

Table 2
¹³C NMR Spectra of Coumarins **1-6** in DMSO-*d*₆

Compound	C2	C3	C4	C4a	C5	C6	C7	C8	C8a	CH ₃
1	162.42	91.54	165.78	120.71	105.29	155.61	116.58	117.92	148.19	55.97
2	162.82	87.46	167.05	108.03	124.75	114.53	163.14	100.79	155.79	56.18
3	162.50	91.60	165.83	123.12	110.40	154.72	121.03	119.89	145.73	
4	162.40	87.75	166.00	107.50	124.45	112.48	161.50	101.93	156.03	
5	162.29	90.62	165.99	115.94	107.08	153.99	117.87	121.31	146.311	57.30
6	162.53	87.20	166.79	107.40	124.47	113.18	162.02	102.37	154.96	57.33

afforded compound **5** in 55% yield. Compound **6** was prepared analogously from **2** via **4** [9], with an overall yield of 48%. ¹H and ¹³C NMR data for compounds **1-6** are listed in Tables 1 and 2, respectively.

EXPERIMENTAL

Melting points were determined in a Reichert Kofler thermopan, and are uncorrected. IR spectra were recorded in a Perkin-Elmer 1640FT spectrometer (ν in cm⁻¹). ¹H and ¹³C NMR spectra were recorded in a Bruker AMX spectrometer at 300 and 75.47 MHz, respectively, using TMS as internal standard (chemical shifts in δ values, *J* in Hz). Mass spectrometry was carried out in a Hewlett Packard 5988A spectrometer. Elemental analyses were performed on a Perkin-Elmer 240B microanalyser. Flash chromatography (FC) was performed on silica gel (Merck 60, 230-400 mesh).

4,6-Dihydroxycoumarin (**3**).

Compound **1** (1 g, 5.2 mmol) was added to a mixture of hydriodic acid (25 ml), acetic anhydride (10 ml) and acetic acid (10 ml), and the mixture was heated at 80 °C for 1 hour. After cooling to room temperature, 100 ml of water was added. The resulting precipitate was isolated by filtration and purified by flash chromatography (FC) using 4:1 CH₂Cl₂/MeOH as eluent. Yield 0.4 g. (45%), mp 286-288 °C (MeOH); RF: 0.22 (4:1 CH₂Cl₂/MeOH); ir: ν 3100-2800, 1663, 1567, 1462, 1325, 1153, 1097, 1002 cm⁻¹; MS *m/z* (%): 178 (M⁺, 96), 150 (M⁺ - CO, 30), 136 (M⁺ - CO₂, 100), 108 (47), 78 (64).

Anal. Calcd. for C₉H₆O₄: C, 62.5; H, 4.20. Found: C, 62.38; H, 4.43.

6-Hydroxy-4-methoxycoumarin (**5**).

A mixture of **3** (1 g, 5.6 mmol), MeOH (40 ml) and concentrated HCl (5 ml) was refluxed for 1.5 hours. The solvent was removed *in vacuo* and the residue was purified by FC using 9:1

CH₂Cl₂/MeOH, yielding the desired compound **5** (0.6 g 55%), and 0.16 g (15%) of the starting coumarin **3**; mp 283-285 °C (EtOH); RF: 0.43 (9:1 CH₂Cl₂/MeOH); ir: ν 3186, 1664, 1571, 1468, 1398, 1243, 1092 cm⁻¹; MS *m/z* (%): 192 (M⁺, 100), 164 (M⁺ - CO, 41), 149 (M⁺ - CO₂, 46), 134 (27), 121 (14), 78 (25).

Anal. Calcd. for C₁₀H₈O₄: C, 60.68; H, 3.39. Found: C, 60.51; H, 3.55.

Acknowledgment.

We thank the Xunta de Galicia (PGIDTOOPXI20317PR) for financial support.

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