Studies on Nepalese Crude Drugs. XIV.¹⁾ New Flavonoids from the Root of *Scutellaria prostrata* JACQ. ex BENTH.²⁾

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Six flavonoids, named scutellaprostins A, B, C, D, E and F, were isolated from the root of *Scutellaria prostrata* JACQ. ex BENTH. (Labiateae). Their structures were established to be (2*R**,3*R**)-6-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-hydroxymethyl-9-phenyl-2,3-dihydro-7*H*-1,4-dioxino[2,3-*h*]chromene-7-one (I), (2*R**,3*R**)-6-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-hydroxymethyl-9-(4-hydroxyphenyl)-2,3-dihydro-7*H*-1,4-dioxino[2,3-*h*]chromene-7-one (II), (2*R**,3*R**)-6-hydroxy-3-(4-hydroxy-3-methoxyphenyl)-2-hydroxymethyl-9-(3,4-dihydroxyphenyl)-2,3-dihydro-7*H*-1,4-dioxino[2,3-*h*]chromene-7-one (III), (2*R**,3*R**)-5-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-8-phenyl-2,3-dihydro-6*H*-1,4-dioxino[2,3-*g*]chromene-6-one (IV), (2*R**,3*R**)-5-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-8-(4-hydroxyphenyl)-2,3-dihydro-6*H*-1,4-dioxino[2,3-*g*]chromene-6-one (V) and (2*R**,3*R**)-5-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-8-(3,4-dihydroxyphenyl)-2,3-dihydro-6*H*-1,4-dioxino[2,3-*g*]chromene-6-one (VI), respectively, by chemical and spectral data. They were synthesized by oxidative coupling of the flavones and coniferyl alcohol in the presence of silver oxide.

Keywords *Scutellaria prostrata*; Labiateae; flavonoid; flavone; scutellaprostin; structure elucidation; biomimetic synthesis

In the previous paper,³⁾ we reported the structural identification of nineteen flavonoids and five phenylethanoid glycosides which were isolated from the root of *Scutellaria prostrata* JACQ. ex BENTH. Further extensive fractionation of the extract of the root led to the isolation of six new flavonoids (I—VI), for which we now give the names, scutellaprostins A, B, C, D, E and F, respectively. The present paper deals with their structural determination.

Compounds I—VI gave dark green colorations with a dil. H₂SO₄ reagent on thin-layer chromatography (TLC), and showed positive color reactions to Mg—HCl. They had absorption bands assignable to hydroxyls, conjugated carbonyl groups and aromatic rings in infrared (IR) spectra. Circular dichroism (CD) spectra revealed them to be racemates.

Scutellaprostin A (I) was obtained as yellow needles, mp 221—222 °C (dec.), C₂₅H₂₀O₈. 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 chelated hydroxyl at the C-5 position.⁴⁾ The proton nuclear magnetic resonance (¹H-NMR) spectrum of I showed the presence of one methoxyl (3H, δ 3.79), two hydroxyls (1H, δ 9.12; 1H, δ 5.09), one chelated hydroxyl (δ 12.25) and one C-3 proton (δ 7.10). In the aromatic region of the spectrum, there were nine proton signals, which appeared as a singlet (1H, δ 6.43) due to the A-ring proton, a double doublet (2H, δ 8.13, *J*=8.2 Hz and 1.7 Hz) and a multiplet (3H, δ 7.53—7.65) due to the non-substituted B-ring protons and an ABC system (H-2'', 5'', and 6'' in Table I) suggesting the presence of a 1,3,4-trisubstituted aromatic ring. In the aliphatic region of the spectrum, the remaining four protons appeared as an AMXY system (H-7'', 8'', 9''a and 9''b in Table I), indicating the presence of a partial structure —CH—CH—CH₂— in I. The methylene proton signals (H-9''a and H-9''b) exhibited downfield shifts by 0.64 and 0.84 ppm when I was acetylated, demonstrating that the methylene bears a hydroxyl. Carbon-13 nuclear magnetic resonance (¹³C-NMR) spectrum of I showed the presence of 25 carbon signals consisting of 21 *sp*² carbons and four *sp*³

carbons bearing oxygen atoms. Among them, 15 *sp*² carbons and one *sp*³ carbon are due to a flavone skeleton and a methoxyl group, respectively. I was, therefore, suggested to have a phenylpropane (C₆—C₃) moiety in the molecule. This was also supported by the mass spectrum (MS) of I, exhibiting fragment ion peaks at *m/z* 180 (F₁) and 137 (F₂). The formation of the former ion can be rationalized in terms of a retro-Diels–Alder cleavage in the dioxane ring. And the latter peak pointed to two oxygen functions in the phenyl ring of a phenylpropane unit to be allocated to a hydroxyl and a methoxyl. The MS of I also exhibited a fragment ion peak originating from the B-ring at *m/z* 105 (C₆H₅—C≡O⁺), which, in conjunction with the ¹H-NMR data, confirmed that no substituents attached to the B-ring.

From these results, I was considered to be a flavone bearing a C₆—C₃ unit, in which the two methine groups of the phenylpropane moiety should be connected with the two oxygens of the flavone molecule forming a benzodioxane bridge. The coupling constant between the H-7'' and H-8'' signals in the dioxane ring was 7.7 Hz, demonstrating that the two hydrogens are *trans*-oriented.

The characterization of flavone and phenylpropane moieties in I was performed chemically as follows. (1) On treatment with pyridine hydrobromide, I afforded a product found to be identical with norwogonin (5,7,8-trihydroxyflavone).⁵⁾ (2) I was treated with alkali to give a product, which was proved to be identical with coniferyl alcohol. This ring opening of the dioxane ring is probably initiated by ionization of the para (4'') phenolic group (Chart 1) since the corresponding 4''-O-methyl ether remains unchanged under the same condition.

Based on these findings, the structure of scutellaprostin A could be restricted to two alternative formulations, I or Ia. Distinction between the two formulae was obtained by selective heteronuclear decoupling experiments according to the strategy developed by Rey *et al.*⁶⁾ towards solving similar problems with regard to coumarinolignoids. In triacetate of I, when the C-7'' and C-8'' hydrogen signals (δ 5.36 and 4.84, respectively) were irradiated, the carbon

signals for C-7 (δ 146.5) and C-8 (δ 129.5), respectively, showed significant sharpening. This result could rule out the possibility of formula Ia.

The structure of scutellaprostin A could thus be formulated as I.

Next, I was synthesized by adoption of the biomimetic approach developed by Merlini *et al.*⁷⁾ for the synthesis of silybin/isosilybin regioisomers. Thus, oxidative coupling of norwogonin and coniferyl alcohol in the presence of Ag_2O afforded I in 45% yield, which was identical in all respects to the natural product. We could find no evidence for the formation of a regioisomer of type Ia or of 7'',8''-*cis*-isomer.

Scutellaprostin B (II) was obtained as yellow needles, mp 255–256 °C (dec.), $\text{C}_{25}\text{H}_{20}\text{O}_9$. The molecular formula suggested the presence of one more hydroxyl group than I. The structural similarity of I and II became evident from MS, ^1H - and ^{13}C -NMR spectral comparison. In the MS of II, the fragment ion peaks at m/z 180 (F_1) and 137 (F_2) suggested the presence of the same phenylpropane unit as I.

The spectrum also showed the ion at m/z 121 ($\text{HO}-\text{C}_6\text{H}_4-\text{C}\equiv\text{O}^+$), which appeared at m/z 105 in I, indicating that the additional hydroxyl group is present in the B-ring. The ^1H -NMR spectrum of II showed the signals of an A_2X_2 type grouping due to the B-ring protons, indicating the presence of a hydroxyl at the C-4' position. In the ^{13}C -NMR spectrum, the signal patterns of the A-, C-, D- and E-rings and of the B-ring were almost identical with those of I and isoscutellarein (5,7,8,4'-tetrahydroxyflavone),⁸⁾ respectively. From these findings, the structure of scutellaprostin B was shown to be II. Chemical evidence for supporting this

structure was secured by the formation of coniferyl alcohol and isoscutellarein by the treatment of II with alkali and with pyridine hydrobromide, respectively. In addition, II was synthesized from isoscutellarein and coniferyl alcohol in the same manner as in the case of I.

