[Chem. Pharm. Bull. 36(9)3654—3658(1988)]

Studies on the Nepalese Crude Drugs. XI.[1] On the Flavonoid Constituents of the Aerial Parts of *Scutellaria discolor* COLEBR.[2]

TSUYOSHI TOMIMORI,*,[a] YUKINORI MIYAICHI,[a] YOSHITAKA IMOTO,[a] HARUHISA KIZU[a] and TSUNEO NAMBA[b]

School of Pharmacy, Hokuriku University,[a] 3 Ho, Kanagawa-machi, Kanazawa 920–11, Japan and Research Institute for Wakan-Yaku, Toyama Medical and Pharmaceutical University,[b] 2630, Sugitani, Toyama 930–01, Japan

(Received February 8, 1988)

From the aerial parts of *Scutellaria discolor* COLEBR., two new flavones (I and II) were isolated together with chrysin, wogonin, apigenin, luteolin, 5,7-dihydroxy-8,2′-dimethoxyflavone, 5,7,4′-trihydroxy-8-methoxyflavone, 5,7-dihydroxy-8,2′,6′-trimethoxyflavone and chrysin 7-*O*-glucuronide. Compounds I and II were identified as 5,7,8-trihydroxyflavone 8-*O*-β-D-glucuronopyranoside and 5,7,2′,6′-tetrahydroxy-8-methoxyflavone 2′-*O*-β-D-(2-*O*-caffeoyl)glucopyranoside, based on spectral and chemical data.

Keywords——*Scutellaria discolor*; Labiatae; flavone; flavone glycoside

In the previous papers,[3] we reported the structural identification of seventeen flavonoids which were isolated from the root of *Scutellaria discolor* COLEBR. collected in Central Nepal. In our further studies on the constituents of the aerial parts of this plant, two new flavones (I and II) and eight known flavones (III—X) were isolated. The present paper deals with their structural determination.

Compounds I—X showed positive color reactions to Mg–HCl, and had absorption bands assignable to hydroxyls, conjugated carbonyl groups and aromatic rings in the infrared (IR) spectra.

Compound I was obtained as yellow needles, mp 212 °C (dec.), $C_{21}H_{18}O_{11}$. On methanolysis, I yielded norwogonin (5,7,8-trihydroxyflavone),[3a] and a sugar fraction, which was identified as methyl glucuronopyranoside methyl ester and the methyl glycoside of glucurono-6,3-lactone by gas-liquid chromatography (GLC).

In the proton (^{1}H-) and carbon-13 (^{13}C-) nuclear magnetic resonance (NMR) spectra of I, an anomeric proton signal at 4.82 ppm (d, $J=7.4$ Hz) and a set of carbon signals due to the sugar moiety including an anomeric carbon signal at 106.4 ppm (d, $J=162.5$ Hz) indicated the presence of a β-glucuronopyranosyl unit in I.

Compound I was methylated with CH_2N_2 to give the dimethyl ether monomethyl ester (Ia), mp 234 °C (dec.), $C_{24}H_{24}O_{11}$. Reduction of Ia with $NaBH_4$ followed by acid hydrolysis gave glucose, which was proved to be the D-form according to the method reported by Oshima and Kumanotani.[4] The position of the sugar in I was concluded to be at the C_8-OH based on the ultraviolet (UV) spectrum and diagnostic shifts showing the presence of free hydroxyls at the C-5 and C-7 positions.[5] From these results, the structure of I was determined to be 5,7,8-trihydroxyflavone 8-*O*-β-D-glucuronopyranoside.

