Studies on the Nepalese Crude Drugs. XII.[1] On the Phenolic Compounds from the Root of *Scutellaria prostrata* JACQ. *ex* BENTH.[2]

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From the root of *Scutellaria prostrata* JACQ. *ex* BENTH., five compounds (I—V) were isolated, together with three known glycosides of phenylethanoid (VI—VIII) and sixteen known flavonoids (IX—XXIV). On the basis of chemical and spectral evidence, I—V were identified as 5,6,2′,6′-tetrahydroxy-7,8-dimethoxyflavone, 5,6,2′-trihydroxy-7,8,6′-trimethoxyflavone, 5,7,2′-trihydroxy-8-methoxyflavone 7-*O*-β-D-glucuronopyranoside, 2-(3-hydroxy-4-methoxyphenyl)ethyl 1-*O*-β-D-glucopyranoside and 2-(3-hydroxy-4-methoxyphenyl)ethyl 1-*O*-β-D-(4-*O*-feruloyl)glucopyranoside, respectively. Compound II has already been synthesized.

Keywords *Scutellaria prostrata*; Labiatae; phenylethanoid; flavonoid; structure elucidation

Scutellaria prostrata JACQ. *ex* BENTH. is a perennial herb of the Labiatae family, and is widely distributed in China, Nepal, Pakistan and India.[3]

As regards the constituents of this plant, no work has been reported. As part of our studies on Nepalese crude drugs and on the flavonoid constituents of the *Scutellaria* species, we have now examined this plant. As described in the experimental section, five new compounds (I—V) were isolated together with three known phenylethanoids (VI—VIII) and sixteen known flavonoids (IX—XXIV) from the ethanol extract of the root of this plant which was collected in Central Nepal. This paper deals with their structural identification.

Compounds I—III 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 274—275 °C (dec.), $C_{17}H_{14}O_8$. The ultraviolet (UV) spectrum of I was characteristic of the flavone series and showed a bathochromic shift by the addition of $AlCl_3$/HCl, indicating the presence of a free hydroxyl at the C-5 position.[4] In addition, the proton nuclear magnetic resonance (^{1}H-NMR) spectrum of I showed a signal at 12.45 ppm confirming the presence of a chelated hydroxyl. The ^{1}H-NMR spectrum also showed the presence of two methoxyls (3.82, 3.95 ppm), three hydroxyls (1H, 9.05 ppm; 2H, 9.90 ppm) and one C-3 proton (6.27 ppm). In the aromatic region of the spectrum, the remaining three protons appeared as a doublet (2H, 6.45 ppm, J=8.2 Hz) and a triplet (1H, 7.14 ppm, J=8.2 Hz). These signals could be assigned to C-3′,5′ and C-4′ protons, respectively, from their chemical shifts and coupling patterns.

Compound I was methylated with CH_2N_2 to give a trimethyl ether (Ia), mp 158 °C (dec.), $C_{20}H_{20}O_8$, which was identical with 5-hydroxy-6,7,8,2′,6′-pentamethoxyflavone prepared from skullcapflavone II (5,2′-dihydroxy-6,7,8,6′-tetramethoxyflavone)[5] by partial methylation with CH_2N_2. I is, therefore, a dimethyl ether of 5,6,7,8,2′,6′-hexahydroxyflavone.

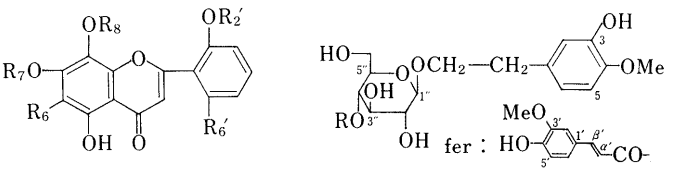
In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum of I, the methoxyl carbon signals appeared down field at 60.8 ppm and 61.6 ppm, indicating that these methoxyls were di-*ortho* substituted by two substituents.[6] This indicated that all the methoxyls were placed in the A-ring. The position of these methoxyls was determined by the long-range selective proton decoupling (LSPD) method[7] in the ^{13}C-NMR spectrum as follows. In the ^{1}H non-decoupling ^{13}C-NMR spectrum of I, one of the carbon singlet when the chelated hydroxyl proton at the C-5 position was selectively irradiated, indicating that the hydroxyl was present at the position *ortho* to the chelated position was selectively irradiated, indicating that the hydroxyl was present at the position *ortho* to the cheleted hydroxyl. The presence of a 5,6-dihydroxy system in I was also supported by the positive $SrCl_2$ test in an ammoniacal methanol solution of I.[8] These results led us to conclude that the methoxyls are present at C-7 and C-8 positions.

