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# Tannins and Related Compounds. XIX.[1] Eight New Gallotannins Containing a Proto-quercitol Core from *Quercus stenophylla* MAKINO. (3)

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By a combination of adsorption and partition chromatography, eight new proto-quercitol gallates (compounds **1**—**8**) have been isolated from the tannin fraction of the bark of *Quercus stenophylla* MAKINO (Fagaceae). Their structures have been characterized mainly by $^1$H-NMR examinations combined with the spin-decoupling techniques as 4,5-di-*O*-gallate (**1**), 3,4,5-tri-*O*-gallate (**2**), 2,4,5-tri-*O*-gallate (**3**), 1,4,5-tri-*O*-gallate (**4**), 1,3,5-tri-*O*-gallate (**5**), 1,3,4,5-tetra-*O*-gallate (**6**), 1,2,4,5-tetra-*O*-gallate (**7**) and 1,2,3,4,5-penta-*O*-gallate (**8**) of proto-quercitol (desoxy-inositol).

**Keywords**——*Quercus stenophylla*; Fagaceae; gallotannin; proto-quercitol gallate; tannase; $^1$H-NMR; spin-decoupling

In previous papers[1,3] on the polyphenolic constituents in the bark of *Quercus stenophylla* MAKINO (Fagaceae), we reported the isolation and structural elucidation of 4′-hydroxy- and 3′,4′-dihydroxyphenethyl alcohol 1-*O*-β-D-glucosides which contain galloyl and hexahydroxydiphenoyl groups in the molecule. Our continuing examination of the tannin ingredients occurring in this plant source has now led to the isolation of eight new proto-quercitol gallates (**1**—**8**). This paper describes the structure determination of these compounds.

By a combination of Sephadex LH-20, Diaion HP-20 and preparative-scale high-performance liquid chromatography (HPLC), compounds **1**—**8** were isolated from the ethyl acetate-soluble portion of the aqueous acetone extract. The homogeneity of these compounds was established by thin-layer chromatography (TLC) and HPLC, and by proton nuclear magnetic resonance ($^1$H-NMR) analysis.

Compound **1** (**1**), a white amorphous powder, $[\alpha]_D$ −107.2°, $C_{20}H_{20}O_{13}\cdot 1/2H_2O$, gave, with the ferric chloride reagent, a blue coloration characteristic of gallotannins. The $^1$H-NMR spectrum of **1** indicated the presence of two galloyl groups ($\delta$ 6.98 and 7.04, each 2H, s). On enzymatic hydrolysis with tannase, **1** furnished gallic acid and a crystalline hydrolysate (**1a**), mp 230—235 °C, $[\alpha]_D$ +27.9° ($H_2O$). The carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum of **1a** showed signals attributable to one methylene ($\delta$ 35.9, t) and five hydroxy-bearing methine carbons ($\delta$ 71.2, 71.5, 73.6, 74.9, 77.2, each d). Since **1a** was negative to the aniline-hydrogen phthalate reagent and no anomeric signal was observed in the $^1$H- and $^{13}$C-NMR spectra, **1a** was presumed to be a pentahydroxycyclohexane. This was further supported by the appearance of the intense molecular ion peak at *m/z* 164 in the field desorption mass spectrum (FD-MS). Only two pentahydroxycyclohexanes, *i.e.* proto-quercitol (desoxy-inositol) and viburnitol (desoxy-*myo*-inositol) have previously been found in plants, and by comparison of the physical data, **1a** was identified as proto-quercitol, which is a common constituent of plants of the genus *Quercus*, and had previously been isolated from the leaves of this plant.[4]

