Two New Flavanones and Two New Chalcones from the Root of *Derris laxiflora* BENTH

Yun-Lian LIN,[a,b] Yuh-Lin CHEN[b] and Yueh-Hsiung KUO*[,a,c]

National Research Institute of Chinese Medicine,[a] Taipei Hsien, Taiwan, R.O.C., Department of Agricultural Chemistry,[b] National Taiwan University, Taipei, R.O.C. and Department of Chemistry,[c] National Taiwan University, Taipei, R.O.C. *Received February 24, 1992*

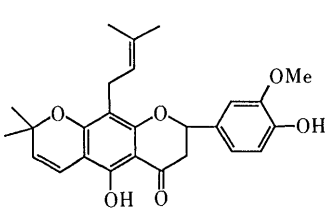
Two new diprenylated flavanones, derriflavanone and *epi*-derriflavanone, and two new diprenylated chalcones, laxichalcone and derrichalcone, have been isolated from the roots of *Derris laxiflora*. Their structures were determined on the basis of spectral and chemical evidence. The two flavanones are an epimeric mixture which can be converted to derrichalcone under basic and acidic conditions.

Keywords *Derris laxiflora*; root; laxifolin, isolaxifolin; derrichalcone; *epi*-derrichalcone

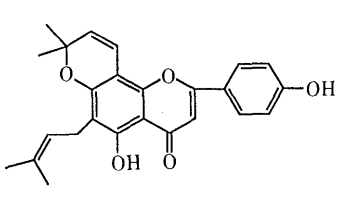
Many interesting components including flavonoids, rotenones, stilbenes, coumarins, aurones, pterocarpans, coumestanes, and glycosides have been identified as constituents of the species of *Derris* (*D.*).[1] The roots of these plants have been reported to possess insecticidal and piscicidal activities. 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.

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 ethyl acetate and water. After repeated purification, six components, flemichapparin-B, 3-methoxylupinifonin, β-amyrin, lupeol, laxichalcone, and lupinifolin, were isolated from the ethyl acetate layer. The water layer was subsequently partitioned with butanol. The butanol layer was subjected to careful separation (repeatedly by silica gel and Sephadex LH-20 chromatography) to yield prunetin, laxifolin, isolaxifolin, derrichalcone, and a yellow crystalline material. The structures of 3′-methoxylupinifonin, laxifolin and isolaxifolin were elucidated as **1**, **2**, and **3**, respectively, in the previous report[2] which also described the identification of four known compounds. The structural elucidation of laxichalcone (**4a**) and derrichalcone (**5a**)[3] was reported in a brief communication. In this full paper we described in detail our study of the structures of laxichalcone (**4a**) and derrichalcone (**5a**), as well as the yellow crystalline material, which was elucidated as an epimeric mixture of derriflavanone (**6a** or **7a**) and *epi*-derriflavanone (**7a** or **6a**).

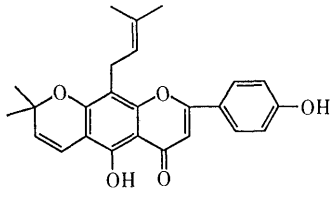
Laxichalcone (**4a**), mp 174—176 °C, red needles from ethanol, was formulated as $C_{25}H_{24}O_5$ on the basis of elementary analysis and the mass spectrum (MS) [M^+ peak at m/z 404]. Its chalcone structure was indicated by the ultraviolet (UV) spectrum (λ_{max}^{MeOH} 251, 265, 277, 377 nm). A bathochromic shift of 65 nm of the longer wavelength band, along with an increase in intensity with NaOMe, showed the presence of a 4-OH group. The bathochromic shift with $AlCl_3$, which did not show any change on the addition of HCl, showed the presence of a chelated OH group. The absence of a bathochromic shift with NaOAc showed the 4′-OH group to be free. The infrared (IR) spectrum shows characteristic absorptions at 1650 cm^{-1} due to chalcone carbonyl, at 1380 and 1373 cm^{-1} due to *gem*-dimethyl and at 830 cm^{-1} due to a *para*-substituted benzene ring. The signals for α and β-protons at δ 7.69 and 7.85 (each 1H, d, J=15.5 Hz) in the proton nuclear magnetic resonance (^{1}H-NMR) spectrum (Table I) also indicated that **4a** is a chalcone. The presence of two 2.2-dimethyl chromene moieties was shown by the signals at δ 1.41 and 1.50 (each 6H, s), 5.64 and 6.54 (each 1H, d, J=10.0 Hz), and 5.62 and 6.51 (each 1H, d, J=10.0 Hz). Further, there were two *ortho*-coupled doublets centered at δ 6.87, 7.54 (each 2H, d, J=8.5 Hz) due to an A_2B_2 system of a *para*-substituted B-ring. Two phenolic OH groups were discernible at δ 10.14 and 14.43 (each 1H, s). The compound formed a diacetate



