

Three New Flavonoids, 3'-Methoxylupinifolin, Laxifolin, and Isolaxifolin from the Roots of *Derris laxiflora* BENTH

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The following constituents were isolated from the roots of *Derris laxiflora* BENTH: flemichapparin-B (1), 3'-methoxylupinifolin (2a), lupinifolin (2b), β -amyrin (3), lupeol (4), prunetin (5), laxifolin (6a), and isolaxifolin (7a). Compounds 2a, 6a, and 7a are new flavonoids, and their structures were determined on the basis of spectral and chemical evidence.

Keywords *Derris laxiflora*; root; flavonoid; 3'-methoxylupinifolin; laxifolin, isolaxifolin

Extensive chemical studies on the constituents of the species of *Derris* (*D.*) have been reported,¹ and many interesting components including flavones, flavonols, chalcones, dihydrochalcones, isoflavans, rotenones, stilbenes, coumarins, aurones, pterocarpanes, coumestans, triterpenes, and glycosides have been isolated. There are only three species of genus *Derris* (Leguminosae) indigenous to Taiwan: *D. trifoliata*, *D. laxiflora*, and *D. oblonga*. The chemical constituents of the first species have been investigated.² The latter two species are climbers and are distributed in forests at low altitudes in southern parts of Taiwan. The roots of both plants have been reported to possess insecticidal and piscicidal activities. In connection with our interest in flavonoids and in view of the biological activity of the root, chemical studies on *D. laxiflora* were undertaken in our laboratory. This paper deals with the chemical constituents of an ethanol extract of the root.

The air-dried roots of *D. laxiflora* were repeatedly extracted with ethanol. The ethanol extract was evaporated *in vacuo* to give a residue which was partitioned with ether and water. After repeated purification by silica gel chromatography, four components, flemichapparin-B (1),³ 3'-methoxylupinifolin (2a) (a new prenylated flavanone), β -amyrin (3),⁴ lupeol (4),⁵ and lupinifolin (2b)⁶ were isolated from the ether layer. The water layer was subsequently partitioned with butanol. The butanol layer was purified repeatedly by silica gel and Sephadex LH-20 chromatography and yielded three components, prunetin (5),⁷ laxifolin (6a), and isolaxifolin (7a). Four known compounds were identified by the comparison of their physical data with those reported in the literature. This paper deals with the structural elucidation of the three new compounds 2a, 6a, and 7a.

3'-Methoxylupinifolin (2a), mp 82–83 °C, yellow needles from methanol, was formulated as C₂₆H₂₈O₆ on the basis of elemental analysis, and gave a positive Mg–HCl test. The infrared (IR) spectrum shows strong absorptions at 3220 (OH) and 1635 cm⁻¹ (chelated CO). Its ultraviolet (UV) spectrum ($\lambda_{\text{max}}^{\text{MeOH}}$ 268, 276, 299, 315 and 367 nm) and signals of an ABX system at δ 2.77 (1H, dd, $J=17.1, 3.0$ Hz), 3.01 (1H, dd, $J=17.1, 12.7$ Hz), 5.29 (1H, dd, $J=12.7, 3.0$ Hz) in the proton nuclear magnetic resonance (¹H-NMR) spectrum (Table I) indicated that 2a is a flavanone.⁸ The addition of sodium acetate caused no bathochromic shift of band II (240–280 nm) in the UV spectrum.⁸ The evidence suggests that the C-7 phenolic hydroxyl group is not free. The doublets at δ 5.48 and 6.62 (each 1H,

$J=9.9$ Hz), and two singlets at δ 1.42 and 1.43 (each 3H) are characteristic of a *cis* double bond and *gem*-dimethyl group of the 2,2-dimethylchromene moiety.⁹ The presence of a C- γ,γ -dimethylallyl group was inferred from the singlets at δ 1.64 and 1.65 (each 3H, br s), the doublet at δ 3.28 (2H, d, $J=7.3$ Hz), and the triplet at δ 5.17 (1H, t, $J=7.3$ Hz).¹⁰ Signals due to three aromatic protons were discernible at δ 6.89 (1H, d, $J=8.9$ Hz), 6.92 (1H, d, $J=8.9$ Hz), and 6.97 (1H, s), and these could be readily assigned to a 1,3,4-