Compound II was obtained as pale yellow needles, mp 207 °C (dec.), $C_{31}H_{28}O_{15}$. The UV spectrum and the diagnostic shifts suggested II to be a 5,7-dihydroxyflavone derivative.[5] The

^{1}H-NMR spectrum of II showed the presence of one methoxyl (3.66 ppm), sugar protons (3.00—5.13 ppm), one C-3 proton (5.95 ppm), two olefinic protons (5.94 and 7.10 ppm, each doublet, $J=15.6$ Hz), four hydroxyls (2H, *ca.* 9.40 ppm; each 1H, *ca.* 10.10 and 10.50 ppm) and one chelated hydroxyl (12.63 ppm). In the aromatic region of the spectrum, there were two singlets (each 1H, 6.28 and 6.92 ppm), three doublets (2H, 6.72 ppm, $J=8.3$ Hz; each 1H, 6.65 and 6.75 ppm, $J=8.8$ Hz) and one triplet (1H, 7.30 ppm, $J=8.3$ Hz). On the hydrolysis of II, caffeic acid and glucose were identified by thin-layer chromatography (TLC). The glucose obtained was confirmed to be the D-form as in the case of I.

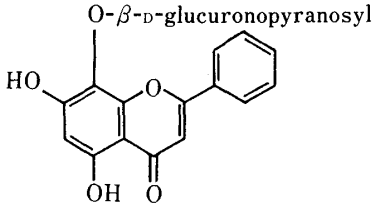
In the ^{1}H- and ^{13}C-NMR spectra of II, an anomeric proton signal at 5.13 ppm (d, $J=8.3$ Hz) and a set of carbon signals due to the sugar moiety including an anomeric carbon signal at 98.4 ppm (d, $J=161.0$ Hz) indicated the presence of a β-D-glucopyranosyl unit.

Methylation of II with CH_2N_2 followed by alkaline hydrolysis gave IIa, mp 157 °C (dec.), $C_{24}H_{26}O_{12}$, $FeCl_3(+)$, and 3,4-dimethoxycinnamic acid. On enzymatic hydrolysis with β-glucosidase, IIa gave rivularin (5,2′-dihydroxy-7,8,6′-trimethoxyflavone)[6] and D-glucose. Based on these findings, II was considered to be the 8- or 6′-methyl ether of 5,7,8,2′,6′-pentahydroxyflavone possessing a caffeoylglucose at C-2′ position.

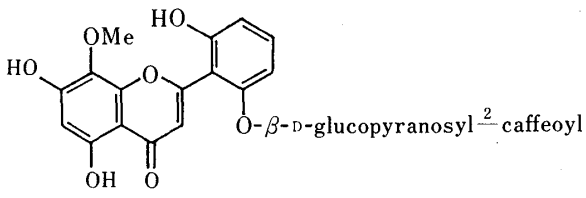
In the ^{13}C-NMR spectrum of II, the carbon signal of the methoxyl appeared downfield at 60.8 ppm, which indicated the methoxyl to be on the C-8 carbon, being di-*ortho*-substituted by two oxygen functions.[7] The linkage between the caffeoyl group and D-glucose in II was determined by the use of acylation shifts[8] in ^{13}C-NMR spectroscopy. In the ^{13}C-NMR spectrum of II, the signals due to C-1″ and C-3″ were shielded by 2.1 and 3.8 ppm, respectively, in comparison with those of IIa, while other signals of the sugar moiety were almost unaffected. These data suggested that the caffeoyl group was linked to C-2″.

From these results, the structure of II was identified as 5,7,2′,6′-tetrahydroxy-8-methoxyflavone 2′-*O*-β-D-(2-*O*-caffeoyl) glucopyranoside.

Compounds III—X were known flavones and were identified as chrysin,[1] wogonin,[3a] apigenin,[1] luteolin,[9] 5,7-dihydroxy-8,2′-dimethoxyflavone,[6a] 5,7,4′-trihydroxy-8-methoxyflavone,[3b] 5,7-dihydroxy-8,2′,6′-trimethoxyflavone[3b] and chrysin 7-*O*-glucuronide,[1] respectively, by direct comparison with authentic samples.



