Studies on the Nepalese Crude Drugs. XIII.¹⁾ On the Flavonoid and Iridoid Constituents of the Root of *Scutellaria grossa* WALL²⁾

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From the root of *Scutellaria grossa* WALL, three new natural flavonoids (I—III) were isolated, together with fifteen known flavonoids (IV, VIII—XXI), two iridoids (V and VI) and *trans*-cinnamic acid (VII). The structures of I—III were shown to be 5-hydroxy-7,8,2',6'-tetramethoxyflavone, 5,6,2'-trihydroxy-7,8-dimethoxyflavone and (2*S*)-5-hydroxy-7,8,2',6'-tetramethoxyflavonone, respectively, on the basis of the chemical and spectral data. Compound I has already been synthesized.

Keywords *Scutellaria grossa*; Labiatae; flavonoid; iridoid; structure elucidation

Scutellaria grossa WALL is an annual herb of the Labiatae family, and is widely distributed in Nepal, Bhutan and India.³⁾

As regards the constituents of this plant, no work has been reported. As part of our studies on the Nepalese crude drugs and on the flavonoid constituents of the *Scutellaria* species, we have now examined this plant. As described in the experimental section, three new natural flavonoids (I—III) were isolated together with fifteen known flavonoids (IV and VIII—XXI), two iridoids (V and VI) and *trans*-cinnamic acid (VII) 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—IV 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 pale yellow needles, mp 199 °C (dec.), C₁₉H₁₈O₇. The ultraviolet (UV) spectrum of I was characteristic of the flavone series, and showed a bathochromic shift by the addition of AlCl₃—HCl indicating the presence of a free hydroxyl at the C-5 position.⁴⁾ The proton nuclear magnetic resonance (¹H-NMR) spectrum of I showed the presence of four methoxyls (each 3H, δ 3.70, 3.92; 6H, δ 3.80), one chelated hydroxyl (δ 12.63) and one C-3 proton (δ 6.32). In the aromatic region of the spectrum, the remaining four protons appeared as a singlet (1H, δ 6.62) for the A-ring proton and a doublet (2H, δ 6.83, *J* = 8.3 Hz) and a triplet (1H, δ 7.52, *J* = 8.3 Hz) for the B-ring protons. The latter two signals could be assigned to C-3', 5' and C-4' protons, respectively, from their chemical shifts and coupling patterns. In the carbon-13 nuclear magnetic resonance (¹³C-NMR) spectrum of I, the carbon signal of one of the four methoxyls appeared down field at δ 61.0, indicating that the methoxyl was di-*ortho* substituted by two substituents.⁵⁾ These data suggested that I was a 5-hydroxy-7,2',6'-trimethoxyflavone derivative with a methoxyl at the C-6 or C-8 position. The position of the methoxyl was determined by the long-range selective proton decoupling (LSPD) method⁶⁾ in the ¹³C-NMR spectrum as follows. In the ¹H non-decoupling ¹³C-NMR spectrum of I, the signal of the carbon attached to an isolated aromatic hydrogen was observed at δ 96.2 (*J* = 7.4 and 162.5 Hz), which changed to a doublet when the chelated hydroxyl proton at the C-5 position was selectively irradiated, indicating that the isolated aromatic proton was present at

the position *ortho* to the chelated hydroxyl, i.e., no substituent was present at the C-6 position. These results led us to conclude that the methoxyl is present at the C-8 position.

I was, therefore, determined to be 5-hydroxy-7,8,2',6'-tetramethoxyflavone.

