[Chem. Pharm. Bull. 31(6)1917—1922(1983)]

Studies on the Constituents of Aceraceae Plants. IV.[1] Carbon-13 Nuclear Magnetic Resonance Spectra of Acerogenin A, Rhododendrol and Related Compounds, and Structure of Aceroside IV from *Acer nikoense*[2]

MASAYOSHI KUBO,[a,3] MASAHIRO NAGAI,*,[b] and TAKAO INOUE[a]

Faculty of Pharmaceutical Sciences[a] and Institute of Medicinal Chemistry,[b] Hoshi University,[4] Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan

(Received November 16, 1982)

The assignment of chemical shifts in the carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra of acerogenin A (**1**), acerogenin B (**2**), rhododendrol (**5**) and related compounds was carried out on the basis of signal multiplicity in the off-resonance spectra, the results of proton selective decoupling, the effect of *O*-methylation of *ortho*-monosubstituted phenols on the aryl carbon shielding, and comparison with NMR data for some known compounds, including the effect of oxidation of *sec*-alcohols to the corresponding ketones on the neighboring carbon shielding. The results offer a useful means for structure elucidation of diarylheptanoids and arylbutanols analogous to **1** and **5**. The ^{13}C NMR spectrum of aceroside IV (**6**), $C_{25}H_{30}O_8$, mp 153°C, $[\alpha]_D$ −39.5°, isolated from the stem bark of *Acer nikoense* (Aceraceae) suggested that **6** is a β-D-glucopyranoside of a new diarylheptanoid, acerogenin C (**17**), $C_{19}H_{20}O_3$, mp 116°C [the ketonic derivative of acerogenin A (**1**)]. The structure of **6** was finally confirmed by chemical means.

Keywords——*Acer nikoense*; Aceraceae; diarylheptanoid; acetogenin A, B, C; aceroside IV; rhododendrol; epirhododendrin; ^{13}C NMR

Structure determinations of acerogenin A (**1**),[5] acerogenin B (**2**),[1] aceroside I (**3**),[6] and epirhododendrin (**4**),[7] isolated from the stem bark of *Acer nikoense* MAXIM. (Aceraceae), have been reported. Acerogenins A and B belong to the diarylheptanoid (C_6–C_7–C_6) class of natural products and have a diphenyl ether structure. Acerogenin A was the first reported example of a diphenyl ether-type diarylheptanoid.

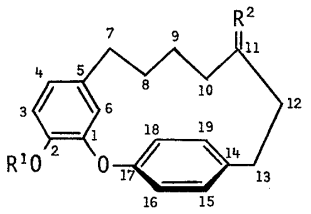
As a continuation of our study on cyclic diarylheptanoids of this type, it seemed desirable to assign the carbon-13 nuclear magnetic resonance (^{13}C NMR) signals of these compounds in order to speed up structure elucidation. This paper deals with assignment of the chemical shifts in the ^{13}C NMR spectra of acerogenin A (**1**), rhododendrol (**5**) and related compounds, and application of the results to structure elucidation of aceroside IV (**6**), a glucoside of a new cyclic diarylheptanoid isolated from the stem bark of the maple tree.

1. ^{13}C NMR Spectra of Acerogenin A (1) and Related Compounds

A ketonic derivative (**7**) of acerogenin A methyl ether (**8**) gives clearly separated signals in its ^1H NMR spectrum.[6] In the ^{13}C NMR spectrum in pyridine, the ketone (**7**) exhibited eighteen signals, two of which were observed as doublets at δ_C 123.6 and 130.9 ppm with high intensities. A singlet at δ_C 210.8 ppm and a quartet at δ_C 56.3 ppm were readily assignable to the carbonyl carbon (C-11) and the methoxyl carbon, respectively. The proton selective decoupling (PSD) technique is an established method for assigning ^{13}C resonances by connecting them with the directly-bound proton signals of known assignment. Application of the PSD technique to the ketone (**7**) led to the conclusion that the signals of the proton-bearing carbons at positions 3, 4, 6, 7, 8, 9, 10, 12, 13, 15(19), and 16(18) appear at δ_C 113.4, 122.4, 118.3, 31.6, 27.8, 20.7, 45.9, 44.3, 32.3, 130.9, and 123.6 ppm respectively. The remaining five singlets are due to quaternary sp^2 carbons (C-1, -2, -5, -14 and -17), and two of them (δ_C 133.7 and 137.4 ppm) are distinguishable from the other three (δ_C 147.4, 151.5 and 157.4 ppm), which