I



II

Fig. 1

Experimental

General Procedures——The instruments used to obtain the physical data were the same as described in the previous paper.[3b] GLC was run on a Shimadzu GC-6AM unit with a flame ionization detector. GLC-1: column, a glass column (2 m × 4 mm i.d.) packed with 5% SE-30 on Chromosorb W (60—80 mesh); column temperature, programmed from 150 °C (20 min hold) to 240 °C at 5 °C/min. GLC-2: column, a fused-silica WCOT column with Carbowax 20M (Shinwa Kako Co., 25 m × 0.2 mm); column temperature, programmed from 110 °C (1 min hold) to 170 °C (10 min hold) at 2 °C/min (lit.,[4] 158 °C). TLC was carried out on Kieselgel 60 F 254 (Merck) with the following solvent systems: $CHCl_3$–MeOH–H_2O-HCOOH (25 : 8 : 1 : 1) (TLC-1), AcOEt–methyl ethyl ketone–H_2O–HCOOH (70 : 30 : 10 : 1) (TLC-2). Spots were detected by spraying diluted H_2SO_4 followed by heating. TLC for sugar was conducted on Avicel SF(Funakoshi) with *n*-BuOH–AcOH–H_2O (4 : 1 : 5) (TLC-3) and the detection was done by spraying aniline hydrogen phthalate reagent.

Extraction and Separation——The dried aerial parts (140 g) of *Scutellaria discolor* COLEBR. collected in Central

Nepal in 1983, were extracted with boiling EtOH. The EtOH extract was concentrated to dryness to give a residue (28 g), which was suspended in H_2O and successively extracted with Et_2O and *n*-BuOH. The Et_2O layer was concentrated and the residue (3.4 g) was chromatographed on silica gel (100 g) using *n*-hexane–acetone (10 : 1→1 : 1) as an eluent to give three fractions, fr. 1—3, in the order of elution. Fraction 1 was subjected to rechromatography on silica gel[solvent : benzene–$CHCl_3$ (1 : 1)] to give IV, VII and IX. Fraction 2, a mixture of two flavonoids, was passed through a silica gel column [solvent : $CHCl_3$–MeOH–H_2O (100 : 2 : 0.1)] to give III and VIII. Fraction 3 was rechromatographed on silica gel[solvent : benzene–AcOEt(100 : 12)] to give V and VI. The *n*-BuOH-soluble portion was concentrated and the residue (8.6 g) was chromatographed on RP-8 (100 g) with a gradient of MeOH–H_2O (1 : 10→1 : 0) as an eluent to give I, II and X. Yields: I (40 mg), II (35 mg), III (10 mg), IV (20 mg), V (15 mg), VI (10 mg), VII (15 mg), VIII (5 mg), IX (10 mg), X (40 mg).

I (5,7,8-Trihydroxyflavone 8-*O*-*β*-D-Glucuronopyranoside)——Yellow needles (MeOH/H_2O), mp 212° C. (dec.). $[\alpha]_D^{14}$ +23.7° (c=0.07, MeOH). *Anal.* Calcd for $C_{21}H_{18}O_{11}$: C, 56.50; H, 4.06. Found: C, 56.24; H, 4.03. Mg–HCl (+). *Rf*: 0.14 (TLC-1), 0.58 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 279 (4.39), 346 (3.68); $\lambda_{max}^{MeOH-NaOMe}$ nm (log ε): 240 sh (4.13), 265 sh (4.31), 284 (4.42), 370 (3.78); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ε): 255 (3.53), 287 sh (4.32), 295 (4.34), 334 (3.90), 405 (3.64); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ε): 257 (4.10), 287 sh (4.32), 295 (4.34), 332 (3.87), 405 (3.59); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ε): 265 sh (4.20), 284 (4.40), 370 (3.79); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ε): 265 sh (4.21), 283 (4.39), 370 (3.73). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1730 (COOH), 1650 (conjugated CO), 1600, 1580, (arom. C=C). ^{1}H-NMR: 3.00—4.20 (m, sugar moiety), 4.82 (1H, d, J=7.4 Hz, anomeric H of glucuronic acid unit), 6.30 (1H, s, 6-H), 7.01 (1H, s, 3-H), 7.58 (3H, m, 3′, 4′, 5′-H), 8.19 (2H, m, 2′, 6′-H), 12.65 (1H, s, 5-OH). ^{13}C-NMR: 163.4 (C-2), 104.8 (C-3), 182.1 (C-4), 157.5 (C-5), 99.2 (C-6, $J_{(C-6)-(6-H)}$=163.2 Hz, $J_{(C-6)-(5-OH)}$=7.4 Hz), 157.6 (C-7), 125.4 (C-8), 149.6 (C-9), 103.7 (C-10), 130.6 (C-1′), 126.8 (C-2′,6′), 129.2 (C-3′, 5′), 132.1 (C-4′), 106.4 (C-1″, J=162.5 Hz), 73.8 (C-2″), 75.3 (C-3″), 71.5 (C-4″), 76.2 (C-5″), 170.2 (C-6″). EI-MS m/z (%): 270 ($C_{15}H_{10}O_5$, 100), 168 ($C_7H_4O_5$, 95).