This is the first report on the isolation of I from natural sources, although I has already been synthesized by us from rivularin (5,2'-dihydroxy-7,8,6'-trimethoxyflavone)¹⁾ by partial methylation.⁷⁾

Compound II was obtained as yellow needles, mp 249—250 °C, C₁₇H₁₄O₇. The UV spectrum and the diagnostic shifts suggested the presence of a hydroxyl at the C-5 position in the flavone nucleus.⁴⁾ The ¹H-NMR spectrum of II showed the presence of two methoxyls (δ 3.90, 3.96), two hydroxyls (1H, δ 9.11; 1H, δ 10.84), one chelated hydroxyl (δ 12.43) and one C-3 proton (δ 7.09). In the aromatic region of the spectrum, the remaining four protons appeared as a multiplet (2H, δ 7.04), a double triplet (1H, δ 7.42, *J* = 1.8 and 7.9 Hz) and a double doublet (1H, δ 7.87, *J* = 1.5 and 8.1 Hz). These signals could be assigned to C-3', 5', C-4' and C-6' protons, respectively, from their chemical shifts and coupling patterns. In the ¹³C-NMR spectrum of II, the methoxyl carbon signals appeared down field at δ 60.9 and 61.8, indicating that these methoxyls were di-*ortho* substituted by two substituents.⁵⁾ These data suggested that all the methoxyls were placed in the A-ring. In the ¹H non-decoupling ¹³C-NMR spectrum of II, one of the carbon signals attached to a hydroxyl was observed at δ 134.1 in the form of a doublet (*J* = 4.7 Hz), which changed to a singlet by LSPD as in the case of I. The methoxyls could therefore, be proven to be placed at the C-7 and C-8 positions. The arrangement of substituents in the A-ring was further confirmed by the ¹³C-NMR spectrum, in which the carbon signals due to the A-ring of II were almost superimposable on those of 5,6,2',6'-tetrahydroxy-7,8-dimethoxyflavone.¹⁾

Thus, the structure of II was established as 5,6,2'-trihydroxy-7,8-dimethoxyflavone.

Compound III was obtained as colorless needles, mp 137 °C, C₁₉H₂₀O₇. The UV spectrum of III was characteristic of the 5-hydroxyflavanone series.⁴⁾ The flavanone nucleus was also confirmed by the ¹H-NMR spectrum, in which the signals due to the C-3 and C-2 protons were observed as an AMX type at δ 2.57 (1H, dd, *J* = 3.3 and 17.2 Hz), δ 3.80 (1H, dd, *J* = 13.2 and 17.2 Hz) and δ 5.98

(1H, dd, $J=3.3$ and 13.2 Hz). The ^1H -NMR spectrum further showed the presence of four methoxys (each 3H, δ 3.52, 3.84; 6H, δ 3.78) and one chelated hydroxyl (δ 12.12). In the aromatic region of the spectrum, the remaining four protons appeared as a singlet (1H, δ 6.22) for the A-ring proton and a doublet (2H, δ 6.74, $J=8.4$ Hz) and a triplet (1H, δ 7.37, $J=8.4$ Hz) for the B-ring protons. These signals for the B-ring could be assigned to C-3', 5' and C-4' protons, respectively, from their chemical shifts and coupling patterns. An isolated aromatic hydrogen in the A-ring was confirmed to be present at the C-6 position by the LSPD method as in the case of I. These findings indicated III to be 5-hydroxy-7,8,2',6'-tetramethoxyflavanone.

It is known that flavanones having (2*S*)-configuration exhibit a positive Cotton effect due to $n\rightarrow\pi^*$ transition (*ca.* 330 nm) and a negative Cotton effect due to $\pi\rightarrow\pi^*$ transition (270–290 nm) in the circular dichroism (CD) spectra.⁸⁾ The CD curve of III exhibited positive and negative maxima at 307 and 279 nm, respectively, which established the (2*S*)-configuration.

The structure of III was finally confirmed by direct comparison with an authentic sample prepared from (2*S*)-5,2'-dihydroxy-7,8,6'-trimethoxyflavanone⁹⁾ by partial methylation with CH_2N_2 .

Thus, III was determined to be (2*S*)-5-hydroxy-7,8,2',6'-tetramethoxyflavanone.

