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ANTHRAQUINONES AND FLAVONOIDS OF *CASSIA LAEVIGATA* ROOTS

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Key Word Index—*Cassia laevigata*; Leguminosae; roots; physcion 8-galactoside; emodin; physcion; ombuin; anthraquinones; flavonoids.

From the root of *Cassia laevigata*, three anthraquinones and one flavonol were isolated, their purity being established by TLC. Two of the anthraquinones were identified as emodin and physcion by mp, mmp, IR, UV, NMR and MS. Emodin and physcion have been reported earlier from many plant sources [1, 2].

The third anthraquinone, $C_{22}H_{22}O_{10}$, was found to be a glycoside which, on acid hydrolysis, gave galactose (PC and osazone) and physcion. The attachment of the sugar moiety at position 8 was established by colour reactions and UV data. The aglycone contained the 1,8-dihydroxy system and gave a positive colour reaction with alkaline zirconium nitrate [3], but the glycoside did not respond to this test, indicating the attachment of sugar residue either at position 1 or 8. In the glycoside the visible absorption maxima in acidic ethanol (415 nm) was hypsochromically shifted by *ca* 15–20 nm relative to aglycone (431 nm). This shift is compatible with glycosidation at one of the α-hydroxyl groups [4].

Permethylation of the glycoside with dimethyl sulphate followed by acid hydrolysis gave 8-hydroxy-1,6-dimethoxy-3-methylanthraquinone (confirmed by mp, mmp, and UV). This confirmed the attachment of the sugar at position 8. That the galactose is in the pyranose form was proved by periodate oxidation when the glycoside consumed 2 mol of periodate per mol and produced 1 mol of formic acid. Thus the glycoside is 1-hydroxy-6-methoxy-3-methylanthraquinone 8-*O*-β-D-galactopyranoside. This is a new anthraquinone glycoside.

The fourth compound, $C_{17}H_{14}O_7$, showed characteristic colour reactions of a flavonol. The compound analysed for three hydroxyl groups (triacetate) and two methoxyl groups (Zeisel, NMR). UV spectral studies indicated the presence of a methoxyl group in position 7 (no shift with NaOAc [5]) and a free hydroxyl group at position 5 (bathochromic shift with $AlCl_3$ [6]). The NMR spectrum showed it to be a 3,5,7,3′,4′-penta-substituted flavone [7]. On $KMnO_4$ oxidation, it gave isovanillic acid, thus placing the methoxyl group at position 4′ and a hydroxyl at position 3′. The compound is, therefore, quercatin 7,4′-dimethyl ether (ombuin), which has been reported before [8, 9].

EXPERIMENTAL

Roots (4 kg) were extracted with EtOH. The conc ethanolic extract was poured in cold H_2O whereby an aq. soln (fraction I) and coloured residue (fraction II) were obtained.

Fraction (I). The aqueous solution was concd and extracted with C_6H_6 and EtOAc, respectively, in a continuous liquid–liquid extractor. The EtOAc fraction was concd, chromatographed on a Si gel column and eluted with C_6H_6–EtOAc (1 : 9). This eluate on concn gave compound $C_{22}H_{22}O_{10}$, mp 192° (d), and was found to contain a single entity on PC and TLC. The glycoside had λ_{max}^{EtOH} nm: 265, 290 and 415. ^{1}H NMR (90 Hz, $CDCl_3$): δ 7.20 (*s*, 1-H, C-2), 7.90 (*s*, 1-H, C-4), 7.45 (*d*, J = 2.5 Hz, C-5) 6.90 (*d*, J = 2.5 Hz, C-7), 3.95 (*s*, 3-H, -OMe), 3.80 (6-H sugar protons) and 5.80 (H-1 galactosyl).

Methylation of the glycoside. The glycoside was methylated with $Me_2SO_4/K_2CO_3/Me_2CO$. The methylated glycoside was hydrolysed with 4 N H_2SO_4. The aglycone was identified as 8-hydroxy-1,6-dimethoxy-3-methylanthraquinone by mp, mmp and UV, and the sugar as galactose by chromatography, co-chromatography and osazone formation.

