Notes

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Study on the Constituents of *Paris quadriforia* L.

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Seven compounds have been isolated from whole plants of *Paris quadriforia* L. and their chemical structures characterized as follows; pennogenin (**1**), pennogenin 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside (**2**), pennogenin 3-*O*-α-L-rhamnopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamno-pyranosyl-(1→2)]-β-D-glucopyranoside (**3**), 22-hydroxyfurostanol 3,26-*O*-bisglycoside corresponding to **3** (**4**), 1-dehydrotrillenogenin (**5**), ecdysterone (**10**) and kaempferol 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (**11**).

In addition, a stimulative effect of **3**, one of the major components, on isolated bull frog heart was observed.

Keywords——*Paris quadriforia*; Liliaceae; pennogenin; pennogenin glycosides; prototype compound of pennogenin glycoside; 1-dehydrotrillenogenin; kaempferol glycoside

In the preceding papers, we have reported on the constituents of *Paris polyphylla* Sm.,[1] *Paris tetraphylla* A. Gray[2] and *Paris verticillata M.v.* Bieb.[3] Among the constituents of European *Paris quadriforia* L., two glycosides named paridin and paristyphnin were reported,[4] of which the former possessed respiratory center-paralyzing activity[5] and pupil size-reducing activity, like eserine. However, chemical characterization of the two glycosides was not described.

For the purpose of clarifying the structure of the biologically active glycoside, we have now surveyed the chemical constituents of this plant collected in Odenwald in West Germany and isolated five steroidal derivatives (**1**—**5**), including a new 18-norspirostanol derivative (**5**), as well as ecdysterone (**10**) and a new flavonol glycoside (**11**). Furthermore, it is suggested that glycoside **3**, one of the main ingredients, has stimulative activity for isolated bull frog heart.

The procedure for extraction and isolation of the compounds is shown in Chart 1.

Compound **1**, mp 230—232°C, $[\alpha]_D$ −106.2°, mass spectrum (MS) (*m/z*): 430 (M^+), was identified (mp, $[\alpha]_D$, thin layer chromatography (TLC), and MS) as pennogenin.[6]

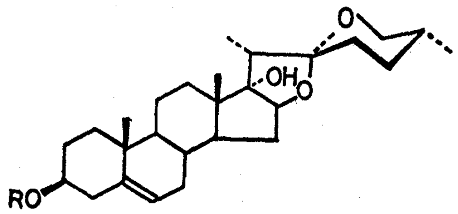
Compound **2**, mp 293—295°C (dec.), $[\alpha]_D$ −103.2°, showed absorptions due to hydroxyl (3400 cm^{-1}) and spiroketal side chain (985, 913, 900, 890 cm^{-1})[7] in its infrared (IR) spectrum. On acid hydrolysis, it yielded kryptogenin as the sapogenol and glucose and rhamnose as sugar components. Since the IR spectrum of **2** exhibited no absorption due to the carbonyl group, kryptogenin was assumed to be an artifact derived from pennogenin (**1**) during acid hydrolysis.[6] Compound **2** was thus identified as pennogenin triglycoside, pennogenin 3-*O*-α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranoside, T-c,[8] previously isolated from *Trillium kamtschaticum* Pall.

Compound **3**, mp 256—258°C (dec.), $[\alpha]_D$ −108.3°, was identified (mp, $[\alpha]_D$, TLC, IR) in the same way as for **2** as pennogenin tetraglycoside, pennogenin 3-*O*-α-L-rhamnopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside, T-g,[8] which has been also obtained from *T. kamtschaticum*. The effect of **3** on the isolated bull

frog heart was investigated by Yagi-Hartung's method. It did not have any effect at concentrations lower than 3.3×10^{-7} g/ml, but it caused a marked increase (approximately 50%) in the amplitude immediately after addition at a concentration of 3.3×10^{-6} g/ml. This was followed by a decline in amplitude, and then by a marked increase (approximately 60%) again with a subsequent gradual increase reaching a peak in 100 to 140 s. There was, however, no change in the heart rate. At a concentration of 3.3×10^{-5} g/ml it caused a slight increase in the amplitude immediately, followed by marked augmentation of the tonus.