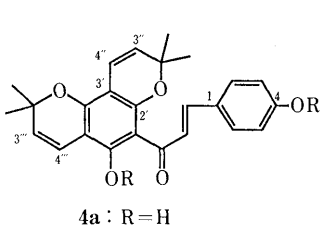
1



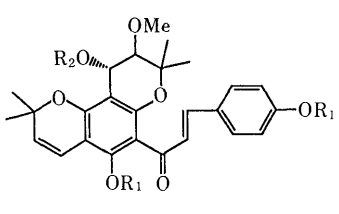
2



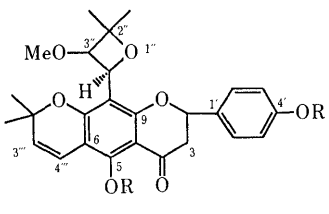
3



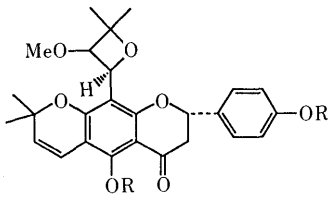
4a : R=H
4b : R=Ac



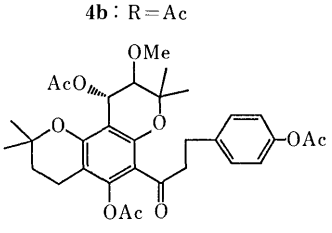
5a : R_1=R_2=H
5b : R_1=R_2=Ac
5c : R_1=Me, R_2=H



6a : R=H
6b : R=Ac



7a : R=H
7b : R=Ac



8

4b [mp 147—148 °C; ν_{max}^{KBr} 1760, 1670 cm^{-1}; δ $CDCl_3$ 2.22, 2.30 (each 3H, s)] on reaction with Ac_2O in pyridine at 60 °C overnight. Based on the above data, laxichalcone can be assigned the structure **4a**. The proposed structure was also supported by the MS fragmentation (Chart 1) and its carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum (Table II).

Derrichalcone (**5a**) crystallized from methanol as red needles, mp 173—175 °C. Elementary analysis and MS *m/z* (%) 452 (M^+, 14) gave its molecular formula as $C_{26}H_{28}O_7$. Its chalcone structure was shown by UV absorption bands at λ_{max}^{MeOH} 234, 247, 277, 286, 301, and 375 nm, and also by ^{1}H-NMR signals (Table I) of the α- and β-protons at δ 7.77 and 7.93, each as a doublet with J=15.5 Hz. A bathochromic shift of 63 nm of the longer wavelength band, along with an increase in intensity with NaOMe, showed the presence of a 4-OH group. The presence of a bathochromic shift with $AlCl_3$, which did not undergo any change with the addition of HCl, showed the presence of a chelated OH group. The absence of a bathochromic shift with NaOAc showed the 4′-OH group to be free. The IR spectrum shows characteristic absorptions at 1630 cm^{-1} due to chalcone carbonyl, and at 830 cm^{-1} due to a *para*-substituted benzene ring, which is also inferred from the signals of an A_2B_2 system of four aromatic protons [δ 7.56, 6.84 (each 2H, d, J=8.4 Hz)] (Table I). The ^{1}H-NMR spectrum of **5a** shows that it contains one 2,2-dimethylchromene [δ 1.42 (6H, s), 5.58, 6.55 (each 1H, d, J=9.8 Hz, 3‴- and 4‴-H)], two phenolic protons [δ 10.18, 14.69 (each 1H, s)], and one 2,2-dimethylchroman with one

TABLE I. ^{1}H-NMR Data for Laxichalcone (**4a**), Derrichalcone (**5a**) and Derriflavanone and *epi*-Derriflavanone (**6a**+**7a**) (300 MHz)