Compound IV was obtained as yellow needles, mp 197°C (dec.), $\text{C}_{21}\text{H}_{18}\text{O}_{11}$. The UV spectrum of IV was characteristic of the 5-hydroxy flavone series.⁴⁾ On methanolysis, IV yielded baicalein¹⁾ (5,6,7-trihydroxyflavone, XIII), and a sugar fraction, which was identified as methyl glucurono-

pyranoside methyl ester and the methyl glycoside of glucurono-6,3-lactone by gas-liquid chromatography (GLC). In the ^1H - and ^{13}C -NMR spectra of IV, an anomeric proton signal at δ 4.94 (d, $J=7.7$ Hz) and a set of carbon signals due to the sugar moiety including an anomeric carbon signal at δ 103.7 indicated the presence of a β -glucuronopyranosyl unit in IV.

The linkage of the sugar to the aglycone was determined by the comparison of the ^{13}C -NMR spectrum of IV with that of XIII. It is known that glycosylation of a phenolic hydroxy group causes a downfield shift of the carbon resonances due to the *ortho*- and *para*-carbons.¹⁰⁾ The ^{13}C -NMR spectrum of IV show that the C-5, C-7 and C-9 signals were lower than the corresponding signals of XIII by δ 5.4–3.1, which can be considered to have been caused by 6-*O*-glycosylation to XIII.

IV was, therefore, identified as baicalein 6-*O*- β -glucuronopyranoside. This compound had already been synthesized¹¹⁾ and also isolated from the leaves of *Oroxylum indicum*¹²⁾ and the metabolites of baicalin and baicalein in rats.¹³⁾

I : $\text{R}_6=\text{H}$, $\text{R}_2'=\text{Me}$, $\text{R}_6'=\text{OMe}$
II : $\text{R}_6=\text{OH}$, $\text{R}_2'=\text{R}_6'=\text{H}$

III

Fig. 1

Chart 1

Compound V was obtained as an amorphous powder, $[\alpha]_D^{31} - 49^\circ$ (MeOH), $C_{24}H_{28}O_{11}$. V showed the absorption maxima at 204 and 277 nm in the UV spectrum and showed the absorption bands corresponding to hydroxyl, conjugated ester, enol ether groups and benzene ring.

On alkaline hydrolysis V afforded catalpol¹⁴⁾ (VI) and *trans*-cinnamic acid (VII).¹⁴⁾ V is, therefore, a monocinnamate of VI. In order to clarify the site of binding of the acyl groups, we used the acylation shifts¹⁵⁾ in ¹³C-NMR spectroscopy. In the ¹³C-NMR spectrum of V, the signals due to the C-8 and C-10 position were shifted downfield by $\delta 3.2$ and upfield by $\delta 2.0$, respectively, in comparison with those of VI, while other signals remained almost unaffected. These data indicated that the cinnamoyl group was linked to the C-10 position of VI.

From these results, the structure of V was identified as 10-cinnamoylcatalpol, which had already been isolated from *Scutellaria altissima* (named scutellarisid-I)¹⁶⁾ and *Globularia alypum* (named globularin).¹⁷⁾

Compounds VIII–XXI are known flavonoids, which were identified as 5-hydroxy-7,8,2'-trimethoxyflavone¹⁸⁾ (VIII), oroxylin A¹⁾ (IX), wogonin¹⁾ (X), chrysin¹⁾ (XI), norwogonin¹⁹⁾ (XII), baicalein¹⁾ (XIII), scutellarein¹⁹⁾ (XIV), luteolin²⁰⁾ (XV), oroxylin A 7-O-glucuronide¹⁾ (XVI), wogonin 7-O-glucuronide¹⁾ (XVII), chrysin 7-O-glucuronide¹⁾ (XVIII), norwogonin 7-O-glucuronide¹⁾ (XIX), baicalin¹⁾ (XX) and scutellarin¹⁹⁾ (XXI), respectively, by direct comparison with authentic samples.

