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Studies on the Constituents of Aceraceae Plants. V.[1] Two Diarylheptanoid Glycosides and an Arylbutanol Apiosylglucoside from *Acer nikoense*[2]

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From the stem bark of *Acer nikoense* Maxim. (Aceraceae), three glycosides were isolated, namely aceroside III (**1**), $C_{30}H_{40}O_{12}$, mp 138—141°C, $[\alpha]_D$ −98.4°, aceroside VI (**2**), $C_{25}H_{32}O_8 \cdot 1/2H_2O$, mp 124—125°C, $[\alpha]_D$ −69.3°, and apiosylepirhododendrin (**3**), amorphous film ($C_{21}H_{32}O_{11}$), $[\alpha]_D$ −59.5°. On acid hydrolysis, **1** yielded acerogenin A (**4**), apiose, glucose, and a partially hydrolyzed product **2**, while **3** afforded (+)-rhododendrol (**11**), apiose, and glucose. Inspection of the carbon-13 nuclear magnetic resonance (^{13}C NMR) and the PRFT-NMR spectra of **1** and **3** disclosed that they are apiosyl-(1→6)-glucosides. The proton nuclear magnetic resonance (^1H NMR) spectral data of their permethylates (**6** and **12**) and the analytical data of methanolysis products of **6** and **12** established the structures of **1**, **2** and **3** as acerogenin A 11-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside, acerogenin A 11-*O*-*β*-D-glucopyranoside and (+)-rhododendrol 2-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-D-glucopyranoside, respectively.

Keywords——*Acer nikoense*; Aceraceae; diarylheptanoid; arylbutanol; apiosylglucoside; aceroside (III, VI); apiosylepirhododendrin; (+)-rhododendrol; PRFT-NMR

In the preceding paper,[1] we reported the results of carbon-13 nuclear magnetic resonance (^{13}C NMR) spectroscopy of diphenyl ether-type diarylheptanoids and arylbutanol derivatives isolated from a maple, *Acer nikoense* Maxim. (Aceraceae), and we successfully applied the spectral results to structure elucidation of aceroside IV, a glucoside of acerogenin C. This paper deals with the isolation and structure determination of three additional glycosides, named aceroside III (**1**), aceroside VI (**2**) and apiosylepirhododendrin (**3**), from the same source.

Aceroside III (**1**), $C_{30}H_{40}O_{12}$, mp 138—141°C, $[\alpha]_D$ −98.4°, was isolated from the ethyl acetate extract and also from the butanol extract of the stem bark and is a comparatively polar compound. It gave positive colorations with ferric chloride and diazo reagents, and showed an absorption maximum at 277 nm (log ε=3.89) in its ultraviolet (UV) spectrum. The UV maximum exhibited a bathochromic shift on addition of alkali. These findings indicated that it has a phenolic function. In the infrared (IR) spectrum, it showed strong and broad absorptions due to hydroxyl groups at 3600—3000 cm^{-1} and 1200—950 cm^{-1} and aromatic ring absorptions at 1590 and 1507 cm^{-1}, suggesting that **1** is a glycoside of an aromatic compound. In fact, it afforded acerogenin A (**4**)[4] as its aglycone on acid hydrolysis.

The ^{13}C NMR chemical shifts of aceroside III (**1**) are summarized in Table I together with those of acerogenin A (**4**), aceroside VI (**2**) (*vide infra*), and the sugar moiety of apiin (**5**), a flavonoid glycoside isolated from parsley.[5] Referring to the ^{13}C NMR spectral results for **4** and related compounds,[1] we could easily assign the chemical shifts of the genin carbons of **1** except for C-10, C-11 and C-12. Twelve signals attributable to sp^3 carbons bearing oxygen were observed. One out of the twelve is due to C-11 of the genin, and this carbon must be linked to the sugar moiety of **1** through an oxygen atom because of the presence of a phenolic function in the molecule **1**. The other eleven signals are attributable to carbons of the sugar

moiety of **1**, two of which at δ_C 103.8 (d) and 110.5 ppm (d) seem to be anomeric carbon signals of the sugar, a disaccharide. The doublet at δ_C 110.5 ppm is probably ascribable to the anomeric carbon of a furanose, since the chemical shift was observed at comparatively low field.[6] Taking into consideration the ^{13}C NMR result for **1** together with the molecular formulae of **1** and **4**, the sugar moiety of aceroside III (**1**) was concluded to be a disaccharide composed of a pentose and a hexose.