Methanolysis of I: A solution of I (10 mg) in 10% HCl–MeOH (2 ml) was heated under reflux on a water bath for 3 h. The reaction mixture was neutralized with Ag_2CO_3. The precipitates were filtered off and the filtrate was concentrated to give the residue, which was chromatographed on silica gel (10 mg) using benzene as an eluent to give yellow needles (MeOH), mp 175 °C (dec.). This product was identified as norwogonin[3b] by direct comparisons (TLC, UV, IR, ^{1}H- and ^{13}C-NMR, mixed fusion) with an authentic specimen. The mother liquor of crystallization was shown to contain methyl glucuronopyranoside methyl ester [t_R 13 min 24 s (both α and β)] and the methyl glycoside of glucurono-6,3-lactone [t_R 6 min 05 s (α, trace), 6 min 48 s (β)] by GLC-1 (as the trimethylsilyl (TMS) ether derivatives).

Methylation of I: An MeOH solution (10 ml) of I (25 mg) was left to stand overnight with ethereal CH_2N_2 (3 ml). After removal of the solvent, the residue was chromatographed on silica gel (10 g) using $CHCl_3$–MeOH (10 : 1) as an eluent and recrystallized from MeOH to give Ia (yield 15 mg) as colorless needles, mp 234 °C (dec.). $[\alpha]_D^{14}$ +18.1 (c=0.07, MeOH). *Anal.* Calcd for $C_{24}H_{24}O_{11}$: C, 59.01; H, 4.95. Found : C, 58.73; H, 4.97. Mg-HCl (+). *Rf*: 0.64 (TLC-1), 0.26 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 270 (4.13), 331 (3.64). No change was observed when the spectrum was determined in the presence of NaOMe, NaOAc or $AlCl_3$. IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 1740 (−$COOCH_3$), 1640 (conjugated CO), 1600, 1590 (arom. C=C). ^{1}H-NMR: 3.45 (−$COOCH_3$), 3.89, 3.96 (each 3H, each s, −OCH_3 ×2), 3.00—3.80 (m, sugar moiety), 4.94 (1H, d, J=5.4 Hz, anomeric H of glucuronic acid unit), 6.70 (1H, s, 6-H), 6.75 (1H, s, 3-H), 7.51 (3H, m, 3′,4′,5′-H), 8.17 (2H, m, 2′,6′-H). ^{13}C-NMR: (* may be reversed) 160.0 (C-2), 107.5 (C-3), 176.0 (C-4), 156.7 (C-5*), 93.9 (C-6), 156.4 (C-7*), 126.1 (C-8), 151.5 (C-9), 107.4 (C-10), 131.1 (C-1′), 126.5 (C-2′, 6′), 128.9 (C-3′,5′), 131.4 (C-4′), 103.7 (C-1″), 73.9 (C-2″), 75.5 (C-3″, 5″), 71.6 (C-4″), 169.1 (C-6″), 51.1 (–COO$\underline{C}H_3$), 56.3, 56.7 (C-5, 7-O$\underline{C}H_3$ ×2). EI-MS m/z (%): 298 ($C_{17}H_{14}O_5$, 100), 269 ($C_{15}H_9O_5$, 40).