Experimental

General Procedures The instruments were the same as described in the previous paper¹⁾ except for the following. Nuclear magnetic resonance (NMR) spectra were taken in dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) on a JNM-GSX-400 spectrometer (¹H-NMR at 400 MHz and ¹³C-NMR at 100 MHz). GLC was run on a Shimadzu GC-6AM unit with a flame ionization detector. GLC: 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. Thin layer chromatography (TLC) was carried out on Kieselgel 60F-254 (Merck) with the following solvent systems: CHCl₃–MeOH–H₂O–AcOH (100:10:1:0.3) (TLC-1), benzene–AcOEt–AcOH (100:60:0.5) (TLC-2), CHCl₃–MeOH–H₂O–HCOOH (25:8:1:0.5) (TLC-3), AcOEt–methyl ethyl ketone–H₂O–HCOOH (6:3:1:1) (TLC-4). Spots were detected by spraying dil. H₂SO₄ followed by heating.

Extraction and Isolation As shown in Chart 1, twenty-one compounds were obtained from the dried root of *Scutellaria grossa* collected at Kalopani, Nepal in September, 1986.

I (5-Hydroxy-7,8,2',6'-tetramethoxyflavone)⁷⁾ Pale yellow needles (MeOH), mp 199°C (dec.). *Anal.* Calcd for C₁₉H₁₈O₇: C, 63.68; H, 5.06. Found: C, 63.42; H, 5.07. EI-MS *m/z* (%): 358 (M⁺, 46), 343 (M⁺–CH₃, 100). Mg–HCl (+). *Rf*: 0.81 (TLC-1), 0.66 (TLC-2). UV λ_{max}^{MeOH} nm (log ϵ): 266 (4.48), 338 (3.84). IR ν_{max}^{KBr} cm^{–1}: 3400 (OH), 1650 (conjugated CO), 1600, 1580 (arom. C=C). ¹H-NMR δ : 3.70, 3.92 (each 3H, each s, OCH₃ × 2), 3.80 (6H, s, 2',6'-OCH₃), 6.32 (1H, s, 3-H), 6.62 (1H, s, 6-H), 6.83 (2H, d, *J* = 8.3 Hz, 3',5'-H), 7.52 (1H, t, *J* = 8.3 Hz, 4'-H), 12.63 (1H, s, 5-OH). ¹³C-NMR δ : 161.7 (C-2), 112.2 (C-3), 182.2 (C-4), 157.0 (C-5), 96.2 (dd, *J* = 7.4, 162.5 Hz, C-6), 158.7 (C-7), 128.6 (C-8), 149.9 (C-9), 104.1 (C-10), 110.2 (C-1'), 158.3 (C-2',6'), 104.6 (C-3',5'), 133.1 (C-4'), 56.2 (C-2',6'-OCH₃), 56.5 (C-7-OCH₃), 61.0 (C-8-OCH₃).

This compound was identified by direct comparisons (UV, IR, ¹H- and ¹³C-NMR) with an authentic sample⁷⁾ prepared from rivularin¹⁾ by partial methylation with CH₂N₂.

II (5,6,2'-Trihydroxy-7,8-dimethoxyflavone) Yellow needles (MeOH), mp 249–250°C. *Anal.* Calcd for C₁₇H₁₄O₇: C, 61.82; H, 4.27. Found: C, 61.91; H, 4.23. EI-MS *m/z* (%): 330 (M⁺, 65), 315 (M⁺–CH₃, 100). Mg–HCl (+). *Rf*: 0.47 (TLC-1), 0.39 (TLC-2). UV λ_{max}^{MeOH} nm (log ϵ): 247 sh (3.98), 283 (4.38), 340 (4.16); $\lambda_{max}^{MeOH-NaOMe}$ nm (log ϵ): 258 sh (4.15), 291 (4.27), 305 sh (4.18), 404 (4.17); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ϵ): 255 sh (3.99), 294 (4.38), 370 (4.28); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ϵ): 255 (4.01), 292 (4.34), 305 sh