Scutellaprostin C (III) was obtained as yellow needles, mp 250–251 °C (dec.), $\text{C}_{25}\text{H}_{20}\text{O}_{10}$. The molecular formula suggested the presence of one more hydroxyl group than II. The ^1H -NMR spectra of II and III were virtually superimposable except for the signal patterns of their B-ring protons, in which an A_2X_2 -system in II was replaced by an ABC-system in III. In the ^{13}C -NMR spectrum of III, the signal patterns of the A-, C-, D- and E-rings and of the B-ring were almost superimposable on those of I and hypolaetin (5,7,8,3',4'-pentahydroxyflavone),⁹⁾ respectively. Coniferyl alcohol and hypolaetin were obtained from III by the same degradation procedure as in the case of I.

Thus, the structure of scutellaprostin C was determined to be as represented by formula III. Compound III was synthesized from hypolaetin and coniferyl alcohol in the same manner as in the case of I.

Scutellaprostin D (IV) was obtained as yellow needles, mp 234–235 °C (dec.), $\text{C}_{25}\text{H}_{20}\text{O}_8$ having the same molecular formula as I. A diagnostic shift in the UV spectrum suggested the presence of a hydroxyl at the C-5 position.⁴⁾ The structural resemblance of IV and I became manifest from MS, ^1H - and ^{13}C -NMR spectral analysis. The MS of IV showed peaks at m/z 180 due to F_1 and at m/z 270 due to $\text{C}_{15}\text{H}_{10}\text{O}_5^+$, which indicated that IV has a trihydroxyflavone moiety. The ^1H -NMR spectrum of IV showed typical signals of a baicalein (5,6,7-trihydroxy-

Fig. 1

Chart 1

TABLE I. ^1H Chemical Shifts of Compounds I—IX, δ (ppm) in $\text{DMSO}-d_6$ (J/Hz in Parentheses)

H	I	II	III	IV	V	VI	VII	VIII	IX
3	7.10 s	6.84 s	6.77 s	7.00 s	6.80 s	6.68 s	6.67 s	6.48 s	6.36 s
6	6.43 s	6.36 s	6.38 s						
8				6.85 s	6.77 s	6.71 s	6.72 s	6.67 s	6.60 s
2'	8.13 br dd (8.2, 1.7)	7.96 d (8.8)	7.45 d (2.2)	8.09 br d (6.7)	7.93 d (8.8)	7.40 d (2.2)	8.01 m	7.83 d (8.8)	7.32 d (2.2)
3'	7.53—7.65 m	6.94 d (8.8)	6.91 d (8.2)	7.53—7.62 m	6.93 d (8.8)	6.89 d (8.1)	7.54—7.61 m	6.89 d (8.8)	6.85 d (8.4)
4'									
5'		6.94 d (8.8)			6.93 d (8.8)			6.89 d (8.8)	7.30 dd (8.4, 2.2)
6'	8.13 br dd (8.2, 1.7)	7.96 d (8.8)	7.48 dd (8.2, 2.2)	8.09 br d (6.7)	7.93 d (8.8)	7.41 dd (8.1, 2.2)	8.01 m	7.83 d (8.8)	7.07 d (1.8)
2''	7.06 d (1.8)	7.05 d (1.7)	7.05 d (1.8)	7.05 d (1.8)	7.04 d (1.8)	7.04 d (1.7)	7.09 d (1.8)	7.06 d (1.8)	6.81 d (8.1)
5''	6.83 d (8.4)	6.83 d (8.2)	6.82 d (8.0)	6.84 d (8.2)	6.82 d (8.1)	6.83 d (8.1)	6.83 d (8.2)	6.81 d (8.1)	6.89 dd (8.1, 1.8)
6''	6.90 dd (8.4, 1.8)	6.89 dd (8.2, 1.7)	6.89 dd (8.0, 1.8)	6.91 dd (8.1, 1.8)	6.89 dd (8.1, 1.8)	6.89 dd (8.1, 1.7)	6.91 dd (8.2, 1.8)	6.89 dd (8.1, 1.8)	4.97 d (7.3)
7''	5.16 d (7.7)	5.12 d (7.9)	5.15 d (7.7)	5.13 d (8.1)	5.11 d (7.7)	5.08 d (8.1)	5.02 d (7.4)	4.97 d (7.0)	4.15 m
8''	4.31 ddd (7.7, 4.4, 2.6)	4.26 ddd (7.9, 4.9, 2.8)	4.30 ddd (7.7, 4.8, 3.0)	4.23 ddd (8.1, 4.1, 2.1)	4.21 ddd (7.7, 4.1, 2.6)	4.20 br d (8.1)	4.19 ddd (7.4, 5.0, 2.9)	4.16 ddd (7.0, 5.0, 3.0)	3.44 m
9''	3.39 ddd (12.5, 5.5, 4.4)	3.45 ddd (12.1, 5.5, 2.8)	3.44 ddd (13.2, 5.5, 4.8)	3.39 ddd (12.4, 5.3, 2.1)	3.37 br dd (12.5, 4.1)	3.36 br dd (12.3, 3.9)	3.48 dd (12.1, 5.0)	3.48 dd (12.1, 5.0)	3.53 br d (12.3)
	3.65 ddd (12.5, 5.5, 2.6)	3.66 ddd (12.1, 5.5, 4.9)	3.70 ddd (13.2, 5.5, 3.0)	3.65 ddd (12.4, 5.3, 4.1)	3.67 ddd (12.5, 2.6)	3.63 br d (12.3)	3.57 dd (12.1, 2.9)	3.53 dd (12.1, 3.0)	3.77 s
OMe	3.79 s	3.80 s	3.78 s	3.79 s	3.79 s	3.79 s	3.79 s	3.76 s	
5-OH	12.25 s	12.38 s	12.43 s	12.94 s	13.09 s	13.12 s			
Ar-OH	9.20 s	9.16 s	9.21 s	9.18 s	9.16 s	9.20 br s	9.12 s	9.18 br s	9.20 br s
		10.36 s	9.44 s		10.33 s	9.45 br s	10.50 s	10.30 br s	9.45 br s
			10.02 s			9.95 br s		10.51 br s	10.00 br s
9''-OH	5.09 t (5.5)	5.03 t (5.5)	5.05 t (5.5)	5.02 t (5.3)	5.00 br s	5.03 br s	4.91 br s	4.95 br s	5.03 br s

flavone) substitution pattern (H-3,8,2',3',4',5' and 6' in Table I). The spectrum also showed signals due to the same phenylpropane moiety as I (H-2'',5'',6'',7'',8'' and 9'' in Table I). Comparison of the ^{13}C -NMR spectrum of IV with that of I revealed that all of the carbon signals due to the phenylpropane moiety and the B- and C-rings of IV appeared at almost the same positions as in the spectrum of I. These findings suggest that IV is also a dioxane-type flavone composed of coniferyl alcohol and baicalein moieties.

IV, on treatment with alkali and with pyridine hydrobromide, produced coniferyl alcohol and baicalein, respectively. Based on these findings, the structure of scutellaprostin D was considered to be restricted to two alternative formulations IV or IVa. The discrimination between the two structures was performed by a selective heteronuclear decoupling experiment in the triacetate of IV. Irradiations of the C-7'' and C-8'' hydrogen signals result

in considerable sharpening of the C-7 and C-6 signals, respectively.

Scutellaprostin D, hence, can be represented as IV. The coupling constant between H-7'' and H-8'' in IV was observed to be 8.1 Hz, demonstrating that the two hydrogens are *trans*-oriented.

IV was synthesized in a similar manner to I as follows. Oxidation of an equimolar mixture of baicalein and coniferyl alcohol in benzene/acetone with Ag_2O afforded a mixture of two compounds (IV and VII). Comparison of the major compound with natural IV established their identity. The second compound (VII) was obtained as colorless needles, mp 206—207 °C (dec.), $\text{C}_{25}\text{H}_{20}\text{O}_8$, having the same molecular formula as IV. The structural similarity of this compound and IV became evident from MS, ^1H - and ^{13}C -NMR spectral comparisons. Inspection of the UV spectrum using a diagnostic reagent⁴⁾ indicated the absence of a free hydroxyl at the C-5 position, which was also