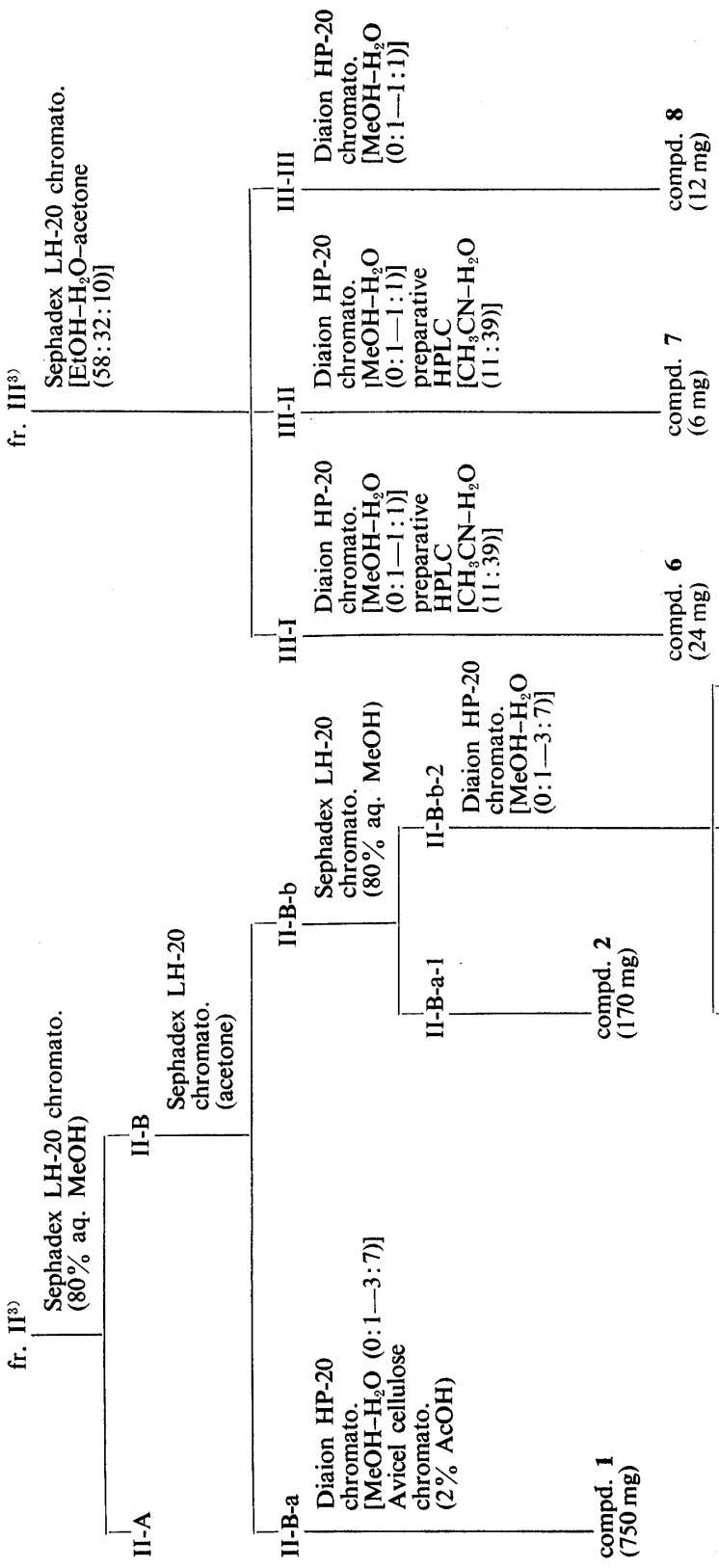
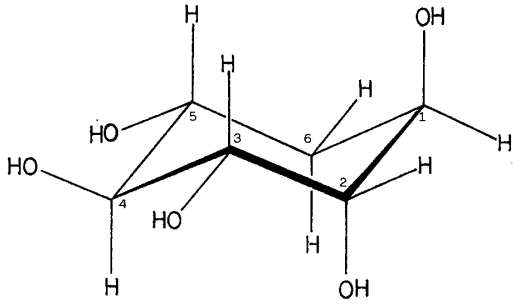
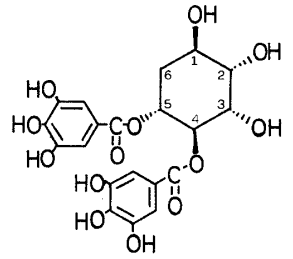



Chart 1



**1a**

Chart 2



**1**

Chart 3

The locations of the two galloyl groups on the cyclohexane nucleus were determined as follows; in the $^1$H-NMR spectrum of **1**, signals due to methines bearing galloyl groups appeared downfield as a triplet ($\delta$ 5.60, $J=10$ Hz) and a multiplet ($\delta$ 5.43). The former triplet signal could be assigned to the C(4)-axial proton on the basis of its large coupling constant (the neighboring C(3)- and C(5)-protons both possess axial orientations). The latter signal was considered to be due to the C(5)-axial proton owing to its multiplicity with a large half-width value, and this was confirmed by a spin-decoupling experiment in dimethylsulfoxide-$d_6$ solution. On irradiation at the frequency of the C(6)-methylene signals ($\delta$ 1.92), this multiplet signal changed into a doublet having a large coupling constant ($J=10$ Hz). Since the C(1)-proton, which was also coupled with the C(6)-methylene, has an equatorial orientation, this multiplet was assignable to the C(5)-proton. On the basis of above-mentioned results, the structure of **1** was characterized as 4,5-di-*O*-galloyl proto-quercitol.

Compounds **2** (**2**), colorless needles, mp 255—258 °C, $[\alpha]_D$ −10.5° (acetone), $C_{27}H_{24}O_{17}\cdot H_2O$, **3** (**3**), colorless granules, mp 207—210 °C, $[\alpha]_D$ +15.0° (acetone), $C_{27}H_{24}O_{17}\cdot 9/2H_2O$, **4** (**4**), colorless granules, mp 219—223 °C, $[\alpha]_D$ +39.1° (MeOH), $C_{27}H_{24}O_{17}\cdot 3/2H_2O$ and **5** (**5**), colorless needles, mp 222—224 °C, $[\alpha]_D$ −11.9° (acetone), $C_{27}H_{24}O_{17}\cdot H_2O$, liberated gallic acid and proto-quercitol (**1a**) on treatment with tannase. The $^1$H-NMR spectra (Figs. 1, 2, 3 and 4) of **2**, **3**, **4** and **5** showed the occurrence of three galloyl groups in each molecule. In additon, three low-field signals corresponding to methine protons geminal to the galloyl groups were observed in each spectrum. The appearance of a low-field triplet attributable to the C(4)-proton in **2**, **3** and **4** clearly indicated the location of a galloyl group at this position, while in **5** a triplet appearing at higher field indicated the absence of a galloyl group at the C(4)-position. Since the C(1)- and C(2)-protons in the proto-quercitol moiety have equatorial orientations, these signals may appear as multiplets having small coupling constants. Based on this consideration coupled with the observations in the spin-decoupling experiments shown in Fig. 1, two upfield multiplets in **2** were assigned to the C(1)- and C(2)-protons, and hence the structure of **2** was concluded to be 3,4,5-tri-*O*-galloyl proto-quercitol. Similar upfield multiplets at $\delta$ 4.22 in **3** and $\delta$ 4.34 in **5** were attributed to the C(1)- and C(2)-protons, respectively, on the basis of a spin-decoupling experiment which demonstrated coupling between this multiplet and C(6)-methylene signals only in the former case (Figs. 2 and 4). A double-doublet signal at $\delta$ 4.44 in **3** was assigned to the C(3)-proton since this signal was shown by the spin-decoupling experiment (Fig. 2) to be coupled with a triplet at $\delta$ 5.77 due to the C(4)-proton, and not to be coupled with the C(6)-methylene signals. Based upon the evidence mentioned above, the structures of **3** and **5** were characterized as 2,4,5- and 1,3,5-tri-*O*-galloyl proto-quercitols, respectively. The assignments of $^1$H-NMR signals of **4** (in acetone-$d_6$ solution) could not be made owing to the overlapping of signals. However, in pyridine-$d_5$ solution, clearly defined signals corresponding to proto-quercitol methine protons were observed, and each signal was assigned by means of spin-decoupling techniques, as shown in Fig. 3. The appearance of signals due to the C(1)-, C(4)- and C(5)-

