Phytochemistry, 1980, Vol. 19, p. 2496. © Pergamon Press Ltd. Printed in England. 0031-9422/80/1101-2496 $02.00/0

6-HYDROXY-4-METHOXY-5-METHYLCOUMARIN FROM *GERBERA JAMESONII**

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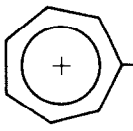
(*Received* 5 *March* 1980)

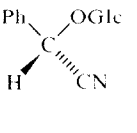
Key Word Index—*Gerbera jamesonii*; Compositae; 6-hydroxy-4-methoxy-5-methylcoumarin; cyanogenic glucoside; prulanrasin.

So far from *Gerbera jamesonii* Bolus only widespread acetylenes [1] have been isolated. In addition to the acetylenes [1], other *Gerbera* species contain typical acetophenone derivatives [2] and also representatives of the unusual 5-methylcoumarins [2–4]. An investigation of a larger quantity of the aerial parts of *G. jamesonii* afforded a glucoside, which is probably prulaurasin (**1**) [5], its structure following from the spectral data of its tetraacetate **2**. Furthermore, a simple coumarin, which turns out to be **3**, was isolated. Acetylation afforded the acetate **4**. Careful comparison of the ^{1}H NMR data of several substituted 5-methylcoumarins [6] clearly shows that the free hydroxyl can only be placed at C-6. In agreement with this assumption, a typical shielding effect of the acetate group (5-methyl) was observed. Also the chemical shift of the methoxy group is only in agreement with its placement in the 4-position [6].

EXPERIMENTAL

The powdered air-dried aerial parts (1 kg) were extracted first with petrol and further with EtOH–H_2O (7:3). The extract obtained was concd *in vacuo*, diluted with H_2O and extracted with Et_2O (A) and with EtOAc (B). Column chromatography (SiO_2) of A using $CHCl_3$ and increasing amounts of EtOAc afforded 50 mg **3**, while B (EtOAc–MeOH, 9:1) gave 700 mg **1**, colourless crystals, mp 120–121° (EtOAc–$CHCl_3$, lit. [5] 121–122°). Acetylation (pyridine, Ac_2O) afforded the tetraacetate **2**, colourless crystals, mp 142–143°. MS *m/e* (rel. int.): M^+ —, 347 (8) (M – PhĊHCN), 331 (6) (M – PhCH(Ȯ)CN), 116, 050 (100) (C_8H_6N = 
—CN). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 7.47 (5H, *s*, Ph). 5.53 (*s*, 7-H), 4.54 (*d*, J = 8 Hz, 1′-H), 5.13 (*m*, 2′-4-H), 3.64 (*m*, 5′-H), 4.27 (*dd*, J'' = 11, 4.5 Hz, 6′$_1$-H), 4.15 (*dd*, J = 11, 2 Hz, 6′$_2$-H), 2.13, 2.02, 1.99 (6H, *s*, OAc).

6-*Hydroxy*-4-*methoxy*-5-*methylcoumarin* (**3**). Colourless crystals, mp 267–268°. IR ν_{max}^{KBr} cm^{-1}: 3300 (OH) 1690, 1610, 1575 (coumarin). MS *m/e* (rel. int.): 206 (100) (M^+): 191 (11) (M – ·Me); 178 (40) (M – CO); 163 (70) (178 – ·Me); ^{1}H NMR ($CDCl_3$/DMSO, 270 MHz): δ 5.60 (*s*, 3-H), 6.91 (*d*, J = 9 Hz, 7-H), 7.05 (*d*, J = 9 Hz, 8-H), 2.44 (*s*, 9-H), 3.91 (*s*, OMe), 9.36 (*br. s*, OH). 2 mg **3** were heated with 0.1 ml Ac_2O for 1 hr at 70°. After evapn 2 mg **4** were obtained. ^{1}H NMR ($CDCl_3$, 270 MHz): 5.71 (*s*, 3-H), 7.20 (*s*, 7,8-H), 2.33 (*s*, 9-H), 3.97 (*s*, OMe), 2.22 (OAc).



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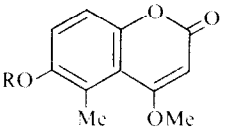

3 R = H
4 R = Ac

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* Part 21 in the series "Naturally Occurring Coumarin Derivatives". For Part 20 see Mahmoud, Z. F., Sarg, T. M., Amer, M. E., Khafagy, S. M. and Bohlmann, F. (1980) *Phytochemistry* **19**, 2029.