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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*	—

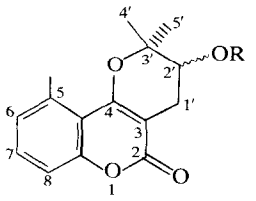
J(Hz): 6,7 = 8.5; 7,8 = 7.5; 1′,2′ = 9.5(**2:** $1'_1$,2′ = 10; $1'_2$,2′ = 8).

EXPERIMENTAL

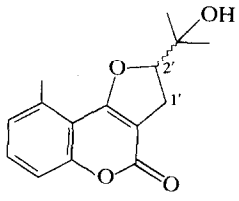
The air-dried aerial parts (62 g) were cut up and extracted with Et_2O. The first extract obtained was separated by column chromatography (Si gel) and further by TLC. Finally 65 mg **1** (Et_2O) and 45 mg of **3** (Et_2O) were obtained.

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.



1 R = H
2 R = Ac



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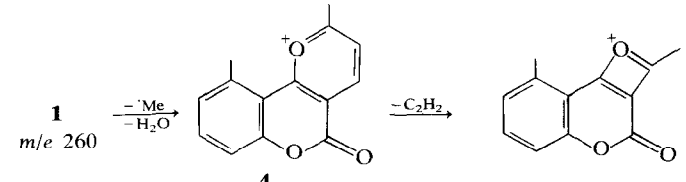

4
m/e 227

m/e 201

1635, 1610, 1575 (aromatic); MS (*m/e* (rel. int.) 260.105 (M^+ 77%) ($C_{15}H_{16}O_4$); 245 (M^+ − Me, 22); 227 (245 − H_2O, 92); 201 (227 − C_2H_2, 100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365 \text{ nm}}{+32.5 \quad +35.0 \quad +40.0 \quad +67.5 \quad +140.0}$$

($c = 0.2$, $CHCl_3$).

1 (10 mg) in 0.5 ml Ac_2O was heated for 1 hr with 10 mg 4-pyrrolidinopyridine [5] at 70°. Usual work-up afforded 8 mg of **2**. IR ($CHCl_3$) cm^{-1}, 1720 (OAc, C=O), 1635, 1605, 1565 (aromatic), 1260 (OAc); MS *m/e* (rel. int.): 302 (M^+ 10%) ($C_{17}H_{18}O_5$); 242 (M^+ − HOAc, 8); 227 (242 − Me, 27); 201 (227 − C_2H_2, 10); 43 ($MeCO^+$, 100).

Isoerlangeafusciol (**3**). Colourless crystals, mp 121° (Et_2O–petrol), IR ($CHCl_3$) cm^{-1}: 3605 (OH), 1720 (C=O), 1630, 1610, 1570 (aromatic), MS *m/e* (rel. int.) 260.105 (M^+, 100%) ($C_{15}H_{16}O_4$); 245 (M^+ − Me, 16); 227 (245 − H_2O, 30); 217 (245 − CO, 41); 201 (227 − C_2H_2, 26); 189 (227 − CO, 88).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365 \text{ nm}}{+35.3 \quad +36.5 \quad +40.0 \quad +68.9 \quad +144.1}$$

($c = 0.17$, $CHCl_3$).

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