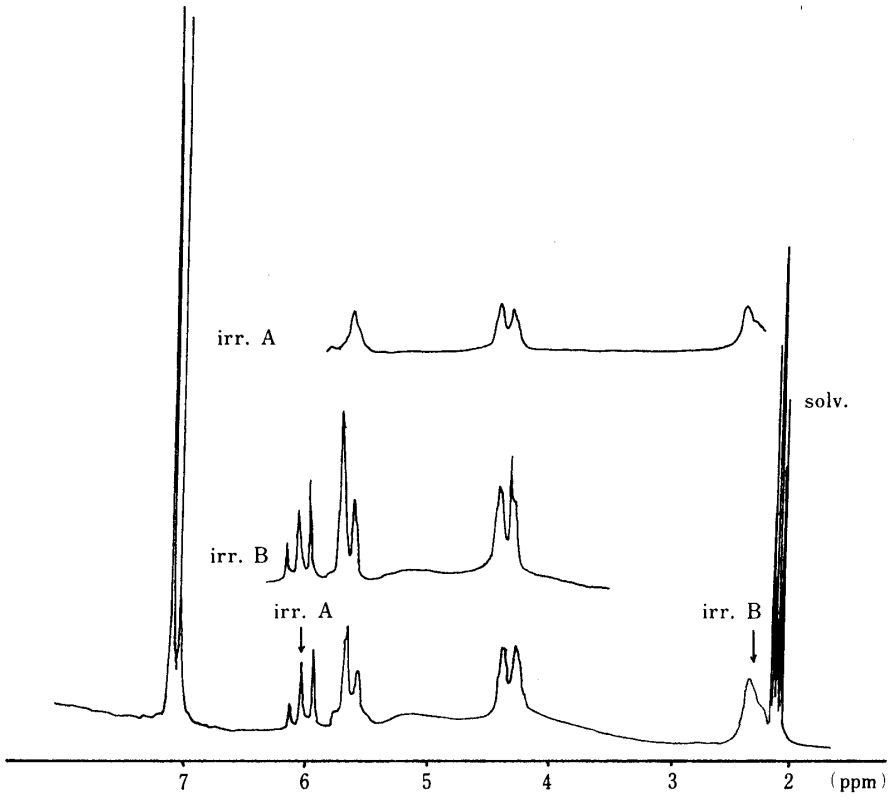



Fig. 1. 100 MHz $^1$H-NMR Spectrum (Spin-decoupled) of Compound **2** (in Acetone-$d_6$)

"irr." indicates irradiation.

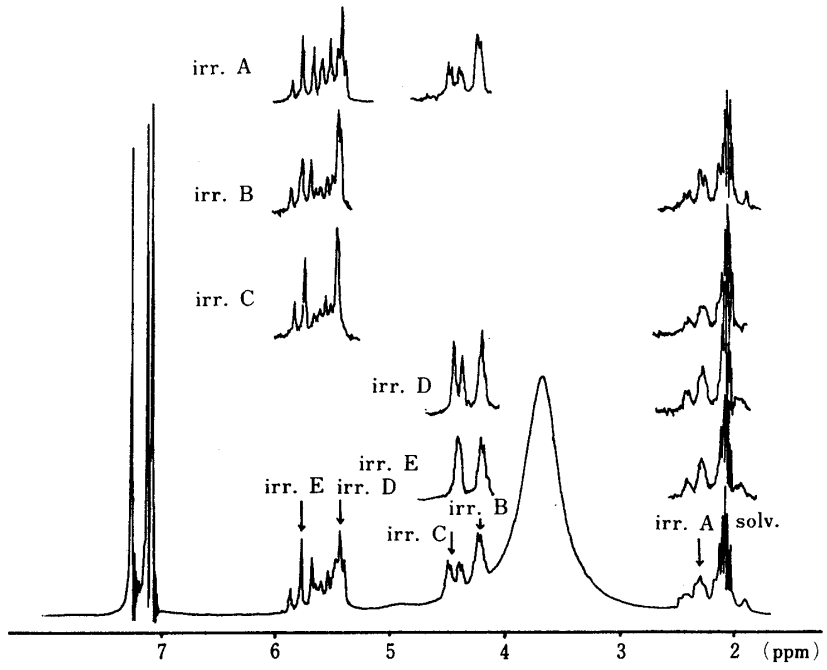



Fig. 2. 100 MHz $^1$H-NMR Spectrum (Spin-decoupled) of Compound **3** (in Acetone-$d_6$)