are attributable to oxygenated carbons, because of their chemical shifts. The singlet at the lowest field was assignable to C-17 by comparing its chemical shift (δ_C 157.4 ppm) with data on (*Z*)-1-propenyl *p*-methylphenyl ether (**9**), *p*-cresol methyl ether (**10**),[8] and 3,4-dimethoxytoluene (**11**, *vide infra*). The remaining four carbons (C-1, -2, -5 and -14) of the ketone (**7**) of acerogenin A (**1**) were not assigned.

In the ^{13}C NMR spectrum of acerogenin A (**1**), singlets at δ_C 132.8, 145.1 and 150.7 ppm correspond without doubt to those at δ_C 135.1, 147.2 and 152.1 ppm, respectively, in the spectrum of its methyl ether (**8**): *O*-methylation of **1** to **8** caused downfield shifts by 2.3, 2.1 and 1.4 ppm for the respective signals. Recently, the effect of *O*-methylation of *ortho*-monosubstituted phenols on the aryl carbon shielding in ^{13}C NMR spectroscopy was reported by Fujita, Nagai and Inoue.[9] They indicated that *O*-methylation gives rise to a downfield shift by an average of 2.5 ppm for *ipso*-carbons, an upfield shift by an average of 4.1 ppm for protonated *ortho*-carbons and a downfield shift by an average of 1.1 ppm for both *para*- and substituted *ortho*-carbons. In addition they assigned all the aryl carbon signals of 3,4-dihydroxytoluene (**12**), 3-methoxy-4-hydroxytoluene (**13**) and 3,4-dimethoxytoluene (**11**). Taking their results into consideration, the singlets at δ_C 150.7, 145.1 and 132.8 ppm in the spectrum of acerogenin A (**1**) were reasonably assigned to C-1, -2 and -5, respectively, and it follows that the singlets at δ_C 139.7 ppm for **1** and at δ_C 140.0 ppm for **8** are due to C-14. Carbon signals due to C-1, -2, -5 and -14 in the spectrum of the ketone (**7**) were determined as listed in Table I in comparison with the above assignment for those carbons of **1**.



1 : R^1=H, R^2=<H/OH

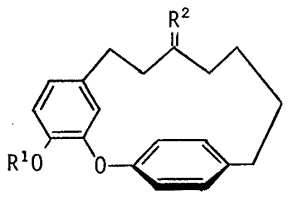
3 : R^1=β-D-glucopyranosyl, R^2=<H/OH

6 : R^1=β-D-glucopyranosyl, R^2=O

7 : R^1=CH_3, R^2=O

8 : R^1=CH_3, R^2=<H/OH

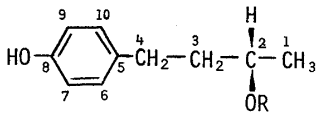
17 : R^1=H, R^2=O



2 : R^1=H, R^2=<H/OH (racemic)