H	**4a**[a]	**5a**[a]	**6a** or **7a**[b]	**7a** or **6a**
2	7.54 d (8.5)	7.56 d (8.4)	5.33 dd (13.0, 3.0)	5.33 dd (13.0, 3.0)
3	6.87 d (8.5)	6.84 d (8.4)	2.79 dd (17.0, 3.0)	2.81 dd (17.0, 3.0)
			3.07 dd (17.0, 13.0)	3.13 dd (17.0, 13.0)
5	6.87 d (8.5)	6.84 d (8.4)		
6	7.54 d (8.5)	7.56 d (8.4)		
2′,6′			7.21 d (8.3)	7.21 d (8.3)
3′,5′			6.01 d (8.3)	6.01 d (8.3)
3″	5.64 d (10.0)	4.52 d (1.8)	3.68 d (7.4)	3.68 d (7.4)
4″	6.54 d (10.0)	4.99 d (1.8)	4.55 d (7.4)	4.55 d (7.4)
3‴	5.62 d (10.0)	5.58 d (9.8)	5.54 d (10.0)	5.54 d (10.0)
4‴	6.51 d (10.0)	6.55 d (9.8)	6.65 d (10.0)	6.65 d (10.0)
H_α	7.69 d (15.5)	7.77 d (15.5)		
H_β	7.85 d (15.5)	7.93 d (15.5)		
OCH_3		3.35 s	3.35 s	3.36 s
2″-CH_3	1.41 s	1.17 s, 1.24 s	1.16 s	1.22 s, 1.25 s
2‴-CH_3	1.50 s	1.42 s	1.45 s, 1.46 s	1.45 s, 1.46 s
OH	10.14 s, 14.43 s	4.87 s, 10.18 s, 14.69 s	6.39 s, 12.40 s	6.39 s, 12.40 s

Figures in parentheses are coupling constants. *a*) In dimethylsulfoxide-d_6. *b*) In $CDCl_3$.

TABLE II. ^{13}C-NMR Data (δ Values) for Laxichalcone (**4a**) and Derrichalcone (**5a**) (75 MHz in DMSO-d_6)

C	**4a**	**5a**	C′	**4a**	**5a**
1	125.9 s	125.8 s	2″	78.3 s[b]	69.6 s
2, 6	130.5 d	130.7 d	3″	125.7 d[c]	96.4 d
3, 5	116.2 d	116.1 d	4″	115.5 d[d]	77.8 d
4	154.2 s[a]	156.8 s	2‴	78.2 s[b]	78.5 s
			3‴	126.4 d[c]	125.5 d
			4‴	115.3 d[d]	115.5 d
1′	105.3 s	105.9 s	α	123.1 d	121.8 d
2′	160.2 s	161.8 s	β	143.5 d	144.2 d
3′	101.9 s	101.1 s	OCH_3		55.6 q
4′	160.3 s	163.7 s	2″-CH_3	27.6 q[e]	24.9 q
5′	102.0 s	101.8 s			25.9 q
6′	155.5 s[a]	160.4 s	2‴-CH_3	27.9 q[e]	28.0 q
			CO	192.2 s	28.1 q
					190.7 s

Assignments established by off-resonance and distortionless enchancement by polarization transfer methods. *a*—*e*) Assignments may be interchanged.

