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The Glycosides of *Plantago major* var. *japonica* Nakai. A New Flavanone Glycoside, Plantagoside

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A new flavanone glucoside, plantagoside (**1**) was isolated from the seeds of *Plantago major* var. *japonica* Nakai (Plantaginaceae) together with aucubin, geniposidic acid, acteoside and syringin. The structure of plantagoside was elucidated to be **1** on the basis of chemical and spectral evidence.

Keywords——*Plantago major* var. *japonica* Nakai; Plantagoside; flavanone glucoside; aucubin; geniposidic acid; acteoside; syringin; ^{13}C NMR

Plantaginis Semen, (車前子, Japanese name, Shazenshi), the seeds of *Plantago asiatica* L. or *P. major* var. *japonica* Nakai (Plantaginaceae), is a well-known crude drug used as a diuretic in traditional Chinese medicine. Earlier investigations of this plant, have resulted in the isolations of succinic acid, adenine, choline and viscous material by Ogata *et al.*[1] and of flavonoid glycosides by Nakaoki *et al.* (plantagin)[2] and by Aritomi (homoplantagin).[3]

This paper deals with the isolation and structure elucidation of a new flavanone glucoside, named plantagoside (**1**), as well as the isolations of the known glycosides aucubin (as the acetate), acteoside (as the tetra-O-methyl ether),[4] syringin (as the acetate)[5] and geniposidic acid (as the geniposide pentaacetate)[6] from the seeds of *P. major* var. *japonica* Nakai.

The crushed seeds of this plant were defatted with chloroform and then extracted with methanol. The methanol extract was purified by column chromatography on charcoal, developing with water, methanol and then acetone. The methanol eluate was rechromatographed on silica gel with a mixture of chloroform and methanol to furnish geniposidic acid, acteoside, aucubin and syringin. The acetone eluate was rechromatographed on polyamide, and elution with H_2O, 10—40% MeOH–H_2O and MeOH gave plantagoside (**1**) and acteoside. Plantagoside (**1**) was obtained as colorless needles, $C_{21}H_{22}O_{12}\cdot 1/2H_2O$, mp 208—211°/241—243° (dec.) (double mp), and gave a brown color with ferric chloride and a reddish-peach color with magnesium-hydrochloric acid in ethanol. The ultraviolet (UV) spectrum of **1** shows absorption maxima at 288 (log ε 4.16) and 322 (sh. 3.16) nm, which shifted to 310 and 374 nm, respectively, on adding aluminum chloride, indicating that **1** is a flavanone derivative. This is also supported by the carbon nuclear magnetic resonance (^{13}C NMR) spectrum. The signals at δ 196.1 (s), 78.5 (d) and 41.9 (t) are attributable to C-4, C-2 and C-3 of flavanone, respectively. Signals of eight quaternary aromatic carbons, four aromatic methines and six carbons of a sugar moiety were also seen (Table I). The chemical shifts of C-2—C-10 are in good agreement with those of naringenin.[7]

Acetylation of **1** with acetic anhydride and pyridine afforded an octaacetate (**2**), $C_{37}H_{38}O_{20}$, mp 138—140°, infrared (IR) spectrum: no OH . The proton (^1H) NMR spectrum of **2** (in $CDCl_3$) shows four alcoholic acetyl methyls (δ 1.98, 2.02, 2.03 and 2.07, each 3H, s), four acetyl methyls [δ 2.25—2.32 (9H, s) and 2.37 (3H, s)] and four aromatic protons [δ 6.53 (1H, d, J=2 Hz), 6.77 (1H, d, J=2 Hz) and 7.02 (2H, s)]. These observations indicate that **1** is a flavanone monoglycoside possessing four phenolic hydroxyls, two of which are attached to the C-5 and C-7 positions of the A-ring.