Reduction of Ia Followed by Hydrolysis: $NaBH_4$ (5 mg) was added to a solution of Ia (10 mg) in MeOH (5 ml) under cooling in an ice-bath, and the mixture was left for 30 min with stirring. After neutralization with diluted AcOH, the reaction mixture was extracted with AcOEt. The AcOEt-soluble portion was washed with water, passed through a silica gel column and evaporated to dryness *in vacuo*. The residue was hydrolyzed with 2 N HCl (2 ml) under reflux for 2 h. The reaction mixture was neutralized with Ag_2CO_3 and the precipitate was filtered off. The filtrate was passed through Sephadex LH-20 with MeOH to give a syrup, which was shown to contain D-glucose by GLC-2 [sugar was converted to the TMS-ether of 1-(L-α-methyl-benzylamino)-1-deoxyalditol (TMS-MBA-alditol) according to Oshima and Kumanotani[4]], t_R 25 min 0 s (TMS-MBA-D-glucitol, t_R 25 min 0 s TMS-MBA-L-glucitol, t_R 24 min 52 s).

II (5,7,2′,6′-Tetrahydroxy-8-methoxyflavone 2′-*O*-*β*-D-(2-*O*-caffeoyl)glucopyranoside)——Pale yellow needles (MeOH/H_2O) mp 207 °C (dec.). $[\alpha]_D^{14}$ −152.4° (c=0.03, MeOH). *Anal.* Calcd for $C_{31}H_{28}O_{15}$: C, 58.12; H, 4.41. Found: C, 57.84; H, 4.42. Mg–HCl (+). *Rf*: 0.27 (TLC-1), 0.59 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 267 (4.23), 305 sh (3.97), 332 (3.99); $\lambda_{max}^{MeOH-NaOMe}$ nm: (log ε): 274 (4.30), 378 (4.16); $\lambda_{max}^{MeOH-AlCl_3}$ nm: (log ε): 275 (4.24), 295 sh (3.98), 325 sh (3.85), 370 (3.99); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ε): 257 (4.25), 279 (4.23), 330 (4.00); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ε): 276 (4.23), 340 (3.92), 380 sh (3.87); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ε): 264 (4.25), 305 sh (3.86), 353 (4.00). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1700 (ester), 1650 (conjugated CO), 1610 (arom. C=C). ^{1}H-NMR (caffeoyl moiety c): 3.66 (3H, s, 8-OCH_3), 3.00—4.00 (m, sugar moiety), 5.13 (1H, d, J=8.3 Hz, anomeric H of glucose unit), 5.94 (1H, d, J=15.6 Hz, cα-H), 5.95 (1H, s, 3-H), 6.28 (1H, s, 6-H), 6.65 (1H, d, J=8.8 Hz, c5-H), 6.72 (2H, d, J=8.3 Hz, 3′,5′-H), 6.75 (1H, d, J=8.8 Hz, c6-H), 6.92 (1H, s, c2-H), 7.10 (1H, d, J=16.1 Hz, cβ-H), 7.30 (1H, t, J=8.3 Hz, 4′-H), 9.40 (2H, br s, OH ×2), 10.10, 10.50 (each 1H, each br s; OH ×2), 12.63 (1H, s, 5-OH). ^{13}C-NMR (caffeoyl moiety c): 160.6 (C-2),

111.9 (C-3), 182.0 (C-4), 156.4 (C-5), 98.8 (C-6), 156.8 (C-7), 127.5 (C-8), 150.8 (C-9), 104.0 (C-10), 110.2 (C-1′), 156.5 (C-2′), 105.4 (C-3′), 132.2 (C-4′), 110.0 (C-5′), 156.0 (C-6′), 98.4 (C-1″, J=161.0 Hz), 73.7 (C-2″), 72.9 (C-3″), 70.0 (C-4″), 77.3 (C-5″), 60.5 (C-6″), 165.1 (cC=O), 115.0 (cC-α), 145.2 (cC-β), 125.7 (cC-1), 113.4 (cC-2), 145.8 (cC-3), 148.2 (cC-4), 115.7 (cC-5), 121.2 (cC-6), 60.8 (C-8-OCH$_3$). EI-MS m/z (%). 316 ($C_{16}H_{12}O_7$, 65), 301 ($C_{15}H_9O_7$, 100). FAB-MS m/z (%): 641 (M^++1, 26), 317 ($C_{16}H_{12}O_7$+1, 75).