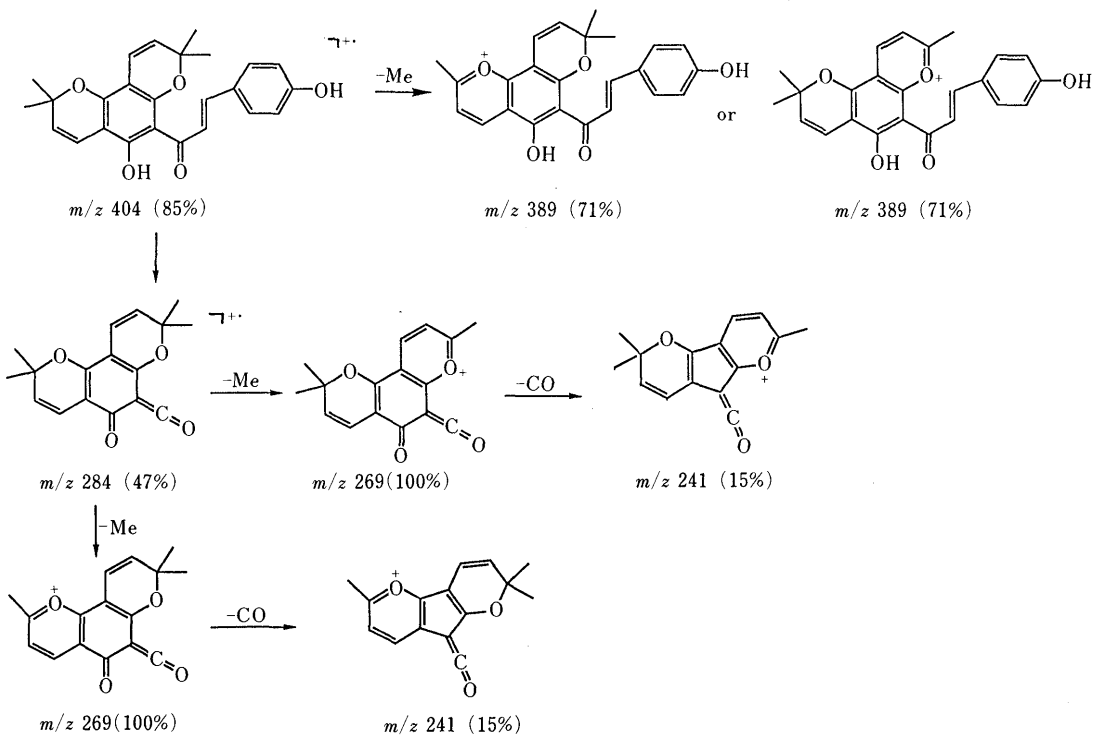


Chart 1

hydroxyl group and one methoxyl group [δ 1.17, 1.24, 3.35 (each 3H, s), 4.52, 4.99 (each 1H, d, $J=1.8$ Hz, 3″- and 4″-H)]. The compound formed a triacetate **5b** [mp 110—111 °C; ν_{max}^{KBr} 1760, 1730 cm^{-1}; δ $CDCl_3$ 1.86, 2.29, 2.32 (each 3H, s), 5.02 (1H, d, $J=3.0$ Hz, 4″-H), and 6.30 (1H, d, $J=10.0$ Hz, 4‴-H)]. The result reveals it to contain two phenolic hydroxyl and one aliphatic hydroxyl groups. The upfield (0.25 ppm) shift of 4‴-H in **5b**[2,4-6] compared with **5a**, as well as the presence of 2.6% nuclear Overhauser effect (NOE) between 4‴-H and 6′-OAc in **5b**, suggests that the chromene group is fused on 4′-C and 5′-C. The aliphatic acetoxy methyl protons in **5b**, seen at higher field (δ 1.86), indicated that the acetoxy group must be located at 4″-C with α-axial orientation, being shielded by the anisotropic effect of the aromatic ring. Proof that the methoxyl group has 3″-C β-axial orientation was provided by the lack of NOE's between the acetoxy and methoxy groups. The reaction of **5a** with methyl iodide and potassium carbonate in acetone under reflux afforded **5c** [amorphous; δ 3.47, 3.72, 3.82 (each 3H, s)], having three methoxyl groups. Hydrogenation of **5b** with Pd–C as a catalyst in methanol yielded a tetrahydrocompound **8** [δ $CDCl_3$ 1.83 (3H, s), and 1.79, 2.52, 2.93, 3.19 (each 2H, t, $J=7.5$ Hz)]. The 4″-C acetoxyl group in **5b** resisted hydrogenolysis due to the steric effect of the axial methoxy group. The proposed structure was also supported by the MS fragments (Chart 2) and ^{13}C-NMR spectra (Table II).

A material obtained as yellow needles [mixture of derriflavanone (**6a** or **7a**) and *epi*-derriflavanone (**7a** or **6a**)] from methanol, mp 103—106 °C, was formulated as $C_{26}H_{28}O_7$ on the basis of elementary analysis and MS *m/z* (%) 452 (M^+, 52), and gave a positive Mg–HCl test. Its flavanone structure was indicated by the UV spectrum (λ_{max}^{MeOH} 229, 237, 265, 271, 297, 308, 360 nm).[7] This yellow crystalline material showed one spot in thin layer chromatography (SiO_2) with several solvent systems. But in its ^{1}H-NMR spectrum (Table I), it exhibits clearly two sets of signals with partial overlapping. The characteristic signals for flavanone are the signals of an ABX system at δ 2.79 (1H, dd, $J=17.1$, 3.0 Hz), 3.07 (1H, dd, $J=17.0$, 13.0 Hz), and 5.33 (1H, dd, $J=13.0$, 3.0 Hz); the other set is at δ 2.81 (1H, dd, $J=17.0$, 3.0 Hz), 3.13 (1H, dd, $J=17.0$, 13.0 Hz), and 5.33 (1H, dd, $J=13.0$, 3.0 Hz). The ^{1}H-NMR ($CDCl_3$) spectrum of the yellow crystalline material shows the presence of 2,2-dimethylchromene, an A_2B_2 system of four aromatic protons, and phenolic protons (δ 12.48, 6.34). The presence of a chelated C-5 hydroxyl was evident, as one of the phenolic protons resonated at low field (δ 12.48). The remainding one prenyl group is distinct from the 2,2-dimethylchromene or γ,γ-dimethylallyl form attached to the A-ring. It was supposed to be a dimethyloxetane form with one methoxy attached to C-3″. The proposed structure was supported by the ^{1}H-NMR spectrum [δ 1.16 (6H, s), 3.35 (3H, s, —OMe), and 3.68, 4.55 (each 1H, d, $J=7.4$ Hz, H-3″ and H-4″); the other set is at δ 1.22, 1.25, 3.36 (each 3H, s), and 3.68, 4.55 (each 1H, d, $J=7.4$ Hz, H-3″ and H-4″)]. The yellow crystalline material formed a diacetate mixture of **6b** and **7b** (Ac_2O/pyridine, 60 °C overnight) [mp 145—147 °C; ν_{max}^{KBr} 1760, 1670 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.29, 2.40 (each 3H, s), and 6.38 (d, $J=10$ Hz, H-4‴)]. The evident downfield shift of phenyl protons in the diacetate compared with the mixture of **6a** and **7a** suggested that the hydroxyl group should be attached to C-4′. The upfield (0.27 ppm) shift of H-4‴ in the mixture