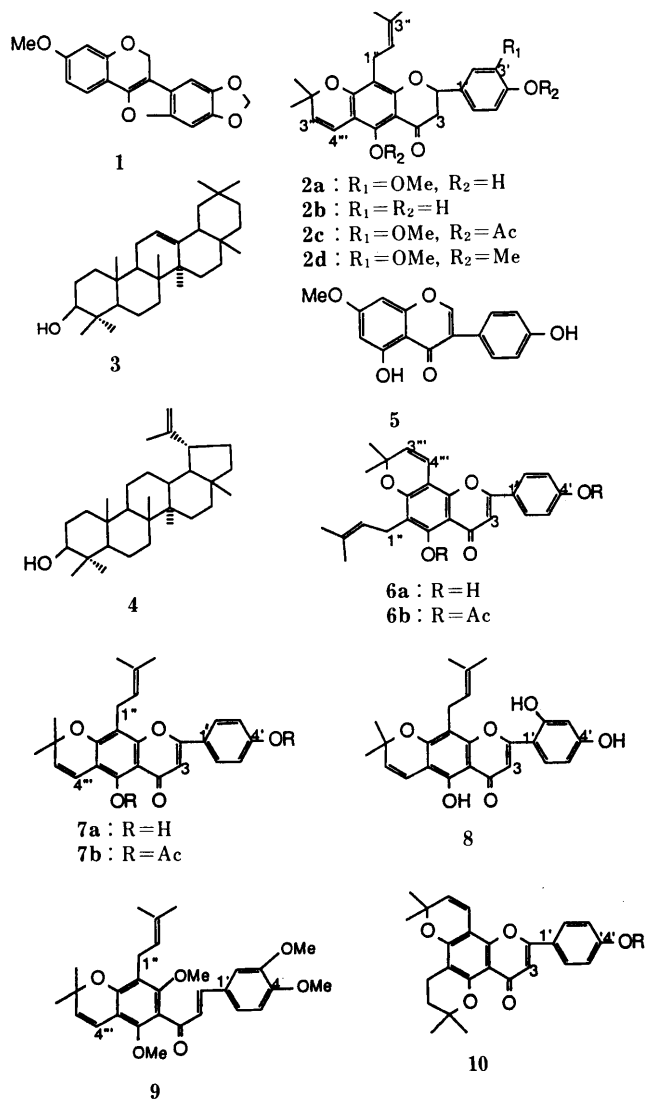
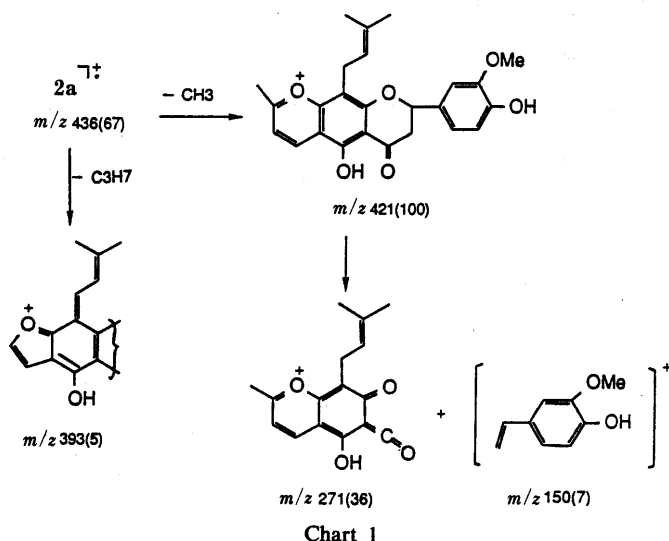


TABLE I. ^1H -NMR Data for 3'-Methoxylupinifolin (**2a**), Lupinifolin (**2b**), Laxifolin (**6a**) and Isolaxifolin (**7a**)