Compound **4**, an amorphous powder, $[\alpha]_D$ −110°, showed no absorption due to spiroketal in its IR spectrum. Enzymic hydrolysis of **4** gave **3** and glucose. Therefore, **4** was assumed to be a furostanol 3,26-bisglycoside corresponding to **4**, 3-*O*-α-L-rhamnopyranosyl-(1→4)-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside, H-d,[9] this compound has already been isolated from *Heloniopsis orientalis* (Thunb.) C. Tanaka.

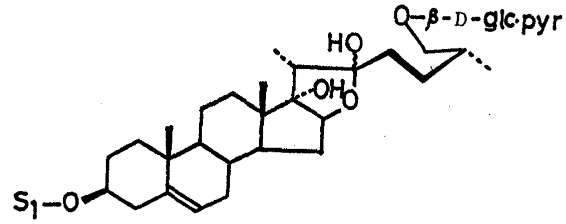
Compound **5**, mp 169—172°C (dec.), $[\alpha]_D$ −135.1°, showed absorptions due to hydroxyl (3700—3020 cm^{-1}), carbonyl (1700) and double bond (1624) and was formulated as $C_{26}H_{34}O_8$ on the basis of its high resolution mass spectrum. Taking into account the sum (26) of the carbons and the fact that it is a highly oxygenated molecule, **5** was supposed to be an 18-norspirostanol derivative such as trillenogenin (**6**).[10] Thus, a comparison of the ^{1}H nuclear magnetic resonance (^{1}H NMR) spectrum of the tetraacetate (**7**) of **5**, mp 200—202°C (dec.), $[\alpha]_D$ −125.0°, MS (*m/z*): 642 (M$^+$), with that of trillenogenin pentaacetate (**8**) was undertaken. The signal pattern of **7** resembled that of **8** and the signals were assigned as shown in the



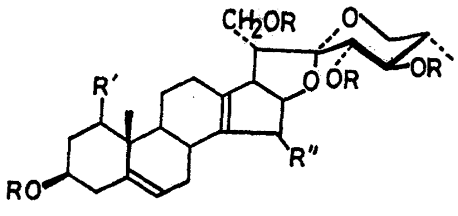
1: R=H

2: R=-β-D-glc·pyr (2: α-L-rha·pyr; 4: α-L-rha·pyr)

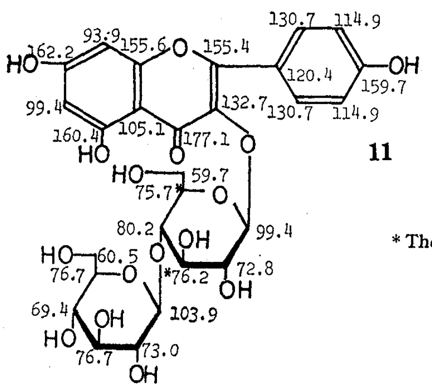
3: R=-β-D-glc·pyr (2: α-L-rha·pyr; 4: α-L-rha·pyr 4← α-L-rha·pyr) (S₁)



4: R=S₁



5 : R=H, R′=R″=⊃O
6 : R=H, R′=βOH, R″=⊃O
7 : R=Ac, R′=R″=⊃O
8 : R=Ac, R′=βOAc, R″=⊃O
9 : R=Ac, R′=βOAc, R″=αOAc



11

* These assignments may be reversed.

Fig. 1

experimental section, but in the ^1H NMR spectrum of **7**, the signals due to one acetoxyl and the methine proton attached to C_1 were absent. Therefore, **5** was suggested to be 1-dehydrotrillenogenin. Reaction of **8** with $NaBH_4$ followed by acetylation afforded the 15-dihydroacetyl compound (**9**) as a major product, whose acetoxyl configuration was determined as α on the basis of its ^1H NMR spectrum (δ 5.37, 1H, br d, J=6 Hz, 15β-H).[11] On the other hand, one of two products derived from **7** in the same manner as described above was identical with **9** in TLC behavior, MS and ^1H NMR. Consequently, **5** was concluded to be 1-dehydrotrillenogenin.