TABLE II. ^{13}C Chemical Shifts of Compounds I–IX, δ (ppm) in $\text{DMSO}-d_6$

C	I	II	III	IV	V	VI	VII	VIII	IX
2	163.1	163.6	163.9	163.5	164.0	164.4	159.4	160.2	160.1
3	105.3	102.9	103.1	104.4	102.1	102.3	107.2	105.3	105.3
4	182.2	181.8	181.9	182.5	182.3	182.3	175.5	175.9	175.6
5	153.0	152.9	153.1	147.8	147.8	148.0	142.5	142.6	142.5
6	99.0	98.6	98.8	128.0	127.9	128.0	129.1	129.2	129.3
7	149.6	149.3	149.4	150.1	149.8	149.9	151.3	151.3	151.9
8	124.6	124.4	124.5	94.7	94.4	94.5	95.9	96.0	95.8
9	144.5	144.3	144.5	149.7	149.5	149.7	151.7	151.8	151.9
10	104.9	104.6	104.8	104.9	104.6	104.8	107.2	107.1	106.7
1'	130.5	121.0	121.4	130.6	121.1	121.5	131.1	121.7	122.0
2'	126.4	128.4	113.6	126.3	128.4	113.4	125.7	127.8	112.9
3'	129.2	115.9	145.7	129.0	115.8	145.8	128.9	115.9	145.7
4'	132.2	161.2	150.0	132.0	161.1	149.8	131.1	160.4	148.9
5'	129.2	115.9	116.0	129.0	115.8	116.0	128.9	115.9	115.9
6'	126.4	128.4	119.2	126.3	128.4	119.1	125.7	127.8	118.0
1''	126.6	126.7	126.8	126.6	126.6	126.8	127.2	127.3	127.3
2''	111.7	111.8	111.8	111.8	111.8	111.9	111.8	111.9	111.8
3''	147.6	147.5	147.6	147.5	147.5	147.7	147.5	147.7	147.6
4''	147.2	147.1	147.2	147.2	147.1	147.3	146.8	147.0	146.9
5''	115.3	115.3	115.4	115.3	115.3	115.4	115.2	115.4	115.3
6''	120.5	120.5	120.6	120.5	120.5	120.7	120.3	120.4	120.4
7''	77.1	77.0	77.0	76.9	76.9	77.1	75.6	75.8	75.7
8''	77.6	77.6	77.6	77.4	77.3	77.5	76.8	77.0	76.9
9''	60.0	60.0	60.1	59.8	59.8	60.0	60.1	60.3	60.2
OMe	55.7	55.7	55.7	55.6	55.6	55.7	55.6	55.8	55.7

confirmed by the ^1H -NMR spectrum showing the absence of a chelated hydroxyl proton. These findings indicated that the $\text{C}_6\text{--C}_3$ unit is attached to the baicalein unit at C-5 and C-6 through a dioxane bridge, and the structure of this compound is considered to be either VII or its regioisomer. The latter structure was ruled out by a selective heteronuclear decoupling experiment in a manner similar to I. The *trans* orientation of the phenyl and hydroxymethyl groups in the dioxane ring is apparent from the coupling constant of a benzylic methine proton ($J=7.4$ Hz). Thus, the structure of this compound was determined to be as represented by the formula VII.

Scutellaprostin E (V) was obtained as yellow needles, mp 240–241 °C (dec.), $\text{C}_{25}\text{H}_{20}\text{O}_9$. The ^1H -NMR spectrum of V was similar to that of IV except for the signals due to the B-ring protons, which appeared as an A_2X_2 -system, indicating the presence of a hydroxyl at the C-4' position. The ^{13}C -chemical shifts of the A-, C-, D- and E-rings of V are almost the same as those of IV, and the ^{13}C -chemical shift of the B-ring of V closely resembles that of scutellarein (5,6,7,4'-tetrahydroxyflavone).⁸⁾ Coniferyl alcohol and scutellarein were detected from V by the same degradation procedure as in the case of I. Scutellaprostin E was thus framed as V. Oxidation of scutellarein and coniferyl alcohol gave a mixture of two products, one of which (main product) was proven to be identical with scutellaprostin E by direct comparison. The second product was obtained as colorless needles, mp 235–236 °C, $\text{C}_{25}\text{H}_{20}\text{O}_9$, whose structure was determined to be VIII by spectroscopic means in the same way described for VII.

Scutellaprostin F (VI) was obtained as yellow needles, mp 204–205 °C (dec.), $\text{C}_{25}\text{H}_{20}\text{O}_{10}$. The molecular formula indicated the presence of one more hydroxyl than V. The ^{13}C -NMR spectrum of VI was closely related to that of V; in particular, the chemical shifts of the signals from the A-, C-, D- and E-rings of VI were almost identical with those

of V. And the ^{13}C -chemical shift of the B-ring of VI was almost identical with that of 6-hydroxyluteolin (5,6,7,3',4'-pentahydroxyflavone).¹¹⁾ Hence, scutellaprostin F can be depicted as VI. The ^1H -NMR spectrum also supported this structure. Oxidation of 6-hydroxyluteolin and coniferyl alcohol gave VI as a main product and IX, colorless needles, mp 213–214 °C, $\text{C}_{25}\text{H}_{20}\text{O}_{10}$, as a minor product. Characterization of IX was performed by spectroscopic means in the same way described for VII.

Experimental

The instruments used to obtain physical data were the same as described in our previous paper.³⁾

Isolation Fractions 16, 20 and 22, described in the previous paper,³⁾ were further examined. Fraction 16 was subjected to chromatography on silica gel [solvent: benzene–dioxane–AcOH (90:15:3)] to give I (120 mg) and IV (98 mg). Fraction 20 was chromatographed on silica gel [solvent: benzene–dioxane–AcOH (90:15:3)] to give II (85 mg) and V (68 mg). Fraction 22 was chromatographed on silica gel [solvent: benzene–dioxane–AcOH (90:20:4)] to give III (70 mg) and VI (59 mg).

Scutellaprostin A (I) Yellow needles (from MeOH), mp 221–222 °C (dec.). $[\alpha]_D^{20} \pm 0^\circ$ ($c=0.05$, MeOH). *Anal.* Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_8$: C, 66.96; H, 4.50. Found: C, 66.91; H, 4.53. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 234 (4.24), 286 (4.45), 370 (3.40); $\lambda_{\text{max}}^{\text{MeOH-NaOMe}}$ nm (log ϵ): 253 (4.27), 289 (4.44), 394 (3.27); $\lambda_{\text{max}}^{\text{MeOH-AlCl}_3}$ nm (log ϵ): 221 (4.35), 236 (4.31), 290 (4.34), 310 (4.38), 346 sh (3.74), 428 (3.42); $\lambda_{\text{max}}^{\text{MeOH-AlCl}_3\text{-HCl}}$ nm (log ϵ): 221 (4.36), 238 (4.29), 290 (4.33), 309 (4.38), 346 sh (3.63), 440 (3.44); $\lambda_{\text{max}}^{\text{MeOH-NaOAc}}$ nm (log ϵ): 285 (4.44), 360 (3.40). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3460 (OH), 1664 (conjugated CO), 1616 (arom. C=C). ^1H -NMR: Table I. ^{13}C -NMR: Table II. EI-MS m/z (%): 448 (M^+ , 100), 270 ($\text{C}_{15}\text{H}_{10}\text{O}_5$, 89), 180 ($\text{C}_{10}\text{H}_{12}\text{O}_3$, 72), 168 ($\text{C}_7\text{H}_4\text{O}_5$, 40), 137 ($\text{C}_8\text{H}_9\text{O}_2$, 97), 124 ($\text{C}_7\text{H}_8\text{O}_2$, 54), 105 ($\text{C}_7\text{H}_5\text{O}$, 27).

Acetylation of I: A mixture of I, Ac_2O and pyridine was kept at 40 °C for 24 h. Usual work up followed by crystallization from $\text{CHCl}_3\text{--MeOH}$ yielded a triacetate as colorless needles, mp 195–197 °C (dec.). *Anal.* Calcd for $\text{C}_{31}\text{H}_{26}\text{O}_{11}$: C, 64.80; H, 4.56. Found: C, 64.73; H, 4.61. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 223 sh (4.52), 272 (4.54), 284 sh (4.36), 315 sh (4.05). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1773, 1753 (acetyl), 1650 (conjugated CO), 1617 (arom. C=C). ^1H -NMR ($\text{DMSO}-d_6$) δ : 6.89 (1H, s, H-3), 6.90 (1H, s, H-6), 8.06 (2H, br dd, $J=7.2$, 1.7 Hz, H-2', 6'), 7.60 (3H, m, H-3',4',5'), 7.35 (1H, d, $J=1.7$ Hz, H-2''), 7.21 (1H, d, $J=8.1$ Hz, H-5''), 7.14 (1H, dd, $J=8.1$,

1.7 Hz, H-6"), 5.36 (1H, d, $J=8.0$ Hz, H-7"), 4.84 (1H, ddd, $J=8.0$, 5.4, 3.5 Hz, H-8"), 4.23 (1H, dd, $J=12.5$, 3.5 Hz, H-9'a), 4.29 (1H, dd, $J=12.5$, 5.4 Hz, H-9'b), 3.83 (3H, s, $-\text{OCH}_3$), 2.06, 2.29, 2.31 (each 3H, s, $-\text{OCOCH}_3$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 160.6 (C-2), 107.4 (C-3), 175.3 (C-4), 141.5 (C-5), 108.4 (C-6), 146.5 (C-7), 129.5 (C-8), 145.9 (C-9), 111.1 (C-10), 130.5 (C-1'), 125.9 (C-2', 6'), 129.0 (C-3', 5'), 131.7 (C-4'), 133.7 (C-1''), 112.2 (C-2''), 151.0 (C-3''), 140.0 (C-4''), 123.0 (C-5''), 120.1 (C-6''), 76.4 (C-7''), 74.5 (C-8''), 61.7 (C-9''), 55.9 ($-\text{OCH}_3$), 20.2 ($-\text{OCOCH}_3 \times 2$), 20.7 ($-\text{OCOCH}_3$), 168.2, 169.0, 169.8 ($-\text{OCOCH}_3$). EI-MS m/z (%): 574 (M^+ , 2), 532 (100), 490 (6), 430 (3), 281 (23), 270 (10), 269 (26), 222 (55), 179 (23).

