), 144.99, 145.13, 145.17 (HHDP C-4, C-4′, C-6, C-6′, Val C-4, C-6, C-6′), 145.87 (2C), 145.93 (4C) (Gal C-3, C-5), 147.05 (Val C-4′), 164.59, 165.55, 167.21 (Gal C-7), 165.12 (Val C-7″), 168.63 (Val C-7′), 169.51 (Val C-7), 167.95 (HHDP C-7), 168.25 (HHDP C-7′); glucose carbons, see Table III.

Nobotanin H (12) An off-white amorphous powder, $[\alpha]_D$ +80° (c=0.5, MeOH). UV λ_{max} (MeOH) nm (log ε): 218 (5.16), 265 (4.83). FAB-MS: m/z 2063 $(M+Na)^+$. *Anal.* Calcd for $C_{89}H_{60}O_{57}\cdot 12H_2O$: C, 47.34; H, 3.72. Found: C, 47.11; H, 3.58. ^1H-NMR, see text and Table I. ^{13}C-NMR (100 MHz, acetone-d_6) δ: 107.33 (HHDP C-3), 108.26 (HHDP C-3′), 110.29 (6C) (Gal C-2, C-6), 114.76 (HHDP C-1), 115.95 (HHDP C-1′), 119.77, 120.10, 121.22 (Gal C-1), 125.69 (2C) (HHDP C-2, C-2′), 136.36 (HHDP C-5′), 136.63 (HHDP C-5), 139.23, 139.58, 139.85 (Gal C-4), 145.07 (HHDP C-4′), 145.10 (HHDP C-6′), 145.17 (HHDP C-4), 145.20 (HHDP C-6), 145.90 (2C), 145.94 (2C), 146.16 (2C) (Gal C-3, C-5), 164.36, 164.59, 167.24 (Gal C-7), 167.76 (HHDP C-7), 168.15 (HHDP C-7′); glucose carbons, see Table III; valoneoyl carbons, see Table IV.

Nobotanin I (13) A light brown amorphous powder, $[\alpha]_D$ +70° (c=0.5, MeOH). UV λ_{max} (MeOH) nm (log ε): 218 (5.22), 275 (4.86). FAB-MS m/z: 2045 $(M+Na)^+$. *Anal.* Calcd for $C_{89}H_{58}O_{56}\cdot 7H_2O$: C, 49.72; H, 3.35. Found: C, 49.93; H, 3.35. ^1H-NMR, see text and Table I. ^{13}C-NMR (100 MHz, acetone-d_6) δ: 107.74 (HHDP C-3), 108.10 (HHDP C-3′), 110.33 (2C), 110.36 (2C) (Gal C-2, C-6), 114.44 (HHDP C-1), 115.95

(HHDP C-1′), 119.88, 120.10, 121.32 (Gal C-1), 125.73, 125.40 (HHDP C-2, C-2′), 136.51 (HHDP C-5), 136.19 (HHDP C-5′), 139.17, 139.61, 139.88 (Gal C-4), 145.15 (HHDP C-4′), 145.19 (HHDP C-4), 145.30 (HHDP C-6), 145.77 (HHDP C-6′), 145.92, 145.96, 146.16 (Gal, C-3, C-5), 164.35, 164.54, 167.23 (Gal C-7), 167.74, 168.14 (HHDP C-7, C-7′); glucose and valoneoyl carbons, see Tables III and IV.

