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New Acylated Flavonol Glucosides in *Allium tuberosum* ROTTLER

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Six flavonoids (**1**—**6**) were isolated from the leaves of *Allium tuberosum* ROTTLER (Liliaceae). Their structures were characterized as 3-*O*-*β*-sophorosyl-7-*O*-*β*-D-(2-*O*-feruloyl)glucosylkaempferol (**1**), 3,4′-di-*O*-*β*-D-glucosyl-7-*O*-*β*-D-(2-*O*-feruloyl)glucosylkaempferol (**2**), 3-*O*-*β*-D-(2-*O*-feruloyl)-glucosyl-7,4′-di-*O*-*β*-D-glucosylkaempferol (**3**), 3,4′-di-*O*-*β*-D-glucosylkaempferol (**4**), 3,4′-di-*O*-*β*-D-glucosylquercetin (**5**) and 3-*O*-*β*-sophorosylkaempferol (**6**) by examination of their physicochemical properties. On partial acid hydrolysis, **1** gave 7-*O*-*β*-D-(2-*O*-feruloyl)glucosylkaempferol (**10**), and on enzymatic hydrolysis, **1** and **3** afforded 3-*O*-*β*-D-glucosyl-7-*O*-*β*-D-(2-*O*-feruloyl)-glucosylkaempferol (**11**) and 3-*O*-*β*-D-(2-*O*-feruloyl)glucosylkaempferol (**14**), respectively. At pH 7.0 or at pH 11.0, or both, the 2-*O*-feruloyl group of **1**, **2**, **10** and **11** migrated to give the corresponding 6-*O*-feruloyl derivatives (**15**, **17**, **16** and **18**). Compounds **1**—**3** and their derivatives **10**, **11**, **14**, **15**, **16**, **17** and **18** are new acylated flavonol glucosides.

Keywords——*Allium tuberosum*; Liliaceae; flavonol; kaempferol; quercetin; ferulic acid; glucoside; acylated flavonol glucoside; acyl migration

Allium tuberosum ROTTLER (Liliaceae) is a perennial herb which has been cultivated widely and whose leaves have been used as food. Various sulfide derivatives,[1] linalool[1] and 3-*O*-rhamnogalactosyl-7-*O*-rhamnosylkaempferol[2] have been isolated from the leaves of *A. tuberosum*. According to the dictionary of Chinese drugs,[3] they have been used for treatment of abdominal pain, diarrhea, hematemesis, snake-bite and asthma. We have attempted to

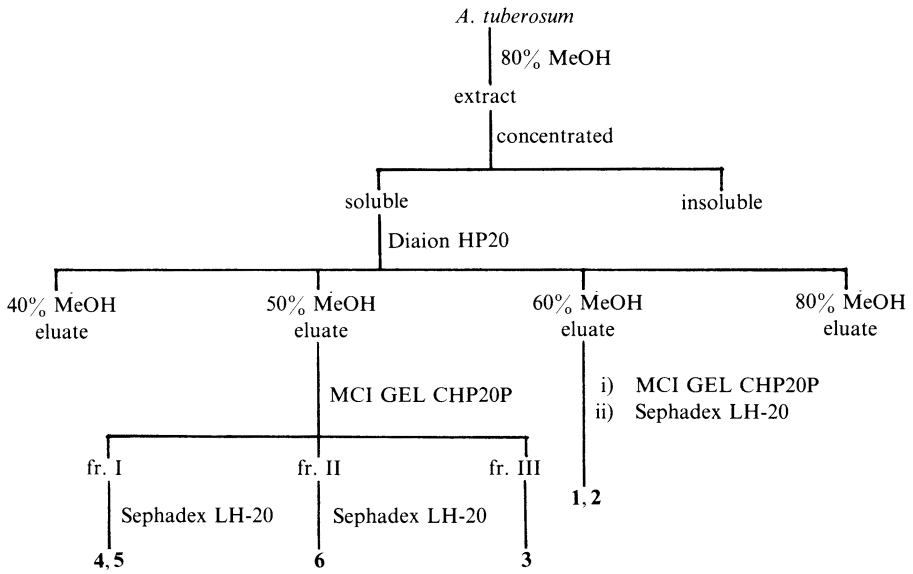


Chart 1

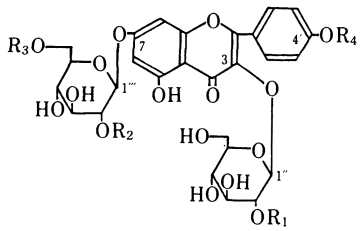
isolate anti-allergic agents from *A. tuberosum*, and have obtained three new acylated flavonol glucosides together with three known flavonol glucosides. This paper deals with the isolation and structural elucidation of these compounds, and the acyl migration of acylated flavonol glucosides.

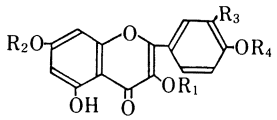
Commercially available fresh leaves of *A. tuberosum* were extracted with 80% methanol, and the extract was treated as shown in Chart 1 to isolate compounds **1**—**6**.

Compound **1** exhibited absorption maxima at 233, 269 and 333 nm in the ultraviolet (UV) spectrum, and its field desorption mass spectrum (FD-MS) showed $[M^+ + K]$ at *m/z* 987 and $[M^+ + Na]$ at *m/z* 971. On acid hydrolysis, **1** gave kaempferol and D-glucose, and on alkaline hydrolysis it afforded ferulic acid and kaempferol glucoside (**8**). Methylation of **1** according to Hakomori's method[4] followed by hydrolysis gave, in a ratio of 2:1, 2,3,4,6-tetra-*O*-methylglucose and 3,4,6-tri-*O*-methylglucose, which were identified as alditol acetates by gas liquid chromatography (GLC) and GLC-mass spectrometry (GLC-MS). Acetylation of **1** afforded a tridecaacetate, the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of which showed the signals of three aromatic and ten aliphatic acetoxyl protons. From these data **1** was found to contain a D-glucosyl (1→2)-D-glucose moiety and a D-glucose moiety attached to kaempferol, and a feruloyl moiety attached to D-glucose.