Partial Methylation of I: I was treated with CH_3N_2 as usual to afford a monomethyl ether as yellow needles (from MeOH), mp 234–244 °C (dec.). *Anal.* Calcd for $\text{C}_{26}\text{H}_{22}\text{O}_8$: C, 67.52; H, 4.80. Found: C, 67.49; H, 4.89. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 230 (4.38), 284 (4.60), 357 (3.40); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 232 (4.46), 284 (4.54), 384 (3.18); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 233 (4.44), 288 (4.46), 307 (4.51), 345 sh (3.78), 430 (3.47); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 233 (4.44), 288 (4.46), 307 (4.51), 345 sh (3.60), 426 (3.45); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 234 (4.61), 325 (3.55), 354 (3.42). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3460 (OH), 1664 (conjugated CO), 1616, 1590 (arom. C=C). $^1\text{H-NMR}$ (DMSO- d_6) δ : 7.07 (1H, s, H-3), 6.45 (1H, s, H-6), 8.11 (2H, brd, $J=8.4$, 1.8 Hz, H-2', 6'), 7.58–7.64 (3H, m, H-3', 4', 5'), 7.08 (1H, d, $J=1.6$ Hz, H-2''), 7.00 (1H, d, $J=8.4$ Hz, H-5''), 7.02 (1H, dd, $J=8.4$, 1.6 Hz, H-6''), 5.20 (1H, d, $J=7.7$ Hz, H-7''), 4.32 (1H, ddd, $J=7.7$, 4.7, 2.6 Hz, H-8''), 3.48 (1H, ddd, $J=12.0$, 5.5, 4.7 Hz, H-9'a), 3.68 (1H, ddd, $J=12.0$, 5.5, 2.6 Hz, H-9'b), 3.77 (6H, s, $-\text{OCH}_3 \times 2$), 5.13 (1H, t, $J=5.5$ Hz, $-\text{OH}$), 12.25 (1H, s, $-\text{OH}$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 163.2 (C-2), 105.4 (C-3), 182.3 (C-4), 153.1 (C-5), 99.1 (C-6), 149.7 (C-7), 124.7 (C-8), 144.6 (C-9), 105.1 (C-10), 130.6 (C-1'), 126.5 (C-2', 6'), 129.3 (C-3', 5'), 132.3 (C-4'), 128.3 (C-1''), 111.3 (C-2''), 148.8 (C-3''), 149.4 (C-4''), 111.7 (C-5''), 120.4 (C-6''), 77.0 (C-7''), 77.7 (C-8''), 60.1 (C-9''), 55.6 ($-\text{OCH}_3$), 55.7 ($-\text{OCH}_3$). EI-MS m/z (%): 462 (M^+ , 100), 194 ($\text{C}_{11}\text{H}_{14}\text{O}_3$, 33), 151 ($\text{C}_9\text{H}_{11}\text{O}_2$, 22).

Scutellaprostin B (II) Yellow needles (from MeOH), mp 255–256 °C (dec.). $[\alpha]_D^{20} \pm 0^\circ$ ($c=0.05$, MeOH). *Anal.* Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_8$: C, 64.65; H, 4.34. Found: C, 64.60; H, 4.41. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 229 (4.45), 285 (4.41), 303 sh (4.32), 310 sh (4.31), 332 sh (4.27); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 233 sh (4.49), 258 (4.49), 281 (4.51), 303 sh (4.31), 400 (4.54); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 237 (4.46), 290 (4.36), 323 (4.34), 357 (4.35), 424 (3.84); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 236 (4.46), 290 (4.36), 322 (4.38), 353 (4.34), 422 (3.82); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 230 sh (4.49), 283 (4.39), 310 sh (4.23), 333 (4.17), 396 (4.11). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3457 (OH), 1667 (conjugated CO), 1612 (arom. C=C). $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. EI-MS m/z (%): 464 (M^+ , 26), 286 ($\text{C}_{15}\text{H}_{10}\text{O}_6$, 100), 180 ($\text{C}_{10}\text{H}_{12}\text{O}_3$, 55), 168 ($\text{C}_7\text{H}_4\text{O}_3$, 81), 137 ($\text{C}_8\text{H}_5\text{O}_2$, 90), 124 ($\text{C}_7\text{H}_5\text{O}_2$, 48), 121 ($\text{C}_7\text{H}_5\text{O}_2$, 20).

Acetylation of II: Ac_2O -pyridine treatment of II yielded a tetraacetate, which was recrystallized from CHCl_3 -MeOH to obtain colorless needles, mp 197–198 °C (dec.). *Anal.* Calcd for $\text{C}_{33}\text{H}_{28}\text{O}_{13}$: C, 62.66; H, 4.46. Found: C, 62.60; H, 4.52. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 224 sh (4.41), 273 (4.39), 284 sh (4.26), 321 sh (4.02). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1766, 1750 (acetyl), 1646 (conjugated CO), 1614, 1590 (arom. C=C). $^1\text{H-NMR}$ (DMSO- d_6) δ : 6.89 (1H, s, H-3), 6.88 (1H, s, H-6), 8.08 (2H, d, $J=8.8$ Hz, H-2', 6'), 7.35 (2H, d, $J=8.8$ Hz, H-3', 5'), 7.35 (1H, brs, H-5''), 7.20 (1H, d, $J=8.1$ Hz, H-5''), 7.13 (1H, brd, $J=8.1$ Hz, H-6''), 5.32 (1H, d, $J=7.7$ Hz, H-7''), 4.82 (1H, ddd, $J=7.7$, 5.2, 3.3 Hz, H-8''), 4.22 (1H, dd, $J=12.5$, 3.3 Hz, H-9'a), 4.27 (1H, dd, $J=12.5$, 5.2 Hz, H-9'b), 3.81 (3H, s, $-\text{OCH}_3$), 2.05, 2.28, 2.29, 2.31 (each 3H, s, $-\text{OCOCH}_3$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 160.0 (C-2), 107.5 (C-3), 175.4 (C-4), 141.6 (C-5), 108.6 (C-6), 146.6 (C-7), 129.6 (C-8), 146.0 (C-9), 111.1 (C-10), 128.2 (C-1'), 127.5 (C-2', 6'), 122.7 (C-3', 5'), 153.1 (C-4'), 133.8 (C-1''), 112.3 (C-2''), 151.2 (C-3''), 140.1 (C-4''), 123.2 (C-5''), 120.2 (C-6''), 76.5 (C-7''), 74.6 (C-8''), 61.8 (C-9''), 56.0 ($-\text{OCH}_3$), 20.4, ($-\text{OCOCH}_3 \times 2$), 20.9 ($-\text{OCOCH}_3 \times 2$), 168.4, 168.9, 169.2, 170.0 ($-\text{OCOCH}_3$). EI-MS m/z (%): 590 (100), 548 (27), 488 (23), 328 (70), 286 (53), 222 (84), 179 (44).