(4.23), 360 (4.24); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ϵ): 285 (4.32), 320 sh (4.06), 347 sh (4.01), 410 (3.89); $\lambda_{max}^{MeOH-NaOAc-H_3BO_3}$ nm (log ϵ): 250 sh (4.02), 285 (4.39), 337 (4.14), 390 sh (3.47). IR ν_{max}^{KBr} cm^{–1}: 3468 (OH), 1664 (conjugated CO), 1612 (arom. C=C). ¹H-NMR δ : 3.90, 3.96 (each 3H, each s, OCH₃ × 2), 7.09 (1H, s, 3-H), 7.04 (2H, m, 3',5'-H), 7.42 (1H, dt, *J* = 1.8, 7.9 Hz, 4'-H), 7.87 (1H, dd, *J* = 1.5, 8.1 Hz, 6'-H), 9.11 (1H, s, 6-OH), 10.84 (1H, s, 2'-OH), 12.43 (1H, s, 5-OH). ¹³C-NMR δ : 161.1 (C-2), 108.5 (C-3), 182.8 (C-4), 142.4 (C-5), 134.1 (d, *J* = 4.7 Hz, C-6), 148.2 (C-7), 132.9 (C-8), 142.1 (C-9), 106.1 (C-10), 117.4 (C-1'), 156.8 (C-2'), 117.2 (C-3'), 133.0 (C-4'), 119.7 (C-5'), 128.3 (C-6'), 60.9, 61.8 (OCH₃ × 2).

III ((2S)-5-Hydroxy-7,8,2',6'-tetramethoxyflavone) Colorless needles (MeOH), mp 137°C. *Anal.* Calcd for C₁₉H₂₀O₇: C, 63.33; H, 5.59. Found: C, 63.26; H, 5.63. EI-MS *m/z* (%): 360 (M⁺, 80), 196 (C₉H₈O₅, 100). Mg–HCl (+). *Rf*: 0.85 (TLC-1), 0.69 (TLC-2). UV λ_{max}^{MeOH} nm (log ϵ): 286 (3.87), 342 (3.26); $\lambda_{max}^{MeOH-NaOMe}$ nm (log ϵ): 286 (3.85), 366 (3.49); $\lambda_{max}^{MeOH-AlCl_3}$ nm (log ϵ): 310 (3.98), 395 (3.27); $\lambda_{max}^{MeOH-AlCl_3-HCl}$ nm (log ϵ): 309 (3.96), 395 (3.27); $\lambda_{max}^{MeOH-NaOAc}$ nm (log ϵ): 286 (3.87), 342 (3.26). IR ν_{max}^{KBr} cm^{–1}: 3400 (OH), 1638 (conjugated CO), 1599 (arom. C=C). ¹H-NMR δ : 3.52, 3.84 (each 3H, each s, OCH₃ × 2), 3.78 (6H, s, 2',6'-OCH₃), 2.57 (1H, dd, *J* = 3.3, 17.2 Hz, *cis* 3-H), 3.80 (1H, dd, *J* = 13.2, 17.2 Hz, *trans* 3-H), 5.98 (1H, dd, *J* = 3.3, 13.2 Hz, 2-H), 6.22 (1H, s, 6-H), 6.74 (2H, d, *J* = 8.4 Hz, 3',5'-H), 7.37 (1H, t, *J* = 8.4 Hz, 4'-H), 12.12 (1H, s, 5-OH). ¹³C-NMR δ : 71.1 (C-2), 39.2 (C-3), 197.7 (C-4), 159.1 (C-5), 92.6 (d, *J* = 7.4, 162.8 Hz, C-6), 160.8 (C-7), 128.5 (C-8), 154.3 (C-9), 102.1 (C-10), 112.8 (C-1'), 158.9 (C-2',6'), 104.8 (C-3',5'), 131.0 (C-4'), 56.0 (C-2',6'-OCH₃), 56.3 (C-7-OCH₃), 60.2 (C-8-OCH₃). CD (*c* = 8.3 × 10^{–5}, MeOH) [θ]_D³¹ (nm): +5225 (307) (positive maximum), –13933 (279) (negative maximum).