From these results, the structure of I was determined to be 5,6,2′,6′-tetrahydroxy-7,8-dimethoxyflavone.

Compound II was obtained as yellow needles, mp 224—225 °C (dec.), $C_{18}H_{16}O_8$, which was identified as 5,6,2′-trihydroxy-7,8,6′-trimethoxyflavone by comparing the physical properties and the ^{1}H-NMR spectral data with those reported by Iinuma *et al.*[9] Compound II has already been synthesized,[9] but this is the first isolation of II from a natural source.

Compound III was obtained as yellow needles, mp 257—259 °C (dec.), $C_{22}H_{20}O_{12}$. The UV spectrum and the diagnostic shifts suggested the presence of a hydroxyl at the C-5 position in the flavone nucleus.[4]

On methanolysis, III yielded scutevulin (5,7,2′-trihydroxy-8-methoxyflavone,[10] IIIa) 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 ^{1}H- and ^{13}C-NMR spectra of III, an anomeric proton signal at 5.25 ppm (d, J=7.3 Hz) and a set of carbon signals due to the sugar moiety including an anomeric carbon signal at 99.7 ppm indicated the presence of a β-glucuronopyranosyl unit



I : R_6=R_6'=OH, R_2'=H, R_7=R_8=Me
II : R_6=OH, R_6'=OMe, R_2'=H, R_7=R_8=Me
III : R_6=R_2'=R_6'=H, R_7=β-D-glu A, R_8=Me
glu A : glucuronopyranosyl

IV : R=H
V : R=fer

Fig. 1

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in III. In the ^{13}C-NMR spectrum of III, the A-ring carbon signals coincided well with those of wogonin 7-*O*-glucuronide,[11] suggesting that III is a 7-*O*-glucuronide of IIIa. On methylation with CH_2N_2, III gave a monomethyl ether monomethyl ester, mp 205—206 °C (dec.), $C_{24}H_{24}O_{12}$, which was identified as 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-*β*-D-glucuronopyranoside methyl ester[12] by direct comparison with an authentic specimen.

Hence III was determined to be 5,7,2′-trihydroxy-8-methoxyflavone 7-*O*-*β*-D-glucuronopyranoside.

Compound IV was obtained as an amorphous powder, $[\alpha]_D^{31}$ −12.9° (MeOH), $C_{15}H_{22}O_8$. IV showed the absorption maxima at 219 (sh) and 280 nm in the UV spectrum and showed the absorption bands corresponding to the hydroxyl group and the benzene ring in the IR spectrum. The ^{1}H-NMR spectrum of IV revealed two methylene protons (2H, 2.70 ppm, m; 1H, 3.55 ppm, dt, J=6.6 and 9.2 Hz and 1H, 3.87 ppm, dt, J=7.0 and 9.2 Hz), one methoxyl (3.71 ppm), one hydroxyl (8.43 ppm) and sugar protons (2.92—4.16 ppm). In the aromatic region of the spectrum, there were two doublets (1H, 6.88 ppm, J=1.8 Hz and 1H, 6.79 ppm, J=8.1 Hz) and one broad doublet (1H, 6.60 ppm, J=8.1 Hz).

On enzymatic hydrolysis with *β*-glucosidase, IV afforded an aglycone (IVa), mp 70—71 °C, $C_9H_{12}O_3$, and glucose, which was proved to be the D-form according to the method reported by Oshima and Kumanotani.[13] IVa was identified as 3-hydroxy-4-methoxyphenethyl alcohol[14] by direct comparison with an authentic sample. In the ^{1}H- and ^{13}C-NMR spectra of IV, an anomeric proton signal at 4.16 ppm (d, J=8.1 Hz) and a set of carbon signals due to the sugar moiety including an anomeric carbon signal at 102.8 ppm indicated the presence of a *β*-glucopyranosyl unit in IV.

