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Flavonoids Syntheses. VI.¹⁾ Synthesis and Spectral Properties of 4-Arylcoumarins (Neoflavones)

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Eight neoflavones were synthesized for examination of their spectral properties. In the mass spectra, 2'-oxygenated neoflavones showed characteristic fragments owing to dehydroxylation or demethoxylation. Other spectral data ultraviolet, proton and carbon-13 nuclear magnetic resonance, however, showed no specific features that could be used to characterize the structures.

Keywords—neoflavone synthesis; 4-arylcoumarin; 2'-oxygenated neoflavone; mass spectrum

4-Arylcoumarins can be regarded as derivatives of flavonoids (C₆–C₃–C₆) on the basis of their biosynthetic pathway²⁾ and their positive color reaction in the Shinoda test (Mg + HCl)³⁾; they are sometimes called neoflavones. These compounds are found in nature in Leguminosae (*Dalbergia*⁴⁾ and *Macherium* spp.⁵⁾ and in Rubiaceae (*Exostemma*⁶⁾ and *Coutarea* spp.⁷⁾). To date, the spectroscopic properties of neoflavones have not been investigated in detail. In this paper, we present some spectral data on neoflavones with simple substitution patterns (1–8) (Chart 1) in order to clarify the differences from those of the relevant flavones.

- 1: R₁ = R₂ = R₃ = R₄ = H
- 2: R₁ = OH, R₂ = R₃ = R₄ = H
- 3: R₂ = OH, R₁ = R₃ = R₄ = H
- 4: R₃ = OH, R₁ = R₂ = R₄ = H
- 5: R₁ = R₄ = OH, R₂ = R₃ = H
- 6: R₁ = OMe, R₂ = R₃ = R₄ = H

- 7: R₅ = H
- 8: R₅ = OH

Chart 1

Synthesis of Eight Neoflavones

The benzoylactic acid ethyl esters required for preparation of the above neoflavones, *i.e.*, the unsubstituted compound (9), 2-isopropoxy- (10), 3-hydroxy- (11), 4-hydroxy- (12), 2,5-diisopropoxy- (13), 2-methoxy- (14), and 3-isopropoxybenzoylactic acid ethyl ester (15), were synthesized from the corresponding acetophenones by condensation with ethyl carbonate in the presence of sodium hydride. The resultant esters were condensed with

TABLE I. Mass Spectral Data for 1—8

	<i>m/z</i> (rel. int.)
1	254 [M ⁺] (100), 226 (99), 225 (12.5), 197 (4.3)
2	270 [M ⁺] (47.6), 253 (14.2), 252 (100), 225 (14.9)
3	270 [M ⁺] (100), 242 (70.4), 213 (31.7)
4	270 [M ⁺] (100), 242 (82), 213 (31.7)
5	286 [M ⁺] (7.8), 269 (47.4), 268 (100), 240 (52.9), 212 (57.9), 184 (18.4), 155 (13.2)
6	284 [M ⁺] (100), 256 (17), 253 (58.5), 242 (34.1), 235 (9.7)
7	238 [M ⁺] (94.7), 210 (100), 181 (34.2), 165 (7.8), 152 (23.7)
8	254 [M ⁺] (79.1), 226 (100), 198 (23.2), 181 (11.6)

TABLE II. ¹³C-NMR Spectral Data for Synthetic Neoflavones (1—5, 7 and 8)

Carbon number	1	2	3	4	5	7	8
2	159.2	160.5	160.1	160.2	160.3	160.1	160.2
3	110.2	110.1	109.9	114.2	109.9	110.3	110.3
4	156.8	154.4	156.9	156.9	157.5	155.5	157.5
5	157.1	156.6	157.2	157.2	156.5	128.0	129.9
6	100.7	99.0	99.3	99.3	98.9	113.2	113.2
7	161.8	161.4	161.8	161.8	161.2	161.5	161.4
8	94.7	94.4	94.8	94.8	94.2	102.6	102.7
9	156.8	157.6	156.9	156.9	157.5	155.4	155.5
10	99.2	102.6	100.8	100.8	101.9	110.6	110.7
1'	139.7	127.9	140.9	130.1	127.9	135.2	136.5
2'	127.3	154.2	114.5 ^{a)}	129.2	154.5	128.3 ^{a)}	115.1
3'	127.4	114.2	156.5	114.2	115.1 ^{a)}	128.9 ^{b)}	155.5
4'	127.8	128.9	114.9 ^{a)}	157.6	115.3 ^{a)}	129.5	116.5
5'	127.4	118.4	128.6	114.2	154.2	128.9 ^{b)}	128.2
6'	127.3	128.3	118.2	129.2	114.7	128.3 ^{a)}	118.9