In ^{13}C NMR spectroscopy of straight chain oligosaccharides, carbons of terminal monosaccharide units have much longer spin-lattice relaxation times (T_1) than those of the inner units. By means of the partially relaxed Fourier-transform (PRFT) NMR method, carbon signals due to individual monosaccharide units can be distinguished from each other.[7] Inspection of the PRFT-NMR spectra of aceroside III (**1**) disclosed that signals at δ_C 65.4 (t), 74.8 (t), 77.4 (d), 80.1 (s), and 110.5 (d) are attributable to the terminal monosaccharide unit (longer T_1 value) of **1**. This terminal monosaccharide, a pentose, showed unique carbon signals, two triplets and one singlet, which strongly suggested that the pentose may be apiose. In fact, ^{13}C NMR signals due to the β-D-apiofuranosyl residue of apiin (**5**) showed a good correspondence with those of aceroside III (**1**) (Table I).

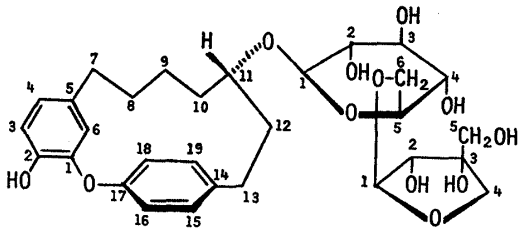
On partial hydrolysis with acetic acid, aceroside III (**1**) yielded a glucoside (**2**) of acerogenin A (**4**), $C_{25}H_{32}O_8 \cdot 1/2H_2O$, mp 124—125°C, $[\alpha]_D$ −69.3°. This glucoside (**2**) was recently found in the ethyl acetate extract from the stem bark of the maple, and is now designated as aceroside VI (**2**).

The ^{13}C NMR spectrum of aceroside VI (**2**) (Table I) in comparison with that of epirhododendrin (**10**) disclosed that the sugar portion of **2** is a β-D-glucopyranosyl residue and that C-11

TABLE I. ^{13}C Chemical Shifts (δ ppm) in C_5D_5N

	Carbon	1	2	4	5	3	10	11
Genin	1	150.6	150.6	150.7		22.4	22.2	24.2
	2	145.1	145.1	145.1		76.1	75.6	66.3
	3	117.1	117.1	117.1		39.6	39.3	42.2
	4	122.3	122.3	122.5		30.9	30.7	31.8
	5	132.5	132.5	132.8		133.2	133.1	133.3
	6	116.7	116.5	116.7		129.8	129.7	129.7
	7	32.2	32.0	32.0		116.0	116.0	115.9
	8	28.2	28.3	28.5		156.6	156.6	156.6
	9	25.1	25.2	25.3		116.0	116.0	115.9
	10	39.6	39.5	39.7		129.8	129.7	129.7
	11	78.0	77.8[a]	69.8				
	12	36.9	36.5	40.9				
	13	32.2	32.3	32.7				
	14	140.1	140.1	139.7				
	15,19	130.3	130.3	130.3				
		132.5	132.5	131.8				
	16,18	123.3	123.2	123.0				
		124.3	124.2	124.2				
	17	156.6	156.5	156.6				
Glucosyl	1	103.8	103.5		99.6	104.4	104.1	
	2	74.8	74.8		78.6	75.1	75.1	
	3	78.7	78.2[a]		77.1	78.3	78.3[a]	
	4	71.2	71.6		70.9	71.7	71.4	
	5	76.3	77.9[a]		78.3	76.7	77.9[a]	
	6	68.1	62.8		61.9	68.8	62.6	
Apiosyl	1	110.5			110.3	110.8		
	2	77.4			77.6	77.6		
	3	80.1			80.3	80.3		
	4	74.8			75.5	74.9		
	5	65.4			65.9	65.6		

a) Assignments in each column may be reversed, but those given are preferred.