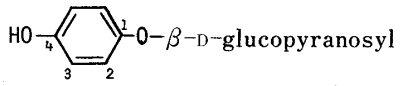
14 : R^1=CH_3, R^2=<H/OH

15 : R^1=CH_3, R^2=O



4 : R=β-D-glucopyranosyl

5 : R=H



16

Chart 1

In the ^1H NMR spectrum of acerogenin A (**1**) in pyridine-d_5,[10] 7-H_2 and 13-H_2 were observed as two multiplets at δ_H 2.24—2.52 and 2.52—2.99 ppm, respectively. Nuclear magnetic double resonance (NMDR) experiments upon irradiation of each of 11-H (δ_H 3.24—3.56 ppm) and 13-H_2 showed that 12-H_2 resonates at δ_H 1.84—2.24 ppm as a multiplet,[10] but 8-, 9- and 10-H_2 appeared at δ_H 0.68—1.48 ppm as a complex overlapping six-proton signal. PSD experiments revealed that C-7, -12 and -13 of **1** resonate at δ_C 32.0, 40.9 and 32.7 ppm,

TABLE I. ^{13}C Chemical Shifts[a]

Carbon	1	8	7	6[b]	2	14	15
1	150.7	152.1 (151.1)	151.5 (151.2)	151.7	150.7	151.9 (151.8)	151.3 (151.3)
2	145.1	147.2 (146.3)	147.4 (147.1)	145.5	145.0	146.8 (146.7)	147.1 (147.1)
3	117.1	113.3 (112.0)	113.4 (112.7)	117.4	117.1	113.1 (112.6)	113.1 (112.5)
4	122.5	122.0 (121.5)	122.4 (122.2)	122.6	122.3	122.0 (121.9)	121.5 (121.6)
5	132.8	135.1 (134.5)	133.7 (133.9)	134.9	133.2	135.3 (135.1)	134.3 (134.3)
6	116.7	116.7 (115.7)	118.3 (117.7)	118.9	116.0	116.0 (115.6)	114.4 (114.3)
7	32.0	32.1 (31.6)	31.6 (31.5)	31.7	30.7	30.8 (30.5)	27.2 (27.2)
8	28.5	28.7 (28.0)	27.8 (27.6)	27.7	37.1	37.1 (36.5)	40.7 (41.0)
9	25.3	25.6 (25.1)	20.7 (20.5)	20.7	70.6	70.7 (72.0)	208.8 (210.2)
10	39.7	39.8 (39.2)	45.9 (46.2)	45.9	39.4	39.3 (38.6)	46.0 (46.1)
11	69.8	69.7 (70.8)	210.8 (212.0)	210.8	23.0	23.0 (22.4)	19.3 (19.2)
12	40.9	41.1 (40.1)	44.3 (44.6)	44.4	28.8	28.8 (28.4)	27.5 (27.5)
13	32.7	32.8 (32.4)	32.3 (32.3)	32.2	35.2	35.3 (35.3)	35.3 (35.6)
14	139.7	140.0 (139.0)	137.4 (137.3)	137.4	139.3	139.5 (139.5)	138.4 (138.7)
15,19	130.3 131.8	130.5 (129.9) 132.0 (131.4)	130.9 (130.8)	130.6 130.9	130.7 131.8	130.9 (130.9) 131.8 (131.9)	131.5 (131.5)
16,18	123.0 124.2	123.2 (123.1) 124.4 (124.2)	123.6 (123.9)	123.6	123.3 123.5	123.4 123.5 (123.6)	123.3 (123.8)
17	156.6	156.4 (155.7)	157.4 (157.4)	157.7	156.2	155.9 (155.8)	155.0 (155.0)
OMe	—	56.4 (56.2)	56.3 (56.4)	—	—	56.3 (56.4)	56.2 (56.4)

a) δ ppm from internal tetramethylsilane (TMS) in C_5D_5N; the figures in parentheses are chemical shifts in $CDCl_3$.
b) In addition to the listed signals, compound **6** showed six signals due to the β-D-glucopyranosyl residue: 102.6 (C-1), 74.6 (C-2), 78.6 (C-3), 71.2 (C-4), 78.2 (C-5) and 62.4 (C-6).