All spectra were measured in DMSO-*d*₆. Assignments bearing the same superscript in any column may be reversed.

phloroglucinol or resorcinol by means of the Pechmann reaction under dry hydrogen chloride to give 5,7-dihydroxy- (1), 5,7-dihydroxy-2'-isopropoxy- (16), 3',5,7-trihydroxy- (3), 4',5,7-trihydroxy- (4), 5,7-dihydroxy-2',5'-diisopropoxy- (17), 5,7-dihydroxy-2'-methoxy- (6), 7-hydroxy-3'-isopropoxy- (18) and 7-hydroxyneoflavone (7), respectively. Further, 16, 17 and 18 were deisopropylated with boron trichloride to give 2',5,7-trihydroxy- (2), 2',5,5',7-tetrahydroxy- (5) and 3',7-dihydroxyneoflavone (8). Among these compounds, 1 and 4 have been described by other investigators.^{7a,8)} Tables I and II show the mass spectral (MS) data and carbon-13 nuclear magnetic resonance (¹³C-NMR) spectral data of the neoflavones thus obtained.

Spectral Properties of the Neoflavones

Ultraviolet (UV) and proton nuclear magnetic resonance (¹H-NMR) spectral data of the neoflavones are given in Experimental. In addition to the bathochromic shifts in the UV after addition of some reagents, two absorption bands, called bands I and II, due to cinnamoyl and benzoyl moieties of the flavone skeleton, are widely utilized to determine the positions of hydroxy groups.⁹⁾ These bands, however, were not observed in the case of the neoflavones. In neoflavones there seems to be no mesomeris effect between the A and B rings. No bathochromic shifts were observed on addition of AcONa and AlCl₃, or MeONa. The latter

Chart 2

results in degradation of the coumarin ring.

In the ^1H -NMR spectra of flavones, the protons at C-2' and C-6' are observed at rather low field, but in the neoflavones all protons of the B ring moiety appear at similar positions, which causes some difficulty in distinguishing the substitution patterns (for example, dioxygenation at C-3',4' or at C-2',5').¹⁰⁾

In the MS of neoflavones, two noteworthy results were obtained. As shown in Chart 2, the neoflavones lacking an O-function at C-2' such as **1**, **3**, **4**, **7** and **8**, showed stable fragments of $[\text{M}^+ - 28]$ caused by decarboxylation. On the other hand, in the case of 2'-oxygenated neoflavones such as **2**, **5** and **6**, dehydroxylation or demethoxylation between C₅-OH and substituents on C-2' occurred to give $[\text{M}^+ - 17]$ or $[\text{M}^+ - 59]$. These characteristic fragmentations have led us to propose a revised structure for 2,5,5'-trihydroxy-7-methoxyneoflavone isolated from *Coutarea hexandra*.¹¹⁾

In the ^{13}C -NMR spectra, all carbons were assigned on the basis of substituent-induced shifts due to hydroxy groups. The chemical shifts of the A and B ring moieties could be independently considered as follows: the chemical shifts of the coumarin moiety of **7**^{12a)} correspond to those of 7-hydroxycoumarin^{12b)} except that of C-4, which is shifted down-field (ca. 11 ppm) by the presence of the B ring. On the other hand, the chemical shifts of the B ring moiety can be assigned by comparison with those of simple benzene derivatives. In the case of flavones, hydroxy or methoxy groups attached at C-2' affect the chemical shift of the C-3 carbon (ca. +3 ppm).¹³⁾ In spite of the similar circumstances, a hydroxy group at C-2' in neoflavone had little influence on the chemical shifts of C-3 and C-5 (C-3, 0 ppm; C-5, -0.6 ppm).