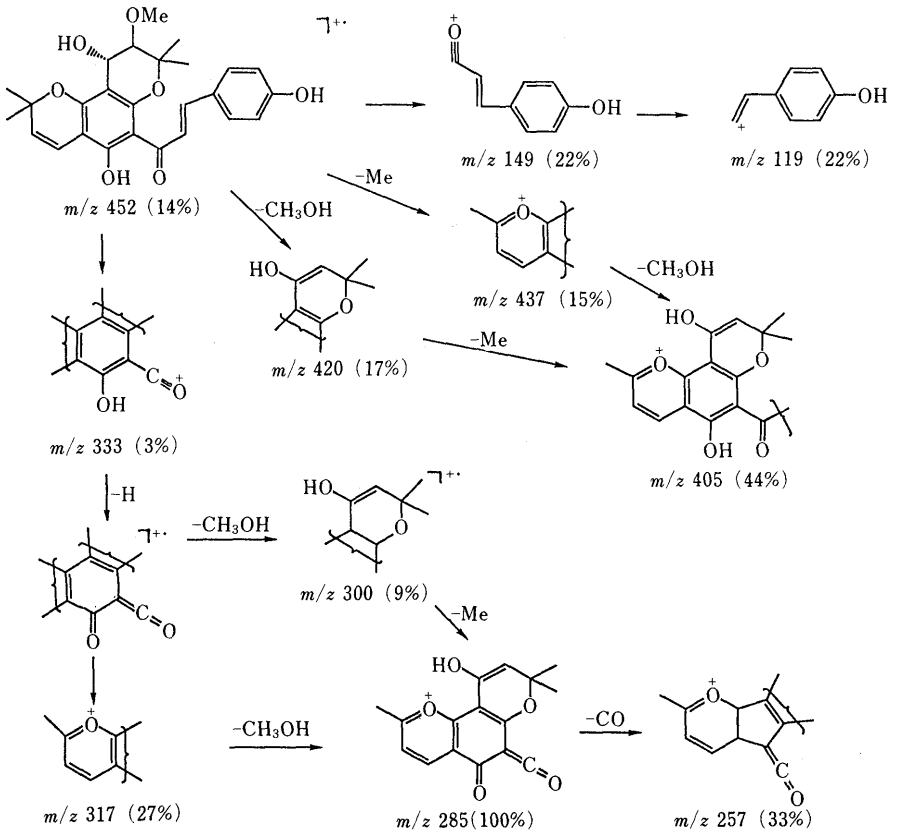


Chart 2

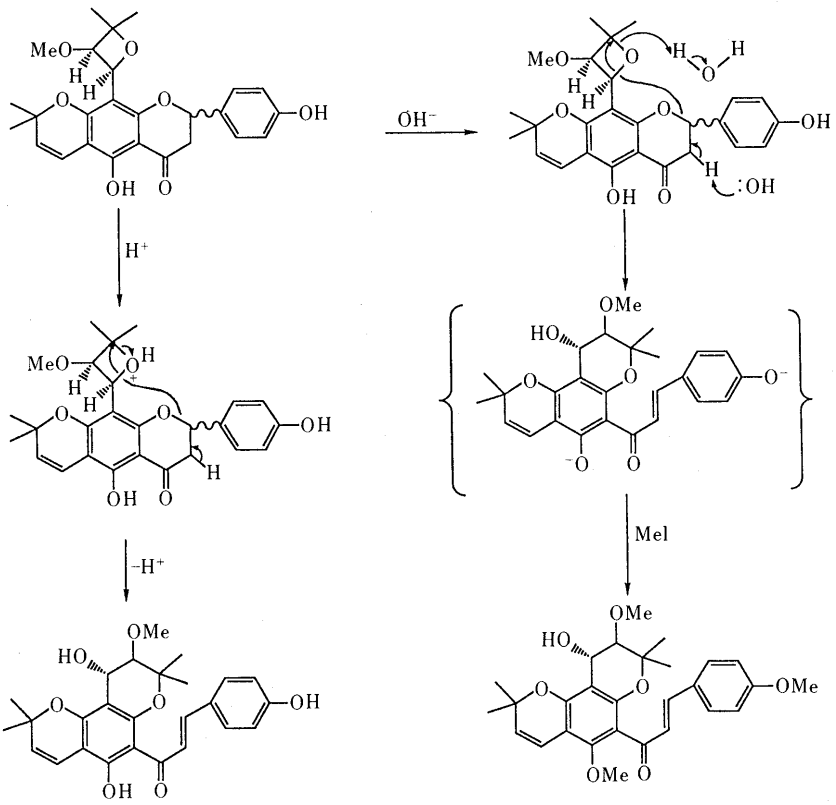


Chart 3

of **6b** and **7b**[2,4-6] compared with the mixture of **6a** and **7a** suggests that the chromene group is fused on C-6 and C-7. Therefore the oxetyl group must be located at C-8. The larger coupling constant ($J=7.4$ Hz) between H-4″ and H-3″ is in favor of the *cis* configuration assignment. The structure was further supported by the following chemical transformation, revealing the labile characteristic of the oxetane. When the mixture of **6a** and **7a** reacted with 6% HCl–MeOH solution at room temperature overnight, only derrichalcone (**5a**) was obtained. The mechanism of this reaction is proposed to be as shown in Chart 3. The protonation on the oxygen atom of oxetane first, followed by cleavage of the C–O bond of oxetane, and the formation of the chroman ring and chalcone may occur simultaneously. The reaction of the mixture of **6a** and **7a** with methyl iodide and potassium carbonate in acetone under reflux gave only a product which was identical with dimethyl derrichalcone (**5c**). The conversion is shown in Chart 3. From the above evidence, derrichalcone and *epi*-derrichalcone are C-2 epimeric isomers and can be assigned the structures **6a** and **7a** or *vice versa*.

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}H and ^{13}C-NMR spectra were run on a Brucker 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 (EIMS) and UV spectra were taken on JEOL JMS-100 and Hitachi U-3200 spectrometers, 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 subjected to partition with ethyl acetate and H_2O (each 1 l). The upper layer was