TABLE II. ^{13}C Chemical Shifts[a]

	C-1	C-2	C-3	C-4	C-5	C-6
2-Butanol	23.4	68.5	32.6	10.5		
2-Butanone	29.2	207.9	36.6	8.0		
Δ[b]	+5.8	+139.4	+4.0	−2.5		
2-Pentanol	24.0	66.7	42.2	19.4	14.3	
2-Pentanone	29.6	207.5	45.4	17.5	13.8	
Δ[b]	+5.6	+140.8	+3.2	−1.9	−0.5	
2-Hexanol	24.0	67.0	39.6	28.5	23.1	14.2
2-Hexanone	29.6	207.5	43.2	26.1	22.4	13.9
Δ[b]	+5.6	+140.5	+3.6	−2.4	−0.7	−0.3

a) δ ppm from internal TMS in C_5D_5N; for the assignments, see ref. 11.
b) Values(Δ) calculated by subtracting the chemical shifts of the alcohol from the corresponding chemical shifts of its ketone.

respectively. On the other hand, inspection of the ^{13}C NMR data (Table II) on 2-butanol, 2-pentanol, 2-hexanol and the corresponding ketones[11] suggested that oxidation of the alcohols into the ketones caused changes in chemical shifts: C-1 and -3 (α-C's to the carbonyl at C-2) showed downfield shifts by 3.2—5.8 ppm; C-4 (β-C to the carbonyl at C-2) showed an upfield shift by 1.9—2.5 ppm. Application of this result to the chemical shifts of C-8, -9 and -10 of the ketone (**7**) led to assignment of δ_C 28.5, 25.3 and 39.7 ppm to C-8, -9 and -10, respectively, of acerogenin A (**1**).

On the basis of all the above results and discussions, the carbon chemical shifts of acerogenin A (**1**), its methyl ether (**7**) and its ketone (**8**) were determined, and are summarized in Table I.

In the ^{13}C NMR spectra of acerogenin B (**2**), its methyl ether (**14**) and its ketone (**15**), chemical shifts of the aromatic carbons were readily assigned as shown in Table I by comparing them with those for acerogenin A (**1**) and its derivatives **7** and **8**. In the spectrum of **15**, three triplets at δ_C 27.2, 35.3 and 40.7 ppm were assigned to C-7, -13 and -8 from the results of PSD experiments, and a triplet at lower field (δ_C 46.0 ppm) was assigned to C-10 (located α

to the carbonyl group at C-9). Two remaining triplets at δ_C 19.3 and 27.5 ppm, showing a large difference between their chemical shifts, must correspond to C-11 and -12. The ketone (**7**) of acerogenin A (**1**) exhibited C-8 and -9 signals at δ_C 27.8 and 20.7 ppm, respectively (Table I). Because C-8 has a position in the molecule (**7**) similar to that of C-12 in its isomeric ketone (**15**), the triplet at δ_C 27.5 ppm was assignable to C-12 of **15**, and the other at δ_C 19.3 ppm to C-11. Interpretation of the ^{13}C signals due to C-7, -8, -10, -11, -12 and -13 of acerogenin B (**2**) was carried out by referring to the effect of oxidation of the secondary alcohols to the corresponding ketones (Table II).

On the basis of the above results, the carbon chemical shifts of acerogenin B (**2**), its methyl ether (**14**) and its ketone (**15**) were assigned, as summarized in Table I.

2. ^{13}C NMR Spectra of Rhododendrol (5) and Epirhododendrin (4)

In the spectrum in pyridine-d_5, (+)-rhododendrol (**5**) showed a quartet ascribable to methyl carbon (C-1), a doublet due to methine carbon (C-2), two triplets due to methylenes at C-3 and -4, and four signals attributable to six aromatic carbons. The aromatic carbon signals were assigned with ease on the basis of an additive relationship for the effects of substituents on aryl carbon shielding.[12] PSD experiments upon irradiation of 3-H_2 (δ_H 1.92 ppm) and 4-H_2 (δ_H 2.85 ppm) showed that C-3 and -4 resonate at δ_C 42.2 and 31.8 ppm, respectively. The assignments for epirhododendrin (**4**), a β-D-glucopyranoside of **5**, were determined by referring to reported glucosidation shifts.[13] These results are listed in Table III.