H	2a	2b	6a	7a
2	5.29 dd (12.7, 3.0) ^a	5.31 dd (12.9, 3.0)		
3	2.77 dd (17.1, 3.0) 3.01 dd (17.1, 12.7)	2.77 dd (17.0, 3.0) 3.00 dd (17.0, 12.9)	6.49 s	6.49 s
2'	6.97 s	7.30 d (9.0)	7.72 d (8.5)	7.72 d (8.7)
3'		6.61 d (9.0)	6.89 d (8.5)	6.89 d (8.7)
5'	6.89 d (8.9)	6.61 d (9.0)	6.89 d (8.5)	6.89 d (8.7)
6'	6.92 d (8.9)	7.30 d (9.0)	7.72 d (8.5)	7.72 d (8.7)
1''	3.28 d (7.3)	3.10 d (7.0)	3.28 d (7.1)	3.47 d (6.9)
2''	5.17 t (7.3)	5.12 t (7.0)	5.16 t (7.1)	5.17 t (6.9)
3''-CH ₃	1.64, 1.65 s	1.63 s	1.61, 1.75 s	1.62, 1.76 s
2'''-CH ₃	1.42, 1.43 s	1.42, 1.43 s	1.42 s	1.41 s
3'''	5.48 d (9.9)	5.48 d (9.9)	5.59 d (10.0)	5.57 d (10.0)
4'''	6.62 d (9.9)	6.61 d (9.9)	6.73 d (10.0)	6.70 d (10.0)
O-CH ₃	3.89 s			

300 MHz in CDCl_3 (TMS as internal standard). a) Figures in parentheses are coupling constants.



trisubstituted benzene ring. A phenolic methyl ether signal was seen at δ 3.89 (3H, s). The singlets at δ 5.81 and 12.25 (each 1H, s), which both disappeared upon addition of D_2O , were assigned to the two phenolic protons.

The substitution pattern of 3'-methoxylupinifolin (**2a**) was determined from ^1H -NMR and mass spectral data. The presence of a chelated C-5 hydroxyl was evident, as one of the phenolic protons resonated at low field (δ 12.25). The non-chelated OH group (δ 5.81) could thus be located either in the A- or B-ring. The mass spectrum (MS) of **2a** (Chart 1) showed fragments at m/z (%) 271 (36) and 150 (7), which can be rationalized only when non-chelated OH and -OMe groups are present in the B-ring, and γ,γ -dimethylallyl and 2,2-dimethylchromene side-chains in the A-ring. The non-chelated OH was assigned to C-4' on the basis of a nuclear Overhauser effect (NOE) experiment, in which NOEs were observed between the -OMe and a signal at δ 6.97 (1H, s, H-2', 20.8% enhancement), showing that -OMe is located at C-3'. Cardillo *et al.*¹¹ have shown that acid cyclization of *ortho*- γ,γ -dimethylallylphenol gives the corresponding chroman. Treatment of **2a** with formic acid

TABLE II. ^{13}C -NMR Data (δ Values) for 3'-Methoxylupinifolin (**2a**), Lupinifolin (**2b**), Laxifolin (**6a**) and Isolaxifolin (**7a**)

C	2a	2b	6a	7a
2	78.8 d	78.5 d	163.7 s	163.0 s
3	43.1 t	43.1 t	103.4 d	103.5 d
4	196.3 s	196.7 s	182.5 s	182.9 s
5	159.2 s	159.4 s	160.8 s	157.0 s
6	102.7 s	102.8 s	100.9 s	105.0 s
7	159.6 s	160.0 s	160.7 s	159.4 s
8	108.4 s	108.7 s	112.6 s	107.6 s
9	156.5 s	156.5 s	158.7 s	154.5 s
10	102.5 s	102.6 s	103.2 s	103.6 s
1'	125.8 s	126.0 s	127.0 s	123.7 s
2'	108.6 d	127.7 d	128.0 d	128.3 d
3'	146.7 s	115.5 d	116.2 d	116.2 d
4'	145.8 s	156.0 s	156.0 s	154.3 s
5'	115.5 d	115.5 d	116.2 d	116.2 d
6'	119.1 d	127.7 d	128.0 d	128.3 d
1''	21.3 t	21.4 t	21.7 t	21.6 t
2''	122.4 d	122.4 d	122.2 d	122.2 d
3''	130.6 s	130.7 s	128.3 s	131.7 s
4''	25.6 q	25.7 q	25.8 q	25.7 q
5''	17.7 q	17.6 q	18.1 q	18.0 q
2'''	78.0 s	78.1 s	77.8 s	78.6 s
3'''	130.8 d	131.1 d	131.4 d	131.9 d
4'''	114.4 d	115.6 d	115.6 d	115.8 d
5'''	28.1 q	28.4 q	28.1 q	28.0 q
6'''	28.2 q	28.3 q	28.2 q	28.1 q
OCH ₃	55.8 q			

75 MHz in CDCl_3 (TMS as internal standard). Assignments established by off-resonance and DEPT methods. s, singlet; d, doublet; t, triplet; q, quartet.