(2S)-5,2'-Dihydroxy-7,8,6'-trimethoxyflavone⁹⁾ was methylated with CH₂N₂ to give a product, mp 137°C, which was identical (UV, IR, ¹H- and ¹³C-NMR) with III.

IV (Baicalein 6-O-β-Glucuronopyranoside)^{11–13)} Yellow needles (MeOH), mp 197°C (dec.). $[\alpha]_D^{31} - 55^\circ$ (*c* = 0.11, MeOH). *Anal.* Calcd for C₂₁H₁₈O₁₁: C, 56.50; H, 4.06. Found: C, 56.55; H, 4.14. EI-MS *m/z* (%): 270 (C₁₅H₁₀O₈, 100). FAB-MS *m/z* (%): 447 (M⁺ + 1, 10), Mg–HCl (+). *Rf*: 0.55 (TLC-3), 0.54 (TLC-4). UV λ_{max}^{MeOH} nm (log ϵ): 245 sh (4.01), 271 (4.37), 316 (4.08). IR ν_{max}^{KBr} cm^{–1}: 3400 (OH), 1734 (COOH), 1658 (conjugated CO), 1624, 1588 (arom. C=C). ¹H-NMR δ : 3.26–3.64 (m sugar moiety), 4.94 (1H, d, *J* = 7.7 Hz, anomeric H of glucuronic acid unit), 6.64 (1H, s, 8-H), 6.97 (1H, s, 3-H), 7.58 (3H, m, 3',4',5'-H), 8.07 (2H, dd, *J* = 1.3, 8.2 Hz, 2',6'-H), 13.05 (1H, s, 5-OH). ¹³C-NMR δ : 163.2 (C-2), 104.7 (C-3), 182.3 (C-4), 152.6 (C-5), 128.1 (C-6), 157.8 (C-7), 94.5 (C-8), 153.1 (C-9), 104.1 (C-10), 130.7 (C-1'), 126.4 (C-2',6'), 129.1 (C-3',5'), 132.0 (C-4'), 103.7 (C-1''), 73.5 (C-2''), 75.3 (C-3''), 71.3 (C-4''), 75.6 (C-5''), 170.1 (C-6'').

Methanolysis of IV: A solution of IV (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 Ag₂CO₃. The precipitates were filtered off and the filtrate was concentrated to give the residue, which was chromatographed on silica gel using CHCl₃ as an eluent to give yellow needles (MeOH), mp 255°C (dec.). This product was identified as baicalein¹⁾ by direct comparisons (TLC, UV, IR, ¹H- and ¹³C-NMR) 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 (as the trimethylsilyl (TMS) ester derivatives).