Compound **10**, mp 240—242°C (dec.), FD-MS (*m/z*): 611 (M^++H) was identical with ecdysterone.[12]

Compound **11**, pale yellow crystals, mp 195—200°C (dec.), $[\alpha]_D$ −134.0°, yielded kaempferol and D-glucose on acid hydrolysis. The mass spectrum of the pentaacetate of **11** exhibited peaks due to the terminal peracetylated diglucosyl cation (*m/z* 619)[13] and the terminal peracetylated glucosyl cation (*m/z* 331).[13] **11** was thus supposed to be kaempferol diglucoside. To determine the locations of the glucosyl→glucosyl and diglucosyl→kaempferol linkages, investigation of the ^{13}C nuclear magnetic resonance (^{13}C NMR) spectrum was undertaken. The signals were assigned as shown in formula **11** by referring to the work of Markham *et al.*[14] The signals due to sugar carbons were also in good accord with those of β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (β-cellobioside).[15] It was concluded that the terminal glucosyl residue was bound with the C_4–OH of another glucosyl moiety and its bisglucosyl residue at the C_3–OH of kaempferol. Accordingly, compound **11** can be represented as kaempferol 3-*O*-β-D-glucopyranosyl-(1→4)-β-D-glucopyranoside.

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-SL automatic polarimeter. IR spectra were obtained with a JASCO IR-G spectrometer. NMR spectra were taken with a JEOL PS-100 spectrometer at 100 MHz (^1H) and a JEOL FX-100 spectrometer at 25.15 MHz (^{13}C); chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard and coupling constants (J) are given in Hz. Mass spectra were recorded on a JMS-01SG mass spectrometer with an accelerating potential of 5.2—6.7 kV and an ionizing potential of 30—70 eV. Field desorption (FD) mass spectra were recorded on a JEOL D-300 machine with an ion source pressure of 3×10^{-7} Torr and an ion source temperature of between 60 and 70°C, and the accelerating voltages were +3 kV for the anode and −5 kV for the slotted cathode plate. TLC was performed on precoated Kieselgel G (Merck) and detection was done by spraying dil. H_2SO_4 reagent followed by heating. TLC for sugar was conducted on Avicel SF (Funakoshi) with aniline hydrogen phthalate as the spraying reagent. Column chromatography was carried out with Kieselgel (0.05—0.5 mesh, Merck), Sephadex LH-20 (25-100) (Pharmacia Fine Chemicals), Amberlite XAD-2 (Organo) and polyamide C-200 (Wako Junyaku).

Extraction and Isolation——The fresh whole plants of *Paris quadriforia* L. were collected in the Odenwald region of West Germany in August 1977. In accordance with Chart 1, seven compounds **1** (5 mg), **2** (610 mg), **3** (620 mg), **4** (720 mg), **5** (30 mg), **10** (10 mg) and **11** (1.2 g) were obtained.

Compound 1——Colorless needles from acetone, mp 230—232°C, $[\alpha]_D^{21}$ −106.2° (c=0.22, $CHCl_3$). MS (*m/z*): 430 (M^+, $C_{27}H_{42}O_4^+$), 415 (M^+-CH_3), 412 (M^+-H_2O), 358 ($M^+-C_4H_8O$), 316 ($M^+-C_6H_{10}O_2$), 298, 214 ($C_{16}H_{22}^+$), 199, 155 ($C_9H_{15}O_2^+$), 153 ($C_9H_{13}O_2^+$), 126 ($C_8H_{14}O^+$). *Anal.* Calcd for $C_{27}H_{42}O_4$: C, 75.31; H, 9.83. Found: C, 75.22; H, 9.91.

Compound 2——Colorless needles from dil. MeOH, mp 293—295°C (dec.), $[\alpha]_D^{20}$ −103.2° (c=1.32, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 985, 913, 900, 890 (spiroketal). *Anal.* Calcd for $C_{45}H_{72}O_{17}\cdot H_2O$: C, 59.85; H, 8.26. Found: C, 59.62; H, 8.22. **2** (4.6 mg) was refluxed with 1 N HCl (2 ml) for 2.5 h. After neutralization, the hydrolysate was examined by TLC for aglycone and on Avicel for sugar. The aglycone was identical with kryptogenin (*Rf* 0.12, solv. *n*-hexane–AcOEt=1:1), and the sugar components were identified as glucose (*Rf* 0.48, solv. the upper layer of *n*-BuOH–pyridine–water (6:2:3)+pyridine (1)) and rhamnose (*Rf* 0.73).

