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Studies on the Constituents of *Thalictrum thunbergii* DC. I

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Three flavone derivatives, TT-a (**1**), TT-b (**2**) and TT-c (**3**), were isolated from *Thalictrum thunbergii* DC. Compound **1** was characterized as apigenin 7,4'-bis-*O*- β -D-allopyranoside, and **2** and **3** were found to be acetyl derivatives of TT-a (**1**).

Keywords—*Thalictrum thunbergii*; Ranunculaceae; flavone glycoside; apigenin alloside

Although many studies on the alkaloids²⁾ in the *Thalictrum* plants have been reported, other constituents have not been extensively examined. In this work, we have isolated three flavone compounds, tentatively named TT-a (**1**), TT-b (**2**) and TT-c (**3**), as major components of the fresh aerial parts of *Thalictrum thunbergii* DC, and determined their chemical structures.

The fresh aerial parts (7.27 kg) of this plant collected in June were extracted with methanol to give an extractive which was separated into TT-a (**1**) (0.57 g, 0.0078%), TT-b (**2**) (2.74 g, 0.038%) and TT-c (**3**) (0.22 g, 0.003%) by silica gel column chromatography.

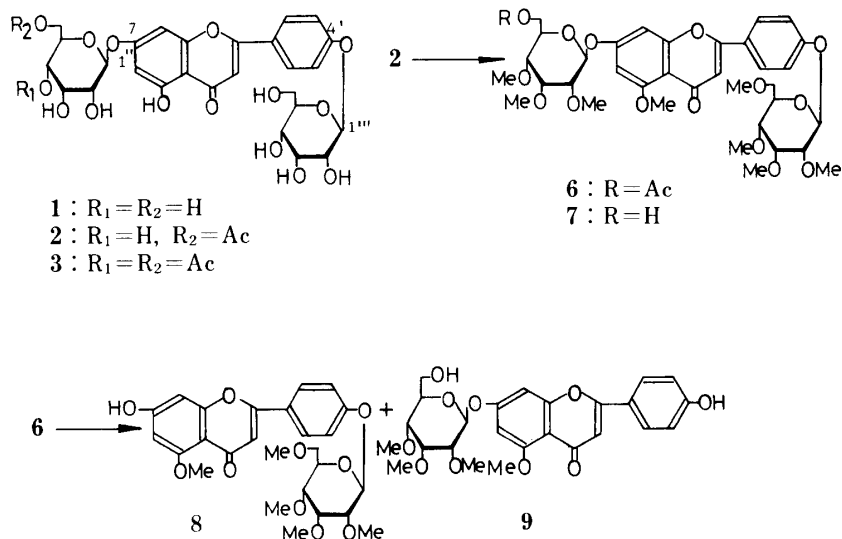
TT-a (**1**), pale yellow needles, mp 248—251 °C, $[\alpha]_D - 138.7^\circ$ (pyridine), gave a dark green coloration with FeCl₃ reagent and showed hydroxyl (3600—3300 cm⁻¹), enone (1665, 1610 cm⁻¹) and aromatic ring (1590, 830 cm⁻¹) absorptions in its infrared (IR) spectrum. Acid hydrolysis of **1** gave apigenin and D-allose, $[\alpha]_D + 11.7^\circ$ (water). The permethyl ether (**4**) of **1** prepared by the Kuhn method³⁾ exhibited a molecular ion at m/z 720, (tetramethylated hexosyl apigenin monomethyl ether)⁺ at m/z 502, (apigenin monomethyl ether)⁺ at m/z 284, and terminal permethylated hexosyl cation at m/z 219 in the electron-impact mass spectrum (EI-MS). Methanolysis of **4** yielded apigenin 5-*O*-monomethyl ether (**5**) and methyl 2,3,4,6-tetra-*O*-methyl α - and β -D-allopyranosides, which were identical with authentic specimens in terms of thin layer chromatographic (TLC) behavior and ¹H nuclear magnetic resonance (NMR) spectra. The absorption maxima at 270.5, 318.5 nm in the ultraviolet (UV) spectrum (in MeOH) of **1** changed to 279.5, 299.5, 338.5, 382.0 nm upon addition of a small amount of AlCl₃, while they showed no change upon addition of NaOAc. It was therefore suggested that D-allopyranosyl moieties are attached to the hydroxyls at both C-7 and C-4' of apigenin. Moreover, the ¹³C-NMR spectrum (in *d*₅-pyridine) of **1** suggested that both D-allopyranosides have β -configurations [allosyl moieties δ : 99.8, 100.8 (C-1'', 1'''), 2 $\times$ 72.0 (C-2'', 2'''), 2 $\times$ 73.1 (C-3'', 3'''), 68.6, 68.7 (C-4'', 4'''), 2 $\times$ 76.6 (C-5'', 5'''), 2 $\times$ 62.6 (C-6'', 6''')].⁴⁾ Consequently, TT-a (**1**) was concluded to be apigenin 7,4'-bis-*O*- β -D-allopyranoside.

