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# ISOFLAVONOIDS FROM *DERRIS SPRUCEANA*

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**Key Word Index**—*Derris spruceana*; Leguminosae; 3-aryl-4-hydroxycoumarins; isoflavone; stilbene.

**Abstract**—Sitosterol, three 3-aryl-4-hydroxycoumarins, one isoflavone and one stilbene were isolated from the roots of *Derris spruceana*. Structures were established through chemical and spectral means.

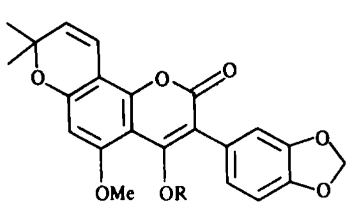
## INTRODUCTION

The genus *Derris* Lour. belongs to the tribe Tephrosieae (*sensu* Polhill and Geesink [1]) or Milletieae (*sensu* Geesink 1984 [2]), of the Leguminosae, subfamily Papilionoidae. Species of this tribe are noted for the profuse production of flavonoids (including isoflavonoids) prenylated in ring A of the skeleton. The species studied in this investigation conforms to the same pattern, having yielded, besides sitosterol, three 3-aryl-4-hydroxycoumarins, one isoflavone and one stilbene.†

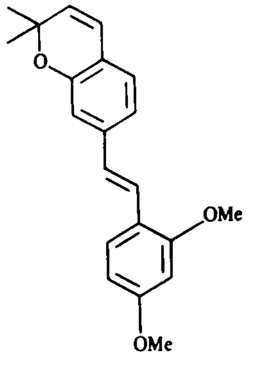
## RESULTS AND DISCUSSION

The material investigated were the whole roots or the root bark of *Derris spruceana* (Benth.) Ducke (= *Lonchocarpus spruceanus* Benth.), a medium sized tree of the lower Amazon, locally known as 'facheiro'. Petroleum ether, ether and acetone extracts were worked up chromatographically on silica gel columns, monitoring the development with the aid of thin-layer chromatography, also on silica gel. Final purification of the isolated compounds was accomplished either on small columns or by preparative TLC. They were numbered **1** to **6**, in accordance with the order of their elution from the columns.

UV spectra were decisive for determining the basic



**1** R = H
**5** R = Me



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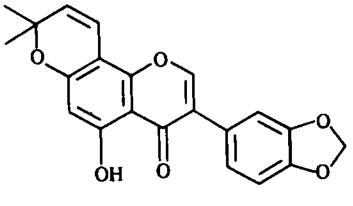
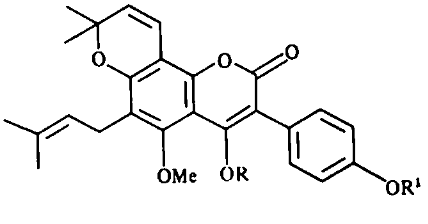


**3**



**6** $R = R^1 = H$
**7** $R = H$; $R^1 = Ac$
**8** $R = R^1 = Ac$

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†For previous work in this field see [3] and references therein.

Table 1. $^1$H NMR data of 3-aryl-4-hydroxycoumarins from *Derris spruceana**

| | Assignment for protons or substituents | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_4$ | | $C_5$ | $C_6$ | 3'-4' | $C_{4'}$ | | | | | | | |
| Compound | OH | OMe | OAc | OMe | H | $CH_2O_2$ | OH | OAc | $-CH_A=CH_B-C(CH_3)_2-O-$ | | | $-CH_{2A}-CH_B=C(CH_3)_2$ | | |
| 1 | 9.71 | | | 4.02 | 6.35 | 5.99 | | | 6.88 | 5.63 | 1.48 | | | |
| 5 | | 3.54 | | 3.92 | 6.3 | 6.02 | | | 6.87 | 5.61 | 1.5 | | | |
| 6 | 10.2 | | | 3.94 | | | 5.92 | | 6.91 | 5.71 | 1.49 | 3.34 | 5.2 | 1.71<br>1.8 |
| 7 | 10.27 | | | 3.96 | | | | 2.31 | 6.92 | 5.7 | 1.49 | 3.37 | 5.2 | 1.72<br>1.8 |
| 8 | | | 2.12 | 3.73 | | | | 2.29 | 6.85 | 5.75 | 1.45 | 3.3 | 5.11 | 1.67<br>1.76 |