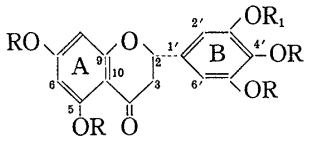
Acid hydrolysis of **1** with 2 N H_2SO_4–EtOH gave glucose and an aglycone, which in turn gave a penta-O-methyl ether (**3**), $C_{20}H_{22}O_7$, mp 176—177° upon methylation with dimethyl sulfate and potassium carbonate in acetone. The ^1H NMR spectrum of **3** shows the presence

Table I. The ^{13}C NMR Data for Plantagoside (**1**) and Related Compounds

Carbon No.	Compounds				
	1[a]	**3**[b]	**4**[c]	**5**[b]	**6**[b]
C-2	78.5	80.2	79.4	79.8	79.4
C-3	41.9	46.4	45.2	46.3	46.2
C-4	196.1	188.0	190.6	188.1	187.7
C-5	163.4	165.7	165.6	165.6	165.6
C-6	95.8	94.6	94.8	94.5	94.5
C-7	166.6	166.7	167.3	166.6	166.7
C-8	95.0	93.7	93.5	93.6	93.8
C-9	162.7	163.3	163.2	163.2	163.3
C-10	101.8	106.8	106.0	106.7	106.7
C-1′	128.7	135.9	135.7	136.0	135.9
C-2′	109.3	105.0	108.6	107.8	113.9
C-3′	145.7	154.6	151.7	151.3	145.3
C-4′	135.1	133.7	139.8	137.3	142.1
C-5′	145.8	154.6	154.3	154.2	154.7
C-6′	106.5	105.0	108.5	103.0	109.5
OCH_3		56.1, 56.2 56.6(×2), 60.2	56.3, 56.4 56.7, 61.4	56.0, 56.1 56.3, 60.5	56.1, 56.2 56.6, 60.6
$OCOCH_3$					20.5, 169.2
Glu C-1	102.3		102.2		
C-2	73.3		74.2		
C-3	77.1		77.5		
C-4	69.8		70.7		
C-5	75.9		77.2		
C-6	60.8		62.0		

a) Measured in DMSO-d_6.
b) Measured in acetone-d_6.
c) Measured in acetone-d_6, D_2O (5: 1).

of five methoxyls [δ 3.82 (s), 3.88 (s) and 3.92 (9H, s)], and C-3 methylene [δ 2.70 (1H, dd, J=16/5 Hz) and 3.07 (1H, dd, J=16/11 Hz)] in the flavanone framework, and four aromatic protons [δ 6.07, 6.18 (each 1H, d, J=2 Hz) and 6.67 (2H, s)]. The mass spectrum of **3** shows the molecular ion peak at m/e 374 (M^+) in addition to peaks at *m/e* 207. 181 and 180 (from the A-ring), and at *m/e* 194 and 179 (from the B-ring).[8]



1: R_1=glucose, R=H
2: R_1=gluc$(OAc)_4$, R=Ac
3: R_1=R=CH_3
4: R_1=glucose, R=CH_3
5: R_1=H, R=CH_3
6: R_1=Ac, R=CH_3

Chart 1

Methylation of **1** with diazomethane afforded a tetra-O-methyl ether (**4**), $C_{25}H_{30}O_{12}\cdot 1/2H_2O$, mp 128—130°, UV λ_{max}^{MeOH} nm (log ε): 226 (4.46), 284 (4.26), 315 (sh. 3.70). The ^1H NMR spectrum of **4** shows the signals of four methoxyls [δ 3.78 (6H, s), 3.82 (3H, s) and 3.85 (3H, s)], a methine proton at C-2 [δ 5.38 (1H, dd, J=11/4.5 Hz)], and four aromatic protons [δ 6.17 (2H, q-like), 6.88 (1H, d, J=2 Hz) and 7.03 (1H, d, J=2 Hz).

Acid hydrolysis of **4** with 2 N H_2SO_4–EtOH afforded glucose and compound (**5**), $C_{19}H_{20}O_7$, mp 79—81°, which gave a brown color with ethanolic ferric chloride and a blue color in the Gibbs test. The ^1H NMR spectrum of **5** shows the presence of four methoxyls at δ 3.82 (3H, s), 3.88 (3H, s) and 3.92 (6H, s), C-2 methine proton at δ 5.28 (1H, dd, J=11/5 Hz), two pairs of *meta*-coupled doublets of aromatic protons [δ 6.07, 6.17, 6.53 and 6.70 (each 1H, d, J=2 Hz)] and a hydroxy proton [δ 5.98 (1H, br.s, disappeared on addition of D_2O)]. The mass spectrum of **5** shows the molecular ion peak (M^+) at *m/e* 360 and peaks derived from the A-ring at *m/e*