Scutellaprostin C (III) Yellow needles (from MeOH), mp 150–251 °C (dec.). $[\alpha]_D^{20} \pm 0^\circ$ ($c=0.05$, MeOH). *Anal.* Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_{10}$: C, 62.50; H, 4.20. Found: C, 62.51; H, 4.26. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 230 sh (4.82), 283 (4.74), 304 sh (4.48), 348 (4.74); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 234 sh (4.75), 270 (4.81), 282 sh (4.77), 304 sh (4.47), 416 (4.75); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 235 sh (4.87), 290 (4.77), 318 sh (4.40), 444 (4.75); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 235 sh (4.82), 290 (4.70), 317 sh (4.50), 366 (4.63); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 282 (4.73), 410 (4.52); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}-\text{H}_3\text{BO}_3}$ nm (log ϵ): 270 sh (4.73), 283 sh (4.73), 307 (4.32), 384 (4.65). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3424 (OH), 1664 (conjugated CO), 1612 (arom. C=C). $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. EI-MS m/z (%): 302 ($\text{C}_{15}\text{H}_{10}\text{O}_7$, 20), 180

($\text{C}_{10}\text{H}_{12}\text{O}_3$, 45), 168 ($\text{C}_7\text{H}_4\text{O}_3$, 21), 137 ($\text{C}_8\text{H}_5\text{O}_2$, 100), 124 ($\text{C}_7\text{H}_5\text{O}_2$, 74). FAB-MS m/z (%): 481 ($\text{M}^+ + 1$, 8), 154 (100).

Acetylation of III: Ac_2O -pyridine treatment of III yielded a pentaacetate as colorless needles (from CHCl_3 -MeOH), mp 224–225 °C (dec.). *Anal.* Calcd for $\text{C}_{35}\text{H}_{30}\text{O}_{15}$: C, 60.87; H, 4.38. Found: C, 60.80; H, 4.41. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 212 (4.46), 272 (4.39), 305 sh (4.12), 335 (3.95). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1758, 1732 (acetyl), 1646 (conjugated CO), 1616 (arom. C=C). $^1\text{H-NMR}$ (DMSO- d_6) δ : 6.91 (1H, s, H-3), 6.94 (1H, s, H-6), 7.96 (1H, d, $J=1.5$ Hz, H-2'), 7.53 (1H, d, $J=8.7$ Hz, H-5'), 8.02 (1H, dd, $J=8.7$, 1.5 Hz, H-6'), 7.34 (1H, brs, H-2''), 7.20 (1H, d, $J=8.1$ Hz, H-5''), 7.13 (1H, brd, $J=8.1$ Hz, H-6''), 5.35 (1H, d, $J=7.7$ Hz, H-7''), 4.83 (1H, ddd, $J=7.7$, 5.5, 3.0 Hz, H-8''), 4.21 (1H, dd, $J=12.5$, 5.5 Hz, H-9'a), 4.27 (1H, dd, $J=12.5$, 3.0 Hz, H-9'b), 3.81 (3H, s, $-\text{OCH}_3$), 2.05, 2.09, 2.28, 2.30, 2.33 (each 3H, s, $-\text{OCOCH}_3$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 159.1 (C-2), 108.0 (C-3), 175.3 (C-4), 141.5 (C-5), 108.6 (C-6), 146.7 (C-7), 129.6 (C-8), 145.9 (C-9), 111.1 (C-10), 129.3 (C-1'), 121.5 (C-2'), 142.6 (C-3'), 144.7 (C-4'), 124.6 (C-5'), 124.5 (C-6'), 133.8 (C-1''), 112.3 (C-2''), 151.2 (C-3''), 140.0 (C-4''), 123.2 (C-5''), 120.2 (C-6''), 76.5 (C-7''), 74.8 (C-8''), 61.5 (C-9''), 56.0 ($-\text{OCH}_3$), 20.3 ($-\text{OCOCH}_3 \times 2$), 20.4 ($-\text{OCOCH}_3 \times 2$), 20.8 ($-\text{OCOCH}_3$), 168.0, 168.1, 168.4, 169.1, 170.0 ($-\text{OCOCH}_3$). EI-MS m/z (%): 648 (80), 606 (31), 588 (17), 546 (22), 504 (13), 386 (18), 344 (31), 222 (100), 179 (24).

Scutellaprostin D (IV) Yellow needles (from MeOH), mp 234–235 °C (dec.). $[\alpha]_D^{20} \pm 0^\circ$ ($c=0.05$, MeOH). *Anal.* Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_8$: C, 66.96; H, 4.50. Found: C, 66.91; H, 4.59. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 219 (4.59), 239 sh (4.31), 280 (4.49), 320 (4.27); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 233 sh (4.50), 256 (4.43), 295 (4.49), 400 (3.46); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 223 (4.55), 287 (4.49), 297 sh (4.44), 348 (4.35), 402 sh (3.58); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 225 (4.56), 287 (4.47), 297 sh (4.43), 345 (4.33), 402 sh (3.58); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 280 (4.49), 321 (4.26). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3280 (OH), 1664 (conjugated CO), 1622 (arom. C=C). $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. EI-MS m/z (%): 448 (M^+ , 59), 270 ($\text{C}_{15}\text{H}_{10}\text{O}_3$, 100), 180 ($\text{C}_{10}\text{H}_{12}\text{O}_3$, 23), 168 ($\text{C}_7\text{H}_4\text{O}_3$, 11), 137 ($\text{C}_8\text{H}_5\text{O}_2$, 40), 124 ($\text{C}_7\text{H}_5\text{O}_2$, 21).

Acetylation of IV: Ac_2O -pyridine treatment of IV yielded a triacetate as colorless needles (from CHCl_3 -MeOH), mp 209–210 °C (dec.). *Anal.* Calcd for $\text{C}_{31}\text{H}_{26}\text{O}_{11}$: C, 64.80; H, 4.56. Found: C, 64.82; H, 4.59. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 217 (4.68), 271 (4.36), 284 sh (4.17), 315 (4.36). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1770, 1752 (acetyl), 1640 (conjugated CO), 1620 (arom. C=C). $^1\text{H-NMR}$ (DMSO- d_6) δ : 6.80 (1H, s, H-3), 7.37 (1H, s, H-8), 8.05 (2H, brd, $J=7.6$, 1.7 Hz, H-2', 6'), 7.58 (3H, m, H-3', 4', 5'), 7.34 (1H, d, $J=1.8$ Hz, H-2''), 7.18 (1H, d, $J=8.1$ Hz, H-5''), 7.12 (1H, dd, $J=8.1$, 1.8 Hz, H-6''), 5.36 (1H, d, $J=7.6$ Hz, H-7''), 4.76 (1H, ddd, $J=7.6$, 5.2, 4.0 Hz, H-8''), 4.11 (1H, dd, $J=12.4$, 5.2 Hz, H-9'a), 4.19 (1H, dd, $J=12.4$, 4.0 Hz, H-9'b), 3.81 (3H, s, $-\text{OCH}_3$), 2.02, 2.28, 2.36 (each 3H, s, $-\text{OCOCH}_3$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 161.1 (C-2), 106.9 (C-3), 175.4 (C-4), 135.6 (C-5), 133.5 (C-6), 148.4 (C-7), 102.5 (C-8), 150.6 (C-9), 111.3 (C-10), 130.7 (C-1'), 126.0 (C-2', 6'), 128.9 (C-3', 5'), 131.6 (C-4'), 133.7 (C-1''), 112.2 (C-2''), 151.0 (C-3''), 139.9 (C-4''), 123.0 (C-5''), 120.1 (C-6''), 76.3 (C-7''), 74.3 (C-8''), 61.6 (C-9''), 55.8 ($-\text{OCH}_3$), 20.2 ($-\text{OCOCH}_3 \times 2$), 20.4 ($-\text{OCOCH}_3$), 168.1, 168.2, 169.7 ($-\text{OCOCH}_3$). EI-MS m/z (%): 574 (M^+ , 4), 532 (100), 490 (9), 430 (6), 281 (13), 270 (49), 222 (42), 179 (17).

Scutellaprostin E (V) Yellow needles (from MeOH), mp 240–241 °C (dec.). $[\alpha]_D^{20} \pm 0^\circ$ ($c=0.05$, MeOH). *Anal.* Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_9$: C, 64.65; H, 4.34. Found: C, 64.69; H, 4.30. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 220 (4.52), 236 sh (4.38), 340 (4.40); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 218 (4.61), 255 (4.37), 293 (4.30), 374 (4.39); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 224 (4.51), 239 sh (4.41), 290 sh (4.24), 309 sh (4.28), 373 (4.45); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 224 (4.51), 238 sh (4.42), 292 sh (4.28), 307 sh (4.31), 364 (4.44); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 223 (4.59), 284 (4.27), 344 (4.29), 408 sh (4.06). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3440 (OH), 1664 (conjugated CO), 1610 (arom. C=C). $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. EI-MS m/z (%): 464 (M^+ , 26), 286 ($\text{C}_{15}\text{H}_{10}\text{O}_6$, 100), 180 ($\text{C}_{10}\text{H}_{12}\text{O}_3$, 55), 168 ($\text{C}_7\text{H}_4\text{O}_3$, 81), 137 ($\text{C}_8\text{H}_5\text{O}_2$, 90), 124 ($\text{C}_7\text{H}_5\text{O}_2$, 48), 121 ($\text{C}_7\text{H}_5\text{O}_2$, 20).