Experimental

Melting points were determined on a Büchi melting point apparatus and are uncorrected. UV spectra were taken on a Hitachi 323 spectrometer. MS were obtained on a JEOL JMS-300 mass spectrometer at 70 eV. ^1H -NMR spectra were taken on a Hitachi R-20B at 60 MHz and chemical shifts are given in δ value (ppm) with tetramethylsilane as an internal standard. ^{13}C -NMR spectra were obtained on a JEOL FX 90 spectrometer operating at 27.5 MHz, spectral width 5000 Hz and 4096 data points. BW-820 MH (Fuji Devision Chemicals, Ltd.) was used for column chromatography.

General Procedures for Synthesis of Benzoylactic Acid Ethyl Esters—A solution of an acetophenone (0.02 mol) dissolved in dry ether (20 ml) was added dropwise to an ethereal solution containing diethyl carbonate (0.01 mol) and sodium hydride (0.05 mol 60% dispersion in mineral oil). The solution was stirred at room temperature, and then refluxed for 7 h. The reaction mixture was poured into water, acidified with hydrochloric acid (2N), and extracted with AcOEt. The AcOEt extract was purified by column chromatography on silica gel with CHCl_3 to give a benzoylactic acid ethyl ester.

General Procedures for Pechmann Condensation—An ethanol solution (30 ml) containing phloroglucinol (or resorcinol) (0.02 mol) and a benzoylactic acid ester (0.02 mol) obtained by the procedure mentioned above was saturated with HCl gas under cooling in an ice bath. The reaction mixture was left at room temperature for 3 d, then poured into water and extracted with AcOEt. The AcOEt extract was purified by recrystallization or by column chromatography on silica gel with $\text{EtOAc}-\text{C}_6\text{H}_{14}$ to yield a neoflavone.

5,7-Dihydroxyneoflavone (1)—A colorless powder, mp 229–230 °C (AcOEt) (lit.^{7a)} mp 234–235 °C), yield 2.5 g (53%). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_4$: C, 70.86; H, 3.96. Found: C, 70.81; H, 4.20. ^1H -NMR ($\text{DMSO}-d_6$) δ : 5.78

(1H, s, H-3), 6.21, 6.33 (1H, each d, $J=2.3$ Hz, H-6 and 8), 7.40 (5H, s, C_6H_5), 10.03, 10.30 (1H, each s, OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 262 (4.1), 334 (4.1). $\lambda^+ \text{NaOMe}$: 285 sh, 382, (dec.). $\lambda^+ \text{AlCl}_3$: 261, 335. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 261, 335. $\lambda^+ \text{AcONa}$: 270, 384. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 261, 335.

2',5,7-Trihydroxyneoflavone (2)—2-Isopropoxyacetophenone: a yellow oil. $^1\text{H-NMR}$ (CCl_4) δ : 1.24 (6H, d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 2.38 (3H, s, Ac), 4.86 (1H, hep, $>\text{CH}$). 2-Isopropoxybenzoylactic acid ethyl ester (**10**): a pale brown oil, yield 3.9 g (77%). $^1\text{H-NMR}$ (CCl_4) δ : 1.20 (3H, t, $J=6$ Hz, CH_2CH_3), 1.39 (6H, d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 3.78 (2H, s, COCH_2CO), 4.02 (2H, q, $J=6$ Hz, CH_2CH_3), 4.60 (1H, hep, $J=6$ Hz, $>\text{CH}$). 5,7-Dihydroxy-2'-isopropoxyneoflavone (**16**): a pale yellow powder, mp 189 °C (dec.) ($\text{AcOEt}-C_6H_{14}$), yield 4 g (67%). $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 1.18 (6H, d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 5.73 (1H, s, H-3), 6.20, 6.30 (1H, each d, $J=3.0$ Hz, H-6 and 8), 6.83—7.60 (4H, m, B ring protons), 9.73, 10.05 (1H, s, OH). **16** was treated with BCl_3 to obtain **2** as a pale yellow powder, mp 249—250 °C ($\text{AcOEt}-C_6H_{14}$). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_5$: C, 66.67; H, 3.73. Found: C, 66.42; H, 4.01. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 5.63 (1H, s, H-3), 6.13, 6.25 (1H, each d, $J=3$ Hz, H-6 and 8), 6.63—7.28 (4H, m, B ring protons), 9.30 (1H, s, OH), 10.35 (2H, brs, 2 $\times$ OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 261 (3.9), 330 (4.0). $\lambda^+ \text{NaOMe}$: 268, 384, (dec.). $\lambda^+ \text{AlCl}_3$: 260 sh, 331. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 260 sh, 331. $\lambda^+ \text{AcONa}$: 268, 379. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 262 sh, 328.