*Chemical shifts in $\delta$ units; solvent $CDCl_3$ with TMS as internal standard ($\delta = 0$).

structures. The nature and position of substituents could be ascertained through interpretation of $^1$H NMR and mass spectra. Further information was obtained through acetylation and by interconversion of compound **1** to **5** by methylation. Mass spectral fragmentation of the 3-aryl-4-hydroxycoumarins conforms to the pattern proposed by Pelter *et al.* [4].

In line with previous observations [5], all three 3-aryl-4-hydroxycoumarins are methoxylated at C-5, a feature which favours the coumarin structure rather than the tautomeric 2-hydroxyisoflavone form.

This is the second report of the presence of 3-aryl-4-hydroxycoumarins in an American species of *Derris*, previous representatives of this class having been described in the Old World species *D. robusta* [6–8] and *D. scandens* [9] and in the South American *D. glabrescens* [10]. With the exception of scandenin (**6**), previously described in *D. scandens* [9], and sitosterol, the remaining compounds are new in the literature. **1** is the 'angular' isomer of the 'linear' robustin [7] and **5** is the corresponding isomer of robustin methyl ether [7].

## EXPERIMENTAL

Mps were determined on the Kofler hot stage and are uncorrected. The silica gel used in the chromatographic columns was type 60, E. Merck, of 0.063–0.2 mm mesh. Elution of the columns was started with petrol (bp 40–80°) followed by solvent mixtures of increasing polarity. UV spectra were taken in MeOH, IR spectra in KBr pellets.

3-*Methylenedioxy* (3′,4′)*phenyl-4-hydroxy-5-methoxy-2″,2″-dimethylchromeno*(5″,6″,7,8)*-coumarin* (**1**). Eluted with hexane–toluene (3:7). Colourless needles from EtOH, mp 202–204°. IR $\nu_{max}$ cm$^{-1}$: 3360, 1705, 1630, 1595. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 232 (4.38), 278 (4.19), 339 (4.07). MS: *m/z* 394 ($M^+$, rel. int. 100%), 379 (45), 233 (19), 217 (61), 189.5 (24). For $^1$H NMR data, see Table 1. Found: *m/z* 394.1058; $C_{22}H_{18}O_7$ requires 394.1053.

2,4-*Dimethoxy-2″,2″-dimethylchromene*(5″,6″,3′,4′)*-stilbene* (**2**). Eluted with toluene. Colourless needles from EtOH, mp 108°. IR $\nu_{max}$ cm$^{-1}$: 1410, 1340, 750, 740. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 318 (1.40), 274 (1.24), 232 (1.30). $^1$H NMR ($CDCl_3$): 1.44 (6H, *s*, *gem*-diMe), 3.84 (6H, *s*, 2 OMe), 5.64 (1H, *d*, $J = 10$ Hz, C-3″), 6.35 (1H, *d*), 6.61 (2H, *d*, $J = 2$ Hz), 6.74 (1H, *d*, $J = 10$ Hz, C-4″), 6.94 (2H, *d*), 7.15 (1H, *d*), 7.28 (2H, *d*). MS: *m/z* 322 ($M^+$, rel. int. 38%), 323 (11), 308 (21), 307 (100), 291 (6), 275 (5), 249 (11), 171 (7), 165 (6), 154 (11), 139 (6), 123 (5), 116 (9), 115 (6). Found: *m/z* 322.1537; $C_{21}H_{22}O_3$ requires 322.1568.