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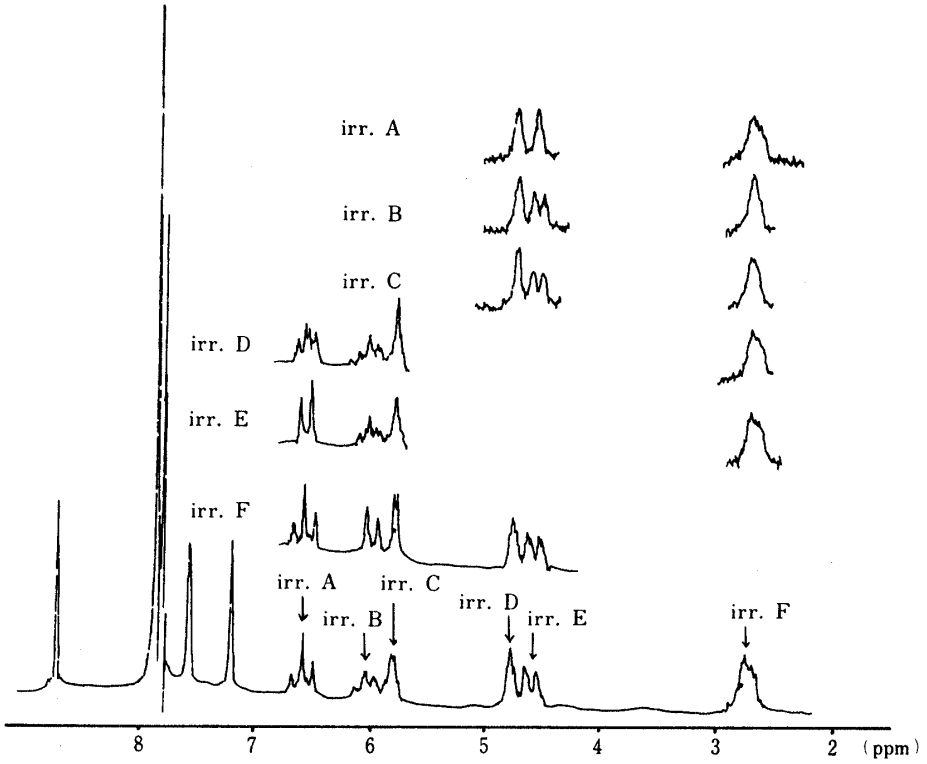



Fig. 3. 100 MHz $^1$H-NMR Spectrum (Spin-decoupled) of Compound **4** (in Pyridine-$d_5$)

"irr." indicates irradiation.

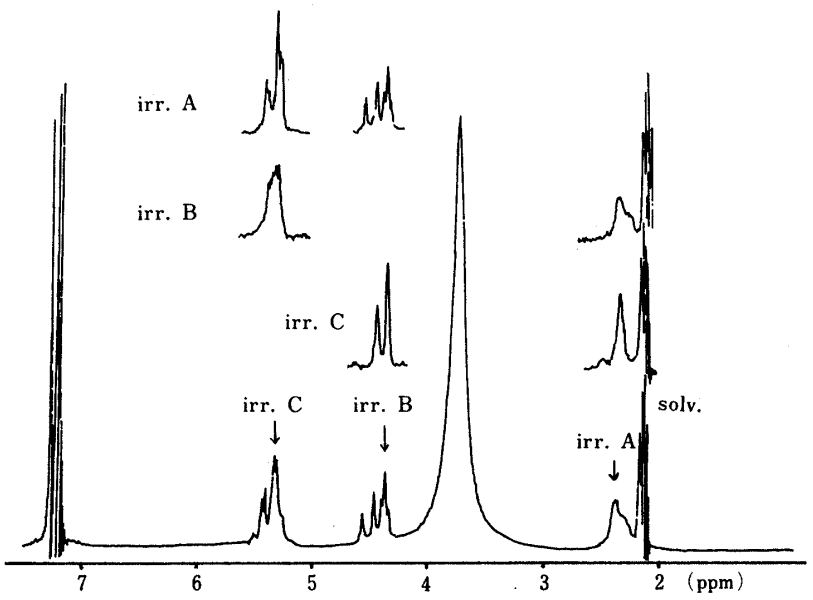



Fig. 4. 100 MHz $^1$H-NMR Spectrum (Spin-decoupled) of Compound **5** (in Acetone-$d_6$)

"irr." indicates irradiation.

protons at lower field indicated the presence of galloyl groups at these positions, and hence the structure of **4** was concluded to be 1,4,5-tri-*O*-galloyl proto-quercitol.

Compounds **6** (**6**), an off-white amorphous powder, $[\alpha]_D$ $-2.7°$ (MeOH), $C_{34}H_{28}O_{21}\cdot 5H_5O$ and **7** (**7**), an off-white amorphous powder, $[\alpha]_D$ $+34.3°$ (MeOH),