In the UV spectrum the diagnostic shifts[5] of **8** on addition of sodium acetate, sodium methoxide or aluminum chloride showed that glucose was linked to kaempferol at C-3 and -7.[6] The ^{1}H-NMR spectrum of **8**, as shown in Table I, exhibited the signals of β-anomeric protons at 4.66, 5.10 and 5.72 ppm, which could be assigned to the anomeric protons of glucose linked to C-2 of glucose, and to C-3 and -7 of kaempferol, respectively. In the ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectrum, as shown in Table II, the signals due to C-3 and -7 were shifted upfield, and the signals due to C-2, -4, -6, -8 and -10 were shifted downfield from those of kaempferol.[7] On partial acid hydrolysis with 1% sulfuric acid, **8** gave 7-*O*-β-D-glucosylkaempferol (**9**) and sophorose.[8a,b] On enzymatic hydrolysis with β-glucosidase, **8** afforded 3-*O*-β-sophorosylkaempferol (**6**).[8a,b] These results suggested that **8** is 3-*O*-β-sophorosyl-7-*O*-β-D-glucosylkaempferol.[8b]

The linkage between the feruloyl group and glucose in **1** was determined from the ^{1}H-





	R_1	R_2	R_3	R_4
1	–Glc	–Fer	–H	–H
2	–H	–Fer	–H	–Glc
3	–Fer	–H	–H	–Glc
8	–Glc	–H	–H	–H
11	–H	–Fer	–H	–H
12	–H	–H	–H	–H
13	–H	–H	–H	–Glc
15	–Glc	–H	–Fer	–H
17	–H	–H	–Fer	–Glc
18	–H	–H	–Fer	–H

	R_1	R_2	R_3	R_4
4	–Glc	–H	–H	–Glc
5	–Glc	–H	–OH	–Glc
6	–Glc^2–Glc	–H	–H	–H
7	–H	–H	–H	–H
9	–H	–Glc	–H	–H
10	–H	–Glc^2–Fer	–H	–H
14	–Glc^2–Fer	–H	–H	–H
16	–H	–Glc^6–Fer	–H	–H

Glc: β-D-glucosyl

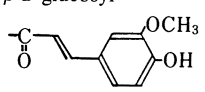
Fer: 

Chart 2

TABLE I. ^{1}H-NMR Spectral Data for Kaempferol Glucosides (in DMSO-d_6–D_2O, J=Hz)

	Kaempferol moiety				Sugar moiety							Feruloyl moiety					
	6 d, J=2	8 d, J=2	2′,6′ d, J=8	3′,5′ d, J=8	1-K3[a] d, J=8	2-K3 t, J=8	1-G2 d, J=8	1-K7 d, J=8	2-K7 t, J=8	6-K7 dd, d[b]	1-K4′ d, J=8	2 d, J=16	3 d, J=16	2′ d, J=2	5′ d, J=8	6′ dd[c]	OMe s
1	6.41	6.80	8.11	6.95	5.69[d]		4.65	5.46	4.97			6.50	7.64	7.31	6.83	7.16[d]	3.80
2	3.42	6.83	8.16	7.19	5.50			5.48	4.97		5.05	6.49	7.62	7.32	6.81	7.14[d]	3.80
3	6.49	6.86	8.18	7.21	5.80	4.92		5.10			5.10	6.53	7.64	7.34	6.84	7.16	3.83
4	6.29	6.53	8.16	7.20	5.51						5.06						
6	6.27	6.51	8.10	6.96	5.71[d]		4.65										
7	6.28	6.54	8.10	7.00													
8	6.48	6.84	8.12	6.97	5.72[d]		4.66	5.10									
9	6.48	6.86	8.12	6.99				5.09									
10	6.40	6.81	8.11	6.98				5.47	4.98			6.47	7.64	7.30	6.82	7.15	3.80
11	6.42	6.80	8.10	6.93	5.48			5.48	4.98			6.50	7.64	7.32	6.82	7.15	3.80
12	6.49	6.84	8.10	6.94	5.51			5.10									
13	6.51	6.87	8.19	7.21	5.54			5.12			5.07						
14	6.22	6.46	8.07	6.94	5.79	4.90						6.51	7.62	7.32	6.83	7.14	3.83
15	6.55	6.85	8.12	6.93	5.70[d]		4.66	5.18		4.21, 4.52		6.47	7.59	7.27	6.82	7.08	3.80
16	6.52	6.82	8.09	6.94				5.18		4.19, 4.54		6.42	7.53	6.94	6.72	7.18	3.76
17	6.59	6.85	8.16	7.18	5.48			5.19		4.21, 4.51	5.03	6.46	7.57	7.23	6.82	7.06[d]	3.81
18	6.57	6.82	8.09	6.92	5.49			5.19		4.20, 4.49		6.47	7.56	7.27	6.80	7.06[d]	3.80

a) Position of glucose proton; the linkage position of glucose to kaempferol (K) or glucose (G) is shown after the hyphen. *b*) Coupling constant: dd, J=12, 8; d, J=8. *c*) J=8, 2. *d*) Broad.

TABLE II. ^{13}C-NMR Spectral Data for Kaempferol Glucosides (in DMSO-d_6)

Carbon	1	2	3	7	8	13	15
Kaempferol moiety							
2	155.7[a]	155.9[a]	156.0[a]	146.8	155.8[a]	156.0	155.8[a]
3	133.1	133.9	133.3	135.7	133.1	133.9	133.1
4	177.5	177.6	177.4	175.9	177.5	177.6	177.6
5	160.9	160.9	160.7	160.7	160.8	160.8	161.0
6	98.9	99.1	99.4	98.3	99.2	99.4	99.0
7	161.9	162.1	162.8	164.0	162.6	162.8	162.5
8	94.5	94.5	94.4	93.5	94.3	94.3	94.5
9	156.1[a]	156.2[a]	156.1[a]	156.2	156.1[a]	156.0	156.1[a]
10	105.7	105.9	105.6	103.0	105.5	105.7	105.6
1′	120.6	123.4	123.1	121.7	120.6	123.5	120.7
2′	131.0	130.6	130.6	129.5	130.9	130.5	130.9
3′	115.2	115.7	115.7	115.4	115.3	115.7	115.2
4′	160.2	159.3	159.6	159.2	160.1	159.2	160.0
5′	115.2	115.7	115.7	115.4	115.3	115.7	115.2
6′	131.0	130.6	130.6	129.5	130.9	130.5	130.9
Feruloyl moiety							
1	165.6	165.6	165.8				166.5
2	114.2	114.2	114.5				114.1
3	145.4	145.5	145.3				145.2
1′	125.5	125.4	125.5				125.4
2′	111.0	110.9	111.0				111.0
3′	147.9	147.9	147.8				147.8
4′	149.3	149.3	149.2				149.3
5′	115.4	115.4	115.4				115.4
6′	123.2	123.2	123.2				123.1
OMe	55.6	55.6	55.6				55.6