From these results, the structure of IV was determined to be 2-(3-hydroxy-4-methoxyphenyl)ethyl 1-*O*-*β*-D-glucopyranoside.

Compound V was obtained as an amorphous powder, $[\alpha]_D^{31}$ −31.2° (MeOH), $C_{25}H_{30}O_{11}$, and had absorption bands assignable to hydroxyl, *α*,*β*-unsaturated carbonyl groups and aromatic rings in the IR spectra.

On alkaline hydrolysis with 0.5 N KOH V afforded IV and *trans*-ferulic acid, which suggested V to be a mono-ferulate of IV. In the ^{13}C-NMR spectrum of V, the carbon signals due to the phenethyl alcohol moiety were observed to be almost superimposable on those of IV, suggesting that the acyl group in V was attached to the glucose moiety. In order to clarify the binding site of the acyl group, we used the acylation shifts[15] in ^{13}C-NMR spectroscopy. In the ^{13}C-NMR spectrum of V, the signals

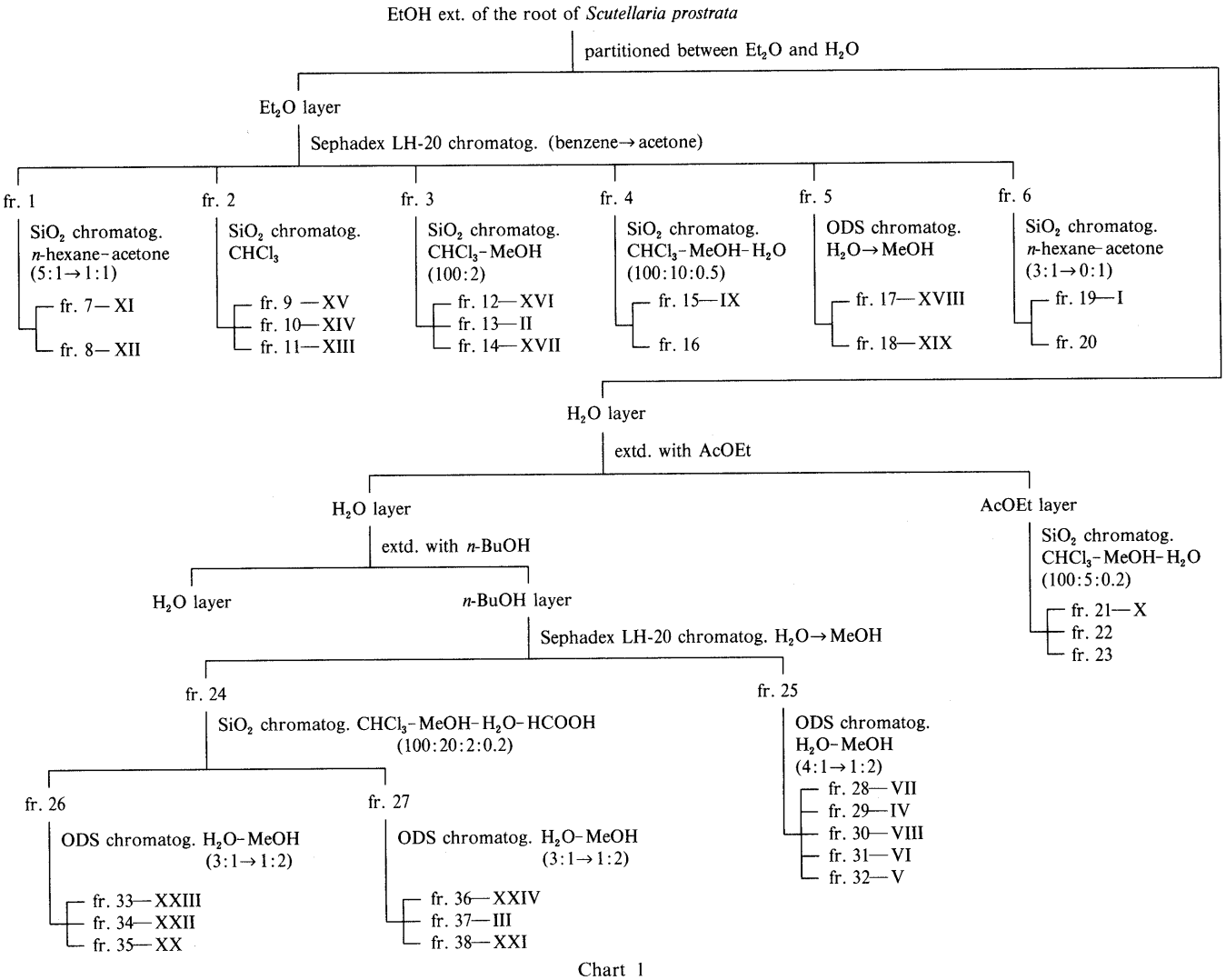

Chart 1

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due to the C-3 and C-5 position of glucose were shifted upfield in comparison with those of IV, while other signals remained almost unaffected. These data indicated that the feruloyl group was linked to the C-4 position of glucose.

From these results, the structure of V was determined to be 2-(3-hydroxy-4-methoxyphenyl)ethyl 1-*O*-*β*-D-(4-*O*-feruloyl)glucopyranoside.

Compounds VI—VIII are known glycosides of phenylethanoid and IX—XXIV are known flavonoids, which were identified as martynoside (VI),[16,17] acteoside (VII),[16,18] leucosceptoside A (VIII),[16] 5,7-dihydroxy-2′-methoxyflavone[19] (IX), 5,7-dihydroxy-2′-methoxyflavone 7-*O*-glucuronide[19b,20] (X), oroxylin A[11] (XI), wogonin[11] (XII), rivularin[10] (XIII), skullcapflavone