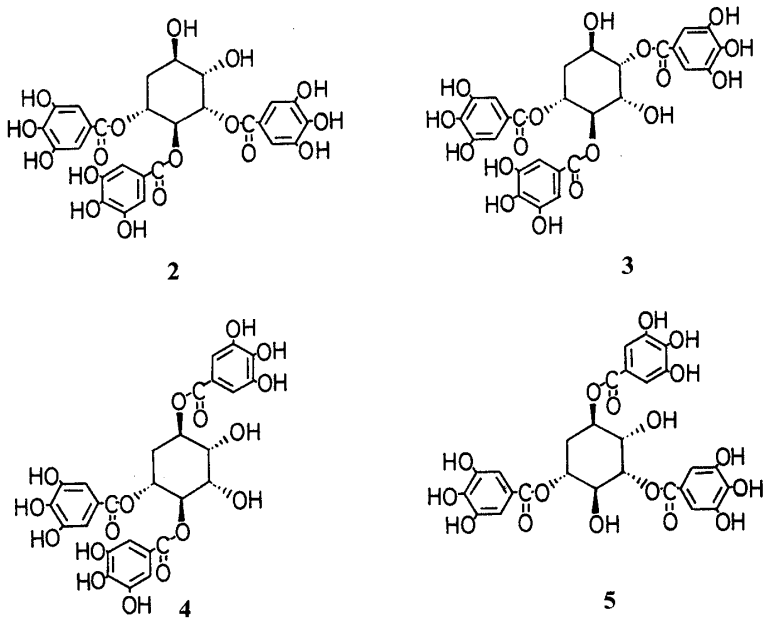


Chart 4

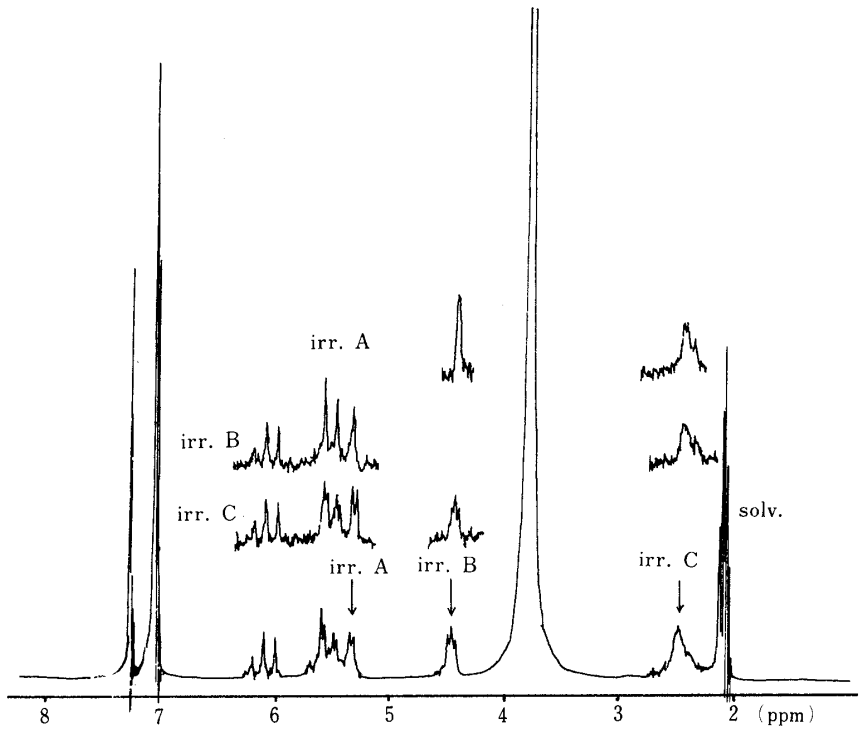
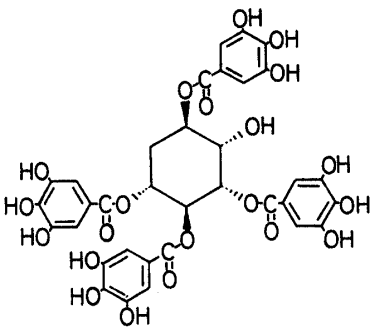



Fig. 5. 100 MHz $^1$H-NMR Spectrum (Spin-decoupled) of Compound **6** (in Acetone-$d_6$ + $D_2O$)

"irr." indicates irradiation.

$C_{34}H_{28}O_{21} \cdot 5H_2O$, each contained four galloyl groups and a proto-quercitol moiety as revealed by $^1$H-NMR analysis and hydrolytic studies. The $^1$H-NMR spectra of **6** and **7** were closely related to each other, showing four lowfield signals attributable to protons geminal to the galloyl groups and one upfield signal due to a methine proton attached to a non-acylated carbon. The locations of the galloyl groups in **6** were determined by means of spin-decoupling experiments as shown in Fig. 5. Upon irradiation at the frequency of the C(6)-methylene signals ($\delta$ 2.48), the upfield multiplet signal at $\delta$ 4.46 did not change, whereas a multiplet at



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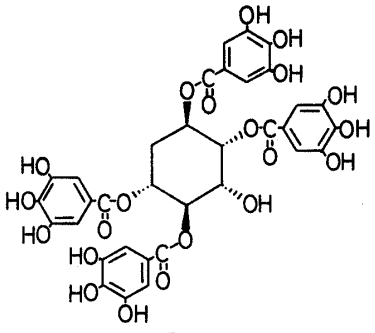

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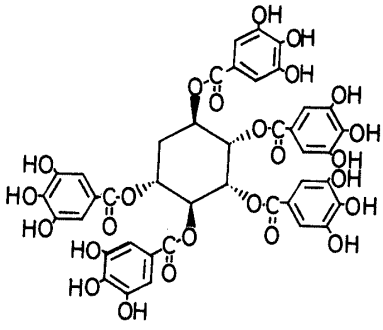
Chart 5