failed to give chroman and only the starting materials was recovered. This result suggested the presence of a C-8 γ,γ -dimethylallyl side-chain in **2a**. Recently, Fukai *et al.*¹² reported that the MS base peaks of 8-prenylated flavanone and 6-prenylated flavanone are $\text{M}^+ - \text{CH}_3$ and $\text{M}^+ - \text{C}_3\text{H}_7$, respectively. Due to the fragment in the MS, the γ,γ -dimethylallyl side-chain was therefore determined to be at C-8 and the structure of **2a** is assigned as 3'-methoxylupinifolin. The structure of **2a** was further confirmed by carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy (Table II).

The reaction of **2a** with methyl iodide and potassium carbonate in dry acetone under reflux gave two products, a trimethoxyflavanone (**2d**) and a chalcone (**9**) [δ 6.91 and 7.34 (each 1H, $J=16$ Hz), δ 3.67, 3.70, 3.88, and 3.88 (each 3H, s)]. Compound **2d**, an amorphous solid, shows three methoxyl signals [δ 3.81 (3H, s) and 3.89 (6H, s)] and an ABX system [δ 2.79 (1H, dd, $J=17.0, 3.1$ Hz), 2.87 (1H, dd, $J=17.0, 13.2$ Hz), and 5.33 (1H, dd, $J=13.2, 3.1$ Hz)] characteristic of the flavanone moiety in its ^1H -NMR spectrum. In an NOE experiment, NOEs were observed between the chromene olefinic proton (δ 6.61) and 5-OMe (δ 3.89) and between H-2' [δ 6.99 (1H, d, $J=2.0$ Hz)] and one methoxyl group [δ 3.81 (3H, s)] in **2d**. The results supported the proposed structure of **2a**.

Laxifolin (**6a**) and isolaxifolin (**7a**) were separated by medium-pressure liquid chromatography (MPLC). The former melted at 259–260 °C. It shows peaks at m/z (%) 404 (M^+ , 70), 389 ($\text{M}^+ - \text{CH}_3$, 49), 361 ($\text{M}^+ - \text{C}_3\text{H}_7$, 100) and 349 ($\text{M}^+ - \text{C}_4\text{H}_9$, 49) in the MS, was formulated as $\text{C}_{25}\text{H}_{24}\text{O}_5$ on the basis of elemental analysis, and gave a positive Mg-HCl test. The UV absorption of **6a** at $\lambda_{\text{max}}^{\text{MeOH}}$

(log ϵ): 236 (4.12), 279 (4.14), 314 (4.18), and 337 (4.06) nm indicated it to be a flavone. The $^1\text{H-NMR}$ spectrum (Table I) of laxifolin (**6a**) showed the presence of one 2,2-dimethylchromene, one γ,γ -dimethylallyl group, one olefinic proton, an A_2B_2 system of four aromatic protons, and two phenolic protons (δ 5.50 and 12.36). Similarly isolaxifolin (**7a**), yellow needles, mp 230–232 °C, was formulated at $\text{C}_{25}\text{H}_{24}\text{O}_5$ based on its elemental analysis. It also gave a positive Mg–HCl test. The $^1\text{H-NMR}$ data (Table I) for isolaxifolin indicated it to possess one 2,2-dimethylchromene, one γ,γ -dimethylallyl group, one olefinic proton, an A_2B_2 system of four aromatic protons, and two phenolic protons (δ 5.96 and 12.47). The UV absorption of isolaxifolin (**7a**) is similar to that of laxifolin (**6a**). The fragment peaks assignable to $\text{M}^+ - \text{CH}_3$, $\text{M}^+ - \text{C}_3\text{H}_7$ and $\text{M}^+ - \text{C}_4\text{H}_9$ in the MS also confirmed the presence of a dimethylchromene and a γ,γ -dimethylallyl group in both compounds.¹³ From the above evidence, laxifolin and isolaxifolin are considered to be isomers. The base peaks, $\text{M}^+ - \text{CH}_3$ (isolaxifolin) and $\text{M}^+ - \text{C}_3\text{H}_7$ (laxifolin), proved the presence of the 8-prenyl group for isolaxifolin and the 6-prenyl group for laxifolin.¹² Acetylation of **6a** and **7a** with acetic anhydride in pyridine at 60 °C overnight afforded the diacetates, **6b** [mp 125–126 °C; $\nu_{\text{max}}^{\text{KBr}}$ 1750 cm^{-1} ; δ 2.33 and 2.45 (each 3H, s)] and **7b** [mp 105–107 °C; $\nu_{\text{max}}^{\text{KBr}}$ 1755 cm^{-1} ; δ 2.32 and 2.45 (each 3H, s)], respectively. In the $^1\text{H-NMR}$ spectrum of **7b**, the signal of H-4''' at δ 6.48 (d) is shifted upfield (0.22 ppm) compared with that in **7a** (δ 6.70, d). On the other hand, the chemical shifts of H-4''' of **6a** and **6b** exhibit opposite shifts. This result provides additional proof that the γ,γ -dimethylallyl side-chain is located at C-6 for laxifolin (**6a**) and at C-8 for isolaxifolin (**7a**).^{14,15} Finally, the location of the γ,γ -dimethylallyl group was determined by chemical transformation of **6a** to chroman (**10**) by heating in acetic acid and sulfonic acid¹⁵ [**10**, mp 272–274 °C; $\nu_{\text{max}}^{\text{KBr}}$ 3300 cm^{-1} ; MS m/z 404 (M^+); δ 1.74 and 2.55 (each 2H, t, $J=7.0$ Hz)]. Under the same conditions, isolaxifolin (**7a**) did not react at all. Thus, the structures of laxifolin and isolaxifolin were established as **6a** and **7a**, respectively. The $^{13}\text{C-NMR}$ data (Table I) also confirm these structures.