Acid Hydrolysis of II: II (0.5 mg) was hydrolyzed with 2 N HCl (1 ml) under reflux for 2 h. The reaction mixture was extracted with AcOEt. From the organic layer, caffeic acid was identified by TLC [Rf: 0.21 (TLC-1), 0.68 (TLC-2)]. The H_2O layer was treated in the same way as described for Ia, and D-glucose was detected by TLC [Rf: 0.15 (TLC-3)] and GLC-2.

Methylation of II with CH_2N_2 and Its Alkaline Hydrolysis: An MeOH–Et_2O solution (10 ml) of II (20 mg) was treated with ethereal CH_2N_2 (1 ml) for a short time. After removal of the solvent, the residue was treated with 1% KOH. After acidification with diluted HCl, the reaction mixture was extracted with Et_2O. The organic layer was washed with H_2O and concentrated to dryness, then the residue was subjected to chromatography on silica gel [solvent: benzene–AcOEt (5:2)] and recrystallized from MeOH to give colorless needles, mp 180 °C (3 mg); this product was identical with 3,4- dimethoxycinnamic acid by direct comparison (TLC, UV, IR and mixed fusion). The aqueous layer was passed through an RP-8 column, and washed with H_2O, then eluted with 40% MeOH. The eluate was concentrated to dryness and the residue was recrystallized from MeOH/H_2O to give IIa, pale yellow needles (12 mg), mp 157 °C (dec.), $[\alpha]_D^{13}$ −4.22 (c=0.14, MeOH). *Anal.* Calcd for $C_{24}H_{26}O_{12}$: C, 56.91; H, 5.17. Found: C, 57.24; H, 5.13. Mg–HCl (+). Rf: 0.58 (TLC-1), 0.54 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 266 (4.27), 305 sh (3.59), 340 (3.41); $\lambda_{max}^{MeOH-NaOMe}$ nm (log ε): 271 (4.25), 376 (3.34); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ε): 276 (4.22), 298 sh (3.85), 320 (3.55), 400 (3.35); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ε): 276 (4.21), 298 sh (3.84), 320 sh (3.48), 400 (3.35); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ε): 266 (4.29), 306 sh (3.67), 340 (3.51); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ε): 265 (4.28), 306 sh (3.63), 340 (3.43). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1660 (conjugated CO), 1610, 1590 (arom. C=C). ^{1}H-NMR: 3.66, 3.79, 3.90 (each 3H, each s, −OCH$_3$×3), 3.00—3.70 (m, sugar moiety), 4.94 (1H, d, J=6.9 Hz, anomeric H of glucose unit), 6.32 (1H, s, 3-H), 6.61 (1H, s, 6-H) 6.86 (1H, d, J=8.3 Hz, 3′-H), 6.92 (1H, d, J=8.3 Hz, 5′-H), 7.49 (1H, t, J=8.3 Hz, 4′-H), 12.70 (1H, s, 5-OH). ^{13}C-NMR: 161.3 (C-2), 112.5 (C-3), 182.4 (C-4), 157.0 (C-5), 96.1 (C-6), 158.5 (C-7), 128.7 (C-8), 150.1 (C-9), 104.4 (C-10), 111.4 (C-1′), 156.2 (C-2′), 107.8 (C-3′), 132.9 (C-4′), 105.5 (C-5′), 158.3 (C-6′), 100.5 (C-1″), 73.2 (C-2″), 76.7 (C-3″), 69.7 (C-4″), 77.2 (C-5″), 60.8 (C-6″), 61.2 (C-8-OCH$_3$), 56.6, 56.2 (C-7, 6′-OCH$_3$). EI-MS m/z (%): 506 (M^+, 20), 344 ($C_{18}H_{16}O_7$, 75), 329 ($C_{17}H_{13}O_7$, 100).