3',5,7-Trihydroxyneoflavone (3)—A pale yellow powder, mp 260 °C ($\text{AcOEt}-C_6H_{14}$), yield 3.7 g (68%). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_5$: C, 66.67; H, 3.73. Found: C, 66.32; H, 3.89. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 5.68 (1H, s, H-3), 6.15, 6.25 (1H, each d, $J=3$ Hz, H-6 and 8), 6.68—7.43 (4H, m, B ring protons), 9.95 (1H, s, OH), 10.32 (2H, s, 2 $\times$ OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 259 (4.1), 334 (4.1). $\lambda^+ \text{NaOMe}$: 268 sh, 380, (dec.). $\lambda^+ \text{AlCl}_3$: 259, 335. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 258, 334. $\lambda^+ \text{AcONa}$: 271 sh, 379. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 259, 335.

4',5,7-Trihydroxyneoflavone (4)—Colorless rectangles, mp 260 °C (AcOEt) (lit.^{6a}) mp 294—295 °C (dec.), yield 2.8 g (52%). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_5$: C, 66.67; H, 3.73. Found: C, 66.91; H, 4.02. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 5.68 (1H, s, H-3), 6.15, 6.25 (1H, each d, $J=3$ Hz, H-6 and 8), 6.73 (2H, d, $J=8$ Hz, H-3' and 5'), 7.15 (2H, d, $J=8$ Hz, H-2' and 6'), 9.48, 9.93, 10.15 (1H, each s, OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 263 (4.0), 335 (4.3). $\lambda^+ \text{NaOMe}$: 275, 373, (dec.). $\lambda^+ \text{AlCl}_3$: 262, 333. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 261, 333. $\lambda^+ \text{AcONa}$: 275, 315, 380. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 262, 333.

2',5,5',7-Tetrahydroxyneoflavone (5)—2,5-Diisopropoxybenzoylactic acid ethyl ester (**13**): a pale yellow oil, yield 4 g (65%). $^1\text{H-NMR}$ (CCl_4) δ : 1.23 (3H, t, $J=6$ Hz, CH_2CH_3), 1.30, 1.35 (6H, each d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 3.86 (2H, s, COCH_2CO), 4.12 (2H, q, $J=6$ Hz, CH_2CH_3), 4.40—4.52 (2H, m, 2 $\times$ CH). 5,7-Dihydroxy-2',5'-diisopropoxyneoflavone (**17**): a pale yellow oil, yield 4.1 g (56%). $^1\text{H-NMR}$ (CDCl_3) δ : 1.10, 1.28 (6H, each d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 4.50—4.55 (2H, m, 2 $\times$ CH), 5.80 (1H, s, H-3), 6.13, 6.35 (1H, each d, $J=3$ Hz, H-6 and 8), 6.75 (3H, brs, H-3', 4' and 6'). **17** was treated with BCl_3 to give **5** as yellow rectangles, mp 280—285 °C (AcOEt). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_6$: C, 62.94; H, 3.52. Found: C, 63.06; H, 3.81. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 5.70 (1H, s, H-3), 6.13, 6.41 (1H, each d, $J=3$ Hz, H-6 and 8), 6.50—6.66 (3H, m, H-3', 4' and 6'). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 261 (4.1), 333 (3.9). $\lambda^+ \text{NaOMe}$: 270 sh, 387, (dec.). $\lambda^+ \text{AlCl}_3$: 261, 333. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 261, 333. $\lambda^+ \text{AcONa}$: 271, 383. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 261, 335.

