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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*; Ranunclaceae; flavone glycoside; apigenin alloside

Although many studies on the alkaloids[2] 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.

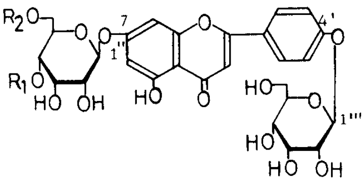
The fresh aerial parts (7.27 kg) of this plant collected in June were extracted with methanol to give an extractive which was separated into TT-a (**1**) (0.57 g, 0.0078%), TT-b (**2**) (2.74 g, 0.038%) and TT-c (**3**) (0.22 g, 0.003%) by silica gel column chromatography.

TT-a (**1**), pale yellow needles, mp 248—251 °C, $[\alpha]_D -138.7°$ (pyridine), gave a dark green coloration with $FeCl_3$ 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, $[\alpha]_D +11.7°$ (water). The permethyl ether (**4**) of **1** prepared by the Kuhn method[3] 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 $AlCl_3$, 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 ^{13}C-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 × 72.0 (C-2″, 2‴), 2 × 73.1 (C-3″, 3‴), 68.6; 68.7 (C-4″, 4‴), 2 × 76.6 (C-5″, 5‴), 2 × 62.6 (C-6″, 6‴)].[4] Consequently, TT-a (**1**) was concluded to be apigenin 7,4′-bis-*O*-β-D-allopyranoside.

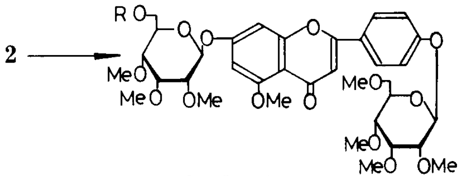
TT-b (**2**), pale yellow needles, mp 257—260 °C, $[\alpha]_D -102.4°$ (pyridine), showed a pattern similar to that of **1** except for the occurrence of an ester absorption (1715 cm^{-1}) in the IR spectrum and $[M+Na^+]$ at *m/z* 659, $[M+H^+]$ at *m/z* 637, $[M+Na^+ - \text{hexose}]$ at *m/z* 497, $[M^+ - \text{hexose}]$ 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-O$\underline{\text{H}}$). The location[5] 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, $[\alpha]_D$ −81.6 ° (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 shifts[5] [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.

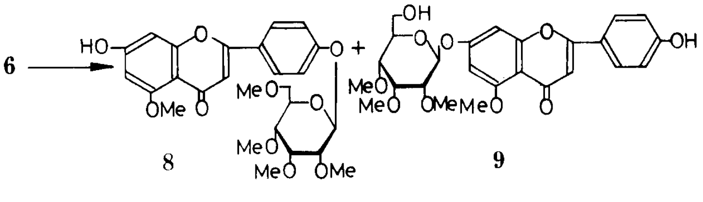
As regards flavonoid derivatives possessing alloside as a sugar component, asiaticalin (kaempferol 3-*O*-β-D-allopyranoside),[6] 4′-*O*-methylisoscutellarein 7-*O*-(6″-*O*-acetyl-β-D-allopyranosyl-(1→2)-β-D-glucopyranoside[7] and chrysoeriol 7-*O*-(β-D-allopyranosyl-(1→2)-β-D-glucopyranoside)[8] have been reported.



1 : R₁=R₂=H
2 : R₁=H, R₂=Ac
3 : R₁=R₂=Ac



6 : R=Ac
7 : R=H



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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 ^{1}H 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_2O (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_2O = 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, $[\alpha]_D^{21}$ $-138.7°$ ($c = 1.06$, pyridine). $FeCl_3$ reagent: dark green. IR ν_{max}^{KBr} cm^{-1}: 3600—3300 (OH), 1665, 1610 (enone), 1590, 830 (arom. ring). UV λ_{max}^{MeOH} nm (log ε): 270.5 (4.57), 318.5 (4.54), $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 279.5 (4.51), 299.5 (4.50), 338.5 (4.56), 382.0 (4.32), $\lambda_{max}^{MeOH+NaOAc}$ 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 ($C_{2',6'}$), 117.1 ($C_{3',5'}$), 161.5 ($C_{4'}$). Anal. Calcd for $C_{27}H_{30}O_{15}$: C, 54.54; H, 5.09. Found: C, 54.34; H, 4.98.

Acid Hydrolysis of 1——A solution of **1** (300 mg) in 2 N 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 ($C_{2',6'}$), 116.8 ($C_{3',5'}$), 162.6 ($C_{4'}$). The filtrate was neutralized with Amberlite IRA-400 to furnish methyl alloside, *Rf* 0.46 (a), which was hydrolyzed with 1 N HCl, neutralized and chromatographed on silica gel with $CHCl_3$–MeOH–H_2O = 7 : 3 : 0.5 to afford D-allose, 73 mg, *Rf* 0.14 (a), $[\alpha]_D^{26}$ $+11.7°$ ($c = 1.20$, H_2O, 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 $C_{36}H_{48}O_{15}$: C, 59.99; H, 6.71. Found: C, 59.81; H, 6.76.