Carbon	1	2	3	8	13	15
3-*O*-Sugar moiety						
1	97.7	100.6	98.1	97.8	100.6	97.9
2	82.4	74.1	74.0[b]	82.3	74.1	82.5
3	76.5	76.6[b]	73.9[b]	76.5	76.3	76.5
4	69.6	69.7[c]	70.1[c]	69.6	69.8[a]	69.5[b]
5	77.4[b]	77.5[d]	77.8[d]	77.4[b]	77.5[b]	77.4
6	60.6[c]	60.8[e]	60.5	60.7[c]	60.8[c]	60.5[c]
1′	104.1			104.0		104.1
2′	74.3			74.3		74.3
3′	76.5			76.5		76.5
4′	69.6			69.6		69.6[b]
5′	76.9			76.9		76.9
6′	60.8[c]			61.0[c]		60.8[c]
7-*O*-Sugar moiety						
1	97.3	97.3	99.9[e]	99.7	99.9[d]	99.6
2	73.0[d]	73.1[f]	73.1[f]	73.0	73.1[e]	73.0
3	73.9[d]	73.8[f]	76.4[g]	76.5	76.3	76.1
4	69.6	69.6[c]	69.5[c]	69.6	69.5[a]	69.5[b]
5	77.3[b]	77.3[d]	77.0[d]	77.1[b]	77.0[b]	73.9
6	60.4[c]	60.7[e]	60.5	60.6[c]	60.7[c]	63.1
4′-*O*-Sugar moiety						
1		99.8	99.6[e]		99.6[d]	
2		73.0[f]	72.9[f]		72.9[e]	
3		76.4[b]	76.3[g]		76.3	
4		69.5[c]	69.5[c]		69.5[a]	
5		77.0[d]	77.0[d]		77.0[b]	
6		60.6[e]	60.5		60.6[c]	

a—*g*) Assignments may be interchangeable within the same column.

and ^{13}C-NMR spectra. The ^{1}H-NMR spectrum of **1** exhibited signals ascribable to kaempferol and feruloyl moieties, along with those of three β-anomeric protons of glucose linked to C-2″, -7 and -3 at 4.65, 5.46 and 5.69 ppm, respectively, and a triplet signal due to a proton on carbon bearing an acyl group at 4.97 ppm. This triplet signal was found to be coupled with H-1‴ by spin decoupling. The acylation shifts[7,9] in ^{13}C-NMR spectroscopy are useful for determining the positions of acyl groups in partially acylated glycosides. In the ^{13}C-NMR spectrum of **1**, the signals due to C-1‴ and -3‴ were shifted upfield in comparison with those of **8**, while other signals remained almost unaffected. These data suggested that the feruloyl group was linked to C-2‴. In order to confirm this assumption, partial and enzymatic hydrolyses of **1** were examined.

On partial acid hydrolysis with 5% sulfuric acid, **1** afforded kaempferol glucoside (**10**). On hydrolysis with 1% potassium hydroxide, **10** gave ferulic acid and **9**. Acetylation of **10** gave a heptaacetate, the ^{1}H-NMR spectrum of which showed the signals of four aromatic and three aliphatic acetoxyl protons. The ^{1}H-NMR spectrum of **10** exhibited the signal of a β-anomeric proton of glucose attached to C-7 at 5.47 ppm and a triplet due to a proton on carbon bearing an acyl group at 4.98 ppm, coupled with each other. Consequently, **10** was established to be 7-*O*-β-D-(2-*O*-feruloyl)glucosylkaempferol.

On enzymatic hydrolysis with crude hesperidinase, **1** afforded kaempferol glucoside (**11**). Treatment of **11** with 1% potassium hydroxide gave ferulic acid and 3,7-di-*O*-β-D-glucosylkaempferol (**12**), which was identified on the basis of the diagnostic shifts[6] in the UV spectrum, and the ^{1}H-NMR spectrum. Acetylation of **11** afforded a decaacetate, the ^{1}H-NMR spectrum of which showed the signals of three aromatic and seven aliphatic acetoxyl protons. The ^{1}H-NMR spectrum of **11** exhibited the signals of two β-anomeric protons and a triplet due to a proton on carbon bearing an acyl group. Therefore, **11** was established to be 3-*O*-β-D-glucosyl-7-*O*-β-D-(2-*O*-feruloyl)glucosylkaempferol.

On the basis of the above results, the structure of compound **1** was established as 3-*O*-β-sophorosyl-7-*O*-β-D-(2-*O*-feruloyl)glucosylkaempferol.

Compounds **2** and **3** exhibited similar absorption maxima in the UV spectrum, and their FD-MS showed $[M^{+}+1]$ at m/z 949. On acetylation **2** and **3** afforded a tridecaacetate, whose ^{1}H-NMR spectra showed the signals of two aromatic and eleven aliphatic acetoxyl protons. Acid hydrolysis of **2** and **3** gave kaempferol and D-glucose, and alkaline hydrolysis afforded ferulic acid and kaempferol glucoside (**13**). These observations indicated that **2** and **3** are isomers in which the positions of the feruloyl group on **13** differ.

Enzymatic hydrolysis of **13** with β-glucosidase gave kaempferol. In the ^{1}H-NMR spectrum of **13**, the signals of three β-anomeric protons of glucose linked to phenolic oxygen were observed at 5.07, 5.12 and 5.54 ppm, the H-3′ and -5′ signals were shifted downfield in comparison with those of **8**, and a hydrogen-bonded 5-OH proton signal was observed at 12.61 ppm in dimethyl sulfoxide-d_6 (DMSO-d_6). In the ^{13}C-NMR spectrum, the C-1′ signal was shifted upfield[7] from that of **8**. From these results and the diagnostic shifts in the UV spectrum, **13** was established to be 3,7,4′-tri-*O*-β-D-glucosylkaempferol, a rare flavonol glycoside that has been isolated only as the *p*-coumarate from *Crambe cordifolia*.[10]

The ^{1}H-NMR spectrum of **2** showed the signals of β-anomeric protons at 5.05, 5.48 and 5.50 ppm, and a triplet due to a proton on carbon bearing an acyl group at 4.97 ppm, coupled with the anomeric proton at 5.48 ppm. In the ^{13}C-NMR spectrum of **2**, the signals due to C-1 and -3 of glucose linked to C-7 or -4′ were shifted upfield compared with those of **13**. Moreover, partial acid hydrolysis of **2** afforded **5**. These data suggested that a feruloyl group is linked to C-2‴. Thus, compound **2** was deduced to be 3,4′-di-*O*-β-D-glucosyl-7-*O*-β-D-(2-*O*-feruloyl)glucosylkaempferol.

The ^{1}H-NMR spectrum of **3** exhibited three β-anomeric signals, and a triplet due to a proton on carbon bearing an acyl group, coupled with the H-1″ proton. In the ^{13}C-NMR

spectrum, the signals due to C-1″ and -3″ were shifted upfield in comparison with those of **13**, while other signals remained almost unaffected.

Enzymatic hydrolysis of **3** with β-glucosidase yielded kaempferol glucoside (**14**), and its FD-MS showed $[M^+ + 1]$ at *m/z* 625. Acetylation of **14** afforded a heptaacetate, the ^{1}H-NMR spectrum of which exhibited the signals of four aromatic and three aliphatic acetoxyl protons. These results showed the elimination of two glucose molecules from **3**. The ^{1}H-NMR spectrum of **14** exhibited the signal of a β-anomeric proton of glucose attached to C-3 at 5.79 ppm, coupled with the triplet signal at 4.90 ppm. In this way, **14** was deduced to be 3-*O*-β-D-(2-*O*-feruloyl)glucosylkaempferol.