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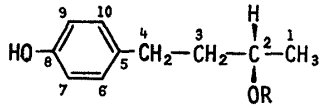
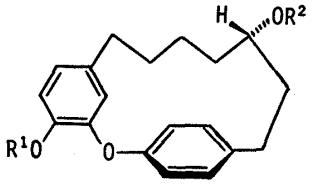


3 : R=β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl
10 : R=β-D-glucopyranosyl
11 : R=H



2 : R^1=H, R^2=β-D-glucopyranosyl
4 : R^1=R^2=H
7 : R^1=CH_3, R^2=H

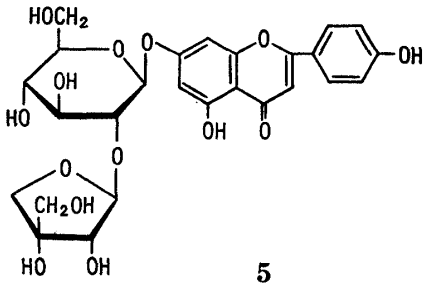


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Chart 1

of its genin appears as a doublet at δ_C 77.8 ppm [corresponding to a doublet at δ_C 78.0 ppm assignable to C-11 of aceroside III (**1**) (Table I)]. Recently Seo *et al.*[8] reported a method for determining the absolute configuration of a secondary hydroxyl group in a chiral secondary alcohol from the glucosidation shifts in ^{13}C NMR spectroscopy. Reverse application of the method to a secondary alcohol with known chirality, acerogenin A (**4**) (11*S* configuration), to determine the chemical shifts of C-10 and C-12 of **2** revealed that two triplets at δ_C 39.5 and 36.5 ppm are assignable to C-10 and C-12, respectively, in the spectrum of **2** [corresponding to the signals at 39.6 and 36.9 ppm due to C-10 and C-12 in the spectrum of aceroside III (**1**) (Table I)]. Comparison of the ^{13}C NMR spectrum of **2** with that of **1** disclosed that C-5 and C-6 of the glucosyl residue of **2** were shifted by −1.6 and +5.3 ppm, respectively, on D-apiofuranosidation of **2** to give **1**, suggesting that the sugar moiety of aceroside III (**1**) is an apiofuranosyl-(1→6)-β-D-glucopyranosyl residue.

Molecular optical rotation difference ($\Delta[M]_D$ −257°)[9a] at 589 nm between **1** and **2** suggests that the D-apiofuranosyl residue is bound as the β-anomer in the molecule **1**, because $\Delta[M]_D$ between apiin (**5**) and cosmosiin is approximately −405°[9b] and because the molecular rotations of methyl 2,3,5-tri-*O*-methyl-α- and -β-D-apiofuranosides are +239° and −163°, respectively.[9c]

The permethylate (**6**) was prepared from aceroside III (**1**) according to Hakomori's method.[10] The permethylate (**6**) exhibited, in its ^1H NMR spectrum, two one-proton doublets at δ_H 4.17 ppm (J=8 Hz) and 5.08 ppm (J=2 Hz), and seven *O*-methyl groups. The coupling constant (J=2 Hz) of one doublet confirmed that the β-anomer is due to the D-apiofuranose unit of aceroside III (**1**),[11] and the other doublet corresponds well to the β-anomeric proton of the D-glucopyranose unit of **1**. On methanolysis with 10% hydrogen chloride in dry methanol, **6** gave acerogenin A methyl ether (**7**),[4] methyl 2,3,4-tri-*O*-methyl-α- and -β-D-glucopyranosides (**8**)[12] and methyl 2,3,5-tri-*O*-methyl-D-apiofuranoside (**9**).[12]

On the basis of all the above findings, we propose the structures acerogenin A 11-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside for aceroside III (**1**) and acerogenin A 11-*O*-β-D-glucopyranoside for aceroside VI (**2**).