Enzymatic Hydrolysis of IIa: A solution of IIa (10 mg) and β-glucosidase (10 mg, from almond, Sigma) in pH 5.0 (diluted HCOOH, 10 ml) was incubated at 37 °C for 15 h. After cooling, the reaction mixture was extracted with AcOEt. The organic layer was washed with water and concentrated to give the residue (5 mg), which was chromatographed on silica gel using Et_2O as an eluent to give yellow needles (MeOH), mp 253 °C. This product was identical with rivularin[7] by direct comparison (TLC, UV, IR, ^{1}H- and ^{13}C-NMR). The H_2O layer was concentrated to dryness and extracted with MeOH. The MeOH-soluble portion was concentrated and the residue was passed through RP-8 with H_2O to give a syrup, which was shown to contain D-glucose by GLC-2.

Identification of III—X——III (mp 285 °C), IV (mp 203 °C), V (mp 350 °C), VI (mp 329 °C), VII (mp 231 °C), VIII (mp 302 °C (dec.)), IX (mp 206 °C (dec.)) and X (mp 226 °C), were identified as chrysin,[1] wogonin,[3a] apigenin,[1] luteolin,[9] 5,7-dihydroxy-8,2′-dimethoxyflavone,[6a] 5,7,4′-trihydroxy-8-methoxyflavone,[3b] 5,7-dihydroxy-8,2′,6′-trimethoxyflavone[3b] and chrysin 7-*O*-glucuronide,[1] respectively, by direct comparisons with authentic specimens (UV, IR, ^{1}H- and ^{13}C-NMR, mixed fusion).

Acknowledgement We are grateful to Dr. N. P. Manandhar, Botanical Survey and Herbarium Section, Department of Medicinal Plants, Ministry of Forests, His Majesty's Government of Nepal, for his identification of *Scutellaria discolor* COLEBR., and to Mrs. R. Igarashi and Miss H. Shimomura of Hokuriku University for elemental analysis and EI and FAB mass measurements. This work was supported in part by a Grant -in Aid (No. 61041032) for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References and Notes

1) Part X: M. Miyaichi, Y. Imoto, H. Kizu and T. Tomimori *Shoyakugaku Zasshi*, **42**, 205 (1988).
2) Presented at the 32nd Annual Meeting of the Japanese Society of Pharmacognosy, Okayama, October 1985.
3) *a*) T. Tomimori, Y. Miyaichi, Y. Imoto, H. Kizu and T. Namba, *Chem. Pharm. Bull.*, **33**, 4457 (1985); *b*) *Idem, ibid.*, **34**, 406 (1986).
4) R. Oshima and J. Kumanotani, *J. Chromatogr.*, **259**, 159 (1983).
5) T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York, 1970, Chapter V.
6) *a*) T. Tomimori, Y. Miyaichi, Y. Imoto and H. Kizu, *Shoyakugaku Zasshi*, **38**, 249 (1984); *b*) C. J. Chou, *J. Taiwam Pharm. Assoc.*, **30**, 36 (1978).

7) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **44**, 2855 (1966); K. Panichpol and P. G. Waterman, *Phytochemistry*, **17**, 1363 (1978).
8) K. Markham, B. Ternai, R. Stanley, H. Geiger and T. Mabry, *Tetrahedron*, **34**, 1389 (1978); T. Yoshida, T. Saito and S. Kadoya, *Chem. Pharm. Bull.*, **35**, 97 (1987); K. Yamasaki, R. Kasai, Y. Masaki, M. Okihara and O. Tanaka, *Tetrahedron Lett.*, **1977**, 1231.
9) T. Tomimori, Y. Miyaichi, Y. Imoto and H. Kizu, *Shoyakugaku Zasshi*, **40**, 432 (1986).