8

Chart 6

TABLE I. $^{13}$C-NMR Spectral Data for Compounds **1**—**6**[a] and **1a**[b]

| | **1a** | **1** | **2** | **3** | **4** | **5** | **6** |
|---|---|---|---|---|---|---|---|
| Proto-quercitol | | | | | | | |
| C-6 | 35.9 (t) | 37.7 (t) | 32.3 (t) | 33.3 (t) | 30.29 (t) | 29.8 (t) | 29.4 (t) |
| C-1—5[c] | 71.2 (d) | 69.4 (d) | 69.3 (d) | 66.6 (d) | 71.1 (3C, d) | 68.7 (d) | 68.7 (d) |
| | 71.5 (d) | 70.7 (d) | 71.0 (d) | 68.6 (d) | 71.9 (d) | 70.4 (d) | 70.8 (d) |
| | 73.6 (d) | 71.4 (d) | 71.2 (d) | 71.3 (d) | 75.0 (d) | 72.2 (d) | 72.0 (d) |
| | 74.9 (d) | 73.9 (d) | 72.3 (d) | 75.6 (d) | | 73.4 (d) | 73.0 (2C, d) |
| | 77.2 (d) | 75.6 (d) | 73.2 (d) | 75.8 (d) | | 75.5 (d) | |
| Galloyl | | | | | | | |
| C-1 | | 121.1 | 120.5 (3C) | 120.9 | 120.9 (2C) | 120.9 | 120.1 (4C) |
| | | 121.3 | | 121.1 (2C) | 121.3 | 121.4 (2C) | |
| C-2 | | 109.7 | 109.7 (3C) | 110.0 (3C) | 110.0 (3C) | 110.0 (2C) | 110.0 (4C) |
| | | 109.8 | | | | 110.2 | |
| C-3 | | 145.8 (2C) | 145.5 (3C) | 145.9 (3C) | 145.9 (2C) | 145.9 (2C) | 145.8 (3C) |
| | | | | | 146.2 | 146.2 | 146.2 |
| C-4 | | 138.9 (2C) | 138.9 (3C) | 139.1 (2C) | 139.0 | 139.1 (2C) | 139.8 (3C) |
| | | | | 139.3 | 139.1 | 139.4 | 140.1 |
| | | | | | 139.4 | | |
| –COO– | | 166.6 | 166.5 (2C) | 166.7 | 166.1 | 166.1 | 166.3 |
| | | 167.4 | 167.1 | 166.8 | 166.6 | 166.9 | 166.7 |
| | | | | 167.6 | 167.6 | 167.1 | 166.8 |
| | | | | | | | 167.5 |

*a*) Measured in acetone-$d_6$ + $D_2O$ with tetramethylsilane as an internal standard.
*b*) Measured in $D_2O$ with sodium 2,2-dimethyl-2-silapentane-5-sulfonate as an internal standard.
*c*) Signals were not individually assigned.

lower field ($\delta$ 5.32) changed into a doublet ($J$ = 4 Hz). Since these two multiplets were shown to be coupled with each other, this observation clearly indicated the multiplet at $\delta$ 4.46 was attributable to the C(2)-proton. Consequently, the C(2)-position in the proto-quercitol moiety lacked a galloyl group, and the structure of **6** was established to be 1,3,4,5-tetra-*O*-galloyl proto-quercitol. The signal appearing at higher field ($\delta$ 4.50, dd, $J$ = 3, 9 Hz) in the $^1$H-NMR spectrum of **7** was assigned to the C(3)-proton on the basis of its coupling pattern (analogous to that found in **3**), thus establishing the structure of **7** as 1,2,4,5-tetra-*O*-galloyl proto-quercitol.

Compound **8** (**8**), an off-white amorphous powder, $[\alpha]_D$ +9.9° (acetone), $C_{41}H_{32}O_{25} \cdot 4H_2O$, was obtained in a small quantity. On enzymatic hydrolysis with tannase, **8** yielded gallic acid and proto-quercitol. The $^1$H-NMR spectrum of **8** showed the presence of five galloyl groups [$\delta$ 6.97 (2H), 7.00 (4H) and 7.06 (4H)] and five methine protons attached to carbons bearing galloyl groups ($\delta$ 5.4—6.0), thus indicating the structure of **8** to be 1,2,3,4,5-

penta-*O*-galloyl proto-quercitol.

Gallotannins have been reported to consist of gallic acid and a variety of polyols such as D-glucose,[5] D-hamamelose,[6] 1,5-anhydro-D-glucitol,[7] methyl glucoside,[8] salidroside[1,3] and quinic acid,[9] and compounds **1**—**8** represent a new class of gallotannins possessing a proto-quercitol moiety.

## Experimental

The instruments and chromatographic conditions used throughout this work were the same as described in the preceding paper[1] except for the following. For cellulose column chromatography and for the detection of a polyalcohol on TLC plates, Avicel micro-crystalline cellulose (Funakoshi) and ammoniacal silver nitrate spray reagent were used, respectively. For HPLC analysis, a Toyo Soda apparatus equipped with an SP 8700 solvent delivery system and a UV-8 model II spectrometer, and a TSK-410 column (4 mm i.d. × 300 mm) were used [mobile phase: $CH_3CN$–50 mM aqueous $NaH_2PO_4$ (11 : 39)]. For preparative-scale HPLC, a TSK-410 column (25 mm i.d. × 300 mm) connected with a Toyo Soda RT-8 differential refractometer was employed.