Fraction (II). The solid mass obtained was refluxed with C_6H_6 and EtOAc, respectively. The C_6H_6 fraction was concd, chromatographed on a Si gel column and eluted with C_6H_6 (100%) and C_6H_6–EtOAc (4 : 1). The C_6H_6 eluate on concn gave physcion, and the C_6H_6–EtOAc (4 : 1) eluate gave emodin. The EtOAc fraction contained only one compound, Ombuin, mp 229°. (Found: C, 61.72; H, 4.28; OMe, 18.50. Calc. for $C_{17}H_{14}O_7$: C, 61.81; H, 4.28; OMe, 18.81%.) UV max in EtOH, 256, 369; +NaOAc, 256; +NaOAc/H_3BO_3, 369; +$AlCl_3$, 427; +$AlCl_3$/HCl 417; +EtONa 419 nm. ^{1}H NMR (90 Hz, $CDCl_3$): δ 3.94 (*s*, 6H, 7,4′-OcMe), 6.40 (*d*, J = 2.5 Hz, 6-H), 6.80 (*d*, J = 2.5 Hz, 8-H), 7.65 (*s*, 2′-H and 6′-H) and 6.95 (*d*, J = 8.5 Hz, 5′-H). MS (70 eV direct inlet) *m/e*: 330(M^+). The triacetate had mp 212°; MS *m/e* 456 (M^+). (Found: Ac, 27.30; Calc. for $C_{17}H_{14}O_7Ac_3$: 28.29%.) UV max in EtOH: 256, 314 nm.

Synthetic anthraquinones. Emodin 6,8-dimethyl ether, mp 213–214°, and emodin 1,6-dimethyl ether, mp 205°, were synthesized by the method of Cameron and Crossley [10]. Mmp tests were carried out with both ethers, and only the latter was undepressed when mixed with the permethylation/hydrolysis product of the new physcion galactoside.

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TWO NEW 5-METHYLCOUMARINS FROM *ERLANGEA FUSCA**

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Key Word Index—*Erlangea fusca*; Compositae; Vernonieae; new 5-methylcoumarins.

So far from the genus *Erlangea* (Compositae, tribe Vernonieae), four species have been investigated [1]. While three species afforded sesquiterpene lactones, one only contained unique 5-methylcoumarins [2], also present in the related genera *Ethulia* [3] and *Bothriocline* [4]. We now have investigated the aerial parts of *E. fusca* S. Moore and again this species contains two new coumarins of this type.

The spectral data show that we are dealing with the two isomeric 5-methylcoumarins, **1** and **3**. While the ^{1}H NMR spectra are very similar, the acetylation of **1** clearly shows that the less polar compound is the isomer with a 6-membered oxygen ring. The ^{1}H NMR signals of the aromatic protons and that of the 5-methyl group are very similar to those of analogous compounds of this type [2–4]. The chemical shift of the other Me groups are characteristic of those at an oxygen bearing carbon, while the position of the signal of the only CH_2-group shows that in both compounds this group is benzylic. Therefore the O-function must be located at C-2′. In the spectrum of the acetate **2** the 1′-H-protons show double doublets, while in the spectra of **1** and **3** these signals collapse to a simple doublet.

In the MS of **1** loss of Me and H_2O leads to a pyrrylium cation (*m/e* 277) (**4**). This fragment most probably loses acetylene (*m/e* 201). In the spectrum of **3** similar fragments can be observed, indicating that rearrangements most probably take place in the M^+ leading perhaps also to **4**, although the relative intensities in the spectra of **1** and **3** are different. We have named **1** erlangeafusciol and **3** isoerlangeafusciol. The isolation of **1** and **3** again shows that the genus *Erlangea* perhaps is not very homogenous. It would be interesting to compare the chemistry with the anatomical aspects.

Table 1. ^{1}H NMR data of **1–3** (270 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**
6-H	7.20 *d(br)*	7.23 *d(br)*	7.19 *d(br)*
7-H	7.39 *dd*	7.41 *dd*	7.39 *dd*
8-H	7.11 *d(br)*	7.06 *d(br)*	7.04 *d(br)*
9-H	2.87 *s(br)*	2.68 *s(br)*	2.68 *s(br)*
$1'_1$-H	3.11 *d*	3.19 *dd*	3.11 *d*
$1'_2$-H		3.08 *dd*	
2′-H	4.83 *t*	5.28 *dd*	4.91 *t*
4′-H	1.35 *s*	1.59 *s*	1.41 *s*
5′-H	1.28 *s*	1.58 *s*	1.31 *s*
OAc	—	2.00 *s*	—

J(Hz): 6,7 = 8.5; 7,8 = 7.5; 1′,2′ = 9.5(**2:** $1'_1$,2′ = 10; $1'_2$,2′ = 8).

EXPERIMENTAL

The air-dried aerial parts (62 g) were cut up and extracted with Et_2O. The first extract obtained was separated by column chromatography (Si gel) and further by TLC. Finally 65 mg **1** (Et_2O) and 45 mg of **3** (Et_2O) were obtained.

Erlangeafusciol (**1**). Colourless crystals, mp 118–119° (Et_2O–petrol), IR ($CHCl_3$) cm^{-1}: 3610 (OH), 1720 (C=O),

* Part 19 in the series "Naturally Occurring Coumarin Derivatives". For Part 18 see Bohlmann, F. and Zdero, C. (1980) *Phytochemistry* **19,** 331.