Another new glycoside, apiosylepirhododendrin (**3**) isolated from *Acer nikoense*, is an

amorphous substance, $[\alpha]_D$ −59.5°, and is more polar than aceroside III (**1**). It has a UV maximum at 277 nm ($E_{1\%}^{1cm}$=29.5), and this maximum shifted to 285 nm on addition of alkali. Taking into consideration its positive coloration with ferric chloride and diazo reagents, it was concluded to be a phenolic substance. On acid hydrolysis, **3** yielded (+)-rhododendrol (**11**),[13] glucose and apiose.[12] The ^{13}C NMR spectral data of **3** are summarized in Table I together with those[1] of epirhododendrin (**10**) and (+)-rhododendrol (**11**). In the ^{13}C NMR spectrum, **3** showed nineteen signals, two (δ_C 129.8 and 116.0 ppm) of which have high intensities and are due to C-6, -10 and C-7, -9, respectively. Thus, **3** is a C_{21} compound. Comparison of carbon signals attributable to the sugar moiety of **3** with those attributable to the β-D-apiofuranosyl-(1→6)-β-D-glucopyranosyl residue of aceroside III (**1**) (Table I) suggests a close similarity of the sugar portions. Inspection of the PRFT-NMR of **3** also gave the same results as in the case of aceroside III (**1**) (*vide supra*). The ^1H NMR spectral data for the permethylate (**12**) of **3** and the analytical data for the methanolysis product of **12** finally established the structure of apiosylepirhododendrin (**3**) as (+)-rhododendrol 2-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside (**3**).

Aceroside III (**1**) and apiosylepirhododendrin (**3**) are apiosylglucosides of a diarylheptanoid **4** and an arylbutanol **11**, respectively, and aceroside VI (**2**) is a glucoside of the diarylheptanoid **4**. The two apiosylglucosides are major constituents of the extract from the stem bark of *Acer nikoense*.

Experimental

All melting points were taken on a Shimadzu micro melting point determination apparatus and are uncorrected. UV and IR spectra, ^{13}C and ^1H NMR spectra, and optical rotations were measured with the machines described in the previous paper.[1] Gas-liquid chromatography (GLC) was run on a Shimadzu GC-4CM with a hydrogen flame ionization detector, and the following conditions were employed: glass column (1.5 m×3 mm), 1.5% OV-17 on Shimalite W (60—80 mesh), carrier gas N_2 (60 ml/min), column temp. 125°C. Thin-layer chromatography (TLC) was performed according to the method previously described.[1] Paper partition chromatography (PPC) was run on filter paper, Toyo Roshi No. 50, and aniline hydrogen phthalate was used as the coloring reagent. Silica gel (Kieselgel 60, 230—400 mesh, Merck), cellulose powder (Avicel, Asahi Kasei Co., Ltd.), and active charcoal powder (Wako Pure Chemical Ind., Ltd.) were used for column chromatographies. A mixture of 1% $FeCl_3$ and 1% $K_3Fe(CN)_6$ (1: 1) was used as the $FeCl_3$ reagent, and diazobenzenesulfonic acid in water was used as the diazo reagent. Analytical samples were dried *in vacuo* overnight at 50—60°C.

Materials——The EtOAc and BuOH extracts described in the experimental section of the previous paper[1] were used as source materials.

Isolation of Aceroside III (1)——A part of the BuOH extract was chromatographed on active charcoal. The column was washed successively with water, water–MeOH, MeOH, and MeOH–BuOH. Fractions on filter eluted with MeOH–BuOH (1: 1) and BuOH afforded a mixture mainly consisting of aceroside I[4] and aceroside III (**1**). The mixture was repeatedly chromatographed on silica gel using $CHCl_3$–MeOH as the developing solvent. Some fractions eluted with $CHCl_3$–MeOH (9: 1) gave a crude crystalline substance, which was recrystallized from MeOH–water to afford aceroside III (**1**), mp 138—141°C, $[\alpha]_D^{22}$ −98.4° (c= 1.1, EtOH). *Anal.* Calcd for $C_{30}H_{40}O_{12}$ (592.62): C, 60.80; H, 6.80. Found: C, 60.44; H, 6.83. IR ν_{max}^{KBr} cm^{-1}: 3400, 2940, 1590, 1520, 1510. UV λ_{max}^{EtOH} nm (log ε): 277 (3.89), (a strong end absorption). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 297 (bathochromic shift). PRFT-NMR: the intervals were 0.1, 0.075, 0.07, and 0.05 s with a recycle time of 3.5 s. $FeCl_3$ reagent: positive (blue). Diazo reagent: positive (orange). Aceroside III (**1**) was also isolated from the EtOAc extract by column chromatography on silica gel.

Hydrolysis of Aceroside III (1) with Sulfuric Acid——A mixture of **1** (100 mg) and 5% aqueous sulfuric acid (7 ml) was heated for an hour under reflux. After dilution with water, the reaction mixture was extracted with ether.