V (10-Cinnamoylcatalpol)^{16,17)} Amorphous powder, $[\alpha]_D^{31} - 49^\circ$ (*c* = 0.15, MeOH). *Anal.* Calcd for C₂₄H₂₈O₁₁: C, 58.53; H, 5.73. Found: C, 58.60; H, 5.69. FAB-MS *m/z* (%): 493 (M⁺ + 1, 20), 149 (C₉H₈O₂ + 1, 90), 103 (C₈H₆ + 1, 100). *Rf*: 0.68 (TLC-3), 0.58 (TLC-4). UV λ_{max}^{MeOH} nm (log ϵ): 204 (4.29), 277 (4.34). IR ν_{max}^{KBr} cm^{–1}: 3400 (OH), 1700 (conjugated ester), 1648 (enol ether), 1580 (arom. C=C). ¹H-NMR δ : 5.00 (2H, m, 1,4-H), 6.39 (1H, dd, *J* = 1.7, 6.1 Hz, 3-H), 2.13 (1H, m, 5-H), 3.86 (1H, brt, *J* = 7.0 Hz, 6-H), 5.36 (1H, d, *J* = 5.5 Hz, 6-OH), 3.50 (1H, s, 7-H), 2.48 (1H, dd, *J* = 7.7, 9.5 Hz, 9-H), 4.12, 4.94 (each 1H, each d, *J* = 12.4 Hz, 10-H), 4.58 (1H, d, *J* = 7.7 Hz, 1'-H (anomeric H)), 2.95 (1H, m, 2'-H), 3.15 (1H, m, 3'-H), 2.97 (1H, m, 4'-H), 3.15 (1H, m, 5'-H), 3.41, 3.71 (each 1H, each m, 6'-H), 4.44 (1H, dd, *J* = 5.5, 7.0 Hz, 6'-H), 6.65 (1H, d, *J* = 16.5 Hz, α -H), 7.66 (1H, d, *J* = 16.5 Hz, β -H), 7.43 (3H, m, 3',4',5'-H), 7.73 (2H, m, 2',6'-H). ¹³C-NMR δ : 93.5 (C-1), 140.4 (C-3), 103.0 (C-4), 37.3 (C-5), 77.0 (C-6), 61.3 (C-7), 61.6 (C-8), 41.9 (C-9), 62.7 (C-10), 98.3 (C-1'), 73.3 (C-2'), 76.5 (C-3'), 70.1 (C-4'), 77.3 (C-5'), 61.5 (C-6'), 134.1 (C-1''), 128.9 (C-2''), 128.4 (C-3''), 130.5 (C-4''), 144.5 (C- β), 118.0 (C- α), 165.8 (CO).

Alkaline Hydrolysis of V: A solution of V (40 mg) in 0.5N KOH was heated on a water bath at 70°C for 1 min. The reaction mixture was

neutralized with dil. HCl and extracted with AcOEt. The organic layer was concentrated to dryness, then the residue was recrystallized from MeOH to give colorless needles (7 mg), mp 133 °C; this product was identical with *trans*-cinnamic acid (VII)¹⁴⁾ by direct comparison (TLC, UV, IR and ¹H-NMR). The aqueous layer was concentrated to give a residue, which was chromatographed on silica gel with CHCl₃-MeOH-H₂O (3:2:0.2) and recrystallized from MeOH to give colorless needles (20 mg), mp 207–208 °C; this product was identical with catalpol (VI)¹⁴⁾ by direct comparison with an authentic sample (TLC, UV, IR, ¹H- and ¹³C-NMR).

Identification of VIII–XXI VIII–XXI were identified as 5-hydroxy-7,8,2'-trimethoxyflavone (VIII, mp 184–186 °C),¹⁸⁾ oroxylin A (IX, mp 202 °C, dec.),¹⁾ wogonin (X, mp 203 °C), chrysin (XI, mp 285 °C),¹⁾ norwogonin (XII, mp 253 °C, dec.),¹⁹⁾ baicalein (XIII, mp 255 °C, dec.),¹⁾ scutellarein (XIV, mp 345 °C, dec.),¹⁹⁾ luteolin (XV, mp 329 °C),²⁰⁾ oroxylin A 7-*O*-glucuronide (XVI, mp 169–255 °C, dec.),¹⁾ wogonin 7-*O*-glucuronide (XVII, mp 270 °C, dec.),¹⁾ chrysin 7-*O*-glucuronide (XVIII, mp 226 °C, dec.),¹⁾ norwogonin 7-*O*-glucuronide (XIX, mp 245 °C, dec.),¹⁾ baicalin (XX, mp 230 °C, dec.)¹⁾ and scutellarin (XXI, mp 360 °C),¹⁹⁾ respectively, by direct comparison with authentic specimens (TLC, UV, IR and ¹H-NMR).

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