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrometer. $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra were run on a Bruker AM 300 at 300 MHz and 75 MHz in the indicated solvent with tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ -values and coupling constants (J) are given in hertz (Hz). Electron impact mass spectra (EI-MS) and UV spectra were taken on JEOL JMS-100 and Hitachi U-3200 instruments, respectively.

Extraction and Isolation The roots of *Derris laxiflora* were crushed into small pieces and dried at 50 °C to give 5.7 kg of raw material, which was extracted with 95% ethanol (50 l) three times (8 h each time) at 60 °C. The combined extracts were evaporated *in vacuo* to give a residue, which was subsequently subjected to partition with ethyl acetate and H_2O (each 1 l). The upper layer was purified by silica gel chromatography with gradient (hexane– CHCl_3) system to afford flemichapparin-B (**1**) (87 mg), 3'-methoxylupinifolin (**2a**) (156 mg), β -amyrin (**3**) (283 mg) and lupeol (**4**) (165 mg) (a crystalline mixture of **3** and **4** was separated on silica gel impregnated with 10% AgNO_3), and lupinifolin (**2b**) (4.6 g). The aqueous layer was subsequently partitioned with BuOH (3 l), and the BuOH layer was purified by silica gel chromatography (CHCl_3 –MeOH gradient) to yield prunetin (**5**) (143 mg) and a yellow crystalline mixture, which was separated by Sephadex LH-20 column chromatography (MeOH) and then silica gel MPLC (hexane:ethyl acetate=3:1) to give laxifolin (**6a**)

(120 mg) and isolaxifolin (**7a**) (128 mg).

Flemichapparin-B (**1**)³: mp 182–184 °C. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 250 (4.08), 328sh (4.35), 338 (4.48), 357 (4.46). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3080, 1640, 1610, 1600, 1510, 1320, 1035, 1015, 935. MS m/z (%): 296 (100). $^1\text{H-NMR}$ (CDCl_3) δ : 3.78 (3H, s), 5.50, 5.97 (each 2H, s), 6.48 (1H, d, $J=2.4$ Hz), 6.52 (1H, dd, $J=8.3$, 2.4 Hz), 6.71 (1H, s), 7.00 (1H, s), 7.35 (1H, d, $J=8.3$ Hz).

3'-Methoxylupinifolin (**2a**): mp 82–83 °C. $[\alpha]_{\text{D}}^{20}$ –250° ($c=0.5$, CHCl_3). MS m/z (%): 436 (M^+ , 67), 421 ($\text{M}^+ - \text{CH}_3$, 100), 271 (36), 243 (17), 231 (11), 215 (61). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 228 (4.34), 268 (4.62), 276 (4.66), 297 (4.11), 315 (4.12), 367 (3.54). UV $\lambda_{\text{max}}^{\text{MeOH} + \text{NaOAc}}$ nm (log ϵ): 226 (4.34), 268 (4.62), 276 (4.66), 314 (4.11), 366 (3.51). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3220, 1635, 1610, 1590, 1510, 1370. $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_6$: C, 71.54; H, 6.47. Found: C, 71.89; H, 6.55.