Compound 3——Colorless needles from dil. MeOH, mp 256—258°C (dec.), $[\alpha]_D^{19}$ −108.3° (c=1.07, MeOH). *Anal.* Calcd for $C_{51}H_{82}O_{21}\cdot 3H_2O$: C, 56.44; H, 8.17. Found: C, 56.21; H, 8.12. IR ν_{max}^{KBr} cm^{-1}: 3400—3200 (OH), 980, 915, 900, 885 (spiroketal).

Effect of 3 on the Isolated Bull Frog Heart——The effect of **3** on the isolated bull frog heart was investigated by Yagi-Hartung's method. The heart movement was recorded on smoked paper. The volume was 3 ml and the bath was aerated continuously during the experiment. The concentration of **3** used in each

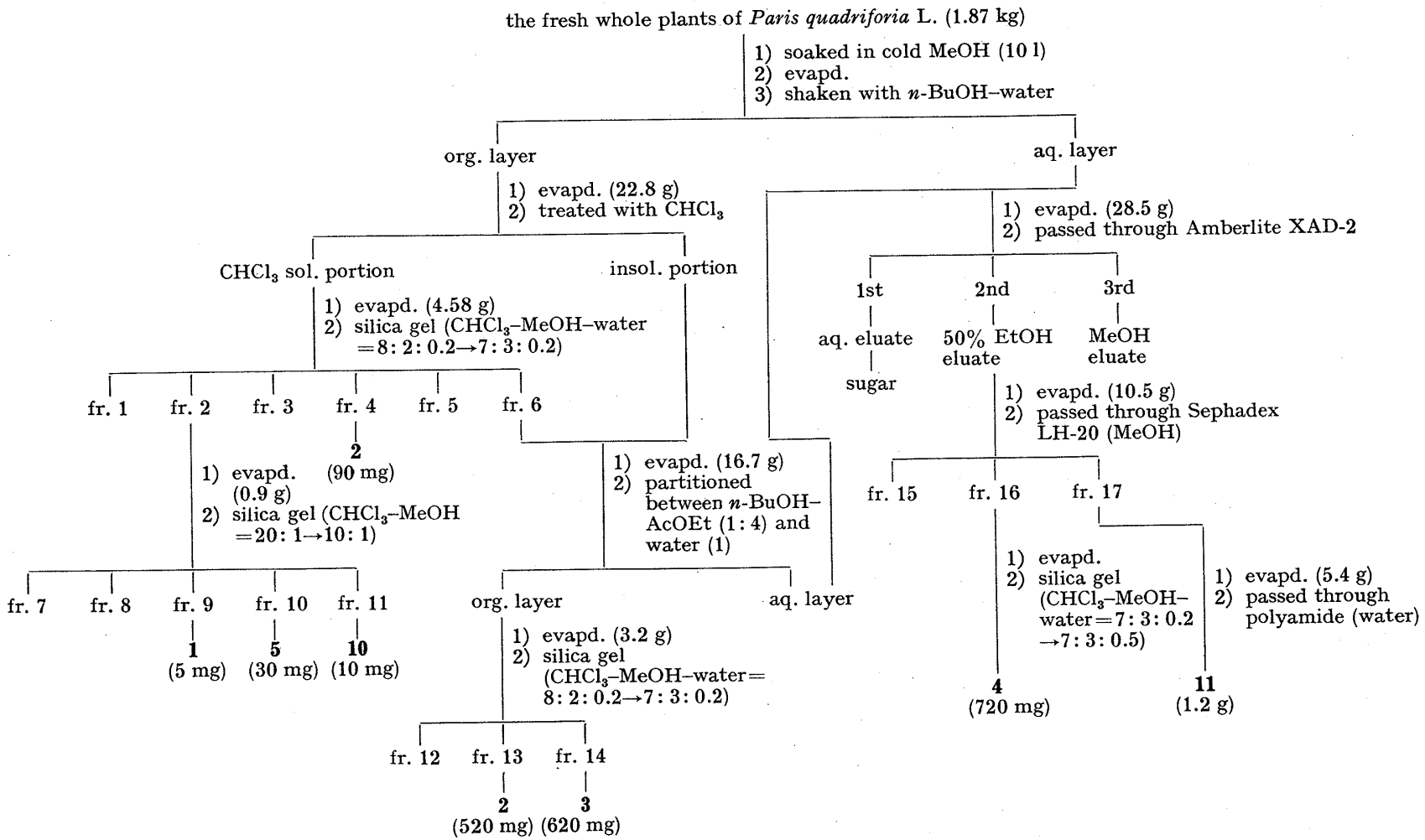


Chart 1

case is given as the final concentration. The experimental work was carried out from spring to summer at room temperature.