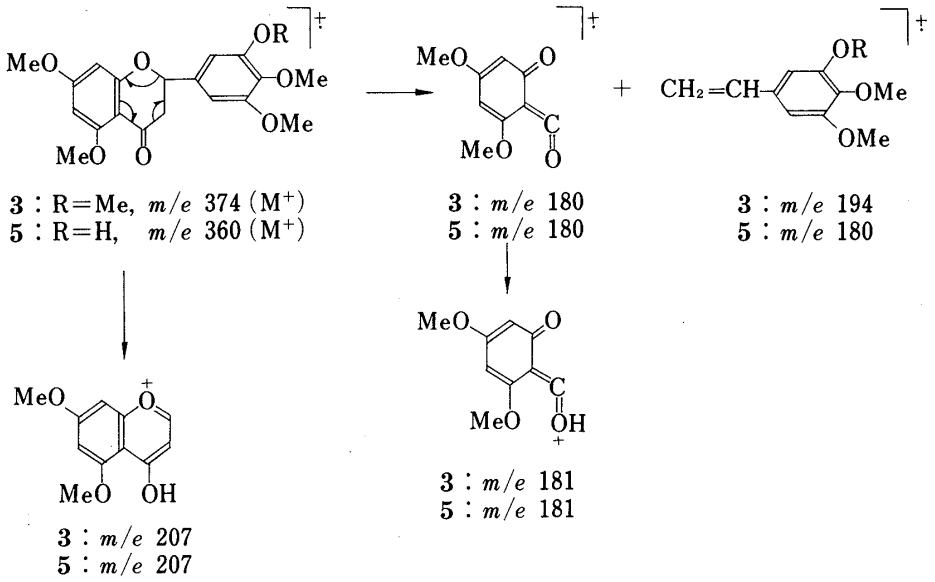


Chart 2

207, 181 and 180. However, the peak at *m/e* 194 derived from the B-ring in the case of **3** was not observed. These results indicate that the hydroxy group of **5** is linked to the B-ring (Chart 2).

In order to clarify the position of the glucose moiety in **1**, the ^{13}C NMR spectra of **3**, **5** and the acetate (**6**) of **5** were measured (Table I). The assignments were based on the reported data for related compounds[9] and standard chemical shift theory.[10] In the spectrum of **3**, the C-3′ carbon signal (δ 154.6) is deshielded by 3.3 ppm, and C-2′ (105.0), C-4′ (133.7) and C-6′ (105.0) are shielded by 2.8, 3.6 and 2.0 ppm, respectively, compared with the signals of **5**, while other carbon signals remain almost unaffected. On going from **5** to **6**, C-3′ is shielded by 6.0 ppm, and C-2′, C-4′ (*ortho* carbon) and C-6′ (*para* carbon) are deshielded by 3.1, 4.8 and 6.5 ppm, respectively. These observations indicate that the glucose moiety of **1** is located at the C-3′ hydroxy group.

Since the optical rotatory dispersion (ORD) spectrum of **1** showed an opposite curve to that of (−)-naringin (C-2: R), **1** most probably has an (*S*)-configuration at C-2[11]. Therefore, the structure of plantagoside was established as (2*S*)-3′-O-β-D-glucopyranosyl-5,7,4′,5′-tetrahydroxy flavanone. Plantagoside has not yet been found in other *Plantago* species such as *P. asiatica*, *P. lanceolata* and *P. camtshatica*.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus (a hot stage type) and are uncorrected. The UV spectra were recorded with a Hitachi 624 digital spectrophotometer and the IR spectra with a Hitachi EPI-G2 unit. The ^1H NMR spectra were recorded with a Varian model T-60 (with tetramethylsilane as an internal standard). The ^{13}C NMR spectra were recorded with a Varian model FT-80A. The mass spectra were measured with a Hitachi double-focusing mass spectrometer. The specific rotations were measured with a JASCO DIP-SL polarimeter and the ORD spectra with a JASCO J-20 spectrophotometer. The gas chromatograph used was a Hitachi model 073 with a hydrogen flame ionization detector. TLC plates were made with silica gel (Kieselgel PF_{254}, Type 60, Merck and DF-5, Camag).