**Isolation**——Fr. II-B (12.7 g),[3] after removal of 4′,6″-di-*O*-gallate, 4″,6″-di-*O*-gallate and 3″,4″,6″-tri-*O*-gallate of salidroside, was subjected to chromatography over Sephadex LH-20 with acetone to give two fractions; fr. II-B-a (5.4 g) and II-B-b (6.1 g). Rechromatography of fr. II-B-a over Diaion HP-20 with an increasing amount of MeOH in $H_2O$ (0—30%) and over Avicel cellulose with 2% acetic acid afforded compound **1** (750 mg). Separation of fr. II-B-b by Sephadex LH-20 column chromatography using 80% aqueous MeOH gave two further fractions; fr. II-B-b-1 (1.87 g) and II-B-b-2 (4.4 g). Crystallization of fr. II-B-b-1 from $H_2O$ yielded compound **2** (170 mg). Fr. II-B-b-2 was rechromatographed over Diaion HP-20 with a mixture of MeOH–$H_2O$ (0 : 1—3 : 7) to give compounds **3** (56 mg), **4** (300 mg) and **5** (120 mg). Similarly, fr. III-1 (4.0 g), fr. III-II (6.7 g) and fr. III-III (6.1 g), which were obtained in the previous paper,[3] were repeatedly chromatographed over Diaion HP-20 with an increasing amount of MeOH in $H_2O$ (0—50%) and over Avicel cellulose with 2% acetic acid to yield fractions containing compounds **6**, **7** and **8**. Purification of these compounds by preparative-scale HPLC [solvent: $CH_3CN$–$H_2O$ (11 : 39)] afforded compounds **6** (24 mg), **7** (6 mg) and **8** (12 mg).

Compound **1** (**1**): A white amorphous powder, $[\alpha]_D^{21}$ −107.2° ($c$=0.67, MeOH), *Anal.* Calcd for $C_{20}H_{20}O_{13}\cdot 1/2H_2O$: C, 50.32; H, 4.47. Found: C, 50.19; H, 4.59. $^1$H-NMR (acetone-$d_6$ + $CD_3OD$): 2.0—2.2 [2H, m, C(6)–H], 3.9—4.2 [3H, m, C(1)–, C(2)– and C(3)–H], 5.43 [1H, m, C(5)–H], 5.60 [1H, t, $J$=10 Hz, C(4)–H], 6.98, 7.04 (each 2H, s, galloyl H). $^1$H-NMR (dimethylsulfoxide-$d_6$): 1.92 [2H, m, C(6)–H], 3.82 [3H, m, C(1)–, C(2)– and C(3)–H], 5.25 [1H, m, C(5)–H], 5.40 [1H, t, $J$=10 Hz, C(4)–H], 6.84, 6.90 (each 2H, s, galloyl H). $^{13}$C-NMR: Table I.

Compound **2** (**2**): Colorless needles ($H_2O$), mp 255—258 °C, $[\alpha]_D^{18}$ −10.5° ($c$=0.68, acetone), *Anal.* Calcd for $C_{27}H_{24}O_{17}\cdot H_2O$: C, 50.79; H, 4.01. Found: C, 51.03; H, 4.00. $^1$H-NMR (acetone-$d_6$): 2.1—2.3 [2H, m, C(6)–H], 4.18 [1H, m, $W/2$=4 Hz, C(1)–H], 4.29 [1H, m, $W/2$=4 Hz, C(2)–H], 5.40—5.76 [2H, m, C(3)– and C(5)–H], 5.90 [1H, t, $J$=10 Hz, C(4)–H], 7.00, 7.05, 7.08 (each 2H, s, galloyl H). $^{13}$C-NMR: Table I.

Compound **3** (**3**): Colorless granules ($H_2O$), mp 207—210 °C, $[\alpha]_D^{21}$ +15.0° ($c$=0.13, acetone), *Anal.* Calcd for $C_{27}H_{24}O_{17}\cdot 9/2H_2O$: C, 46.22; H, 4.74. Found: C, 45.94; H, 4.68. $^1$H-NMR (acetone-$d_6$): 1.9—2.5 [2H, m, C(6)–H], 4.22 [1H, m, $W/2$=4 Hz, C(1)–H], 4.44 [1H, dd, $J$=10, 4 Hz, C(3)–H], 5.4—5.7 [2H, m, C(2)– and C(5)–H], 5.77 [1H, t, $J$=10 Hz, C(4)–H], 7.07, 7.11, 7.24 (each 2H, s, galloyl H). $^{13}$C-NMR: Table I.

Compound **4** (**4**): Colorless granules ($H_2O$), mp 219—223 °C, $[\alpha]_D^{20}$ +39.1° ($c$=0.40, MeOH), *Anal.* Calcd for $C_{27}H_{24}O_{17}\cdot 3/2H_2O$: C, 50.08; H, 4.20. Found: C, 49.58; H, 4.45. $^1$H-NMR (acetone-$d_6$ + $D_2O$): 2.2—2.5 [2H, m, C(6)–H], 4.0—4.3 [2H, m, C(2)– and C(3)–H], 5.2—5.4 [1H, m, C(1)– and C(5)–H], 5.72 [1H, t, $J$=9 Hz, C(4)], 7.04, 7.11, 7.21 (each 2H, s, galloyl H). $^1$H-NMR (pyridine-$d_5$): 2.6—2.9 [2H, m, C(6)–H], 4.58 [1H, dd, $J$=8, 3 Hz, C(3)–H], 4.77 [1H, br s, $W/2$=4 Hz, C(2)–H], 5.80 [1H, m, C(1)–H], 6.04 [1H, t, $J$=9 Hz, C(5)–H], 6.58 [1H, t, $J$=9 Hz, C(4)–H], 7.58 (2H, s, galloyl H), 7.86 (4H, s, galloyl H). $^{13}$C-NMR: Table I.