Acetylation of V: Ac_2O -pyridine treatment of V yielded a tetraacetate as colorless needles (from CHCl_3 -MeOH), mp 199–200 °C (dec.). *Anal.* Calcd for $\text{C}_{33}\text{H}_{28}\text{O}_{13}$: C, 62.66; H, 4.46. Found: C, 62.59; H, 4.52. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 219 (4.67), 275 sh (4.27), 292 sh (4.18), 326 (4.37). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1772, 1754 (acetyl), 1644 (conjugated CO), 1618 (arom. C=C). $^1\text{H-NMR}$ (DMSO- d_6) δ : 6.79 (1H, s, H-3), 7.35 (1H, s, H-8), 8.08 (2H, d, $J=8.8$ Hz, H-2', 6'), 7.35 (2H, d, $J=8.8$ Hz, H-3', 5'), 7.35 (1H, d, $J=1.8$ Hz, H-2''), 7.17 (1H, d, $J=8.1$ Hz, H-5''), 7.11 (1H, dd, $J=8.1$, 1.8 Hz, H-6''), 5.35 (1H, d, $J=7.7$ Hz, H-7''), 4.74 (1H, ddd, $J=7.7$, 5.2, 4.1 Hz, H-8''), 4.08 (1H, dd, $J=12.5$, 5.2 Hz, H-9'a), 4.18 (1H, dd, $J=12.5$, 4.1 Hz, H-9'b), 3.80 (3H, s, $-\text{OCH}_3$), 2.00, 2.27, 2.31, 2.35 (each 3H, s, $-\text{OCOCH}_3$). $^{13}\text{C-NMR}$ (DMSO- d_6) δ : 160.5 (C-2), 106.9 (C-3), 175.5

(C-4), 135.7 (C-5), 133.6 (C-6), 148.5 (C-7), 102.6 (C-8), 150.6 (C-9), 111.4 (C-10), 128.3 (C-1'), 127.6 (C-2', 6'), 122.5 (C-3', 5'), 152.9 (C-4'), 133.7 (C-1''), 112.2 (C-2''), 151.1 (C-3''), 140.0 (C-4''), 123.0 (C-5''), 120.1 (C-6''), 76.3 (C-7''), 74.4 (C-8''), 61.6 (C-9''), 55.9 (—OCH₃), 20.2, 20.3, 20.5, 20.8 (—OCOCH₃), 168.2, 168.3, 168.8, 169.8 (—OCOCH₃). EI-MS *m/z* (%): 632 (M⁺, 2), 590 (100), 548 (16), 488 (11), 328 (52), 286 (28), 222 (67), 179 (33).

Scutellaprostin F (VI) Yellow needles (from MeOH), mp 204—205 °C (dec.). $[\alpha]_D^{20} \pm 0^\circ$ (*c* = 0.05, MeOH). *Anal.* Calcd for C₂₅H₂₀O₁₀: C, 62.50; H, 4.20. Found: C, 62.45; H, 4.29. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 220 sh (4.61), 237 sh (4.40), 261 (4.12), 284 (4.28), 352 (4.39); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 258 (4.40), 294 (4.28), 394 (4.32); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 224 (4.58), 285 (4.26), 311 sh (4.05), 433 (4.46); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 224 (4.56), 240 sh (4.36), 265 (4.05), 290 (4.24), 302 sh (4.20), 376 (4.40); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 282 (4.23), 354 (4.19), 414 (4.06); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}-\text{H}_3\text{BO}_3}$ nm (log ϵ): 266 (4.27), 282 (4.23), 378 (4.37). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3428 (OH), 1664 (conjugated CO), 1610 (arom. C=C). ¹H-NMR: Table I. ¹³C-NMR: Table II. EI-MS *m/z* (%): 480 (M⁺, 3), 302 (C₁₅H₁₀O₇, 77), 180 (C₁₀H₁₂O₃, 63), 168 (C₇H₄O₅, 28), 137 (C₈H₉O₂, 100), 124 (C₇H₈O₂, 61).

Acetylation of VI: Ac₂O-pyridine treatment of VI yielded a pentaacetate as colorless needles (from CHCl₃-MeOH), mp 181—181 °C (dec.). *Anal.* Calcd for C₃₅H₃₀O₁₅: C, 60.87; H, 4.38. Found: C, 60.89; H, 4.40. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 215 (4.79), 270 (4.43), 314 (4.44). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1772, 1742 (acetyl), 1644 (conjugated CO), 1616 (arom. C=C). ¹H-NMR (DMSO-*d*₆) δ : 6.84 (1H, s, H-3), 7.38 (1H, s, H-8), 8.01 (1H, d, *J* = 2.2 Hz, H-2'), 7.49 (1H, d, *J* = 9.2 Hz, H-5'), 8.01 (1H, dd, *J* = 9.2, 2.2 Hz, H-6'), 7.33 (1H, d, *J* = 1.8 Hz, H-2''), 7.17 (1H, d, *J* = 8.1 Hz, H-5''), 7.10 (1H, dd, *J* = 8.1, 1.8 Hz, H-6''), 5.36 (1H, d, *J* = 7.7 Hz, H-7''), 4.75 (1H, ddd, *J* = 7.7, 5.2, 3.7 Hz, H-8''), 4.07 (1H, dd, *J* = 12.4, 5.2 Hz, H-9'a), 4.17 (1H, dd, *J* = 12.4, 3.7 Hz, H-9'b), 3.79 (3H, s, —OCH₃), 2.00, 2.27, 2.32, 2.33, 2.35 (each 3H, s, —OCOCH₃). ¹³C-NMR (DMSO-*d*₆) δ : 159.7 (C-2), 107.4 (C-3), 175.5 (C-4), 135.7 (C-5), 133.7 (C-6), 148.7 (C-7), 102.8 (C-8), 150.7 (C-9), 111.4 (C-10), 129.5 (C-1'), 121.7 (C-2'), 142.5 (C-3'), 144.6 (C-4'), 124.8 (C-5'), 124.5 (C-6'), 133.8 (C-1''), 112.2 (C-2''), 151.1 (C-3''), 140.0 (C-4''), 123.1 (C-5''), 120.2 (C-6''), 76.4 (C-7''), 74.4 (C-8''), 61.7 (C-9''), 56.0 (—OCH₃), 20.3 (—OCOCH₃ × 2), 20.4 (—OCOCH₃ × 2), 20.6 (—OCOCH₃), 168.0, 168.2, 168.3, 168.4, 169.9 (—OCOCH₃). EI-MS *m/z* (%): 690 (M⁺, 7), 648 (33), 606 (22), 588 (52), 546 (100), 504 (48), 386 (35), 344 (26), 302 (29), 222 (28), 179 (21).

Treatment of I—VI with Pyridine Hydrobromide To freshly fused pyridine hydrobromide (450 mg) was added each of the compounds I—VI (15 mg), and the mixture was heated at 210—220 °C for 15 min. The reaction mixture was cooled and poured into ice-water. After extraction with AcOEt, the extract was washed with water and dried over anhydrous Na₂SO₄. The solution was evaporated to dryness and the residue was crystallized from MeOH to give the respective flavones, which were identified as norwogonin, isoscutellarein, hypolaetin, baicalein, scutellarein and 6-hydroxyluteolin, respectively, by direct comparisons with authentic specimens (TLC, UV, IR, ¹H-NMR, mixed fusion).

Treatment of I—VI with Alkali A solution of each of the compounds I—VI (10 mg) in 0.5N KOH (3 ml) was heated at 75 °C for 2.5 h. The reaction mixture was acidified with diluted HCl and extracted with AcOEt. The organic layer was washed with water and dried over anhydrous Na₂SO₄. The solution was evaporated to dryness and the residue was chromatographed on silica gel using CHCl₃ to give colorless needles (3 mg) (from benzene-petr. ether), mp 75 °C; this product was shown to be identical with coniferyl alcohol by direct comparison (IR, ¹H-NMR, mixed fusion).

Oxidative Coupling of Norwogonin and Coniferyl Alcohol with Ag₂O (Formation of I) Norwogonin (500 mg) and coniferyl alcohol (320 mg) were dissolved in dry benzene-acetone (18:5) (200 ml). Ag₂O (925 mg) was added and the suspension was stirred at 55 °C. The reaction was monitored by TLC and interrupted when one of the starting materials was no longer detectable by TLC. The reaction mixture was then filtered and evaporated to dryness. The residue obtained was purified by column chromatography on a silica gel with CHCl₃-MeOH-H₂O (100:10:2) to give compound I (365 mg), which was identical to scutellaprostin A by direct comparison (TLC, $[\alpha]_D$, IR, ¹H- and ¹³C-NMR).