(i) The organic layer was washed with water, dried, and concentrated to give a crystalline residue. Recrystallization of the residue from MeOH afforded colorless needles (28 mg), mp 151—152°C, $[\alpha]_D^{20}$ +58.0° (c=1.0, EtOH). This compound was shown to be identical with an authentic sample of acerogenin A (**4**) on the basis of mixed mp determination and IR spectral comparison.

(ii) The aqueous layer was neutralized with dilute $Ba(OH)_2$, and then filtered in order to remove precipitates ($BaSO_4$). The filtrate was concentrated to a syrupy residue under reduced pressure. The residue was found to be a mixture of D-glucose and D-apiose. TLC: solvent, BuOH–acetone–water (4: 5: 1); Rf 0.36

(D-glucose), 0.62 (D-apiose). PPC: solvent, BuOH–acetic acid–water (6: 1: 2); *Rf* 0.22 (D-glucose), 0.35 (D-apiose).

Partial Hydrolysis of Aceroside III (1) with Acetic Acid——A mixture of **1** (510 mg) and 50% aqueous acetic acid (20 ml) was heated for 1.5 h under reflux, and then concentrated to dryness under reduced pressure. The residue was mixed with water and extracted with EtOAc. The organic layer was washed with water, and concentrated to an oily residue. The residue was chromatographed on silica gel (30 g) using $CHCl_3$–EtOH–EtOAc–water (40: 40: 110: 10). After elution of acerogenin A (**4**), the partially hydrolyzed product (**2**) was eluted. Recrystallization (twice) of the crude **2** from EtOH afforded **2**, prisms, mp 124—125°C, $[\alpha]_D^{23}$ −69.3° (c=1.0, EtOH). *Anal.* Calcd for $C_{25}H_{32}O_8 \cdot 1/2H_2O$ (469.53): C, 63.95; H, 7.08. Found: C, 64.01; H, 7.39. IR ν_{max}^{KBr} cm^{-1}: 3350, 2900, 2840, 1590, 1510, 1500.

Permethylation of Aceroside III (1)——According to Hakomori's method, NaH (1 g) was stirred with dimethyl sulfoxide (DMSO, 10 ml) at 65°C for 45 min under N_2 gas flow. Next, **1** (80 mg) in DMSO (2 ml) was added and the mixture was stirred at room temperature for an hour under N_2 gas flow. CH_3I (5 ml) was then added and the reaction mixture was allowed to stand at room temperature for 2 h with stirring. After dilution with water, the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried, and concentrated to a syrup. The syrup was repeatedly methylated by the above procedure until the IR spectrum (in CCl_4) of the reaction product showed no hydroxyl absorption between 3600—3100 cm^{-1}. The final methylation product was chromatographed on silica gel using benzene–EtOAc (20: 1) to afford an oily permethylate (**6**). High MS *m/e*: 690.3615 calcd for $C_{37}H_{54}O_{12}(M^+)$. Found: 690.3642. ^1H NMR δ ($CDCl_3$): 3.34 (3H, s), 3.41 (6H, s), 3.53 (3H, s), 3.55 (3H, s), 3.62 (3H, s), 3.95 (3H, s), 4.17 (1H, d, J=8), 5.08 (1H, d, J=2).

Methanolysis of the Permethylate (6)——A solution of **6** in 10% methanolic HCl was refluxed for 2 h. The reaction mixture was neutralized with Ag_2CO_3 and then filtered. The filtrate was concentrated *in vacuo*, and the oily residue was chromatographed on silica gel. Elution with benzene–acetone (4: 1) yielded *O*-methyl sugars and acerogenin A methyl ether (**7**) separately. The latter product (**7**), mp 123—124°C was shown to be identical with an authentic sample of **7** on the basis of mixed mp determination and TLC and ^1H NMR comparisons. The *O*-methyl sugar was found to be a mixture of methyl 2,3,4-tri-*O*-methyl-α- and -β-D-glucopyranosides (**8**) and methyl 2,3,5-*O*-methyl-D-apiofuranoside (**9**). TLC: solvent, benzene–acetone (4: 1), *Rf* 0.19 and 0.25 (**8**), 0.46 (**9**). GLC: t_R (min) 15.8 and 22.6 (**8**), 9.5 (**9**).