The above results established compound **3** as 3-*O*-β-D-(2-*O*-feruloyl)glucosyl-7,4′-di-*O*-β-D-glucosylkaempferol.

Compound **4** exhibited absorption maxima at 267 and 344 nm in the UV spectrum, and its FD-MS showed $[M^+ + 1]$ at *m/z* 611. Acid hydrolysis of **3** afforded kaempferol and D-glucose. In the ^{1}H-NMR spectrum two β-anomeric proton signals were observed at 5.06 and 5.51 ppm, and the signals due to H-3′ and -5′ were shifted downfield in comparison with those of **7**. From these data and the diagnostic shifts in the UV spectrum, glucose is linked to C-3 and -4′. Compound **4** was thus established to be 3,4′-di-*O*-β-D-glucosylkaempferol.[11]

Compound **5** exhibited absorption maxima at 267 and 348 nm in the UV spectrum, and its FD-MS showed $[M^+ + 1]$ at *m/z* 627. On acid hydrolysis, **5** afforded quercetin and D-glucose. In the ^{1}H-NMR spectrum two β-anomeric proton signals were observed at 4.92 and 5.53 ppm, and the signal due to H-5′ was shifted downfield from that of quercetin. These data and the diagnostic shifts in the UV spectrum showed that glucose is linked to quercetin at C-3 and -4′. Consequently, compound **5** was established to be 3,4′-di-*O*-β-D-glucosylquercetin, which has been isolated from *Allium cepa*,[8a,12] *Allium ascalonicum*,[13] and *Ribes* species.[14]

Compound **6** was identified as 3-*O*-β-sophorosylkaempferol, which was obtained from **8** by enzymatic hydrolysis with β-glucosidase.

As compound **1** seemed to be unstable during the process of separation, the stability of **1** was examined. Compound **1** was dissolved in pH 3.2, 7.0 and 8.0 buffer solutions and the stability at 100 °C was checked by high-performance liquid chromatography (HPLC). After heating for 3 h, the chromatogram of the pH 3.2 solution was not changed, but at pH 7.0, as shown in Fig. 1, the peak of **1** at t_R 7.8 min disappeared, and peaks a and b were observed at t_R 3.7 and 11.7 min. At pH 8.0, the peak of **1** disappeared and peak a, which was identified as **8** formed by alkaline hydrolysis of **1**, was recognized.

The product in peak b was obtained as colorless needles (**15**), whose UV spectrum closely resembled that of **1**. The ^{1}H-NMR spectrum of its acetate showed the signals of three

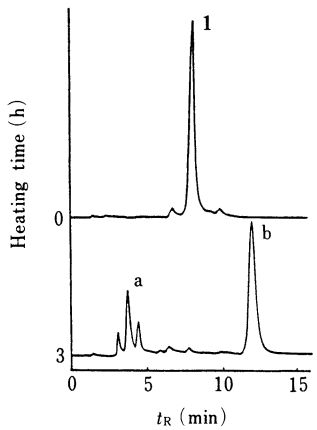


Fig. 1. Chromatogram of **1** before and after Heating at 100 °C at pH 7.0

Column, Nucleosil $_5C_{18}$ (4.6 × 250 mm); mobile phase, MeOH–H_2O (45 : 55); flow rate, 1.0 ml/min; detection, UV 254 nm; oven temperature, 40 °C.

aromatic and ten aliphatic acetoxyl protons. On alkaline hydrolysis, **15** afforded ferulic acid and **8**. These results indicated that **15** is an isomer of **1** whose feruloyl position on **8** differs from that of **1**. In the ^{1}H-NMR spectrum of **15**, doublet and double doublet proton signals at 4.21 and 4.52 ppm coupled with each other ($J=12$ Hz) were observed instead of a triplet signal in the ^{1}H-NMR spectrum of **1**. In the ^{13}C-NMR spectrum, the signals due to C-5 and -6 of one of the glucosyl moieties were shifted upfield and downfield, respectively, from those of **8**. These data suggested that the feruloyl group was linked to C-6 of glucose.

In order to clarify the linkage between the feruloyl and glucose moieties, partial acid hydrolysis of **15** was performed. Hydrolysis of **15** with 5% sulfuric acid afforded kaempferol glucoside (**16**). Acetylation of **16** gave a heptaacetate, the ^{1}H-NMR spectrum of which showed the signals of four aromatic and three aliphatic acetoxyl protons. On alkaline hydrolysis, **16** yielded ferulic acid and **9**. In the ^{1}H-NMR spectrum of **16**, doublet and double doublet proton signals due to H-6″ were observed at 4.19 and 4.54 ppm. Compound **16** was thus deduced to be 7-*O*-*β*-D-(6-*O*-feruloyl)glucosylkaempferol.

From the above, **15** was established to be 3-*O*-*β*-sophorosyl-7-*O*-*β*-D-(6-*O*-feruloyl)-glucosylkaempferol, so that the feruloyl group had migrated from C-2‴ to C-6‴ of the same molecule. Acyl migration in partially acylated carbohydrates is known[15] under various conditions, especially under mild alkaline conditions. Therefore, **1** was treated with pH 11.0 buffer at room temperature to afford **15**.

A similar acyl migration was observed in **2**, **10** and **11**——in the case of **10** and **11**, only in buffer at pH 11.0, on account of the low solubility of these compounds in pH 7.0 buffer solution——to afford the corresponding 6-*O*-feruloylates **17**, **16** and **18**, respectively. The structures of these substances were elucidated by FD-MS, UV spectra and ^{1}H-NMR spectra.

Six flavonol glycosides were isolated from *A. tuberosum*, four of them being rare C-4′ glycosides. Compounds **1**, **2**, **3**, **10**, **11**, **14**, **15**, **16**, **17** and **18** are new acylated flavonol glucosides. Compounds **1**, **2**, **10**, **11**, **15** and **16** have significant inhibitory effects on the homologous passive cutaneous anaphylaxis reaction in rats at the dose of 2.5 mg/kg (i.v.). Further biological studies are in progress.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. UV spectra were measured on a Hitachi 323 or 228 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were taken at 200 and 50.3 MHz, respectively, with a Varian XL-200 spectrometer, and chemical shifts are expressed in δ (ppm) values with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). FD-MS were obtained on a JEOL JMS-01SG2 spectrometer. Optical rotation was measured on a Perkin–Elmer 141 or Horiba SEPA 200 polarimeter. GLC was performed on a Hitachi 163 apparatus with a flame ionization detector using a glass column (3 mm i.d. × 2 m) packed with 3% OV-225 on Gas Chrom Q (100—200 mesh); injection temperature, 280 °C; column temperature, 170 °C; carrier gas, N_2 55 ml/min. GLC mass spectrometry (GLC-MS) was performed with the chromatographic column coupled to a JEOL JMS D-300 mass spectrometer. HPLC was carried out on a Hewlett–Packard 1084B apparatus. TLC was performed on Kieselgel 60F_{254} (Merck) using the following solvents: (A) EtOAc saturated with H_2O; (B) BuOH–AcOH–H_2O (4 : 1 : 5, upper); (C) BuOH–iso-PrOH–H_2O (5 : 3 : 1). The spots were detected by UV irradiation, $FeCl_3$ reagent or *p*-anisaldehyde–H_2SO_4 reagent. D-Glucose was detected by using glucose oxidase (Sigma) followed by bromphenol blue. Acetylation was carried out with acetic anhydride–pyridine in the usual way.