Oxidative Coupling of Isoscutellarein and Coniferyl Alcohol with Ag₂O (Formation of II) A mixture of isoscutellarein (320 mg) and coniferyl alcohol (210 mg) in benzene-acetone (18:5) (460 ml) in the presence of Ag₂O (570 mg) as treated by a procedure similar to that described for the formation of I. The resulting product was purified by chromatography on a silica gel with CHCl₃-MeOH-H₂O (100:10:2) to give compound II (190 mg), which was identical to scutellaprostin B by direct comparison

(TLC, $[\alpha]_D$, ¹H- and ¹³C-NMR).

Oxidative Coupling of Hypolaetin and Coniferyl Alcohol with Ag₂O (Formation of III) A mixture of hypolaetin (500 mg) and coniferyl alcohol (300 mg) in benzene-acetone (18:5) (500 ml) in the presence of Ag₂O (800 mg) was treated by a procedure similar to that described for the formation of I. The resulting product was purified by chromatography on a silica gel with CHCl₃-MeOH-H₂O (100:10:2) to give compound III (290 mg), which was identical with scutellaprostin C by direct comparison (TLC, $[\alpha]_D$, ¹H- and ¹³C-NMR).

Oxidative Coupling of Baicalein and Coniferyl Alcohol with Ag₂O (Formation of IV and VII) A mixture of baicalein (1 g) and coniferyl alcohol (670 mg) in benzene-acetone (18:5) (400 ml) in the presence of Ag₂O (1.8 g) was treated by a procedure similar to that described for the formation of I. The resulting product was chromatographed on silica gel with a gradient of CHCl₃-MeOH (100:0→100:20) as an eluent to give compounds IV (570 mg) and VII (145 mg). Compound IV was identical with scutellaprostin D by direct comparison (TLC, $[\alpha]_D$, ¹H- and ¹³C-NMR).

Compound VII: Colorless needles (from MeOH), mp 206—207 °C (dec.). $[\alpha]_D^{25} \pm 0^\circ$ (*c* = 0.05, MeOH). *Anal.* Calcd for C₂₅H₂₀O₉: C, 66.96; H, 4.50. Found: C, 66.92; H, 4.51. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 215 (4.37), 237 (4.07), 274 (4.26), 314 (3.98); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 248 (4.25), 267 (4.29), 357 (3.73); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 215 (4.36), 237 sh (4.05), 275 (4.23), 314 (3.95); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 215 (4.30), 238 (4.04), 277 (4.19), 320 (3.82); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 270 (4.15), 356 (3.58). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3400 (OH), 1638 (conjugated CO), 1588 (arom. C=C). ¹H-NMR: Table I. ¹³C-NMR: Table II. EI-MS *m/z* (%): 448 (M⁺, 52), 270 (C₁₅H₁₀O₅, 100), 180 (C₁₀H₁₂O₃, 23), 168 (C₇H₄O₅, 11), 137 (C₈H₉O₂, 40), 124 (C₇H₈O₂, 23).

Acetylation of VII: Ac₂O-pyridine treatment of VII yielded a triacetate as colorless needles (from CHCl₃-MeOH), mp 206—207 °C (dec.). *Anal.* Calcd for C₃₁H₂₆O₁₁: C, 64.80; H, 4.56. Found: C, 64.73; H, 4.60. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 217 (4.44), 274 (4.49), 303 (4.12), 330 (3.85). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1774, 1750 (acetyl), 1648 (conjugated CO), 1616 (arom. C=C). ¹H-NMR (DMSO-*d*₆) δ : 6.84 (1H, s, H-3), 7.31 (1H, s, H-8), 8.06 (2H, m, H-2', 6'), 7.54—7.61 (3H, m, H-3', 4', 5'), 7.33 (1H, d, *J* = 1.5 Hz, H-2''), 7.16 (1H, d, *J* = 8.1 Hz, H-5''), 7.10 (1H, dd, *J* = 8.1, 1.5 Hz, H-6''), 5.27 (1H, d, *J* = 7.0 Hz, H-7''), 4.65 (1H, ddd, *J* = 7.0, 5.5, 3.1 Hz, H-8''), 4.06 (1H, dd, *J* = 12.5, 5.5 Hz, H-9'a), 4.20 (1H, dd, *J* = 12.5, 3.1 Hz, H-9'b), 3.78 (3H, s, —OCH₃), 2.02, 2.27, 2.33 (each 3H, s, —OCOCH₃). ¹³C-NMR (DMSO-*d*₆) δ : 160.6 (C-2), 107.6 (C-3), 175.8 (C-4), 142.7 (C-5), 131.9 (C-6), 143.1 (C-7), 104.8 (C-8), 150.6 (C-9), 112.2 (C-10), 130.7 (C-1'), 126.1 (C-2', 6'), 129.1 (C-3', 5'), 131.7 (C-4'), 134.3 (C-1''), 112.2 (C-2''), 151.0 (C-3''), 139.7 (C-4''), 123.0 (C-5''), 120.0 (C-6''), 75.5 (C-7''), 73.8 (C-8''), 61.6 (C-9''), 55.9 (—OCH₃), 20.2 (—OCOCH₃), 20.4 (—OCOCH₃ × 2), 167.7, 168.5, 170.0 (—OCOCH₃). EI-MS *m/z* (%): 574 (M⁺, 4), 532 (100), 490 (9), 430 (6), 281 (13), 270 (49), 222 (42), 179 (17), 147 (8), 131 (13).

Oxidative Coupling of Scutellarein and Coniferyl Alcohol with Ag₂O (Formation of V and VIII) A mixture of scutellarein (235 mg) and coniferyl alcohol (148 mg) in benzene-acetone (18:5) (400 ml) in the presence of Ag₂O (400 mg) was treated by a procedure similar to that described for the formation of I. The resulting product was chromatographed on silica gel with a gradient of CHCl₃-MeOH (100:0→100:20) as an eluent to give compounds V (109 mg) and VIII (32.8 mg). Compound V was identical to scutellaprostin E by direct comparison (TLC, $[\alpha]_D$, ¹H- and ¹³C-NMR).

Compound VIII: Colorless needles (from MeOH), mp 235—236 °C (dec.). $[\alpha]_D^{25} \pm 0^\circ$ (*c* = 0.05, MeOH). *Anal.* Calcd for C₂₅H₂₀O₉: C, 64.65; H, 4.34. Found: C, 64.58; H, 4.40. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 219 (4.56), 278 (4.35), 328 (4.39); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 235 sh (4.49), 252 sh (4.38), 273 (4.27), 322 (4.19), 380 (4.51); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 219 (4.56), 279 (4.32), 331 (4.36), 400 (3.62); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 220 sh (4.52), 281 (4.27), 305 sh (4.18), 347 sh (4.18), 393 (4.28); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 276 (4.44), 305 sh (4.11), 358 (4.27). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 3300 (OH), 1634 (conjugated CO), 1608, 1576 (arom. C=C). ¹H-NMR: Table I. ¹³C-NMR: Table II. EI-MS *m/z* (%): 464 (M⁺, 15), 286 (C₁₅H₁₀O₆, 100), 180 (C₁₀H₁₂O₃, 23), 168 (C₇H₄O₅, 34), 137 (C₈H₉O₂, 34).