TT-b (**2**), pale yellow needles, mp 257—260 °C, $[\alpha]_D - 102.4^\circ$ (pyridine), showed a pattern similar to that of **1** except for the occurrence of an ester absorption (1715 cm⁻¹) in the IR spectrum and $[M + Na^+]$ at m/z 659, $[M + H^+]$ at m/z 637, $[M + Na^+ - \text{hexose}]$ at m/z 497, $[M^+ - \text{hexose}]$ at m/z 474, $[M + Na^+ - \text{hexose mono} \cdot \text{Ac}]$ at m/z 455, $[M^+ - \text{hexose mono} \cdot \text{Ac}]$ at m/z 432 in the field desorption mass spectrum (FD-MS). Weak alkaline treatment afforded a more polar substance identical with TT-a (**1**). The ¹H-NMR spectrum (in *d*₆-DMSO) of **2** showed the presence of one acetyl group (δ 2.00) and the other signals were assigned as

follows; δ 6.36 (1H, d, $J=2.0$ Hz, 6-H), 6.82 (1H, d, $J=2.0$ Hz, 8-H), 6.94 (1H, s, 3-H), 7.16 (2H, d, $J=8.0$ Hz, 3',5'-H), 8.07 (2H, d, $J=8.0$ Hz, 2',6'-H), 12.8 (1H, s, 5-OH). The location⁵⁾ of the acetyl group could be easily deduced to be at C-6'' or C-6''' on the allosyl residues from the ^{13}C -NMR spectrum of **2** [allosyl moieties δ : 100.0, 71.8, 72.9, 69.0, 73.4, 65.0 (C-1''-6'' or C-1'''-6'''), 100.8, 72.1, 73.1, 68.7, 76.6, 62.7 (C-1'''-6''' or C-1''-6'')]. Kuhn methylation of **2** afforded two products, **6**, EI-MS (m/z): 748 (M^+), 284 (apigenin mono·Me⁺), 247 (monoacetyl trimethyl allosyl⁺), 219 (tetramethyl allosyl⁺), and **7**, EI-MS (m/z): 706 (M^+), 284 (apigenin mono·Me⁺), 219 (tetramethyl allosyl⁺). Compound **7** corresponds to the desacetyl derivative of **6**. Partial methanolysis of **6** gave two products, **8** and **9**, of which the latter showed no acetyl absorption in the IR spectrum and gave peaks due to M^+ (m/z 488), apigenin monomethyl ether cation (m/z 284) and trimethyl allosyl cation (m/z 205) in the EI-MS. Compound **9** upon methanolysis yielded methyl 2,3,4-tri-*O*-methyl- α -D-allopyranoside and its anomer along with an apigenin derivative. The ^{13}C -NMR spectrum of **9** exhibited shifts of +0.8, -2.3 and +1.9 ppm at C-6, C-7 and C-10, respectively, in comparison with the signals of **5**, suggesting that the allosyl derivatives in **9** is linked to the hydroxyl at C-7 on **5**. Therefore, the structures for compounds **6**, **7**, **8** and **9** were represented as shown in the Formulae and TT-b (**2**) was characterized as 7-*O*-(6''-mono-*O*-acetyl- β -D-allopyranosyl) apigenin 4'-*O*- β -allopyranoside.