Compound 4——A white powder (mp 193—200°C) from dil. acetone, $[\alpha]_D^{21}$ −110° (c=1.02, pyridine), IR ν_{max}^{KBr} cm^{-1}: 3400 (OH). When **4** (*Rf* 0.09, solv. $CHCl_3$–MeOH–water=7: 3: 0.5) was refluxed with MeOH, it changed into a less polar substance, the 22-OMe compound (*Rf* 0.17). A mixture of **4** (5 mg), almond emulsin (5 mg) and dist. water (2 ml) was incubated at 37°C for 18 h, then examined by TLC (solv. $CHCl_3$–MeOH–water (7: 3: 0.5)). A glycoside identical with **3** (*Rf* 0.40) and glucose (*Rf* 0.13) were detected.

Compound 5——Colorless needles from dil. MeOH, mp 169—172°C (dec.), $[\alpha]_D^{20}$ −135.1° (c=0.56, MeOH). *Anal.* Calcd for $C_{26}H_{34}O_8$: C, 65.80; H, 7.22. Found: C, 65.78; H, 7.17. IR ν_{max}^{KBr} cm^{-1}: 3700—3020 (OH), 1700 (C=O), 1624 (C=C), 975, 926, 879, 828 (spiroketal). UV λ_{max}^{EtOH} nm 248 (ε=12300). MS (m/z): 474 (M^+, $C_{26}H_{34}O_8$), 456 (M^+-H_2O), 438 (M^+-2H_2O), 386 ($C_{22}H_{26}O_6^+$), 373, 368 ($C_{22}H_{24}O_5^+$), 355 ($C_{21}H_{23}O_5^+$), 337 ($C_{21}H_{21}O_4^+$), 327, 281, 149, 121, 60.

Tetraacetate (7) of 5——**5** (15 mg) was acetylated with Ac_2O–pyridine (1: 1, 2 ml) in the usual manner to yield the acetate (**7**), colorless needles (11 mg) from MeOH, mp 200—202°C, $[\alpha]_D^{20}$ −125.0° (c=1.10, $CHCl_3$), MS (m/z): 642 (M^+, $C_{34}H_{42}O_{12}^+$), 600 ($M^+-C_2H_2O$), 582 (M^+-AcOH), 540 ($C_{30}H_{36}O_9^+$), 522 (M^+-2AcOH), 480 ($C_{28}H_{32}O_7^+$), 462 (M^+-3AcOH), 457, 438 ($C_{26}H_{30}O_6^+$), 402 (M^+-4AcOH), 396 ($C_{24}H_{28}O_5^+$), 355, 337, 264, 198, 181. ^{1}H NMR ($CDCl_3$) δ: 0.89 (3H, d, J=6 Hz, 25-CH_3), 1.32 (3H, s, 10-CH_3), 2.00, 2.03, 2.08, 2.14 (3H each, all s, 4×OCOCH_3), 4.14 (1H, dd, J=8, 10 Hz, 21-H), 4.41 (1H, dd, J=6, 10 Hz, 21-H′), 4.41 (1H, d, J=6 Hz, 16-H), 4.85 (1H, m, 3-H), 5.01 (1H, d, J=10 Hz, 23-H), 5.17 (1H, t, J=10 Hz, 24-H), 5.76 (1H, m, 6-H).