Extraction and Separation——Commercially available fresh leaves of *Allium tuberosum* ROTTLER (Liliaceae, 59 kg) were extracted with 80% MeOH (300 l) at room temperature for 12 d, and the extract was concentrated in order to remove MeOH. The residual solution was allowed to stand overnight, and the resulting precipitate was filtered off. The filtrate was passed through a Diaion HP20 (Mitsubishi Chemical Industry Ltd.) column. The column was washed with H_2O and then eluted with an H_2O–MeOH stepwise gradient. The 60% MeOH eluate was repeatedly chromatographed on MCI GEL CHP20P (Mitsubishi Chemical Industry Ltd.) with a linear gradient from 40% MeOH to 80% MeOH, and on Sephadex LH-20 with 50% MeOH to yield **1** (1.04 g) and **2** (0.29 g). The 50% MeOH eluate was rechromatographed on MCI GEL CHP20P with a linear gradient from 30% MeOH to 60% MeOH to give

three fractions (fractions I to III). Fraction III was concentrated to afford **3** (0.24 g). Fractions I and II were rechromatographed on Sephadex LH-20 with 50% MeOH to yield **4** (0.25 g) and **5** (0.14 g) from fraction I, and **6** (0.13 g) from fraction II.

Properties of 1——Yellow amorphous powder, mp 212—215 °C (H_2O–EtOH). $[\alpha]_D^{22}$ −84.9° (c = 1.00, pyridine). *Anal.* Calcd for $C_{43}H_{48}O_{24} \cdot H_2O$: C, 53.42; H, 5.21. Found: C, 53.27; H, 4.98. FD-MS *m/z*: 987 (M^+ + K), 971 (M^+ + Na). UV λ_{max}^{EtOH} nm (log ε): 233 (4.36), 246 (4.27), 269 (4.31), 333 (4.42). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Acetate of 1——Colorless amorphous powder, mp 129—130 °C (EtOH). *Anal.* Calcd for $C_{69}H_{74}O_{37} \cdot H_2O$: C, 54.76; H, 5.06. Found: C, 54.38; H, 4.88. ^{1}H-NMR ($CDCl_3$) δ: 1.89—2.10 (30H, each s, OAc × 10), 2.34, 2.36, 2.44 (each 3H, s, Ar–OAc), 3.88 (3H, s, OCH_3), 5.82 (1H, d, J = 8 Hz, H-1″ anomeric), 6.38 (1H, d, J = 16 Hz, CH = CHCO), 6.70 (1H, d, J = 2 Hz, H-6), 7.00 (1H, d, J = 2 Hz, H-8), 7.25 (2H, d, J = 8 Hz, H-3′,5′), 7.73 (1H, d, J = 16 Hz, CH = CHCO), 8.01 (2H, d, J = 8 Hz, H-2′,6′).

Acid Hydrolysis of 1——A solution of **1** (3 mg) in 1 N HCl (1 ml) was heated at 100 °C for 5 h. After cooling, the reaction mixture was extracted with EtOAc. The organic layer was washed with H_2O and dried over Na_2SO_4, then concentrated to dryness to yield a yellow powder, which was identified as kaempferol by comparison with an authentic sample. The aqueous layer was neutralized with Dowex 1-X2 (CO_3^{2-}) and concentrated to obtain D-glucose which was identified by TLC comparison with an authentic sample.

Alkaline Hydrolysis of 1——A solution of **1** (20 mg) in 1% KOH was allowed to stand overnight. After acidification with 1 N HCl, the reaction mixture was extracted with ether. The organic layer was concentrated to dryness and the residue was recrystallized from H_2O to yield colorless needles (2 mg), which were identified as ferulic acid by comparison with an authentic sample. The aqueous layer was passed through an MCI GEL CHP20P column (pH 3.0 HCl), which was washed successively with pH 3.0 HCl and H_2O, then eluted with 80% MeOH. The eluate was concentrated to dryness and the residue was recrystallized from EtOH to yield a pale yellow amorphous powder **8** (13 mg), mp 207—209 °C. *Anal.* Calcd for $C_{33}H_{40}O_{21} \cdot 3H_2O$: C, 47.94; H, 5.61. Found: C, 48.33; H, 5.27. FD-MS *m/z*: 811 (M^+ + K), 795 (M^+ + Na). UV λ_{max}^{EtOH} nm (log ε): 267 (4.42), 349 (4.38); λ^{+NaOAc}: 267 (4.42), 351 (4.35); λ^{+NaOMe}: 276 (4.41), 395 (4.46); λ^{+AlCl_3}: 275 (4.41), 302 (4.13), 348 (4.33), 395 (4.21). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Partial Acid Hydrolysis of 8——A solution of **8** (30 mg) in 1% H_2SO_4 (2 ml) was heated at 100 °C for 45 min. After cooling, the reaction mixture was extracted with EtOAc. The organic layer was chromatographed on silica gel with EtOAc–EtOH (1 : 1) to yield 7-*O*-β-D-glucosylkaempferol (**9**, 4 mg) as a yellow amorphous powder, which was identified on the basis of diagnostic shifts in the UV spectrum,[6] and the ^{1}H-NMR spectrum (Table I). The aqueous layer was neutralized with Dowex 1-X2 (CO_3^{2-}) and concentrated to obtain sophorose which was identified by TLC comparison with an authentic sample.

Enzymatic Hydrolysis of 8——A solution of **8** (20 mg) and β-glucosidase (20 mg, from almond, Sigma) in pH 5.0 MacIlvaine buffer (20 ml) was incubated at 37 °C for 5 h. After cooling, the reaction mixture was extracted with BuOH. The organic layer was washed with water and concentrated to dryness to yield 3-*O*-β-sophorosylkaempferol (**6**, 12 mg) as a yellow amorphous powder which was identified on the basis of the diagnostic shifts in the UV spectrum,[6] and the ^{1}H-NMR spectrum (Table I).