TT-c(**3**), pale yellow needles, mp 168—170 °C, $[\alpha]_{\text{D}} -81.6^\circ$ (pyridine), was also supposed to be related to **1** and **2** from the evidence of the FeCl_3 coloration and the IR spectrum, in which **3** showed absorption due to an ester group (1720—1715 cm^{-1}). Comparative ^{13}C -NMR spectral investigation of **1**, **2** and **3** revealed that **3** is a bis-*O*-allopyranosyl apigenin derivative, like **1** and **2**, and that two acetyl groups (δ 20.7, 20.8, 170.1, 170.6) are attached to one (7-*O*- or 4'-*O*-allopyranosyl) of the two allopyranosyl moieties in **3**; their locations were estimated at the C-4'' and 6'', or C-4''' and 6''' hydroxyls from the esterification shifts⁵⁾ [allosyl moieties δ : 99.8, 71.3, 70.6, 70.1, 70.5, 63.6 (C-1''-6'' or C-1'''-6'''), 100.7, 72.1, 73.1, 68.7, 76.7, 62.6 (C-1'''-6''' or C-1''-6'')]. Partial alkaline hydrolysis (2% NaHCO_3 -MeOH-pyridine) gave two products identical with **1** and **2**. It was therefore deduced that the two acetyl groups were bound with the hydroxyls at C-4'' and C-6'' of the 7-*O*-allopyranosyl residue, namely **3** is 7-*O*-(4'',6''-di-*O*-acetyl- β -D-allopyranosyl) apigenin 4'-*O*- β -D-allopyranoside.

As regards flavonoid derivatives possessing alloside as a sugar component, asiaticalin (kaempferol 3-*O*- β -D-allopyranoside),⁶⁾ 4'-*O*-methylisoscuteallarein 7-*O*-(6''-*O*-acetyl- β -D-allopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranoside⁷⁾ and chrysoeriol 7-*O*-(β -D-allopyranosyl-(1 $\rightarrow$ 2)- β -D-glucopyranoside)⁸⁾ have been reported.



Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus (hot stage type) and are uncorrected. The optical rotations were measured with a Union PM-201 automatic digital polarimeter. The UV spectra were obtained with a Hitachi 330 spectrometer, and the IR spectra were recorded with a Hitachi 215 spectrometer. The NMR spectra were run on a JEOL PS-100 spectrometer and a JEOL FX-200 spectrometer (100 and 200 MHz for ^1H and 50.1 MHz for ^{13}C -NMR). Chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard. The EI-MS and FD-MS spectra were recorded on a JEOL JMS D-300 spectrometer. Thin layer chromatography was done on precoated Kieselgel 60 F_{254} plates (Merck) with CHCl_3 -MeOH-H $_2$ O (7:3:0.5 v/v, a) and CHCl_3 -MeOH (20:1 v/v, b) unless otherwise specified, and detection was achieved by spraying 10% H_2SO_4 followed by heating.

Extraction and Isolation of Flavonoids—The fresh aerial parts (7.27 kg) of *Thalictrum thunbergii* DC cultivated at the Botanical Garden of this Faculty were extracted with refluxing MeOH (31 l), and a residue (525.6 g) was obtained by evaporation of the MeOH extract. The extractive was defatted with *n*-hexane and partitioned between *n*-BuOH and water. Evaporation of the BuOH layer gave a residue (82.3 g), which was column-chromatographed with CHCl_3 -MeOH-H $_2$ O=9:2:0.1 as the solvent to afford fr. 1–12. TT-a (**1**) (0.57 g) was obtained from fr. 8 and 9, TT-b (**2**) (2.74 g) from fr. 5 and TT-c (**3**) (0.22 g) from fr. 3.

TT-a (1)—Yellowish needles, *Rf* 0.32 (a), mp 248–251 °C, $[\alpha]_D^{21} -138.7^\circ$ ($c=1.06$, pyridine). FeCl_3 reagent: dark green. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3600–3300 (OH), 1665, 1610 (enone), 1590, 830 (arom. ring). UV $\lambda_{\text{max}}^{\text{MeOH}} \text{nm}$ (log ϵ): 270.5 (4.57), 318.5 (4.54), $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3} \text{nm}$ (log ϵ): 279.5 (4.51), 299.5 (4.50), 338.5 (4.56), 382.0 (4.32), $\lambda_{\text{max}}^{\text{MeOH} + \text{NaOAc}} \text{nm}$ (log ϵ): 270.0 (4.55), 319.0 (4.53). ^{13}C -NMR (d_5 -pyridine) δ : 164.3, 104.8, 182.7, 162.4, 99.7, 164.2, 95.2, 157.8, 106.5 (C_2 – C_{10}), 124.6 (C_1), 128.4 ($\text{C}_{2',6'}$), 117.1 ($\text{C}_{3',5'}$), 161.5 (C_4). Anal. Calcd for $\text{C}_{27}\text{H}_{30}\text{O}_{15}$: C, 54.54; H, 5.09. Found: C, 54.34; H, 4.98.