purified by silica gel chromatography with a gradient (hexane–$CHCl_3$) system to afford flemichapparin-B (87 mg), 3′-methoxylupinifolin (**1**) (156 mg), β-amyrin (283 mg), lupeol (165 mg), laxichalcone (**4a**) (58 mg), and lupinifolin (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 (143 mg) and a yellow crystalline mixture, which was also separated by Sephadex LH-20 column chromatography (MeOH) and then silica gel medium pressure liquid chromatography (MPLC) (hexane–ethyl acetate, 3 : 1) to give laxifolin (**2**) (120 mg) and isolaxifolin (**3**) (128 mg). The fraction eluted after compounds **2** and **3** was a mixture of orange crystals, which was also subjected to Sephadex LH-20 column chromatography (MeOH) to give derrichalcone (**5a**) (32 mg) and a mixture of derriflavanone (**6a** or **7a**) and *epi*-derriflavanone (**7a** or **6a**) (180 mg) in 1 : 1 ratio. We could not purify the latter mixture with an open column, even with MPLC or high performance liquid chromatography (HPLC). The physical data for flemichapparin-B, 3′-methoxylupinifolin (**1**), β-amyrin, lupeol, prunetin, lupinifolin, laxifolin (**2**), and isolaxifolin (**3**) were described in a previous paper.[2] Those for other compounds are as follows:

Laxichalcone (**4a**): mp 174—176 °C. UV λ_{max}^{MeOH} nm (log ε): 251 (4.25), 265 (4.25), 272 (4.27), 377 (4.35); +NaOMe 252 (4.14), 279 (4.28), 390 (4.25), 442 (4.52); +$AlCl_3$ 266 (4.21), 282 (4.21), 3.08 (4.05), 364 (4.10), 412 (4.38). IR ν_{max}^{KBr} cm^{-1}: 3200, 1650, 1630, 1600, 1580, 1520, 1510. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. *Anal.* Calcd for $C_{25}H_{24}O_5$: C, 74.18; H, 5.97. Found: C, 74.24; H, 5.98.