I[21] (XIV), chrysin[22] (XV), baicalein[23] (XVI), 5,7,4′-trihydroxy-8-methoxyflavone[11] (XVII), 5,7,2′-trihydroxyflavone[24] (XVIII), scutevulin[10] (XIX), chrysin 7-*O*-glucuronide[22] (XX), oroxylin A 7-*O*-glucuronide[25] (XXI), wogonin 7-*O*-glucuronide[11] (XXII), baicalin[23] (XXIII) and norwogonin 7-*O*-glucuronide[26] (XXIV), respectively, by direct comparison with authentic samples. Some biological activities of the isolated compounds are under investigation.

Experimental

General Procedures The instruments were the same as described in the previous paper[1] except for the following. NMR spectra were taken in dimethyl sulfoxide-d_6 (DMSO-d_6) on a JNM-GSX-400 spectrometer (^{1}H-NMR at 400 MHz and ^{13}C-NMR at 100 MHz). 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.,[13] 158 °C). Thin layer chromatography (TLC) was carried out on Kieselgel 60F-254 (Merck) with the following solvent systems: $CHCl_3$–MeOH–H_2O–AcOH (100 : 10 : 1 : 0.3) (TLC-1), benzene–AcOEt–AcOH (100 : 60 : 0.5) (TLC-2), $CHCl_3$–MeOH–H_2O–HCOOH (25 : 8 : 1 : 0.5) (TLC-3), AcOEt–methyl ethyl ketone–H_2O–HCOOH (6 : 3 : 1 : 1) (TLC-4). Spots were detected by spraying dil. H_2SO_4 followed by heating.

Extraction and Separation As shown in Chart 1, twenty-four compounds, I (50 mg), II (100 mg), III (20 mg), IV (60 mg), V (80 mg), VI (270 mg), VII (150 mg), VIII (230 mg), IX (30 mg), X (30 mg), XI (30 mg), XII (70 mg), XIII (50 mg), XIV (20 mg), XV (40 mg), XVI (200 mg), XVII (20 mg), XVIII (15 mg), XIX (15 mg), XX (30 mg), XXI (20 mg), XXII (50 mg), XXIII (800 mg) and XXIV (20 mg) were obtained from the dried root of *Scutellaria prostrata* (1.5 kg) collected in Nepal in 1986.