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

	Carbon	**5**	**4**	Carbon	**16**
Genin	1	24.2	22.2	1	151.3
	2	66.3	75.6	2,6	116.4
	3	42.2	39.3	3,5	118.4
	4	31.8	30.7	4	153.5
	5	133.3	133.1		
	6,10	129.7	129.7		
	7,9	115.9	116.0		
	8	156.6	156.6		
Glucosyl	1		104.1		103.0
	2		75.1		74.6
	3		78.3		78.1
	4		71.4		70.9
	5		77.9		78.0
	6		62.6		62.1

3. Structure Elucidation of Aceroside IV (6)

During silica gel chromatographic separation of the ethyl acetate extract of the stem bark, aceroside IV (**6**) was isolated as a minor constituent from a fraction less polar than aceroside I (**3**). Aceroside IV (**6**), colorless needles, $C_{25}H_{30}O_8$, mp 153°C, $[\alpha]_D^{16}$ −39.5°, gave a negative coloration in the ferric chloride–potassium ferricyanide and diazo reactions. The infrared (IR) spectrum of **6** shows carbonyl absorption (1700 cm^{-1}) in addition to hydroxyl and aromatic ring absorptions.

As shown in Table I, the ^{13}C NMR spectrum of **6** revealed that the aglycone moiety was extremely similar to the ketone (**7**) of acerogenin A methyl ether (**8**) except for methyl and sugar moiety signals. The sugar moiety gave signals characteristic of a β-D-glucopyranosyl group in comparison with the signals of arbutin (**16**) listed in Table III. These results suggested that **6** is a glucopyranoside of acerogenin A ketone, a new diarylheptanoid of diphenyl ether type.

In order to confirm the above suggestion, **6** was hydrolyzed, and an aglycone named acerogenin C (**17**), $C_{19}H_{20}O_3$, mp 116°C, was obtained, while glucose was detected by thin-layer

chromatography (TLC) and paper chromatography (PPC). Acerogenin C (**17**) gave almost the same ^{1}H NMR spectrum as the ketone (**7**), except for two singlets due to a phenolic hydroxyl group at δ_H 5.55 ppm in **17** and a methyl group at δ_H 3.93 ppm in **7**.[6] Acerogenin C was finally derived into its methyl ether, mp 124—125°C, which was found to be identical with the ketone (**7**) on the basis of mixed mp, and TLC, IR and mass spectral (MS) comparisons.

Consequently, the structure of aceroside IV (**6**) was established as acerogenin C (acerogenin A ketone) β-D-glucopyranoside (Chart 1).

Aceroside IV (**6**) is a novel glucoside of a diphenyl ether–type diarylheptanoid. Diarylheptanoids are distributed in several families of plants. The proposed assignments of the chemical shifts in the ^{13}C NMR spectra of acerogenin A (**1**), acerogenin B (**2**) and related compounds should be useful for future structure elucidations of naturally occurring diarylheptanoids of diphenyl ether type.

Experimental

All melting points were taken on a Shimadzu micro melting point determination apparatus and are uncorrected. IR spectra were obtained with a Hitachi IR-215 spectrometer, and ultraviolet (UV) spectra were recorded on a Shimadzu UV-200 double beam spectrometer. ^{13}C and ^{1}H NMR spectra were taken with a JEOL JNM FX-100 spectrometer in pyridine-d_5 and $CDCl_3$ as solvents with tetramethylsilane as an internal standard. Chemical shifts are given on the δ scale (ppm) and coupling constants (J values) are expressed in Hz. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Optical rotations were determined with a JASCO DIP-181 automatic polarimeter in a dm tube. MS were measured with a JEOL JMS-300 mass spectrometer. TLC was performed on Kieselgel 60 F_{254} precoated plates (Merck), and detection was carried out by UV irradiation (254 nm) and by spraying 10% H_2SO_4 followed by heating.