Extraction

The crushed seeds of *P. major* var. *japonica* NAKAI (100 g) were defatted with $CHCl_3$ and extracted with hot MeOH. The combined MeOH extract (8.1 g) was chromatographed on charcoal (48 g); the column was developed with H_2O, MeOH and then acetone. A part of the extract (1.28 g) of the MeOH eluate (2.245 g) was subjected to silica gel column chromatography with MeOH–$CHCl_3$ mixtures of increasing polarity (5—20% MeOH–$CHCl_3$) (each fraction, 100 ml); fr. 9—10 (12% MeOH–$CHCl_3$, 51 mg), fr. 11—20 (15% MeOH–$CHCl_3$, 167 mg), fr. 21—23 (20% MeOH–$CHCl_3$, 119 mg). The acetone extract (1.893 g) was chro-

matographed on polyamide (20 g) with H_2O, 10% MeOH–H_2O, 20—40% MeOH–H_2O and then MeOH. The fraction eluted with 20—40% MeOH–H_2O gave plantagoside (**1**) (1042 mg).

Plantagoside (1)——Recrystallization of **1** from MeOH gave colorless needles, mp 208—211°/241—243° (dec.), $[\alpha]_D^{25}$ −44.4° (c=0.61, MeOH). ORD (c=0.07, MeOH) $[\alpha]^{25}$ (nm): 0° (340), −3943° (300) (trough), 0° (281), +3098° (270) (peak), −352° (240) (trough). UV λ_{max}^{MeOH} nm (log ε): 288 (4.16), 322 (sh, 3.16). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 310 (4.51), 374 (3.74). IR ν_{max}^{KBr} cm^{-1}: 3400, 1640, 1590, 1460. ^{1}H NMR (δ in acetone-d_6): 5.38 (1H, dd, J=12/4 Hz, C_2–H), 5.97 (2H, br, s), 6.78 (1H, d, J=2 Hz), 6.95 (1H, d, J=2 Hz), 12.15 (1H, s, quenched with D_2O). The ^{13}C NMR spectral data are given in Table I. *Anal.* Calcd for $C_{21}H_{22}O_{12}\cdot 1/2H_2O$: C, 53.05; H, 4.88. Found: C, 53.05; H, 4.96.

Acetylation of 1——A solution of **1** (91 mg) in Ac_2O (0.5 ml) and pyridine (1 ml) was allowed to stand at room temperature for 48 hr. The reaction mixture was poured into ice-water and extracted with AcOEt. The organic layer was washed with water, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by preparative TLC (P. TLC) (DF-5, $CHCl_3$: MeOH=5: 1) to furnish **2** as colorless needles (from EtOH, 67 mg). mp 138—140°, $[\alpha]_D^{28}$ −64.85° (c=0.59, MeOH). UV λ_{max}^{MeOH} nm (log ε): 260 (3.99), 314 (3.53). IR ν_{max}^{KBr} cm^{-1}: 1770, 1755, 1695, 1680, 1610. ^{1}H NMR (δ in $CDCl_3$): 1.98, 2.02, 2.03, 2.07 (each 3H, s, 4×OAc), 2.25—2.32 (9H, s, 3×OAc), 2.37 (3H, s, OAc), 6.53 (1H, d, J=2 Hz), 6.77 (1H, d, J=2 Hz), 7.02 (2H, s). *Anal.* Calcd for $C_{37}H_{38}O_{20}$: C, 55.36; H, 4.77. Found: C, 54.97; H, 4.73.