β -Amyrin (**3**)⁴: mp 196–197 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3280, 1380, 1370, 1035, 995, 875, 810. MS m/z (%): 426 (M^+ , 2), 411 (1), 218 (100), 203 (62), 189 (26). $^1\text{H-NMR}$ (CDCl_3) δ : 0.77, 0.81, 0.85, 0.85, 0.92, 0.95, 0.98, 1.11 (each 3H, s), 3.20 (1H, dd, $J=10.2$, 5.7 Hz), 5.16 (1H, t, $J=3.3$ Hz).

Lupeol (**4**)⁵: mp 206–208 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3420, 3040, 1635, 1010, 980, 870. MS m/z (%): 426 (M^+ , 12), 411 (6), 218 (42), 207 (60), 203 (38), 189 (100), 175 (37), 135 (60), 121 (60). $^1\text{H-NMR}$ (CDCl_3) δ : 0.74, 0.77, 0.81, 0.92, 0.94, 1.01 (each 3H, s), 1.66 (3H, brs), 2.34 (1H, dt, $J=11.0$, 5.6 Hz), 3.16 (1H, dd, $J=11.0$, 5.6 Hz), 4.56, 4.66 (each 1H, brs).

Prunetin (**5**)⁷: mp 178–179 °C. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 262 (4.69), 327 (3.79). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3360, 1660, 1610, 1560, 1510, 1050, 945, 820, 745. MS m/z (%): 284 (M^+ , 100), 166 (14), 138 (5), 118 (2). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 3.80 (3H, s), 6.26, 6.40 (each 1H, d, $J=2.1$ Hz), 6.78, 7.28 (each 2H, d, $J=8.5$ Hz), 8.04 (1H, s), 9.28, 12.82 (each 1H, s, –OH).

Lupinifolin (**2b**)⁹: mp 178–179 °C. MS m/z (%): 406 (M^+ , 82), 391 (100), 271 (27), 243 (10), 215 (29). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 266 (4.52), 275 (4.56), 299 (3.95), 314 (3.99), 366 (3.39). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3240, 1640, 1610, 1590, 1520. $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II.

Laxifolin (**6a**): mp 259–260 °C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3430, 1645, 1605, 1580, 1510, 1175, 1125, 835. MS m/z (%): 404 (M^+ , 70), 389 (49), 361 (100), 349 (49). $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_5$: C, 74.25; H, 5.94. Found: C, 74.20; H, 5.97.

Isolaxifolin (**7a**): mp 230–232 °C. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 234 (4.25), 282 (4.15), 311 (4.13), 341 (4.10). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400, 1655, 1605, 1560, 1510, 1205, 1170, 1125, 830. MS m/z (%): 404 (26), 389 (100), 361 (26), 349 (13). $^1\text{H-NMR}$: Table I. $^{13}\text{C-NMR}$: Table II. Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_5$. Found: C, 74.19; H, 5.98.

Acetylation of 2a with Acetic Anhydride and Pyridine 3'-Methoxylupinifolin (**2a**) (5 mg) was allowed to react with Ac_2O (1 ml) in pyridine (0.5 ml) at 60 °C overnight. Usual work-up gave a diacetate (**2c**) (5 mg). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1750, 1670, 1600, 1500, 1200, 1155. $^1\text{H-NMR}$ (CDCl_3) δ : 1.42, 1.43, 1.63, 1.69, 2.31, 2.39, 3.84 (each 3H, s), 2.71 (1H, dd, $J=16.8$, 2.5 Hz), 2.93 (1H, dd, $J=16.8$, 13.2 Hz), 3.28 (2H, d, $J=7.0$ Hz), 5.17 (1H, t, $J=7.0$ Hz), 5.40 (1H, dd, $J=13.2$, 2.5 Hz), 5.63, 6.36 (1H, d, $J=10.0$ Hz), 6.97 (1H, dd, $J=8.0$, 1.2 Hz), 7.05 (1H, d, $J=8.0$ Hz), 7.07 (1H, d, $J=1.2$ Hz).