Acid Hydrolysis of Nobotanins G (6), H (12) and I (13) A solution of **6** (10 mg) in 5% H_2SO_4 (2 ml) was refluxed for 6 h, and after being cooled, the reaction mixture was extracted with EtOAc. The HPLC analysis of the EtOAc extract showed the presence of gallic acid (**7**), ellagic acid (**8**) and valoneoyl dilactone (**9**), as the products. HPLC conditions: YMC Pack A312 (ODS), 0.01 M phosphate buffer–EtOH–EtOAc (85 : 10 : 5), **7** t_R 1.3 min, **8** t_R 10.5 min, **9** t_R 7.5 min. Identification of these products were further confirmed by methylation of the EtOAc extract with diazomethane followed by preparative thin-layer chromatography (TLC) [SiO_2, benzene–acetone 15 : 1] to give **7a** [1.3 mg; MS *m/z* 226 (M^+)], **8a** [0.5 mg; MS *m/z* 358 (M^+)] and **9a** [0.5 mg; MS *m/z* 568 (M^+)]. The aqueous layer was neutralized with ion exchange resin (Amberlite IRA 410) and evaporated off. Glucose was detected by gas liquid chromatography (GLC) of the trimethylsilyl ether of the residue. GLC conditions: 2.5% OV-17 on Chromosorb W, column temperature, 170 °C, N_2 flow rate 50 ml/min. Acid hydrolysis of nobotanins H (**12**) and I (**13**) under similar conditions gave the same products, respectively.

Partial Hydrolysis of Nobotanin G (6) A solution of **6** (83 mg) in H_2O (80 ml) was refluxed for 25 h under an N_2 atmosphere. The concentrated reaction mixture was chromatographed over MCI-gel CHP-20P [H_2O→aqueous MeOH (10%→20%→25%→30%→35%→40%)]. The 20% MeOH eluate gave strictinin (**2**) (2 mg) and the hydrolyzate (**11**) (3 mg), while the 30% MeOH eluate furnished the hydrolyzate (**10**) (6 mg). Unreacted nobotanin G (**6**) (10 mg) was recovered from the 35% MeOH eluate.

Hydrolyzate (**10**): ^{1}H-NMR (500 MHz, acetone-d_6–D_2O) δ: 5.61 [d, J=8.2 Hz, glucose (Gluc) H-1], 5.15 (t, J=10.0 Hz, Gluc H-4), 4.11 (br d, J=11.5 Hz, Gluc H-6), 3.60 (dd, J=8.2, 9.0 Hz, Gluc H-2), 3.78—3.90 (m, Gluc H-3, H-5, H-6), aromatic protons, see text.

Hydrolyzate (**11**): A light brown amorphous powder, $[\alpha]_D$ +52° (c=0.7, MeOH), ^{1}H-NMR (500 MHz, acetone-d_6+D_2O) δ: 6.93, 7.09, 7.20 (each 2H, s, Gal), 6.09, 6.70, 7.06 (each 1H, s, Val), 6.14 (d, J=8.5 Hz, Gluc H-1), 4.90 (dd, J=8.5, 9.5 Hz, Gluc H-2), 5.41 (t, J=9.5 Hz, Gluc H-3), 3.82 (t, J=9.5 Hz, Gluc H-4), 3.88 (m, Gluc H-5 and H-6), 3.75 (dd, J=6, 12.5 Hz, Gluc H-6), 5.65 (d, J=8.5 Hz, Gluc H-1′), 3.61 (dd, J=8.5′, 9.5 Hz, Gluc H-2′), 3.71 (t, J=9.5 Hz, Gluc H-3′), 5.39 (t, J=9.5 Hz, Gluc H-4′), *ca.* 3.35 (overlapped with HDO, Gluc H-5′), 4.73 (d, J=12.5 Hz, Gluc H-6′), 3.89 (dd, J=2.0, 12.5 Hz, Gluc H-6′).

Partial Hydrolysis of Nobotanin H (12) An aqueous solution (60 ml) of **12** (60 mg) was refluxed for 9 h. The concentrated reaction mixture was subjected to column chromatography over Sephadex LH-20 development with EtOH→EtOH–MeOH (8 : 2) to give strictinin (**2**) (1.6 mg) and nobotanin G (**6**) (3 mg), which were identified by ^{1}H-NMR.

Transformation of Nobotanin I (13) into Nobotanin H (12) An aqueous solution (5 ml) of **13** (5 mg) was kept standing at 37 °C for 100 h. The HPLC analysis of the reaction mixture showed complete transformation of **13** into nobotanin H (**12**) [HPLC conditions: YMC A312 (ODS) column; 0.01 M phosphate buffer–EtOH–EtOAc (40 : 40 : 15 : 5); t_R 3.41 min]. The identity of the product with **12** was confirmed by ^{1}H-NMR spectral comparison after removal of the solvent.

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