Methylation Analysis of 1——A solution of **1** (3 mg) and sodium methylsulfinylmethide (0.5 mM) in DMSO (0.5 ml) was allowed to stand overnight at room temperature. Methyl iodide (0.1 ml) was added and the reaction mixture was stirred at room temperature for 90 min. After dilution with water, the reaction mixture was extracted with $CHCl_3$, and the dried organic layer was concentrated to dryness. The residue was hydrolyzed with 90% formic acid at 100 °C for 2 h, and with 0.5 N H_2SO_4 (1 ml) at 100 °C for 16 h. After neutralization with $BaCO_3$ solution, the reaction mixture was centrifuged and the supernatant was concentrated to dryness. The residue was reduced with 0.5% sodium borohydride (0.5 ml) at room temperature for 1 h. Boric acid was removed by distillation with MeOH and the residue was acetylated with acetic anhydride–pyridine (1 : 1, 0.5 ml) at 100 °C for 2 h. The reaction mixture was concentrated to dryness and the residue was examined by GLC and GLC-MS, which indicated the presence of 2,3,4,6-tetra-*O*-methyl-1,5-*O*-diacetylglycitol (t_R 7.1 min) and 3,4,6-tri-*O*-methyl-1,2,5-*O*-triacetylglycitol (t_R 12.9 min) in a ratio of 2 : 1.

Partial Acid Hydrolysis of 1——A solution of **1** (50 mg) in 5% H_2SO_4 was heated at 100 °C for 100 min. After cooling, the resulting precipitate was filtered to give a yellow-brown powder, which was recrystallized from EtOH to afford **10** (10 mg) as a pale yellow amorphous powder, mp 215—217 °C. $[\alpha]_D^{22}$ +32.0° (c = 0.20, pyridine). *Anal.* Calcd for $C_{31}H_{28}O_{14} \cdot 2H_2O$: C, 56.37; H, 4.88. Found: C, 56.82; H, 4.71. FD-MS *m/z*: 625 (M^+ + 1). UV λ_{max}^{EtOH} nm (log ε): 235 (4.26), 248 (4.34), 271 (4.26), 330 (4.41), 378 sh (4.28). ^{1}H-NMR: Table I. Alkaline hydrolysis of **10** afforded ferulic acid and **9**.

Acetate of 10——Colorless amorphous powder, mp 131—133 °C (EtOH). *Anal.* Calcd for $C_{45}H_{42}O_{21} \cdot 1/2H_2O$: C, 58.25; H, 4.67. Found: C, 58.21; H, 4.83. ^{1}H-NMR ($CDCl_3$) δ: 2.04, 2.07, 2.08 (each 3H, s, OAc), 2.31, 2.32, 2.36, 2.42 (each 3H, s, Ar–OAc), 3.88 (3H, s, OCH_3), 6.38 (1H, d, J = 16 Hz, CH = CHCO), 6.76 (1H, d, J = 2 Hz, H-6), 7.02 (1H, d, J = 2 Hz, H-8), 7.37 (2H, d, J = 8 Hz, H-3′,5′), 7.73 (1H, d, J = 16 Hz, CH = CHCO), 7.84 (2H, d, J = 8 Hz, H-2′,6′).

Enzymatic Hydrolysis of 1——A solution of **1** (100 mg) and crude hesperidinase (200 mg, Tanabe Seiyaku Co.,

Ltd.) in pH 4.0 MacIlvaine buffer (25 ml) was incubated at 37 °C for 40 h. After cooling, the resulting precipitate was collected and washed with water to yield **11** (61 mg) as a yellow amorphous powder, mp 200—205 °C. $[\alpha]_D^{22}$ −48.7° (c=0.27, 0.1 N NaOH). *Anal.* Calcd for $C_{37}H_{38}O_{19}\cdot 2H_2O$: C, 54.02; H, 5.15. Found: C, 53.77; H, 5.03. FD-MS m/z: 787 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 233 (4.39), 246 (4.33), 269 (4.34), 333 (4.47). ^{1}H-NMR: Table I. Alkaline hydrolysis of **11** afforded ferulic acid and 3,7-di-*O*-β-D-glucosylkaempferol (**12**). ^{1}H-NMR: Table I.

Acetate of 11——Colorless amorphous powder, mp 155—157 °C (EtOH). *Anal.* Calcd for $C_{57}H_{58}O_{29}\cdot 2H_2O$: C, 55.07; H, 5.03. Found: C, 55.38; H, 4.64. ^{1}H-NMR ($CDCl_3$) δ: 1.91, 1.99, 2.01, 2.04, 2.08, 2.08, 2.10 (each 3H, s, OAc), 2.32, 2.34, 2.43 (each 3H, s, Ar–OAc), 3.87 (3H, s, OCH_3), 5.56 (1H, d, J=8 Hz, H-1″ anomeric), 6.36 (1H, d, J=16 Hz, CH=CHCO), 6.70 (1H, d, J=2 Hz, H-6), 7.00 (1H, d, J=2 Hz, H-8), 7.23 (2H, d, J=8 Hz, H-3′,5′), 7.71 (1H, d, J=16 Hz, CH=CHCO), 8.03 (2H, d, J=8 Hz, H-2′,6′).

Properties of 2——Pale yellow amorphous powder, mp 214—217 °C (H_2O–EtOH). $[\alpha]_D^{22}$ −39.9° (c=0.26, pyridine). *Anal.* Calcd for $C_{43}H_{48}O_{24}\cdot 2H_2O$: C, 52.44; H, 5.32. Found: C, 52.75; H, 5.52. FD-MS m/z: 949 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 232 (4.38), 268 (4.37), 328 (4.47). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. Acid hydrolysis of **2** gave kaempferol and D-glucose, and partial acid hydrolysis afforded **10**.

Acetate of 2——Colorless needles, mp 201—205 °C (EtOH). *Anal.* Calcd for $C_{69}H_{74}O_{37}\cdot 1/2H_2O$: C, 55.09; H, 5.03. Found: C, 54.81; H, 5.56. ^{1}H-NMR ($CDCl_3$) δ: 1.90—2.12 (33H, each s, OAc×11), 2.34, 2.44 (each 3H, s, Ar–OAc), 3.88 (3H, s, OCH_3), 5.82 (1H, d, J=8 Hz, H-1″ anomeric), 6.38 (1H, d, J=16 Hz, CH=CHCO), 6.70 (1H, d, J=2 Hz, H-6), 7.00 (1H, d, J=2 Hz, H-8), 7.25 (2H, d, J=8 Hz, H-3′,5′), 7.73 (1H, d, J=16 Hz, CH=CHCO), 8.01 (2H, d, J=8 Hz, H-2′,6′).

Properties of 3——Colorless amorphous powder, mp 235—238 °C (H_2O). $[\alpha]_D^{22}$ −206° (c=0.22, pyridine). *Anal.* Calcd for $C_{43}H_{48}O_{24}\cdot 3H_2O$: C, 51.50; H, 5.43. Found: C, 51.64; H, 5.31. FD-MS m/z: 949 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 232 (4.47), 269 (4.55), 327 (4.66). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. Acid hydrolysis of **3** afforded kaempferol and D-glucose.