I (5,6,2′,6′-Tetrahydroxy-7,8-dimethoxyflavone) Yellow needles (MeOH), mp 274—275 °C (dec.). *Anal.* Calcd for $C_{17}H_{14}O_8$: C, 58.96; H, 4.08. Found: C, 59.03; H, 4.16. EI-MS *m/z* (%): 346 (M^+, 80), 331 ($M^+ - CH_3$, 100), 197 ($C_8H_5O_6$, 65). Mg–HCl (+), $SrCl_2$ (+). *Rf*: 0.28 (TLC-1), 0.30 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 231 sh (4.26), 278 (4.30), 318 sh (3.93), 372 sh (3.47); $\lambda_{max}^{MeOH-NaOMe}$ nm (log ε): 245 sh (4.20), 288 (4.03), 349 (3.83), 380 sh (3.70); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ε): 232 sh (4.31), 295 (4.28), 345 (4.08), 420 (3.45); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ε): 292 (4.29), 335 (4.05), 420 (3.41); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ε): 278 (4.27), 321 sh (3.89); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ε): 279 (4.33), 326 (3.73), 387 sh (3.37). IR ν_{max}^{KBr} cm^{-1}: 3388 (OH), 1662 (conjugated CO), 1626 (arom. C=C). ^{1}H-NMR: 3.82, 3.95 (each 3H, each s, OCH_3 × 2), 6.27 (1H, s, 3-H), 6.45 (2H, d, *J* = 8.2 Hz, 3′,5′-H), 7.14 (1H, t, *J* = 8.2 Hz, 4′-H), 9.90 (2H, s, 2′,6′-OH), 9.05 (1H, s, 6-OH), 12.45 (1H, s, 5-OH). ^{13}C-NMR: 162.6 (C-2), 111.2 (C-3), 182.5 (C-4), 142.9 (C-5), 133.8 (C-6), 147.9 (C-7), 132.7 (C-8), 142.8 (C-9), 106.1 (C-10), 108.2 (C-1′), 156.6 (C-2′,6′), 106.5 (C-3′,5′), 132.7 (C-4′), 60.8, 61.6 (OCH_3 × 2).

Methylation of I: I was methylated with CH_2N_2 to give a trimethyl ether (Ia), yellow needles (MeOH), mp 158 °C (dec.). *Anal.* Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.73; H, 5.22. EI-MS *m/z* (%): 388 (M^+, 75), 373 ($M^+ - CH_3$, 100), 211 ($C_9H_7O_6$, 30). Mg–HCl (+). *Rf*: 0.80 (TLC-1), 0.60 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 268 (4.37), 310 sh (3.90), 350 sh (3.63); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ε): 281 (4.34), 300 sh (4.19), 327 (4.01), 405 (3.64). IR ν_{max}^{KBr} cm^{-1}: 3480 (OH), 1664 (conjugated CO), 1620, 1582 (arom. C=C). ^{1}H-NMR: 3.79 (9H, s, OCH_3 × 3), 3.83, 4.02 (each 3H, each s, OCH_3 × 2), 6.37 (1H, s, 3-H), 6.83 (2H, d, *J* = 8.3 Hz, 3′,5′-H), 7.53 (1H, t, *J* = 8.3 Hz, 4′-H), 12.60 (1H, s, 5-OH). ^{13}C-NMR: 162.0 (C-2), 112.2 (C-3), 182.7 (C-4), 146.4 (C-5), 136.1 (C-6), 152.9 (C-7), 132.8 (C-8), 148.8 (C-9), 106.4 (C-10), 110.2 (C-1′), 158.3 (C-2′,6′), 104.6 (C-3′,5′), 133.2 (C-4′), 56.2 (C-2′,6′-O$\underline{C}$H$_3$), 60.6, 60.8, 61.6 (OCH_3 × 3). Ia was identical (TLC, UV, IR, ^{1}H- and ^{13}C-NMR, mixed fusion) with 5-hydroxy-6,7,8,2′,6′-pentamethoxyflavone prepared from skullcapflavone II (5,2′-dihydroxy-6,7,8,6′-tetramethoxyflavone)[5] by methylation with CH_2N_2.