3′,4′-*Methylenedioxy-5-hydroxy-2″,2″-dimethylchromeno* (5″,6″,7,8)*-isoflavone* (**3**). Eluted with toluene–$CH_2Cl_2$ (3:7). Yellow needles from EtOH, mp 180°. IR $\nu_{max}$ cm$^{-1}$: 1410 (*gem*-diMe), 3100 (OH), 1650 (C=O . . . HO), 780. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 270 (1.40). $^1$H NMR ($CDCl_3$): $\delta$1.48 (6H, *s*, *gem*-diMe), 5.58 (1H, *d*, $J = 10$ Hz, C-A), 6.0 (2H, *s*, $OCH_2O$), 6.30 (1H, *s*, C-6), 6.68 (1H, *d*, $J = 10$ Hz, H-B), 6.90–7.10 (3H, *m*, C-2′,5′,6′), 7.88 (1H, *s*, C-2), 12.86 (1H, *s*, C=O . . . HO). MS: *m/z* 364 ($M^+$, rel. int. 68%), 349 (100), 203 (17), 174 (42). Anal.: C, 68.9; H, 4.6. Calc. for $C_{21}H_{16}O_6$: C, 69.22; H, 4.43.

*Sitosterol* (**4**). Eluted with $CH_2Cl_2$–$CHCl_3$ (9:1). Colourless plates from EtOH, mp 147–150°. Identified by comparison (IR, $^1$H NMR, MS, TLC, mp and mmp) with an authentic sample.

3-*Methylenedioxy*(3′,4′)*phenyl-4,5-dimethoxy-2″,2″-dimethylchromeno*(5″,6″,7,8)*-coumarin* (**5**). Eluted with $CH_2Cl_2$. Slightly yellowish cryst. from EtOH, mp 195°. IR $\nu_{max}$ cm$^{-1}$: 1705, 1610, 1570. UV $\lambda_{max}^{MeOH}$ nm (log $\varepsilon$): 235 (4.50), 289 (4.25), 349 (4.16). MS: *m/z* 408 ($M^+$, rel. int. 53%), 393 (100), 365 (5), 350 (6), 233 (28), 217 (11), 197 (10), 174 (10), 149 (41), 57 (97), 55 (62). For $^1$H NMR data, see Table 1. Anal.: C, 67.40; H, 4.98. Calc. for $C_{23}H_{20}O_7$: C, 67.64; H, 4.94.

3-p-*Hydroxyphenyl-4-hydroxy-5-methoxy-6-prenyl-2″,2″-dimethylchromeno*(5″,6″,7,8)*-coumarin* (**6**, scandenin). Eluted with $CHCl_3$. Colourless needles from EtOH, mp 232–234° (lit. [9] 232–234°). IR $\nu_{max}$ cm$^{-1}$: 3300, 1680, 1635, 1595. UV $\lambda_{max}^{MeOH}$ (log $\varepsilon$): 237 (4.63), 286 (4.20), 340 (4.21). MS: *m/z* 434 ($M^+$, rel. int. 100%), 435 (33), 420 (23), 419 (55), 301 (6), 300 (5), 285 (29), 257 (9), 245 (14), 217 (9), 121 (7). For $^1$H NMR data, see Table 1. Anal.: C, 71.73; H, 6.01; Calc. for $C_{26}H_{26}O_6$: C, 71.89; H, 5.99.

*Scandenin 4′-acetate* (**7**). Acetylation of scandenin (**6**) with $Ac_2O$/Py according to [9]. Colourless needles from MeOH, mp 198–200°. Mp and spectral data consistent with lit. [9].

*Scandenin diacetate* (**8**). Acetylation of scandenin (**6**) with $Ac_2O$/NaOAc according to [9]. Colourless needles from MeOH, mp 154–155°. Mp and spectral data consistent with lit. [9].

*Interconversion of* **1** *to* **5**. (a) 1 hr under reflux in $Me_2CO/Me_2SO_4$. (b) **1** treated with $CH_2N_2$ in MeOH gave cryst. **5** in quantitative yield. Pale yellow needles, mp 195°, mixt. with **5** no depression. Spectra identical with those of the natural substance.

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