Acid Hydrolysis of 1 followed by Methylation, giving 3——A solution of **1** (152 mg) in 2 N H_2SO_4–EtOH (1: 1, 2 ml) was heated on a boiling water bath for 2 hr. After cooling, the reaction mixture was extracted with AcOEt. The AcOEt extract was washed with water and concentrated *in vacuo* to give an aglycone (yield 97 mg). $(CH_3)_2SO_4$ (0.2 ml) and K_2CO_3 (400 mg) were added to a solution of this aglycone (40 mg) in dry acetone (4 ml). The reaction mixture was stirred at 60° for 2 hr. The precipitate was filtered off, and the solution was concentrated *in vacuo* to give a residue, which was purified by P. TLC ($CHCl_3$: MeOH= 20: 1) to furnish **3** as colorless needles (from EtOH, 19.8 mg). mp 176—177°. UV λ_{max}^{MeOH} nm (log ε): 283 (4.03), 312 (sh, 3.47). IR ν_{max}^{KBr} cm^{-1}: 1660, 1608, 1595, 1570. ^{1}H NMR (δ in $CDCl_3$): 2.70 (1H, dd, J=16/5 Hz, C_3–H), 3.07 (1H, dd, J=16/11 Hz, C_3–H), 3.82 (3H, s), 3.88 (3H, s), 3.92 (9H, s) (5×OMe), 5.33 (1H, dd, J=11/5 Hz, C_2–H), 6.07 (1H, d, J=2 Hz), 6.18 (1H, d, J=2 Hz), 6.67 (2H, s, $C_{2',6'}$–H). The ^{13}C NMR spectral data are given in Table I. MS, *m/e* (%): 374 (M^+, 100), 207 (22), 194 (94), 181 (73), 180 (22), 179 (61), 151 (19). *Anal.* Calcd for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.41; H, 5.98. The aqueous layer was concentrated to dryness and the residue was trimethylsilylated by the usual method. The presence of glucose was demonstrated by GLC. Conditions: column, 2% OV-17 on Uniport Q, 3 mm×2 m, oven temperature, 170°, injection temperature, 220°, carrier gas, N_2; flow 38 ml/min. t_R (min): 7.8 and 11.2.

Partial Methylation of 1, giving 4——A solution of **1** (98 mg) in MeOH (20 ml) was treated with CH_2N_2 in a refrigerator for 24 hr. The reaction mixture was concentrated and purified by P.TLC (acetone: benzene: AcOH=60: 20: 0.1) to give colorless needles (**4**) (from EtOH, 58 mg). mp 128—130°. UV λ_{max}^{MeOH} nm (log ε): 226 (4.46), 284 (4.26), 315 (sh, 3.70). IR ν_{max}^{KBr} cm^{-1}: 3400, 1670, 1605, 1570. ^{1}H NMR (δ in acetone-d_6): 3.78 (6H, s, 2×OMe), 3.82 (3H, s, OMe), 3.85 (3H, s, OMe), 5.38 (1H, dd, J=11/4.5 Hz), 6.17 (2H, q-like), 6.88 (1H, d, J=2 Hz), 7.03 (1H, d, J=2 Hz). The ^{13}C NMR spectral data are given in Table I. *Anal.* Calcd for $C_{25}H_{30}O_{12}\cdot 1/2H_2O$: C, 56.49; H, 5.88. Found: C, 56.79; H, 5.84.

Acid Hydrolysis of 4——A solution of **4** (30 mg) in 2 N H_2SO_4–EtOH (1: 1, 2 ml) was heated on a boiling water bath for 3 hr. After cooling, the reaction mixture was extracted with AcOEt. The organic layer was washed with water and concentrated *in vacuo* to give **5** as colorless needles (from EtOH, 14 mg). mp 79—81°. UV λ_{max}^{MeOH} nm (log ε): 223 (3.78), 283 (3.58), 315 (sh, 2.98). IR ν_{max}^{KBr} cm^{-1}: 3350, 1650, 1610, 1570. ^{1}H NMR (δ in $CDCl_3$): 2.43—3.27 (2H, m), 3.82 (3H, s, OMe), 3.88 (3H, s, OMe), 3.92 (6H, s, 2×OMe), 5.28 (1H, dd, J=11/5 Hz, C_2–H), 5.98 (1H, br. s, quenched with D_2O), 6.07 (1H, d, J=2 Hz), 6.17 (1H, d, J= 2 Hz), 6.53 (1H, d, J=2 Hz), 6.70 (1H, d, J=2 Hz). The ^{13}C NMR spectral data are given in Table I. MS, *m/e* (%): 360 (M^+, 100), 242 (18), 207 (20), 181 (83), 180 (41), 167 (31), 143 (21), 115 (33). *Anal.* Calcd for $C_{19}H_{20}O_7$: C, 63.32; H, 5.59. Found: C, 63.50; H, 5.62.