II (5,6,2′-Trihydroxy-7,8,6′-trimethoxyflavone) Yellow needles (MeOH), mp 224—225 °C (dec.). *Anal.* Calcd for $C_{18}H_{16}O_8$: C, 60.00; H, 4.48. Found: C, 60.12; H, 4.46. EI-MS *m/z* (%): 360 (M^+, 70), 345 ($M^+ - CH_3$, 100), 197 ($C_8H_5O_6$, 50). Mg–HCl (+), $SrCl_2$ (+). *Rf*: 0.45 (TLC-1), 0.36 (TLC-2). UV λ_{max}^{MeOH} nm (log ε): 277 (4.27), 317 sh (3.88), 368 sh (3.44); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ε): 293 (4.20), 346 (3.96), 418 sh (3.43); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ε): 292 (4.22), 338 (3.96), 430 (3.31); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ε): 276 (4.21), 368 sh (3.58); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ε): 277 (4.30), 368 sh (3.44). IR ν_{max}^{KBr} cm^{-1}: 3384 (OH), 1662 (conjugated CO), 1622 (arom. C=C). ^{1}H-NMR: 3.75, 3.80, 3.95 (each 3H, each s, OCH_3 × 3), 6.28 (1H, s, 3-H), 6.62 (2H, d, *J* = 8.2 Hz, 3′,5′-H), 7.32 (1H, t, *J* = 8.2 Hz, 4′-H), 9.13 (1H, br s, 6-OH), 10.13 (1H, s, 2′-OH), 12.40 (1H, s, 5-OH). ^{13}C-NMR: 162.0 (C-2), 111.4 (C-3), 182.4 (C-4), 143.0 (C-5), 134.0 (C-6), 148.0 (C-7), 132.8 (C-8), 142.8 (C-9), 106.1 (C-10), 109.0 (C-1′), 156.5 (C-2′), 108.7 (C-3′), 132.3 (C-4′), 102.2 (C-5′), 158.2 (C-6′), 55.8 (C-6′-O$\underline{C}$H$_3$), 60.9, 61.6 (OCH_3 × 2).

III (5,7,2′-Trihydroxy-8-methoxyflavone 7-*O*-*β*-D-Glucuronopyranoside Yellow needles (MeOH), mp 257—259 °C (dec.). $[\alpha]_D^{31}$ −101° (*c* = 0.04, MeOH). *Anal.* Calcd for $C_{22}H_{20}O_{12}$: C, 55.46; H, 4.23. Found: C, 55.38; H, 4.06. EI-MS *m/z* (%): 300 ($C_{16}H_{12}O_6$, 50), 285 ($C_{15}H_9O_6$, 100). FAB-MS *m/z* (%): 477 ($M^+ + 1$, 35), 301 ($C_{16}H_{12}O_6 + 1$, 100). Mg–HCl (+). *Rf*: 0.40 (TLC-3), 0.48 (TLC-4). UV λ_{max}^{MeOH} nm (log ε): 275 (4.26), 342 (3.93); $\lambda_{max}^{MeOH-NaOMe}$ nm (log ε): 233 sh (4.24), 261 sh (4.19), 272 (4.22), 387 (4.07); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ε): 284 (4.25), 297 (4.22), 353 (4.00), 382 sh (3.81); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ε): 284 (4.26), 298 (4.21), 350 (4.10), 383 sh (3.80); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ε): 213 (4.62), 218 sh (4.61), 275 (4.38), 341 (4.04); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ε): 214 (4.64), 219 sh (4.63), 275 (4.33), 345 (4.00). IR ν_{max}^{KBr} cm^{-1}: 3456 (OH), 1736 (COOH), 1654 (conjugated CO), 1616 (arom. C=C). ^{1}H-NMR: 3.85 (3H, s, 8-OCH_3), 3.31—3.98 (m, sugar moiety), 5.25 (1H, d, *J* = 7.3 Hz, anomeric H of glucuronic acid unit), 6.69 (1H, s, 6-H), 7.14 (1H, s, 3-H), 7.04 (1H, br t, *J* = 7.4 Hz, 5′-H), 7.08 (1H, br d, *J* = 8.4 Hz, 3′-H), 7.42 (1H, dt, *J* = 1.5, 7.7 Hz, 4′-H), 7.88 (1H, dd, *J* = 1.5, 8.1 Hz, 6′-H), 12.61 (1H, s, 5-OH). ^{13}C-NMR: 161.7 (C-2), 109.0 (C-3), 182.4 (C-4), 155.9 (C-5), 98.4 (C-6), 155.9 (C-7), 129.2 (C-8), 149.2 (C-9), 105.1 (C-10), 117.2 (C-1′), 157.1 (C-2′), 117.1 (C-3′), 133.1 (C-4′), 119.6 (C-5′), 128.3 (C-6′), 99.7 (C-1″), 72.9 (C-2″), 75.2 (C-3″), 71.4 (C-4″), 75.9 (C-5″), 170.4 (C-6″), 61.4 (C-8-O$\underline{C}$H$_3$).