Extraction and Fractionation——The dried stem bark (5 kg) of *Acer nikoense* was cut into small pieces and extracted seven times with MeOH under reflux. The MeOH extract (709 g) was mixed with hot water (1.5 l). After cooling, the mixture in a separatory funnel was extracted successively with ether, EtOAc and BuOH to afford the ether extract (94 g), EtOAc extract (220 g) and BuOH extract (290 g).

Isolation of Aceroside IV (6)——A part of the EtOAc extract was chromatographed on silica gel using $CHCl_3$–MeOH (9: 1) to give a fraction containing mainly aceroside I (**3**). Since TLC of this fraction showed that it contained compounds less polar than aceroside I (**3**), the fraction was re-chromatographed in order to separate these compounds from each other, affording aceroside IV (**6**) and subsequently a mixture of aceroside I (**3**) and another new glycoside, aceroside VI.[14] Crude aceroside IV (**6**) was purified by repeated chromatography on silica gel, and recrystallization from MeOH provided **6** as colorless needles, mp 153°C, $[\alpha]_D^{16}$ −39.5° (c=1.0, EtOH). *Anal.* Calcd for $C_{25}H_{30}O_8$: C, 65.49; H, 6.60. Found: C, 65.60; H, 6.62. IR ν_{max}^{KBr} cm^{-1}: 3400, 2930, 2875, 1700, 1587, 1510, 1500. UV λ_{max}^{EtOH} nm (log ε): 273 (3.99). UV $\lambda_{max}^{EtOH+NaOH}$ nm: unchanged. TLC: solvent, $CHCl_3$–MeOH (6: 1); *Rf* 0.48.

Hydrolysis of Aceroside IV (6)——A solution of **6** (10 mg) in MeOH (3 ml) was treated with 10% HCl (3 ml), and the mixture was refluxed for 2 h. After cooling, the reaction mixture was diluted with water (20 ml) and extracted with ether and then with EtOAc. The organic layers were combined and concentrated *in vacuo*. The residue was recrystallized from MeOH to give acerogenin C (**17**) as colorless needles, mp 116°C, $[\alpha]_D^{20}$ ±0° (c=1.0, EtOH). High MS *m/e*: Calcd for $C_{19}H_{20}O_3$(M$^+$) 296.1410. Found: 296.1408. IR ν_{max}^{KBr} cm^{-1}: 3400, 2925, 2850, 1700, 1590, 1510, 1500. UV λ_{max}^{EtOH} nm (log ε): 275 (3.838). UV $\lambda_{max}^{EtOH+NaOH}$ nm: 297 (bathochromic shift). ^{1}H NMR δ ($CDCl_3$): 1.09 (m, 9-H_2), 1.37 (m, 8-H_2), 1.90 (m, 10-H_2), 2.44 (m, 7-H_2), 2.61 (m, 12-H_2), 2.96 (m, 13-H_2), 5.55 (s, 2-OH), 5.64 (d, J=2, 6-H), 6.63 (dd, J=2 and 8, 4-H), 6.85 (d, J=8, 3-H), 6.99 and 7.19 (AA′BB′ q, J=9, 16(18)- and 15(19)-H_4). The aqueous layer was neutralized with Ag_2CO_3 and concentrated *in vacuo*. Glucose was detected in the residue by TLC and PPC. TLC: solvent, BuOH–acetone–H_2O (4: 1: 2); *Rf* 0.49 (glucose). PPC: paper, Toyo Roshi No. 50; solvent, BuOH–AcOH–H_2O (6: 1: 2); coloring reagent, aniline hydrogen phthalate; *Rf* 0.22 (glucose).