Compound **5** (**5**): Colorless needles ($H_2O$), mp 222—224 °C, $[\alpha]_D^{20}$ −11.9° ($c$=0.81, acetone), *Anal.* Calcd for $C_{27}H_{24}O_{17}\cdot H_2O$: C, 50.79; H, 4.10. Found: C, 50.73; H, 4.57. $^1$H-NMR (acetone-$d_6$ + $D_2O$): 2.2—2.5 [2H, m, C(6)–H], 4.34 (1H, t, $J$=3 Hz, C(2)–H], 4.44 [1H, t, $J$=9 Hz, C(4)–H], 5.30 [1H, m, C(1)–H], 5.2—5.5 [1H, m, C(5)–H], 5.35 [1H, dd, $J$=9, 3 Hz, C(3)–H], 7.16, 7.19, 7.24 (each 2H, s, galloyl H). $^{13}$C-NMR: Table I.

Compound **6** (**6**): An off-white amorphous powder, $[\alpha]_D^{21}$ −2.7° ($c$=0.71, MeOH), *Anal.* Calcd for $C_{34}H_{28}O_{21}\cdot 5H_2O$: C, 47.34; H, 4.44. Found: C, 46.94; H, 4.37. $^1$H-NMR (acetone-$d_6$ + $D_2O$): 2.3—2.6 [2H, m, C(6)–H], 4.46 [1H, m, $W/2$=4 Hz, C(2)–H], 5.32 [1H, m, $W/2$=4 Hz, C(1)–H], 5.52 [1H, dd, $J$=9, 4 Hz, C(3)–H], 5.5—5.7 [1H, m, C(5)–H], 6.09 [1H, t, $J$=9 Hz, C(4)–H], 7.02, 7.26 (each 2H, s, galloyl H), 7.05 (4H, s, galloyl H). $^{13}$C-NMR: Table I.

Compound **7** (**7**): An off-white amorphous powder, $[\alpha]_D^{21}$ +34.3° ($c$=0.14, MeOH), *Anal.* Calcd for $C_{34}H_{28}O_{21}\cdot 5H_2O$: C, 47.34; H, 4.44. Found: C, 46.92; H, 4.29. $^1$H-NMR (acetone-$d_6$ + $D_2O$): 1.9—2.6 [2H, m, C(6)–H], 4.50 [1H, dd, $J$=9, 3 Hz, C(3)–H], 5.40—5.68 [3H, m, C(1)–, C(2)– and C(5)–H], 5.85 [1H, t, $J$=9 Hz, C(4)–H],

7.10, 7.17, 7.26, 7.29 (each 2H, s, galloyl H).

Compound **8** (**8**): An off-white amorphous powder, $[\alpha]_D^{18}$ +9.9° ($c$=0.52, acetone), *Anal.* Calcd for $C_{41}H_{32}O_{25}\cdot 4H_2O$: C, 49.40; H, 4.04. Found: C, 49.28; H, 4.21. $^1$H-NMR (acetone-$d_6$): 2.1—3.0 [2H, m, C(6)–H], 5.4—6.0 [5H, m, C(1)–, C(2)–, C(3)–, C(4)– and C(5)–H], 6.97 (2H, s, galloyl H), 7.00, 7.06 (each 4H, s, galloyl H).

**Enzymatic Hydrolysis of 1 with Tannase**——A solution of **1** (230 mg) in $H_2O$ (4.5 ml) containing dimethylsulfoxide (0.5 ml) was incubated with tannase at 37 °C for 2 h. The reaction mixture was concentrated to dryness *in vacuo*, and the residue was treated with MeOH. The MeOH-soluble portion was chromatographed over Sephadex LH-20 (80% aqueous MeOH) and silica gel [$CHCl_3$–MeOH–$H_2O$ (7 : 3 : 1), lower layer] to furnish gallic acid (130 mg) and a hydrolysate (**1a**), colorless needles, mp 230—235 °C, $[\alpha]_D^{21}$ +27.9° ($c$=1.1, $H_2O$). FD-MS $m/z$: 164 ($M^+$). $^1$H-NMR ($D_2O$): 1.63—2.13 [2H, m, C(6)–H], 3.3—4.1 [5H, m, C(1)–, C(2)–, C(3)–, C(4)– and C(5)–H]. $^{13}$C-NMR: Table I. **1a** was shown to be identical with proto-quercitol by comparison of its physical constants with those reported in the literature.[4)]

**Enzymatic Hydrolysis of 2—8 with Tannase**——A solution of a gallotannin in $H_2O$ (3 mg/1 ml) was incubated with tannase at 37 °C for 1 h. The solvent was evaporated off *in vacuo*, and the residue was treated with MeOH. The MeOH-soluble portion was subjected to TLC examination; *Rf* 0.65 (gallic acid), 0.15 (proto-quercitol) [cellulose plate; *n*-BuOH–AcOH-$H_2O$ (6 : 1 : 2)]; *Rf* 0.74 (gallic acid), 0.35 (proto-quercitol) [Avicel cellulose plate; *n*-BuOH–pyridine–$H_2O$ (6 : 4 : 3)]; *Rf* 0.76 (gallic acid), 0.08 (proto-quercitol) [silica gel plate; benzene–ethyl formate–formic acid (1 : 7 : 1)].

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