Isolation of Aceroside VI (2)——The EtOAc extract (10 g) was chromatographed on silica gel (500 g) using $CHCl_3$–EtOH–EtOAc–water (80: 80: 160: 23). On TLC using the same solvent, crude aceroside VI (**2**) obtained from the column chromatographic separation was detected as a single spot with a slightly higher *Rf* value than that of aceroside I.[4] On the other hand, TLC of crude **2** using $CHCl_3$–MeOH (9: 1) showed that **2** has the same *Rf* value as aceroside I and that the crude **2** was slightly contaminated with less polar aceroside IV.[1] Repeated recrystallization of the crude **2** from EtOH provided pure aceroside VI (**2**), prisms (180 mg), mp 124—125°C. This product was shown to be identical with **2** described in "Partial Hydrolysis of **1** with Acetic Acid" above, by mixed mp determination and IR, and TLC comparisons.

Isolation of Apiosylepirhododendrin (3)——The EtOAc extract was chromatographed on silica gel using 3—50% MeOH in $CHCl_3$. Elution with 12—20% MeOH in $CHCl_3$ afforded a mixture of aceroside III (**1**) and apiosylepirhododendrin (**3**). The mixture was chromatographed on cellulose powder using $CHCl_3$–MeOH (9: 1). The chromatographic fractions containing a substance more polar than aceroside III (**1**) were combined and re-chromatographed on silica gel with $CHCl_3$–MeOH (9: 1), yielding apiosylepirhododendrin (**3**) as a slightly brown-colored film, $[\alpha]_D^{30}$ −59.5° (c=2.7, EtOH). (Calculated molecular formula: $C_{21}H_{32}O_{11}$). IR ν_{max}^{KBr} cm^{-1}: 3350, 2925, 2878, 1610, 1590, 1510. UV $E_{1\%}^{1cm}$ 29.5 (maximum at 277 nm), (a strong end absorption). The maximum shifted to 285 nm on addition of aqueous NaOH. $FeCl_3$ reagent: positive (blue). Diazo reagent: positive (orange). Apiosylepirhododendrin (**3**) was also isolated from the BuOH extract by a combination of chromatographies on active charcoal powder and silica gel.

Hydrolysis of Apiosylepirhododendrin (3) with Sulfuric Acid——Apiosylepirhododendrin (**3**) (110 mg) was hydrolyzed in a manner similar to that employed in the case of aceroside III (**1**) above. The aglycone, obtained as prisms (from MeOH), mp 81—82°C, $[\alpha]_D^{18}$ +17.0° (c=1.6, EtOH), was identical with an authentic sample of (+)-rhododendrol (**11**) on the basis of mixed mp determination and IR, and TLC comparisons. The sugar fraction was found to be a mixture of D-glucose and D-apiose by TLC and PPC. (The results for the sugar fraction were the same as those obtained in "Hydrolysis of Aceroside III (**1**) with Sulfuric Acid (ii)" above).

Permethylation of Apiosylepirhododendrin (3)——Apiosylepirhododendrin (**3**) (100 mg) was methylated in a manner similar to that employed in the case of aceroside III (**1**) above. Permethylate (**12**), oil. High MS *m/e*: 558.3040 calcd for $C_{28}H_{46}O_{11}$ (M^+). Found: 558.3093. ^1H NMR δ ($CDCl_3$): 3.37, 3.44, 3.51, 3.625, 3.632, 3.78 (all s, 7×CH_3O), 4.30 (1H, d, J=7), 5.08 (1H, d, J=2).

Methanolysis of Permethylate (12)——The permethylate (**12**) (80 mg) was methanolyzed in a manner similar to that employed in the case of the permethylate (**6**) above. The methylated aglycone was confirmed to be (+)-rhododendrol methyl ether by TLC and ^1H NMR analyses. The *O*-methylated sugar was found to be a mixture of methyl 2,3,4-tri-*O*-methyl-α- and -β-D-glucopyranosides (**8**) and methyl 2,3,5-tri-*O*-methyl-D-apiofuranoside (**9**) by TLC and GLC. (The results for the *O*-methyl sugars were the same as those obtained

in "Methanolysis of the Permethylate (**6**)" above).

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