Acetylation of 5——A solution of **5** (67 mg) in Ac_2O (1 ml) and pyridine (1 ml) was allowed to stand at room temperature overnight. The reaction mixture was poured into ice-water and extracted with AcOEt. The AcOEt extract was dried over Na_2SO_4 and concentrated *in vacuo*, then purified by P.TLC (benzene: acetone=4: 1) to give a monoacetate (**6**) (yield, 48 mg) as amorphous powder, $[\alpha]_D^{28}$=0° (c=1.1, MeOH). IR ν_{max}^{KBr} cm^{-1}: 1770, 1678, 1608, 1570. ^{1}H NMR (δ in $CDCl_3$): 2.32 (3H, s, OAc), 2.53—3.28 (2H, m), 3.83 (3H, s, OMe), 3.87 (3H, s, OMe), 3.92 (6H, s, 2×OMe), 5.33 (1H, dd, J=11/5 Hz), 6.08 (1H, d, J=2 Hz), 6.17 (1H, d, J=2 Hz), 6.82 (1H, d, J=2 Hz), 6.92 (1H, d, J=2 Hz). The ^{13}C NMR spectral data are given in Table I. *Anal.* Calcd for $C_{21}H_{22}O_8\cdot 1/2H_2O$: C, 61.31; H, 5.64. Found: 61.34; H, 5.39.

Isolation and Identification of Known Glycosides

Aucubin and Geniposidic Acid——A solution of fr. 11—20 (167 mg) in Ac_2O (0.5 ml) and pyridine (0.5 ml) was allowed to stand at room temperature overnight. The reaction mixture was poured into ice-water and extracted with AcOEt. The AcOEt extract was separated by P.TLC (DF-5, $CHCl_3$: MeOH=10: 1) to give band A (25 mg) and band B (62 mg). Band A was recrystallized from ether to give colorless needles, mp 128—129°, IR ν_{max}^{KBr} cm^{-1}: 1750, 1660, 1382, 1370. This product was identified as aucubin hexaacetate by direct comparison with an authentic sample (mixed mp, IR and TLC). A part of the band B (27 mg) was

treated with CH_2N_2 in a refrigerator for 5 min. The reaction mixture was concentrated and purified by P.TLC (ether) to give colorless needles (from EtOH, 20.6 mg), mp 135—136°, IR ν_{max}^{KBr} cm^{-1}: 1750, 1710, 1640, 1440. This product was identified as geniposide pentaacetate by direct comparison with an authentic sample (mixed mp, IR and ^1H NMR).

Syringin——The H_2O eluate (204 mg) from polyamide column chromatography was purified by P.TLC ($CHCl_3$: MeOH: H_2O=35: 15: 3) to give a white amorphous powder (5.6 mg), which was acetylated with Ac_2O and pyridine at room temperature overnight. The reaction mixture was poured into ice-water and the crystalline substance was recrystallized from EtOH to give colorless needles (8.6 mg), mp 110—112°, IR ν_{max}^{KBr} cm^{-1}: 1760, 1750, 1595, 1510. ^1H NMR (δ in $CDCl_3$): 2.01 (9H, s, 3×OAc), 2.02 (3H, s, OAc), 2.09 (3H, s, OAc), 3.81 (6H, s, 2×OMe), 4.69 (2H, d, J=6 Hz), 6.15 (1H, dt, J=17/6 Hz), 6.53 (1H, d, J=17 Hz), 6.55 (2H, s). *Anal.* Calcd for $C_{27}H_{34}O_{14}$: C, 55.66; H, 5.88. Found: C, 55.55; H, 5.94. This compound was identified as syringin pentaacetate by direct comparison with an authentic sample (mixed mp, IR and ^1H NMR).

Acteoside——A mixture of the 10% MeOH–H_2O eluate (160 mg), $(CH_3)_2SO_4$ (0.2 ml) and K_2CO_3 (400 mg) in dry acetone (4 ml) was stirred at room temperature for 21 hr. The precipitate was filtered off, and the filtrate was purified by P.TLC (DF-5, $CHCl_3$: MeOH=5: 1) to give a white amorphous powder (yield, 24.6 mg). IR ν_{max}^{KBr} cm^{-1}: 3450, 1720, 1630, 1600, which was identified as acteoside tetra-O-methyl ether by direct comparison with an authentic sample (IR, ^1H NMR and TLC).

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