Acid Hydrolysis of 1—A solution of **1** (300 mg) in 2N HCl–MeOH (20 ml) was refluxed for 5.5 h. The precipitate (84.1 mg) was collected by filtration and recrystallized to afford yellowish needles (25 mg), identical with apigenin. Yellowish needles, *Rf* 0.80 (a), mp > 300 °C. ^{13}C -NMR (d_5 -pyridine) δ : 165.8, 103.9, 182.7, 163.1, 100.0, 164.5, 94.8, 158.2, 105.0 (C_2 – C_{10}), 122.3 (C_1), 128.8 ($\text{C}_{2',6'}$), 116.8 ($\text{C}_{3',5'}$), 162.6 (C_4). The filtrate was neutralized with Amberlite IRA-400 to furnish methyl alloside, *Rf* 0.46 (a), which was hydrolyzed with 1N HCl, neutralized and chromatographed on silica gel with CHCl_3 -MeOH-H $_2$ O=7:3:0.5 to afford D-allose, 73 mg, *Rf* 0.14 (a), $[\alpha]_D^{26} +11.7^\circ$ ($c=1.20$, H $_2$ O, after 5 h).

Methylation of 1—A suspension of **1** (100 mg), dimethylformamide (DMF) (8 ml), CH_3I (7 ml) and Ag_2O (500 mg) was stirred overnight at room temperature (Kuhn method). Usual work-up of the reaction mixture afforded the permethyl ether (**4**) as a syrup (51 mg). EI-MS (m/z): 720 (M^+), 502 (apigenin mono·Me + hexose tetra·Me) $^+$, 284 (apigenin mono·Me) $^+$, 219 (hexose tetra·Me) $^+$, 187 (m/z 219 – MeOH) $^+$. Anal. Calcd for $\text{C}_{36}\text{H}_{48}\text{O}_{15}$: C, 59.99; H, 6.71. Found: C, 59.81; H, 6.76.

Methanolysis of 4—A solution of **4** (32 mg) in 2N HCl–MeOH (4 ml) was refluxed for 1.5 h and neutralized with 3% KOH–MeOH. The deposited salt was filtered off and the filtrate was chromatographed on Sephadex LH-20 with MeOH to give apigenin 5-monomethyl ether (**5**) and permethylated α - and β -D-allopyranosides. **5**: Pale yellowish needles, *Rf* 0.10 (solv. CHCl_3 -MeOH = 10:1 v/v). ^1H -NMR (d_5 -pyridine) δ : 3.80 (3H, s, OMe), 6.68 (1H, d, $J=2$ Hz, 6-H), 6.83 (1H, s, 3-H), 6.90 (1H, d, $J=2$ Hz, 8-H), 7.15 (2H, d, $J=8$ Hz, 3',5'-H $_2$), 7.84 (2H, d, $J=8$ Hz, 2',6'-H $_2$). ^{13}C -NMR (d_6 -DMSO) δ : 160.4, 105.9, 175.7, 159.9, 96.5, 162.5, 95.2, 159.0, 107.0 (C_2 – C_{10}), 121.4 (C_1), 127.7 ($\text{C}_{2',6'}$), 115.8 ($\text{C}_{3',5'}$), 160.5 (C_4), 55.8 (OMe). Anal. Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_5$: C, 67.60; H, 4.26. Found: C, 67.42; H, 4.31. Methyl 2,3,4,6-tetra-*O*-methyl β -D-allopyranoside: *Rf* 0.62 (b). ^1H -NMR (CDCl_3) δ : 3.30–3.60 (5 $\times$ OMe), 4.52 (1H, d, $J=8$ Hz, anomeric proton). Methyl 2,3,4,6-tetra-*O*-methyl α -D-allopyranoside: *Rf* 0.52 (b). ^1H -NMR (CDCl_3) δ : 3.30–3.60 (5 $\times$ OMe), 4.65 (1H, d, $J=4$ Hz, anomeric proton).