$NaBH_4$ Reduction of 8——$NaBH_4$ (30 mg) was added portionwise to a solution of **8** (100 mg) in a mixture of $CHCl_3$ (3 ml) and MeOH (5 ml) at room temperature. The reaction mixture was stirred for 30 min at room temperature, neutralized with 10% AcOH and evaporated to dryness *in vacuo* to give a residue, which was passed through a Sephadex LH-20 column with MeOH to afford the product. This product was acetylated with Ac_2O–pyridine (2 ml each) to give the crude acetate, which was purified by silica gel column chromatography using *n*-hexane–AcOEt (2: 1) as the solvent to provide **9** (38 mg), *Rf* 0.27 (*n*-hexane–AcOEt=2: 1) and an unidentified compound (7 mg), *Rf* 0.19. **9**: A white powder (mp 90—95°C), $[\alpha]_D^{23}$ −123.4° (c=0.31, $CHCl_3$), *Anal.* Calcd for $C_{38}H_{50}O_{14}$: C, 62.45; H, 6.90. Found: C, 62.12; H, 6.92. MS (m/z): 730 (M^+), 688, 670, 610, 592, 550, 532, 490, 472, 430, 412, 398, 352, 292, 260, 232. ^{1}H NMR ($CDCl_3$) δ: 0.83 (3H, d, J=6 Hz, 25-CH_3), 1.14 (3H, s, 10-CH_3), 2.01, 2.02, 2.05, 2.06, 2.08, 2.16 (3H each, all s, 6×OCOCH_3), 3.55 (2H, d, J=8 Hz, 26-H_2), 4.04 (1H, dd, J=9, 11 Hz, 21-H), 4.36 (1H, dd, J=6, 11 Hz, 21-H′), 4.60—5.11 (5H, 1α, 3α, 16α, 23β, 24α-H_5), 5.37 (1H, br d, J=6 Hz, 15-H), 5.66 (1H, m, 6-H).

$NaBH_4$ Reduction of 7——**7** (8.4 mg) was reduced with $NaBH_4$ (6 mg) in the same manner as **8**. The reduction products were acetylated (Ac_2O, pyridine, 0.7 ml each) and chromatographed on silica gel (solv. *n*-hexane–AcOEt=2: 1) to give two compounds, *Rf* 0.27 (3 mg) and 0.23 (4 mg) (solv. *n*-hexane–AcOEt=2: 1), of which the former (less polar substance) was identical with **9** in terms of MS, FT-PMR spectra and TLC behavior.

Compound 10——Colorless needles from dil. MeOH, mp 240—242°C, *Rf* 0.13 (solv. $CHCl_3$–MeOH=20: 3), *Anal.* Calcd for $C_{27}H_{44}O_7\cdot H_2O$: C, 65.03; H, 9.30. Found: C, 65.12; H, 9.26.

Compound 11——Pale yellow crystals from dil. MeOH, mp 195—200°C (dec.), $[\alpha]_D^{21}$ −134.3° (c=1.01, pyridine). Mg–HCl, Zn–HCl tests: positive. IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1650, 1600. FD-MS (m/z): 611 (M^++H), 448, 286. ^{1}H NMR (pyridine-d_5) δ: 5.44, 5.78 (each 1H, d, J=6 Hz, 2×glucosyl anomeric proton), 6.76 (1H, d, J=2 Hz, 6-H), 6.10 (1H, d, J=2 Hz, 8-H), 7.38, 8.48 (2H each, AA′BB′ quartet, J=8 Hz, 2′,3′,5′,6′-H_4). ^{13}C NMR (DMSO-d_6): see formula **11**. **11** (103 mg) was acetylated with Ac_2O–pyridine (2 ml each) in the usual manner to yield the acetate (59 mg) as a white powder (mp 125—126°C), $[\alpha]_D^{21}$ −80.8° (c=1.01, pyridine), MS (m/z): 619 (terminal peracetylated di-glucosyl cation), 331 (terminal peracetylated glucosyl cation).

Acid Hydrolysis of 11——**11** (15 mg) was hydrolyzed with 6% HCl–MeOH (5 ml) under reflux for 3 h on a hot bath. The mixture was cooled, and the deposited aglycone was collected by filtration and recrystallized from MeOH to afford yellow crystals (4 mg), mp 275—278°C (dec.), MS (m/z): 286 (M^+), identical with kaempferol, while the filtrate was neutralized with aq. K_2CO_3 and passed through Sephadex LH-20 with MeOH to give a syrup (6 mg), $[\alpha]_D^{22}$ +49.2° (c=0.25, water), which was examined by PPC (*Rf* 0.44, solv. *n*-BuOH–AcOH–water=6: 1: 5) and on Avicel (*Rf* 0.17, solv. the same as for PPC); D-glucose was detected as the sugar component.

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