Methanolysis of 4——A solution of **4** (32 mg) in 2 N 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). ^{1}H-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 ($C_{2',6'}$), 115.8 ($C_{3',5'}$), 160.5 ($C_{4'}$), 55.8 (OMe). *Anal.* Calcd for $C_{16}H_{12}O_5$: 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). ^{1}H-NMR ($CDCl_3$) δ: 3.30—3.60 (5 × 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). ^{1}H-NMR ($CDCl_3$) δ: 3.30—3.60 (5 × OMe), 4.65 (1H, d, $J = 4$ Hz, anomeric proton).

TT-b (2)——Pale yellowish needles, *Rf* 0.53 (a), mp 257—260 °C, $[\alpha]_D^{20}$ $-102.4°$ ($c = 1.03$, pyridine). $FeCl_3$ reagent: dark green. IR ν_{max}^{KBr} cm^{-1}: 3600—3300 (OH), 1715 (OAc), 1665, 1610 (enone), 1590, 830 (arom. ring). UV λ_{max}^{MeOH} nm (log ε): 264.0 (4.03), 311.0 (4.01), $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 274.0 (3.99), 290.5 (3.96), 333.0 (4.05), 374.5 (3.83), $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 264.5 (4.02), 313.0 (4.00). FD-MS (*m/z*): 659 ($M + Na^+$), 637 ($M + H^+$), 497 ($M + Na^+ -$ hexose), 474 ($M^+ -$ hexose), 455 ($M + Na^+ -$ hexose mono · Ac), 432 ($M^+ -$ hexose mono · 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 ($C_{2',6'}$), 117.2 ($C_{3',5'}$), 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 $C_{29}H_{32}O_{16}$: 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 1 N 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, $[\alpha]_D^{22}$ $-136.2°$ ($c = 1.03$, 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), $[\alpha]_D^{22}$ $-73.5°$ ($c = 1.02$, $CHCl_3$). 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}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 × OMe), 3.94 (3H, s, 5-OMe), 5.36, 5.40 (each 1H, d, $J=8$ Hz, 2 × 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′-H_2), 7.78 (2H, d, $J=8$ Hz, 2′,6′-H_2). *Anal.* Calcd for $C_{57}H_{48}O_{16}$: C, 59.35; H, 6.46. Found: C, 59.17; , 6.51. **7**: A syrup, *Rf* 0.24 (b), $[\alpha]_D^{22}$ −64.0° ($c=$ 1.00, $CHCl_3$). EI-MS (m/z): 706 (M^+), 284, 219, 205 (trimethyl allosyl cation), 187, 173 (m/z 205 − MeOH). ^{1}H-NMR ($CDCl_3$) δ: 3.38, 3.46, 3.48, 3.60, 3.62, 3.64, 3.66 (each 3H, s, 7 × OMe), 3.92 (3H, s, 5-OMe), 5.38, 5.46 (each 1H, $J=$ 8 Hz, 2 × 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′-H_2), 7.80 (2H, d, $J=8$ Hz, 2′,6′-H_2). *Anal.* Calcd for $C_{35}H_{46}O_{15}$: 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 $C_{26}H_{30}O_{10}$: 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 ν_{max}^{KBr} cm^{-1}: 3600—3300 (OH), 1665, 1610 (enone), 1590, 830 (arom. ring). ^{13}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 ($C_{2',6'}$), 115.7 ($C_{3',5'}$), 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 × OMe); assignments marked * may be reversed. *Anal.* Calcd for $C_{25}H_{28}O_{10}$: 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 D-allopyranosides along with **5**. Methyl 2,3,4-tri-*O*-methyl β-D-allopyranoside: A syrup, *Rf* 0.37 (b). ^{1}H-NMR ($CDCl_3$) δ: 3.3—3.6 (4 × 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, *Rf* 0.77 (b). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, OAc), 3.3—3.6 (4 × OMe), 4.60 (1H, d, $J=$ 8 Hz, anomeric proton). Methyl 2,3,4-tri-*O*-methyl α-D-allopyranoside: A syrup, *Rf* 0.27 (b). ^{1}H-NMR ($CDCl_3$) δ: 3.3—3.6 (4 × 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, *Rf* 0.72 (b). ^{1}H-NMR ($CDCl_3$) δ: 2.03 (3H, s, OAc), 3.3—3.6 (4 × 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, *Rf* 0.58 (a), mp 168—170°C, $[\alpha]_D^{21}$ −81.6° ($c=1.03$, pyridine). $FeCl_3$ reagent: dark green. IR ν_{max}^{KBr} cm^{-1}: 3600—3300 (OH), 1720—1715 (OAc), 1665, 1610 (enone), 1590, 840 (arom. ring). UV λ_{max}^{MeOH} nm (log ε): 269.5 (4.47), 317.5 (4.45), $\lambda_{max}^{MeOH+AlCl_3}$ nm (log ε): 279 (4.42), 299.0 (4.40), 337.5 (4.48), 382.0 (4.24), $\lambda_{max}^{MeOH+NaOAc}$ nm (log ε): 268.0 (4.47), 316.5 (4.45). ^{13}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 ($C_{2',6'}$), 117.1 ($C_{3',6'}$), 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 × OAc), 100.7, 72.1, 73.1, 68.7, 76.7, 62.6 ($C_{1'''}$–$C_{6'''}$). *Anal.* Calcd for $C_{31}H_{34}O_{17}$: 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–H_2O = 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}C-NMR spectra.

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