TT-b (2)—Pale yellowish needles, *Rf* 0.53 (a), mp 257–260 °C, $[\alpha]_D^{20} -102.4^\circ$ ($c=1.03$, pyridine). FeCl_3 reagent: dark green. IR $\nu_{\text{max}}^{\text{KBr}} \text{cm}^{-1}$: 3600–3300 (OH), 1715 (OAc), 1665, 1610 (enone), 1590, 830 (arom. ring). UV $\lambda_{\text{max}}^{\text{MeOH}} \text{nm}$ (log ϵ): 264.0 (4.03), 311.0 (4.01), $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3} \text{nm}$ (log ϵ): 274.0 (3.99), 290.5 (3.96), 333.0 (4.05), 374.5 (3.83), $\lambda_{\text{max}}^{\text{MeOH} + \text{NaOAc}} \text{nm}$ (log ϵ): 264.5 (4.02), 313.0 (4.00). FD-MS (m/z): 659 ($\text{M} + \text{Na}^+$), 637 ($\text{M} + \text{H}^+$), 497 ($\text{M} + \text{Na}^+ - \text{hexose}$), 474 ($\text{M}^+ - \text{hexose}$), 455 ($\text{M} + \text{Na}^+ - \text{hexose mono}\cdot\text{Ac}$), 432 ($\text{M}^+ - \text{hexose mono}\cdot\text{Ac}$). ^{13}C -NMR (d_5 -pyridine) δ : 164.3, 104.9, 182.8, 162.6, 99.8, 164.2, 95.5, 157.8, 106.6 (C_2 – C_{10}), 124.7 (C_1), 128.5 ($\text{C}_{2',6'}$), 117.2 ($\text{C}_{3',5'}$), 161.6 (C_4), 100.0, 71.8, 72.9, 69.0, 73.4, 65.0 (7-*O*-allosyl C_1 – C_6), 20.5, 170.1 (OAc), 100.8, 72.1, 73.1 68.7, 76.6, 62.7 (4'-*O*-allosyl C_1 – C_6). Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{O}_{16}$: C, 54.72; H, 5.07. Found: C, 54.66; H, 5.11.

Alkaline Treatment of TT-b (2)—A solution of **2** (121 mg) in 3% KOH–MeOH (6 ml) was allowed to stand for 1 h at room temperature, then neutralized with 1N HCl–MeOH and evaporated to dryness *in vacuo* to give a residue, which was recrystallized from MeOH, affording yellowish crystals (103 mg), mp 246–252 °C, $[\alpha]_D^{22} -136.2^\circ$ ($c=1.03$, pyridine), identical with TT-a (**1**).

Methylation of 2—**2** (500 mg) was methylated by the Kuhn method (DMF 30 ml, CH_3I and Ag_2O 3.3 g). Usual work-up of the reaction mixture gave the product, which was separated by silica gel column chromatography with CHCl_3 -MeOH = 50:1 to afford **6** (257 mg) and **7** (50 mg). **6**: A syrup, *Rf* 0.39 (b), $[\alpha]_D^{22} -73.5^\circ$ ($c=1.02$, CHCl_3). EI-