Methanolysis of III: A solution of III (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 using benzene as an eluent to give yellow needles (MeOH), mp 278 °C (dec.). This product was identified as scutevulin[10] 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 III: III was methylated with CH_2N_2 to give pale yellow needles (MeOH), mp 205—206 °C (dec.), $C_{24}H_{24}O_{12}$, which was identified as 5,7-dihydroxy-8,2′-dimethoxyflavone 7-*O*-*β*-D-glucuronopyranoside methyl ester[12] by direct comparison with an authentic specimen.

IV (2(3-Hydroxy-4-methoxyphenyl)ethyl 1-*O*-*β*-D-Glucopyranoside) Amorphous powder. $[\alpha]_D^{31}$ −12.9° (*c* = 0.33, MeOH). *Anal.* Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.68; H, 6.83. EI-MS *m/z* (%): 330 (M^+, 2), 137 ($C_8H_9O_2$, 100). FAB-MS *m/z* (%): 353 ($M^+ + Na$, 23), 331 ($M^+ + 1$, 20). *Rf*: 0.45 (TLC-3), 0.27 (TLC-4). UV λ_{max}^{MeOH} nm (log ε): 219 sh (4.30), 280 (3.93). IR ν_{max}^{KBr} cm^{-1}: 3460 (OH), 1596 (arom. C=C). ^{1}H-NMR: 2.70 (2H, m, β-H), 2.92—3.49 (m, sugar moiety), 3.55 (1H, dt, *J* = 6.6, 9.2 Hz, α-H), 3.71 (3H, s, 4-OCH_3), 3.87 (1H, dt, *J* = 7.0, 9.2 Hz, α-H), 4.16 (1H, d, *J* = 8.1 Hz, anomeric H of glucose unit), 6.60 (1H, br d, *J* = 8.1 Hz, 6-H), 6.68 (1H, d, *J* = 1.8 Hz, 2-H), 6.79 (1H, d, *J* = 8.1 Hz, 5-H), 8.43 (1H, br s, 3-OH). ^{13}C-NMR: 131.3 (C-1), 116.3 (C-2), 146.4 (C-3), 146.1 (C-4), 112.9 (C-5), 119.3 (C-6), 69.8 (C-α), 35.1 (C-β), 102.8 (C-1″), 73.5 (C-2″), 76.9 (C-3″), 70.1 (C-4″), 76.8 (C-5″), 61.1 (C-6″), 55.7

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(C-4-O$\underline{C}$H$_3$).

Enzymatic Hydrolysis of IV: A solution containing IV (20 mg) and β-glucosidase (20 mg, from almond, Sigma) (pH 5.0 dil. HCOOH, 20 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, which was recrystallized from MeOH/H_2O to give colorless needles (5 mg), mp 70—71 °C. This product was identical with 3-hydroxy-4-methoxyphenethyl alcohol[14] by direct comparison (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 an RP-8 column with H_2O to give a syrup, which was shown to contain D-glucose by GLC-2 [as the TMS-MBA-alditol, t_R 25 min 00 s (TMS-MBA-D-glucitol, t_R 25 min 00 s; TMS-MBA-L-glucitol, t_R 24 min 52 s)].