Acetylation of VIII: Ac₂O-pyridine treatment of VIII yielded a tetraacetate as colorless needles (from CHCl₃-MeOH), mp 213—214 °C (dec.). *Anal.* Calcd for C₃₃H₂₈O₁₃: C, 62.66; H, 4.46. Found: C, 62.68; H, 4.52. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 217 sh (4.52), 277 (4.53), 305 (4.25), 335 (3.85). IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1772, 1744 (acetyl), 1648 (conjugated CO), 1616 (arom. C=C). ¹H-NMR (DMSO-*d*₆) δ : 6.83 (1H, s, H-3), 7.31 (1H, s, H-8), 8.10 (2H, d, *J* = 8.8 Hz, H-2', 6'), 7.33 (2H, d, *J* = 8.8 Hz, H-3', 5'), 7.33 (1H, d, *J* = 1.8 Hz, H-2''), 7.16 (1H, d, *J* = 8.2 Hz, H-5''), 7.09 (1H, dd, *J* = 8.2, 1.8 Hz, H-6''), 5.27 (1H, d, *J* = 7.0 Hz, H-7''), 4.64 (1H, m,

H-8"), 4.20 (1H, dd, $J=12.6, 3.4$ Hz, H-9"a), 4.06 (1H, dd, $J=12.6, 5.9$ Hz, H-9"b), 3.77 (3H, s, $-\text{OCH}_3$), 2.01, 2.27, 2.30, 2.32 (each 3H, s, $-\text{OCOCH}_3$). ^{13}C -NMR (DMSO- d_6) δ : 160.0 (C-2), 107.6 (C-3), 175.9 (C-4), 142.7 (C-5), 132.0 (C-6), 143.2 (C-7), 104.9 (C-8), 150.7 (C-9), 112.2 (C-10), 128.3 (C-1'), 127.7 (C-2', 6'), 122.7 (C-3', 5'), 153.1 (C-4'), 134.4 (C-1''), 112.2 (C-2''), 151.1 (C-3''), 139.8 (C-4''), 123.1 (C-5''), 120.0 (C-6''), 75.6 (C-7''), 73.9 (C-8''), 61.7 (C-9''), 56.0 ($-\text{OCH}_3$), 20.3 ($-\text{OCOCH}_3$), 20.5 ($-\text{OCOCH}_3 \times 2$), 21.0 ($-\text{OCOCH}_3$), 167.9, 168.6, 170.1 ($-\text{OCOCH}_3$). EI-MS m/z (%): 632 (M^+ , 27), 590 (14), 530 (13), 488 (12), 328 (70), 327 (100), 286 (49), 222 (53), 179 (22), 131 (24).

Oxidative Coupling of 6-Hydroxyluteolin and Coniferyl Alcohol with Ag_2O (Formation of VI and IX) A mixture of 6-hydroxyluteolin (1.9 g) and coniferyl alcohol (1.13 g) in benzene-acetone (18:5) (1900 ml) in the presence of Ag_2O (3.2 g) was treated by a procedure similar to that described for the formation of I. The resulting product was chromatographed on silica gel with a gradient of CHCl_3 -MeOH (100:0 $\rightarrow$ 100:20) as an eluent to give compounds VI (650 mg) and IX (105 mg). Compound VI was identical to scutellaprostin F by direct comparison (TLC, $[\alpha]_D$, ^1H - and ^{13}C -NMR).

Compound IX: Colorless needles (from MeOH), mp 213–214 °C (dec.). $[\alpha]_D^{25} \pm 0^\circ$ ($c=0.05$, MeOH). Anal. Calcd for $\text{C}_{25}\text{H}_{20}\text{O}_{10}$: C, 62.50; H, 4.20. Found: C, 62.45; H, 4.29. Mg-HCl (+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 222 sh (4.60), 238 (4.35), 281 (4.24), 343 (4.35); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOMe}}$ nm (log ϵ): 259 sh (4.42), 294 sh (4.08), 334 (4.02), 394 (4.39); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3}$ nm (log ϵ): 221 sh (4.54), 239 sh (4.38), 279 (4.24), 432 (4.24); $\lambda_{\text{max}}^{\text{MeOH}-\text{AlCl}_3-\text{HCl}}$ nm (log ϵ): 221 sh (4.52), 238 sh (4.34), 285 (4.21), 376 (4.21); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}}$ nm (log ϵ): 277 (4.38), 323 sh (4.34), 376 (4.32); $\lambda_{\text{max}}^{\text{MeOH}-\text{NaOAc}-\text{H}_3\text{BO}_3}$ nm (log ϵ): 264 sh (4.31), 278 sh (4.29), 368 (4.34). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3460 (OH), 1636 (conjugated CO), 1614 (arom. C=C). ^1H -NMR: Table I. ^{13}C -NMR: Table II. EI-MS m/z (%): 302, ($\text{C}_{15}\text{H}_{10}\text{O}_7$, 100), 168 ($\text{C}_7\text{H}_4\text{O}_5$, 51), 137 ($\text{C}_8\text{H}_9\text{O}_2$, 13).

Acetylation of IX: Ac_2O -pyridine treatment of IX yielded a pentaacetate as colorless needles (from CHCl_3 -MeOH), mp 213–215 °C (dec.). Anal. Calcd for $\text{C}_{35}\text{H}_{30}\text{O}_{15}$: C, 60.87; H, 4.38. Found: C, 60.90; H, 4.43. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 219 sh (4.59), 278 (4.63), 307 sh (4.26), 340 sh (3.94). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1773, 1749 (acetyl), 1650 (conjugated CO), 1617 (arom. C=C). ^1H -NMR (DMSO- d_6) δ : 6.87 (1H, s, H-3), 7.31 (1H, s, H-8), 8.03 (1H, br s, H-2'), 7.48 (1H, d, $J=8.8$ Hz, H-5'), 8.02 (1H, dd, $J=8.8, 2.2$ Hz, H-6'), 7.33 (1H, d, $J=1.8$ Hz, H-2''), 7.16 (1H, d, $J=8.2$ Hz, H-5''), 7.10 (1H, dd, $J=8.2, 1.8$ Hz, H-6''), 5.26 (1H, d, $J=7.0$ Hz, H-7''), 4.64 (1H, m, H-8''), 4.06 (1H, dd, $J=12.6, 5.7$ Hz, H-9'a), 4.20 (1H, dd,

$J=12.6, 3.3$ Hz, H-9'b), 3.78 (3H, s, $-\text{OCH}_3$), 2.02, 2.28, (each 3H, s, $-\text{OCOCH}_3$), 2.32, (6H, s, $-\text{OCOCH}_3 \times 2$), 2.33 (3H, s, $-\text{OCOCH}_3$). ^{13}C -NMR (DMSO- d_6) δ : 159.0 (C-2), 108.0 (C-3), 175.7 (C-4), 142.7 (C-5), 132.0 (C-6), 143.1 (C-7), 104.8 (C-8), 150.6 (C-9), 112.2 (C-10), 129.1 (C-1'), 121.7 (C-2'), 142.5 (C-3'), 144.5 (C-4'), 124.6 (C-5'), 124.4 (C-6'), 134.2 (C-1''), 112.2 (C-2''), 151.0 (C-3''), 139.8 (C-4''), 123.0 (C-5''), 120.0 (C-6''), 75.6 (C-7''), 73.9 (C-8''), 61.6 (C-9''), 55.9 ($-\text{OCH}_3$), 20.2 ($-\text{OCOCH}_3$), 20.3 ($-\text{OCOCH}_3 \times 2$), 20.4 ($-\text{OCOCH}_3 \times 2$), 167.7, 168.0, 168.2, 168.4, 170.0 ($-\text{OCOCH}_3$). EI-MS m/z (%): 690 (M^+ , 18), 648 (11), 588 (7), 546 (12), 504 (4), 427 (24), 385 (100), 343 (43), 302 (31), 222 (91), 179 (61).

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References and Notes

- 1) Part XIII: Y. Kikuchi, Y. Miyaichi and T. Tomimori, *Chem. Pharm. Bull.*, **39**, 1051 (1991).
- 2) Presented at the 109th Annual Meeting of the Pharmaceutical Society of Japan, Nagoya, April 1989 and the 36th Annual Meeting of the Japanese Society of Pharmacognosy, Kumamoto, October 1989.
- 3) Y. Kikuchi, Y. Miyaichi, Y. Yamaguchi, H. Kizu and T. Tomimori, *Chem. Pharm. Bull.*, **39**, 1047 (1991).
- 4) T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, New York, 1970, Chapter V.
- 5) T. Tomimori, Y. Miyaichi, Y. Imoto, H. Kizu and Y. Tanabe, *Yakugaku Zasshi*, **103**, 607 (1983).
- 6) A. B. Ray, S. K. Chattopadhyay, S. Kumar, D. Konno, Y. Kiso and H. Hikino, *Tetrahedron*, **41**, 209 (1985).
- 7) L. Merlini, A. Zanarotti, A. Pelter, M. P. Rochefort and R. Hänsel, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 775.
- 8) Y. Miyaichi, Y. Imoto, H. Saida and T. Tomimori, *Shoyakugaku Zasshi*, **42**, 216 (1988).
- 9) Synthesized from 5,8-dihydroxy-7,3',4'-trimethoxyflavone¹¹⁾ by demethylation with pyridine hydrobromide.
- 10) T. Tomimori, Y. Miyaichi, Y. Imoto and H. Kizu, *Yakugaku Zasshi*, **38**, 249 (1984).
- 11) Synthesized according to the literature [N. Morita, *Chem. Pharm. Bull.*, **8**, 66 (1960)].