Acetate of 3——Colorless amorphous powder, mp 186—188 °C (EtOH). *Anal.* Calcd for $C_{69}H_{74}O_{37}\cdot H_2O$: C, 54.76; H, 5.06. Found: C, 54.55; H, 4.91. ^{1}H-NMR ($CDCl_3$) δ: 1.94—2.14 (33H, each s, OAc×11), 2.35, 2.43 (each 3H, s, Ar–OAc), 3.90 (3H, s, OCH_3), 5.86 (1H, d, J=8 Hz, H-1″ anomeric), 6.38 (1H, d, J=16 Hz, CH=CHCO), 6.69 (1H, d, J=2 Hz, H-6), 6.95 (1H, d, J=2 Hz, H-8), 7.70 (1H, d, J=16 Hz, CH=CHCO), 8.02 (2H, d, J=8 Hz, H-2′,6′).

Alkaline Hydrolysis of 3——A solution of **3** (158 mg) was hydrolyzed with 1% KOH (30 ml) and worked up in the same way as **1** to obtain ferulic acid and **13** (61 mg) as a pale yellow amorphous powder, mp 210—213 °C (H_2O–EtOH). $[\alpha]_D^{22}$ −91.0° (c=0.22, pyridine). *Anal.* Calcd for $C_{33}H_{48}O_{21}\cdot 2H_2O$: C, 49.01; H, 5.48. Found: C, 49.41; H, 5.35. FD-MS m/z: 773 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 268 (4.35), 321 (4.18), 347 (4.18); λ^{+NaOAc}: 268 (4.36), 321 (4.21), 347 (4.18); λ^{+NaOMe}: 287 (4.35), 391 (3.88); λ^{+AlCl_3}: 278 (4.30), 338 (4.23), 394 (3.96). ^{1}H-NMR (DMSO-d_6) δ: 12.61 (1H, s, 5-OH); (DMSO-d_6–D_2O): Table I. ^{13}C-NMR: Table II. Enzymatic hydrolysis of **13** with β-glucosidase afforded kaempferol.

Alkaline Hydrolysis of 2——A solution of **2** was hydrolyzed with 1% KOH and worked up in the same way as **1** to identify ferulic acid and **13**.

Enzymatic Hydrolysis of 3——A solution of **3** (40 mg) and β-glucosidase (120 mg) in pH 5.0 MacIlvaine buffer (80 ml) was incubated at 37 °C for 3 d. The reaction mixture was extracted with EtOAc and the organic layer was concentrated to yield a brown residue, which was chromatographed on a Sephadex LH-20 column with MeOH to yield **10** (7 mg) as pale yellow prisms, mp 183—185 °C (EtOH). *Anal.* Calcd for $C_{31}H_{28}O_{14}\cdot 2H_2O$: C, 56.37; H, 4.88. Found: C, 56.17; H, 4.83. FD-MS m/z: 625 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 236 (4.32), 268 (4.31), 330 (4.45). ^{1}H-NMR: Table I.

Properties of 4——Pale yellow amorphous powder, mp 207—210 °C. *Anal.* Calcd for $C_{27}H_{30}O_{16}\cdot H_2O$: C, 51.60; H, 5.13. Found: C, 51.37; H, 5.13. FD-MS m/z: 611 ($M^+ + 1$). UV λ_{max}^{MeOH} nm (log ε): 267 (4.39), 344 (4.19); λ^{+NaOAc}: 276 (4.54), 371 (4.11); λ^{+NaOMe}: 276 (4.51), 372 (4.14); λ^{+AlCl_3}: 276 (4.35), 302 (4.17), 343 (4.24), 393 (4.10). ^{1}H-NMR: Table I. Acid hydrolysis of **4** afforded kaempferol and D-glucose.

Properties of 5——Yellow amorphous powder, mp 208—212 °C. *Anal.* Calcd for $C_{27}H_{30}O_{17}\cdot H_2O$: C, 50.32; H, 5.00. Found: C, 50.26; H, 4.86. FD-MS m/z: 627 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 268 (4.31), 349 (4.24); λ^{+NaOAc}: 276 (4.45), 323 (4.13) 366 (4.16); λ^{+NaOMe}: 275 (4.46), 382 (4.14); λ^{+AlCl_3}: 277 (4.34), 298 (4.10), 351 (4.18), 396 (4.13); $\lambda^{+NaOAc+H_3BO_4}$: 268 (4.21), 353 (4.20); λ^{+AlCl_3+HCl}: 278 (4.35), 347 (4.21), 395 (4.08). ^{1}H-NMR (DMSO-d_6–D_2O) δ: 4.92 (1H, d, J=8 Hz, H-1‴ anomeric), 5.53 (1H, d, J=8 Hz, H-1″ anomeric), 6.25 (1H, d, J=2 Hz, H-6), 6.49 (1H, d, J=2 Hz, H-8), 7.25 (1H, d, J=8 Hz, H-5′), 7.65 (1H, br dd, J=8, 2 Hz, H-6′), 7.68 (1H, d, J=2 Hz, H-2′). Acid hydrolysis of **5** afforded quercetin and D-glucose.

Properties of 6——Yellow needles, mp 195—198 °C (EtOH). *Anal.* Calcd for $C_{27}H_{30}O_{16}\cdot 2H_2O$: C, 50.16; H, 5.30. Found: C, 50.50; H, 4.96. FD-MS m/z: 611 ($M^+ + 1$). UV λ_{max}^{EtOH} nm (log ε): 267 (4.38), 350 (4.30); λ^{+NaOAc}: 275 (4.33), 300 (4.11), 365 (4.10); λ^{+NaOMe}: 276 (4.54), 328 (4.29), 406 (4.52); λ^{+AlCl_3}: 277 (4.38), 304 (4.21), 348 (4.30), 397 (4.26). ^{1}H-NMR: Table I.

Stability Test of Compound 1——A 0.1% solution of compound **1** at pH 3.2 (0.1 M acetate buffer), pH 7.0 or pH 8.0 (0.1 M phosphate buffer) was heated at 100 °C for 3 h, and the stability of **1** was checked by HPLC.

Procedures of Acyl Migration——i) A solution of 1% 2-*O*-acylated flavonol glucoside in 0.1 M pH 7.0 phosphate buffer was heated at 100 °C for 3 h, and allowed to stand overnight at 5 °C. The resulting precipitate was collected by centrifugation and washed with water to afford 6-*O*-acylated flavonol glucoside.

ii) A solution of 0.1% 2-*O*-acylated flavonol glucoside in 0.1 M pH 11.0 Na_2HPO_4–NaOH buffer was allowed to stand at room temperature for 3—8 h, and the solution was acidified with 1 N HCl. The resulting precipitate was collected by centrifugation and washed with water to afford 6-*O*-acylated flavonol glucoside.