5,7-Dihydroxy-2'-methoxyneoflavone (6)—2-Methoxybenzoylactic acid ethyl ester (**14**): a colorless oil, yield, 2.2 g (49%). $^1\text{H-NMR}$ (CCl_4) δ : 1.13 (3H, t, $J=6$ Hz, CH_2CH_3), 3.78 (3H, s, OMe), 3.88 (2H, s, COCH_2), 4.04 (2H, q, $J=6$ Hz, CH_2CH_3), 6.78—7.55 (4H, m, B ring protons). **6**: mp 178—180 °C (dec.) (AcOEt), a pale yellow powder, yield 3.2 g (56%). *Anal.* Calcd for $\text{C}_{16}\text{H}_{12}\text{O}_5$: C, 67.60; H, 4.26. Found: C, 67.68; H, 4.11. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 3.63 (3H, s, OCH₃), 5.63 (1H, s, H-3), 6.05, 6.20 (1H, each d, $J=2.5$ Hz, H-6 and 8), 6.83—7.45 (4H, m, B ring protons), 9.73, 10.08 (1H, each s, OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 261 (4.1), 330 (4.0). $\lambda^+ \text{NaOMe}$: 275, 381, (dec.). $\lambda^+ \text{AlCl}_3$: 261, 331. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 261, 330. $\lambda^+ \text{AcONa}$: 254, 378. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 261, 331.

7-Hydroxyneoflavone (7)—Colorless needles, mp 230—235 °C (EtOH), yield 2.5 g (52%). *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_3$: C, 75.62; H, 4.23. Found: C, 75.52; H, 4.39. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 6.05 (1H, s, H-3), 6.80—7.38 (3H, m, H-5, 6 and 8), 7.55 (5H, brs, C_6H_5), 10.20 (1H, s, OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 238 (4.1), 330 (4.2). $\lambda^+ \text{NaOMe}$: 254, 379, (dec.). $\lambda^+ \text{AlCl}_3$: 257, 330. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 258, 330. $\lambda^+ \text{AcONa}$: 254, 378. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 257, 331.

3',7-Dihydroxyneoflavone (8)—3-Isopropoxybenzoylactic acid ethyl ester (**15**): a pale brown oil, yield 4.1 g (82%). $^1\text{H-NMR}$ (CCl_4) δ : 1.20 (3H, t, $J=6$ Hz, CH_2CH_3), 1.30 (6H, d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 3.85 (2H, s, COCH_2CO), 4.15 (2H, q, $J=6$ Hz, CH_2CH_3), 4.60 (1H, hep, $J=6$ Hz, $>\text{CH}$). 7-Hydroxy-3'-isopropoxyneoflavone (**20**): a colorless powder, mp 120 °C (EtOH), yield 3.7 g (63%). $^1\text{H-NMR}$ (CCl_4) δ : 1.71 (6H, d, $J=6$ Hz, $(\text{CH}_3)_2\text{CH}$), 4.45 (1H, hept., $(\text{CH}_3)_2\text{CH}$), 6.25 (1H, s, H-3), 6.83—7.15 (7H, m, aromatic protons). **8**: mp 260 °C (EtOH), a colorless powder. *Anal.* Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_4$: C, 70.86; H, 3.96. Found: C, 70.80; H, 4.01. $^1\text{H-NMR}$ ($\text{DMSO}-d_6$) δ : 6.10 (1H, s, H-3), 6.62—7.45 (7H, m, aromatic protons), 9.70, 10.50 (1H, each s, OH). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 238 (4.3), 330, (4.2). $\lambda^+ \text{NaOMe}$: 244, 376, (dec.). $\lambda^+ \text{AlCl}_3$: 238, 328. $\lambda^+ \text{AlCl}_3/\text{HCl}$: 238, 328. $\lambda^+ \text{AcONa}$: 242, 378. $\lambda^+ \text{AcONa}/\text{H}_3\text{BO}_3$: 273 sh, 330.

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