MS (m/z): 748 (M^+), 284 (apigenin 5-monomethyl ether cation), 247 (monoacetyl trimethyl allosyl cation), 187 (m/z 219 – MeOH or/and m/z 247 – AcOH). $^1\text{H-NMR}$ (CDCl_3) δ : 2.02 (3H, s, OAc), 3.36, 3.43, 3.45, 3.60, 3.62, 3.64, 3.67 (each 3H, s, 7 $\times$ OMe), 3.94 (3H, s, 5-OMe), 5.36, 5.40 (each 1H, d, $J=8$ Hz, 2 $\times$ anomeric proton), 6.44 (1H, d, $J=2$ Hz, 6-H), 6.56 (1H, s, 3-H), 6.70 (1H, d, $J=2$ Hz, 8-H), 7.08 (2H, d, $J=8$ Hz, 3',5'-H₂), 7.78 (2H, d, $J=8$ Hz, 2',6'-H₂). *Anal.* Calcd for $\text{C}_{57}\text{H}_{48}\text{O}_{16}$: C, 59.35; H, 6.46. Found: C, 59.17; H, 6.51. **7**: A syrup, R_f 0.24 (b), $[\alpha]_D^{22} -64.0^\circ$ ($c=1.00$, CHCl_3). EI-MS (m/z): 706 (M^+), 284, 219, 205 (trimethyl allosyl cation), 187, 173 (m/z 205 – MeOH). $^1\text{H-NMR}$ (CDCl_3) δ : 3.38, 3.46, 3.48, 3.60, 3.62, 3.64, 3.66 (each 3H, s, 7 $\times$ OMe), 3.92 (3H, s, 5-OMe), 5.38, 5.46 (each 1H, $J=8$ Hz, 2 $\times$ anomeric proton), 6.44 (1H, m, 6-H), 6.58 (1H, s, 3-H), 6.70 (1H, m, 8-H), 7.10 (2H, d, $J=8$ Hz, 3',5'-H₂), 7.80 (2H, d, $J=8$ Hz, 2',6'-H₂). *Anal.* Calcd for $\text{C}_{35}\text{H}_{46}\text{O}_{15}$: C, 59.48; H, 6.56. Found: C, 59.31; H, 6.52. Acetylation of a small amount of **7** gave an acetate identical with **6**.

Partial Methanolysis of 6—A solution of **6** (258 mg) in 0.5 N HCl–MeOH (10 ml) was refluxed for 3 h and neutralized with 3% KOH–MeOH. The deposited salt was filtered off and the filtrate was subjected to Sephadex LH-20 (solv. MeOH) then silica gel (solv. CHCl_3 –MeOH = 50:1) column chromatographies to furnish **8** (7.5 mg) and **9** (27.4 mg). **8**: A syrup, EI-MS (m/z): 502 (M^+), 284 (apigenin 5-monomethyl ether), 219 (permethylated allosyl cation). *Anal.* Calcd for $\text{C}_{26}\text{H}_{30}\text{O}_{10}$: C, 62.14; H, 6.02. Found: C, 62.02; H, 5.98. **9**: A syrup, EI-MS (m/z): 488 (M^+), 284, 205 (trimethyl allosyl cation). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3600–3300 (OH), 1665, 1610 (enone), 1590, 830 (arom. ring). $^{13}\text{C-NMR}$ (d_6 -DMSO) δ : 160.4, 106.0, 175.6, 160.2, * 97.3, 160.2, * 95.7, 158.7, 108.9 (C_2 – C_{10}), 121.2 (C_1), 127.8 (C_2 – C_6), 115.7 (C_3 – C_5), 160.9 (C_4), 60.2, 73.7, 74.3, 76.3, 79.6, 97.0 (allosyl moiety), 56.0, 56.4, 57.4, 60.5 (4 $\times$ OMe); assignments marked * may be reversed. *Anal.* Calcd for $\text{C}_{25}\text{H}_{28}\text{O}_{10}$: C, 61.47; H, 5.78. Found: C, 61.23; H, 5.61.

Methanolysis of 9—A solution of **9** (10 mg) in 2 N HCl–MeOH (2 ml) was refluxed for 4 h and neutralized to give the product, which was separated by silica gel column chromatography to afford α and β anomers of methyl 2,3,4-tri-*O*-methyl β -D-allopyranosides along with **5**. Methyl 2,3,4-tri-*O*-methyl β -D-allopyranoside: A syrup, R_f 0.37 (b). $^1\text{H-NMR}$ (CDCl_3) δ : 3.3–3.6 (4 $\times$ OMe), 4.60 (1H, d, $J=8$ Hz, anomeric proton). Acetylation with Ac_2O and pyridine of the above sugar gave the corresponding acetate, methyl 2,3,4-tri-*O*-methyl-6-*O*-monoacetyl β -D-allopyranoside, a syrup, R_f 0.77 (b). $^1\text{H-NMR}$ (CDCl_3) δ : 2.03 (3H, s, OAc), 3.3–3.6 (4 $\times$ OMe), 4.60 (1H, d, $J=8$ Hz, anomeric proton). Methyl 2,3,4-tri-*O*-methyl α -D-allopyranoside: A syrup, R_f 0.27 (b). $^1\text{H-NMR}$ (CDCl_3) δ : 3.3–3.6 (4 $\times$ OMe), 4.76 (1H, d, $J=4$ Hz, anomeric proton). Acetylation of the above compound gave methyl 2,3,4-tri-*O*-methyl-6-*O*-monoacetyl α -D-allopyranoside, a syrup, R_f 0.72 (b). $^1\text{H-NMR}$ (CDCl_3) δ : 2.03 (3H, s, OAc), 3.3–3.6 (4 $\times$ OMe), 4.79 (1H, d, $J=4$ Hz, anomeric proton).