Properties of 15——Compound **15** was obtained from **1** by methods i and ii above. Colorless needles, mp 214—217 °C (MeOH–H_2O). $[\alpha]_D^{22}$ −212° (*c*=0.26, pyridine). *Anal.* Calcd for $C_{43}H_{48}O_{24}\cdot 2H_2O$: C, 52.44; H, 5.32. Found: C, 52.38; H, 5.09. FD-MS *m/z*: 987 (M^++K), 971 (M^++Na). UV λ_{max}^{EtOH} nm (log ε): 233 (4.31), 247 (4.21), 268 (4.22), 333 (4.33). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. Alkaline hydrolysis of **15** afforded ferulic acid and **8**.

Acetate of 15——Colorless amorphous powder, mp 129—131 °C (EtOH). *Anal.* Calcd for $C_{69}H_{74}O_{37}\cdot 2H_2O$: C, 54.12; H, 5.13. Found: C, 53.93; H, 4.64. ^{1}H-NMR ($CDCl_3$) δ: 1.90—2.11 (30H, each s, OAc×10), 2.34, 2.36, 2.41 (each 3H, s, Ar–OAc), 3.88 (3H, s, OCH_3), 5.79 (1H, d, *J*=8 Hz, H-1″ anomeric), 6.40 (1H, d, *J*=16 Hz, CH=C<u>H</u>CO), 6.70 (1H, d, *J*=2 Hz, H-6), 6.98 (1H, d, *J*=2 Hz, H-8), 7.24 (2H, d, *J*=8 Hz, H-3′,5′), 7.68 (1H, d, *J*=16 Hz, C<u>H</u>=CHCO), 8.02 (2H, d, *J*=8 Hz, H-2′,6′).

Partial Acid Hydrolysis of 15——A solution of **15** (78 mg) in 5% H_2SO_4–EtOH (1:1, 20 ml) was refluxed for 100 min, then the reaction mixture was concentrated and the resulting precipitate was filtered and recrystallized from EtOH to afford **16** (23 mg) as yellow needles, mp 238—243 °C. $[\alpha]_D^{22}$ −128° (*c*=0.13, MeOH). *Anal.* Calcd for $C_{31}H_{28}O_{14}\cdot 2H_2O$: C, 56.37; H, 4.88. Found: C, 56.73; H, 4.44. FD-MS *m/z*: 625 (M^++1). UV λ_{max}^{EtOH} nm (log ε): 235 (4.35), 247 (4.35), 270 (4.45), 329 (4.57), 376 sh (4.47). ^{1}H-NMR: Table I. Compound **16** was also obtained from **10** by acyl migration by method ii. Alkaline hydrolysis of **16** afforded ferulic acid and **9**.

Acetate of 16——Colorless needles, mp 189—191 °C (EtOH). *Anal.* Calcd for $C_{45}H_{42}O_{21}\cdot 2H_2O$: C, 56.61; H, 4.86. Found: C, 57.06; H, 4.43. ^{1}H-NMR ($CDCl_3$) δ: 2.06 (3H, s, OAc), 2.09 (6H, s, OAc×2), 2.32, 2.34, 2.36, 2.38 (each 3H, s, Ar-OAc), 3.84 (3H, s, OCH_3), 6.37 (1H, d, *J*=16 Hz, CH=C<u>H</u>CO), 6.76 (1H, d, *J*=2 Hz, H-6), 7.22 (2H, d, *J*=8 Hz, H-3′,5′), 7.65 (1H, d, *J*=16 Hz, C<u>H</u>=CHCO), 7.82 (2H, d, *J*=8 Hz, H-2′,6′).

Properties of 17——**17** was obtained from **2** by acyl migration by methods i and ii. Pale yellow amorphous powder, mp 233—236 °C (MeOH). $[\alpha]_D^{22}$ −149° (*c*=0.20, pyridine). *Anal.* Calcd for $C_{43}H_{48}O_{24}\cdot 4H_2O$: C, 50.59; H, 5.53. Found: C, 50.23; H, 5.09. FD-MS *m/z*: 949 (M^++1). UV λ_{max}^{EtOH} nm (log ε): 232 (4.59), 243 (4.59), 269 (4.63), 328 (4.71). ^{1}H-NMR: Table I. ^{13}C-NMR: Table II.

Acetate of 17——Colorless amorphous powder, mp 179—180 °C (EtOH). *Anal.* Calcd for $C_{69}H_{74}O_{37}$: C, 55.40; H, 4.99. Found: C, 55.18; H, 4.93. ^{1}H-NMR ($CDCl_3$) δ: 1.90—2.13 (33H, each s, OAc×11), 2.36, 2.39 (each 3H, s, Ar–OAc), 3.88 (3H, s, OCH_3), 5.63 (1H, d, *J*=8 Hz, H-1″ anomeric), 6.43 (1H, d, *J*=16 Hz, CH=C<u>H</u>CO), 6.73 (1H, d, *J*=2 Hz, H-6), 7.02 (1H, d, *J*=2 Hz, H-8), 7.70 (1H, d, *J*=16 Hz, C<u>H</u>=CHCO), 8.02 (2H, d, *J*=8 Hz, H-2′,6′).

Properties of 18——Compound **18** was obtained from **11** by acyl migration by method i. Colorless amorphous powder, mp 253—255 °C (EtOH). $[\alpha]_D^{22}$ −157° (*c*=0.20, pyridine). *Anal.* Calcd for $C_{37}H_{38}O_{19}\cdot 4H_2O$: C, 51.75; H, 5.40. Found: C, 51.45; H, 5.40. FD-MS *m/z*: 787 (M^++1). UV λ_{max}^{EtOH} nm (log ε): 234 (4.32), 244 (4.34), 267 (4.31), 332 (4.43). ^{1}H-NMR: Table I.

Acetate of 18——Colorless amorphous powder, mp 128—132 °C (EtOH). *Anal.* Calcd for $C_{57}H_{58}O_{29}\cdot H_2O$: C, 54.29; H, 5.12. Found: C, 54.06; H, 4.72. ^{1}H-NMR ($CDCl_3$) δ: 1.92, 2.00, 2.02, 2.06, 2.08, 2.08, 2.11 (each 3H, s, OAc), 2.33, 2.34, 2.38 (each 3H, s, Ar–OAc), 3.86 (3H, s, OCH_3), 5.56 (1H, d, *J*=8 Hz, H-1″ anomeric), 6.38 (1H, d, *J*=16 Hz, CH=C<u>H</u>CO), 6.70 (1H, d, *J*=2 Hz, H-6), 6.98 (1H, d, *J*=2 Hz, H-8), 7.66 (1H, d, *J*=16 Hz, C<u>H</u>=CHCO), 8.02 (2H, d, *J*=8 Hz, H-2′,6′).

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