Derrichalcone (**5a**): mp 173—175 °C. UV λ_{max}^{MeOH} nm (log ε): 234 (4.36), 247 (4.34), 277 (4.23), 286 (4.23), 301 (4.15), 375 (4.66); +NaOMe 239 (4.53), 276 (4.53), 288 (4.50), 300 (4.36), 321 (4.26),438 (4.83); +$AlCl_3$ 253 (4.74), 286 (4.26), 368 (4.57), 410 (4.67). IR ν_{max}^{KBr} cm^{-1}: 3400, 1630, 1600, 1540, 1510, 1350, 1150. ^{1}H-NMR: Table I. ^{13}C-NMR: Table II. *Anal.* Calcd for $C_{26}H_{28}O_7$: C, 69.01; H, 6.24. Found: C, 69.08; H, 6.22.

Mixture of Derriflavanone and *epi*-Derriflavanone (**6a**+**7a**): mp 103—105 °C. UV λ_{max}^{MeOH} nm (log ε): 229 (4.29), 237 (4.22), 265 (4.61), 271 (4.66), 297 (4.08), 308 (4.01), 360 (3.45). IR ν_{max}^{KBr} cm^{-1}: 3350, 1660, 1620, 1570, 1515, 1380, 1160, 1120, 890. MS m/z (%): 452 (M^+, 52), 437 (26), 421 (6), 381 (100), 362 (45), 347 (75), 251 (60), 243 (17), 227 (60). ^{1}H-NMR: Table I. *Anal.* Calcd for $C_{26}H_{28}O_7$: Found: C, 69.09; H, 6.20.

Acetylation of Laxichalcone (4a) with Acetic Anhydride and Pyridine Laxichalcone (**4a**) (5 mg) was allowed to react with Ac_2O (0.5 ml) in

pyridine (0.5 ml) at 60 °C overnight. Usual work-up gave the diacetate **4b** (5 mg). IR ν_{max}^{KBr} cm^{-1}: 1760, 1670, 1640, 1590, 1500, 1200. ^{1}H-NMR ($CDCl_3$) δ: 1.38, 1.44 (each 6H, s), 2.22, 2.30 (each 3H, s), 5.54, 6.62 (each 1H, d, J=10.0 Hz, H-3″, H-4″), 5.56, 6.22 (each 1H, d, J=9.8 Hz, H-3‴, H-4‴), 7.02, 7.45 (each, 1H, d, J=16.0 Hz, H_α, H_β), 7.09, 7.53 (each 2H, d, J=8.9 Hz, H-3, -5 and H-2, -6).

Acetylation of Derrichalcone (5a) Acetylation of **5a** (5 mg) in the same way as mentioned above yielded **5b** (5 mg). IR ν_{max}^{KBr} cm^{-1}: 1760, 1730, 1650, 1610, 1590, 1500, 1420, 1360, 1180, 1140. ^{1}H-NMR ($CDCl_3$) δ: 1.46, 1.46, 1.48, 1.53 (each 3H, s), 1.86, 2.29, 2.32, 3.47 (3H, s), 4.80, 5.02 (each 1H, d, J=3 Hz, H-3″, H-4″), 5.58, 6.30 (each 1H, d, J=10.0 Hz, H-3‴, H-4‴), 7.08, 7.54 (each 2H, d, J=8.4 Hz, H-3, -5 and H-2, -6), 7.32, 7.58 (each 1H, d, J=15.9 Hz, H_α, H_β).

Methylation of 5a A mixture of derrichalcone (**5a**) (6 mg), methyl iodide (1 ml), acetone (5 ml), potassium carbonate (1 g), and a few drops of dimethyl sulfoxide 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 an amorphous compound, a trimethylflavanone (**5c**) (4 mg). IR ν_{max}^{KBr} cm^{-1}: 3440, 1625, 1590, 1505, 1250, 1160, 1130, 1095. ^{1}H-NMR ($CDCl_3$) δ: 1.20, 1.26, 1.44, 1.47, 3.47, 3.73, 3.82 (each 3H, s) 4.40, 5.01 (each 1H, d, J=1.4 Hz, H-3″, H-4″), 5.52, 6.54 (each 1H, d, J=10.0 Hz, H-3‴, H-4‴), 6.88, 7.50 (each 2H, d, J=8.5 Hz, H-3, -5 and H-2, -6), 7.09, 7.53 (each 1H, d, J=15.9 Hz, H_α, H_β).