V (2-(3-Hydroxy-4-methoxyphenyl)ethyl 1-*O*-β-D-(4-*O*-Feruloyl)glucopyranoside) Amorphous powder. $[\alpha]_D^{31}$ −31.2° (c=0.33, MeOH). *Anal.* Calcd for $C_{25}H_{30}O_{11}$: C, 59.28; H, 5.97. Found: C, 59.44; H, 6.04. EI-MS m/z (%): 207 ($C_7H_{11}O_7$, 66), 150 ($C_9H_{10}O_2$, 100), 137 ($C_8H_9O_2$, 40). FAB-MS m/z (%): 529 (M^++Na, 8), 507 (M^++1, 15). *Rf*: 0.67 (TLC-3), 0.69 (TLC-4). UV λ_{max}^{MeOH} nm (log ε): 220 sh (4.11), 231 (4.03), 291 sh (3.90), 330 (4.06). IR ν_{max}^{KBr} cm^{-1}: 3470 (OH), 1703 (α,β-unsaturated CO), 1600 (arom. C=C). ^{1}H-NMR: 2.74 (2H, m, β-H), 3.35—3.48 (m, sugar moiety), 3.62 (1H, dt, J=7.0, 9.6 Hz, α-H), 3.73 (3H, s, 4-OCH$_3$), 3.82 (3H, s, 3′-OCH$_3$), 3.91 (1H, dt, J=7.3, 9.6 Hz, α-H), 4.30 (1H, d, J=7.7 Hz, anomeric H of glucose unit), 4.60 (1H, t, J=9.5 Hz, 4″-H), 6.47 (1H, d, J=15.8 Hz, α′-H), 6.63 (1H, dd, J=1.8, 8.1 Hz, 6-H), 6.69 (1H, d, J=1.8 Hz, 2-H), 6.80 (1H, d, J=8.1 Hz, 5′-H), 6.81 (1H, d, J=8.1 Hz, 5-H), 7.12 (1H, dd, J=1.8, 8.1 Hz, 6′-H), 7.33 (1H, d, J=1.8 Hz, 2′-H), 7.55 (1H, d, J=15.8 Hz, β′-H), 8.78 (1H, s, 3-OH), 9.58 (1H, s, 4′-OH). ^{13}C-NMR: 131.1 (C-1), 116.3 (C-2), 146.3 (C-3), 146.1 (C-4), 112.3 (C-5), 119.4 (C-6), 70.0 (C-α), 35.0 (C-β), 102.8 (C-1″), 73.6 (C-2″), 74.1 (C-3″), 71.3 (C-4″), 74.7 (C-5″), 60.9 (C-6″), 125.6 (C-1′), 111.1 (C-2′), 147.9 (C-3′), 149.4 (C-4′), 115.5 (C-5′), 123.2 (C-6′), 145.3 (C-β′), 114.5 (C-α′), 166.0 (CO), 55.7 (C-4, 3′-O$\underline{C}$H$_3$).

Alkaline Hydrolysis of V: A solution of V (20 mg) in 0.5 N KOH was heated on a water bath at 70 °C for 1 min. The reaction mixture was neutralized with dil. HCl and concentrated to give a residue. The residue was chromatographed on silica gel, and successively eluted with $CHCl_3$–MeOH–H_2O–HCOOH (25:4:0.4:0.2) (solvent-1) and (25:6:0.6:0.3) (solvent-2). The solvent-1 eluate was concentrated and recrystallized from MeOH/H_2O to give colorless needles, mp 168 °C. This product was identical with ferulic acid by direct comparison (TLC, UV, IR and mixed fusion). The solvent-2 eluate was concentrated to give colorless amorphous (10 mg); this product was identified as IV by comparison with an authentic sample (TLC, UV, IR, ^{1}H- and ^{13}C-NMR).

Identification of VI—XXIV: VI (amorphous powder), VII (amorphous powder), VIII (amorphous powder), IX (mp 266—267 °C, dec.), X (mp 198—199 °C, dec.), XI (mp 202 °C, dec.), XII (mp 203 °C), XIII (mp 259 °C), XIV (mp 253 °C), XV (mp 285 °C), XVI (mp 255 °C), XVII (mp 302 °C), XVIII (mp 284 °C), XIX (mp 278 °C, dec.), XX (mp 226 °C, dec.), XXI (mp 169—170 °C, dec.), XXII (mp 270 °C, dec.), XXIII (mp 230 °C, dec.), XXIV (mp 245 °C, dec.) were identified as martynoside,[16,17] acteoside,[16,18] leucosceptoside A,[16] 5,7-dihydroxy-2′-methoxyflavone,[19] 5,7-dihydroxy-2′-methoxyflavone 7-*O*-glucuronide,[19b,20] oroxylin A,[11] wogonin,[11] rivularin,[10] skullcapflavone I,[21] chrysin,[22] baicalein,[23] 5,7,4′-trihydroxy-8-methoxyflavone,[11] 5,7,2′-trihydroxyflavone,[24] scutevulin,[10] chrysin 7-*O*-glucuronide,[22] oroxylin A 7-*O*-glucuronide,[25] wogonin 7-*O*-glucuronide,[11] baicalin[23] and norwogonin 7-*O*-glucuronide,[26] respectively, by direct comparison with authentic specimens (UV, IR, ^{1}H- and ^{13}C-NMR).

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