Methylation of 2a A mixture of 3'-methoxylupinifolin (**2a**) (20 mg), methyl iodide (1 ml), dry acetone (5 ml), anhydrous potassium carbonate (1 g), and a few drops of dimethyl sulfoxide (DMSO) was heated under reflux for 24 h. The mixture was filtered, and the filtrate was evaporated to dryness. The residue was subsequently purified by silica gel chromatography (CHCl_3) to afford two amorphous compounds, a trimethoxyflavanone (**2d**) (10 mg) [$\text{IR } \nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1670, 1580, 1510, 1150, 1110. $^1\text{H-NMR}$ (CDCl_3) δ : 1.41, 1.43, 1.64, 1.65, 3.81, 3.89 (each 3H, s), 2.79 (1H, dd, $J=17.1$, 3.1 Hz), 2.97 (1H, dd, $J=17.1$, 13.0 Hz), 3.28 (2H, d, $J=7.2$ Hz), 5.19 (1H, t, $J=7.2$ Hz), 5.33 (1H, dd, $J=13.0$, 3.1 Hz), 5.57, 6.61 (each 1H, d, $J=10.1$ Hz), 6.87 (1H, d, $J=8.0$ Hz), 6.97 (1H, dd, $J=8.0$, 2.0 Hz), 6.99 (1H, d, $J=2.0$ Hz)] and a chalcone (**9**) (9 mg) [$\text{IR } \nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1660, 1635, 1580, 1500, 1130. $^1\text{H-NMR}$ (CDCl_3) δ : 1.43, 1.43, 1.67, 1.76, 3.67, 3.70, 3.88, 3.88 (each 3H, s), 3.27 (2H, d, $J=7.1$ Hz), 5.18 (1H, t, $J=7.1$ Hz), 5.59, 6.52 (each 1H, d, $J=10.0$ Hz), 6.83 (1H, d, $J=8.4$ Hz), 6.91, 7.34 (each 1H, d, $J=16.0$ Hz), 7.05 (1H, d, $J=1.9$ Hz), 7.10 (1H, dd, $J=8.4$, 1.9 Hz)].

Acetylation of Laxifolin (6a) and Isolaxifolin (7a) Acetylation of **6a** (5 mg) and **7a** (5 mg) in the same way as mentioned above yielded **6b** (5 mg) and **7b** (5 mg) respectively. **6b**: IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1750, 1645, 1635, 1590, 1500, 1190. $^1\text{H-NMR}$ (CDCl_3) δ : 1.45, 1.45, 1.65, 1.65, 2.33, 2.45 (each 3H, s), 3.25 (2H, d, $J=7.1$ Hz), 5.08 (1H, t, $J=7.1$ Hz), 5.71, 6.84 (each 1H, d, $J=10.0$ Hz), 6.53 (1H, s), 7.23, 7.84 (each 2H, d, $J=8.5$ Hz). **7b**: IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 1755, 1645, 1630, 1590, 1500, 1195. $^1\text{H-NMR}$ (CDCl_3) δ : 1.46, 1.46, 1.67, 1.81, 2.32, 2.45 (each 3H, s), 3.56 (2H, d, $J=6.8$ Hz), 5.21 (1H,

t, $J=6.8$ Hz), 5.74, 6.48 (each 1H, d, $J=10.0$ Hz), 6.53 (1H, s), 7.22, 7.85 (each 2H, d, $J=8.5$ Hz).

The Chroman 10 from 6a by Acidic Cyclization A mixture of laxifolin (6a) (5 mg), acetic acid (1 ml), and concentrated H_2SO_4 (0.2 ml) was heated at $100^\circ C$ overnight and then allowed to stand at room temperature for 36 h. The reaction mixture was poured into excess ice water. The organic compounds were extracted with ethyl acetate and purified by silica gel column chromatography ($MeOH-CHCl_3$, 5:95) to give the chroman (10) (3 mg) [mp $272-274^\circ C$. IR ν_{max}^{KBr} cm^{-1} : 3300, 1650, 1160, 1565, 1500. MS m/z (%): 404 (50), 389 (100), 361 (35), 349 (31). 1H -NMR ($DMSO-d_6$) δ : 1.29, 1.43 (each 6H, s), 1.74, 2.55 (each 2H, t, $J=7.0$ Hz), 5.74, 6.84 (each 1H, d, $J=10.1$ Hz), 6.31 (1H, s), 6.64, 7.66 (each 2H, d, $J=8.5$ Hz)].

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