Methanolysis of 8—Methanolysis of **8** (3 mg) with 2 N HCl–MeOH gave **5** and methyl 2,3,4,6-tetra-*O*-methyl α - and β -D-allopyranosides (on TLC).

TT-c (3)—Yellowish needles, R_f 0.58 (a), mp 168–170°C, $[\alpha]_D^{21} -81.6^\circ$ ($c=1.03$, pyridine). FeCl_3 reagent: dark green. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3600–3300 (OH), 1720–1715 (OAc), 1665, 1610 (enone), 1590, 840 (arom. ring). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 269.5 (4.47), 317.5 (4.45), $\lambda_{\text{max}}^{\text{MeOH} + \text{AlCl}_3}$ nm (log ϵ): 279 (4.42), 299.0 (4.40), 337.5 (4.48), 382.0 (4.24), $\lambda_{\text{max}}^{\text{MeOH} + \text{NaOAc}}$ nm (log ϵ): 268.0 (4.47), 316.5 (4.45). $^{13}\text{C-NMR}$ (d_5 -pyridine) δ : 164.3, 104.9, 182.8, 162.6, 99.8, 164.0, 95.5, 157.8, 106.7 (C_2 – C_{10}), 124.6 (C_1), 128.5 (C_2 – C_6), 117.1 (C_3 – C_6), 161.6 (C_4), 99.8, 71.3, 70.6, 70.1, 70.5, 63.6 (C_1 – C_6), 20.7, 20.8, 170.1, 170.6 (2 $\times$ OAc), 100.7, 72.1, 73.1, 68.7, 76.7, 62.6 (C_1 – C_6). *Anal.* Calcd for $\text{C}_{31}\text{H}_{34}\text{O}_{17}$: C, 54.87; H, 5.05. Found: C, 58.91; H, 5.91.

Alkaline Treatment of TT-c (3)—TT-c (**3**), 85 mg, was treated with a mixture of 2% NaHCO_3 solution (6 ml), MeOH (6 ml) and pyridine (2 ml) at room temperature for 1 h and neutralized with 1 N HCl–MeOH. The product was separated by silica gel column chromatography (solv. CHCl_3 –MeOH– $\text{H}_2\text{O}=8:2:0.2$) to afford two compounds identical with TT-a (**1**), 15 mg, and TT-b (**2**), 21 mg, on the basis of mp, and $^{13}\text{C-NMR}$ spectra.

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References and Notes

- 1) Present address: Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-honmachi, Kumamoto 862, Japan.
- 2) T. Tomimatsu, *Shoyakugaku Zasshi*, **30**, 1 (1976).
- 3) R. Kuhn, H. Trischmann and I. Löw, *Angew. Chem.*, **67**, 32 (1955).
- 4) $^{13}\text{C-NMR}$ chemical shifts (d_5 -pyridine) of methyl β -D-allopyranoside: δ 103.0, 72.2, 72.8, 68.9, 75.8, 62.9 (C_1 – C_6), 56.5 (Me).
- 5) D. E. Dorman and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 4463 (1971).
- 6) T. Okuyama, K. Hosoyama, Y. Hiraga, G. Kurono and T. Takemoto, *Chem. Pharm. Bull.*, **26**, 3071 (1978).
- 7) V. M. Chari, R. J. Grayer-Barkmeizer, J. B. Harborne and B.-G. Österdahl, *Phytochemistry*, **20**, 1977 (1981).
- 8) R. M. Rabanal, S. Valverde, M. Martin-Lomas, B. Rodriguez and V. M. Chari, *Phytochemistry*, **21**, 1830 (1982).