Catalytic Hydrogenation of 5b Compound **5b** (5 mg) was dissolved in 5 ml of MeOH, then 10 mg of 5% Pd–C suspended in 5 ml of MeOH was added and the mixture was saturated with H_2. After 1 h, the catalyst was removed by filtration and washed several times with MeOH. After purification, the combined filtrate yielded **8** [an amorphous solid; ν_{max}^{KBr} cm^{-1}: 1760, 1730, 1660, 1610, 1500, 1460, 1360, 1190. ^{1}H-NMR ($CDCl_3$) δ: 1.32, 1.35, 1.43, 1.48, 1.83, 2.26, 2.30, 3.44 (each 3H, s), 1.79, 2.52, 2.93, 3.19 (each 2H, t, J=7.5 Hz), 4.75, 4.95 (each 1H, d, J=3.0 Hz), 6.95, 7.18 (each 2H, d, J=8.4 Hz).

Acetylation of the Mixture of 6a and 7a Acetylation of the mixture of **6a** and **7a** (5 mg) in the same way as mentioned above yielded **6b** and **7b** (5 mg) [ν_{max}^{KBr} cm^{-1}: 1760, 1670, 1600, 1190, 1160, 1110, 1000, 890, 840, 810, 750. ^{1}H-NMR ($CDCl_3$) δ: 1.14, 1.17, 1.43, 1.43, 2.29, 2.40, 3.32 (each 3H, s), 2.74 (1H, dd, J=13.0, 3.0 Hz), 2.93 (1H, dd, J=17.0, 13.0 Hz), 3.61, 4.57 (each 1H, d, J=7.0 Hz), 5.43 (1H, dd, J=13.0, 3.0 Hz), 5.65, 6.38 (each 1H, d, J=10.0 Hz), 7.12, 7.42 (each 2H, d, J=8.5 Hz). One of epimer: δ 1.10, 1.22, 1.43, 1.43, 2.29, 2.40, 3.34 (each 3H, s), 2.77 (1H, dd, J=17.0, 3.0 Hz), 2.96 (1H, dd, J=17.0, 13.0 Hz), 3.59, 4.56 (each 1H, d, J=7.0 Hz), 5.40 (1H, d, J=13.0, 3.0 Hz), 5.65, 6.38 (each 1H, d, J=10.0 Hz), 7.12, 7.40 (each 2H, d, J=8.5 Hz).

Rearrangement of the Mixture of 6a and 7a to Derrichalcone (5a) by Acid The mixture of **6a** and **7a** (5 mg) was dissolved in 6% HCl methanol solution at room temperature overnight. The reaction mixture was treated by a usual method to give only derrichalcone (**5a**) (3 mg) after silica gel chromatography.

Conversion of the Mixture of 6a and 7a to Dimethylderrichalcone (5c) Methylation of the mixture of **6a** and **7a** (10 mg) in the same way as mentioned above yielded only a product (7 mg) identical with dimethylderrichalcone (**5c**) (5 mg).

Acknowledgement This research was supported by the National Science Council of the R.O.C.

References

1) *a*) M. C. Do Nascimento and W. B. Mors, *Phytochemistry*, **20**, 147 (1981); *b*) Y. Obara, H. Matsubara and K. Munakata, *Agr. Biol. Chem.*, **40**, 1245 (1976); *c*) T. Komada, T. Yamakawa and Y. Minoda, *ibid.*, **44**, 2387 (1980); *d*) S. S. Chibber and R. P. Sharma, *Phytochemistry*, **18**, 1082 (1979); *idem*, *ibid.*, **19**, 1857 (1980); *e*) M. Garcia, M. H. C. Kano, D. M. Vieir, M. C. De Nasciments and W. B. Mors, *ibid.*, **25**, 2425 (1986).
2) Y. L. Lin, Y. L. Chen and Y. H. Kuo, *Chem. Pharm. Bull.*, **39**, 3132 (1991).
3) Y. L. Lin, Y. L. Chen and Y. H. Kuo, *Chem. Express*, **6**, 747 (1991).
4) T. M. Smalberger, R. Vleggaar and J. C. Webber, *Tetrahedron*, **30**, 3927 (1974).
5) M. Shabbir, A. Zaman, L. Crombie, B. Tuck and D. A. Whiting, *J. Chem. Soc.* (*C*), **1968**, 1899.
6) A. K. Singhal, R. P. Sharma, G. Thyagrajan, W. Herz and S. V. Govinelan, *Phytochemistry*, **19**, 929 (1980).
7) T. J. Mabry, K. R. Markham and M. B. Thomas, "The Systematic Identification of Flavonoids," Springer-Verlag, Berlin, 1970, Chapter V, VIII.