Methylation of Acerogenin C (17)——An excess of dimethyl sulfate was added to a solution of **17** (10 mg) in 10% NaOH. The solution was stirred for 5 min and the resulting precipitates were extracted with ether. The ether layer was dried and concentrated. The residue was recrystallized from MeOH to give the methyl ether as colorless needles (7 mg), mp 124—125°C; this product was found to be identical with the ketone (**7**) derived from acerogenin A (**1**) by mixed mp determination, and TLC, IR and MS comparisons.

Acknowledgement The authors are indebted to Mr. K. Higashiyama for measuring the NMR spectra. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, which is gratefully acknowledged.

References and Notes

1) Part III: M. Kubo, T. Inoue, and M. Nagai, *Chem. Pharm. Bull.*, **28**, 1300 (1980).
2) This work was presented at the 22nd Symposium on the Chemistry of Natural Products, Fukuoka, Oct. 1979. An amendment is proposed in this paper to the assignments of some ^{13}C chemical shifts described in the Abstracts of Papers reported at the Symposium.
3) Present address: *Tsumura Laboratory, Izumi-Honcho 1-9-9, Komae-shi, Tokyo 201, Japan.*
4) Formerly *Hoshi College of Pharmacy.*
5) M. Nagai, M. Kubo, M. Fujita, T. Inoue, and M. Matsuo, *J. Chem. Soc., Chem. Commun.*, **1976**, 338.
6) M. Nagai, M. Kubo, M. Fujita, T. Inoue, and M. Matsuo, *Chem. Pharm. Bull.*, **26**, 2805 (1978).
7) T. Inoue, Y. Ishidate, M. Fujita, M. Kubo, M. Fukushima, and M. Nagai, *Yakugaku Zasshi*, **98**, 41 (1978).
8) Aromatic carbon chemical shifts: **9** in $CDCl_3$, 156.0 (C-1), 116.3 (C-2), 130.5 (C-3), 131.7 (C-4) ("^{13}C FT NMR Spectra," Vol. 1, The Application Laboratory of JEOL Analytical Instrument Division, p. 10); **10** in C_5D_5N, 158.2 (C-1), 114.3 (C-2), 130.3 (C-3), 129.8 (C-4).
9) M. Fujita, M. Nagai, and T. Inoue, *Chem. Pharm. Bull.*, **30**, 1151 (1982). Aromatic carbon chemical shifts of **11** in DMSO-d_6: 129.7 (C-1), 112.9 (C-2), 148.6 (C-3), 146.7 (C-4), 111.9 (C-5), 120.6 (C-6).
10) In reference 6 (Experimental section), the chemical shifts of 10-H_2 and 12-H_2 of **1** were erroneously reported, and the assignments should be reversed.
11) *a*) ^{13}C Chemical shifts for 2-methylbutane and 2-methylpentane were reported by D.M. Grant and E.G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964); *b*) ^{13}C Chemical shifts for 2-methylhexane were calculated according to L.P. Lindeman and J.Q. Adams, *Anal. Chem.*, **43**, 1245 (1971) [ref. 11*c*, pp. 50—55]; *c*) ^{13}C Chemical shifts for 2-butanol, 2-pentanol and 2-hexanol were calculated from those for the above three 2-methylalkanes on the basis of chemical shift changes on replacement of a methyl group by a polar substituent described in "Carbon-13 Nuclear Magnetic Resonance Spectroscopy," 2nd. ed., G.C. Levy, R.L. Lichter, and G.L. Nelson, John Wiley and Sons, New York, 1980, p. 58 and 62.
12) P.C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1846 (1961); *idem*, *J. Chem. Phys.*, **38**, 1432 (1963).
13) S. Seo, Y. Tomita, K. Tori, and Y. Yoshimura, *J. Am. Chem. Soc.*, **100**, 3331 (1978); R. Kasai, M. Suzuo, J. Asakawa, and O. Tanaka, *Tetrahedron Lett.*, **1977**, 175.
14) Isolation and structure elucidation of aceroside VI are to be described in the accompanying paper (Studies on the Constituents of Aceraceae Plants. V).