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STRUCTURAL REVISION OF FOUR COUMARINS FROM *PTEROCAULON* SPECIES

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Key Word Index—*Pterocaulon*; Compositae; structural revision; trioxxygenated coumarins.

Abstract—The structures of two 5,6,7-trioxxygenated coumarins, named sabandinol and sabandinone, isolated from *Pterocaulon virgatum*, have been revised. The new structures assigned were regioisomers and were identified on the basis of additional spectroscopic data and X-ray crystallographic data. Also the structural revision of two trioxxygenated coumarins from *Pterocaulon balansae* and *P. lanatum* is presented. © 1997 Elsevier Science Ltd. All rights reserved

In our previous work, we reported the isolation and identification of two coumarins from the chloroform extract of the aerial parts of *Pterocaulon virgatum* L. DC [1]. Their structures were established as **1** and **2** by comparison of their physical and spectroscopic data (UV, IR, EI-MS, mp) with sabandinol [2] and sabandinone, respectively [3]. Based on the literature data available at that time [2, 3], the complete identity of the compounds from *P. virgatum* L. DC with sabandinol and sabandinone was made clear.

Further isolation and identification of 5-methoxy-6,7-methylenedioxcoumarin (**3**) and 5-(3-methyl-2-butenyloxy)-6,7-methylenedioxcoumarin (**4**) as new coumarins from the same plant [4], has now allowed us to revise the structures of the coumarins, originally identified as **1** and **2**, as the regioisomers 5-(2,3-dihydroxy-3-methylbutyloxy)-6,7-methylenedioxcoumarin (**5**) and 5-(3-methyl-2-oxobutyloxy)-6,7-methylenedioxcoumarin (**6**), respectively. This is the first report on these two new 5,6,7-trioxxygenated coumarins (**5**) and (**6**).

RESULTS

On comparison of additional spectroscopic data (^{13}C NMR and 500 MHz ^1H NMR, Tables 1 and 2), of coumarins assigned as **1** and **2** with those of coumarin **4**, the structure of which was unambiguously determined by X-ray diffraction [4], and combining

all the structural elements, the regioisomers **5** and **6** were attributed as the correct structures for these two coumarins. The ^1H and ^{13}C NMR data of these three compounds matched completely with the structure of a 5,6,7-trioxxygenated coumarin.

The isolation of coumarin **7** was reported from related *Pterocaulon* species, namely *P. balansae* Chodat and *P. lanatum* O. Kuntze [5]. The positioning of the *O*-substituents on the coumarin nucleus was established on the basis of acidic cleavage of coumarin **8**, also isolated from the same sources [5]. The latter coumarin was first isolated from *Pteronia glabrata* and the structure was determined by the aromatic solvent induced shift (ASIS) observed for the methylenedioxy and methyleneoxy signals in the ^1H NMR spectrum [6]. A synthesis of coumarin **8** [7] revealed that the spectroscopic properties of this compound differed from the coumarin that was isolated from *P. lanatum* and *P. balansae* [5]. Accordingly, the synthetic and natural compound must have a different structure. However, the authors did not propose an alternative structure [7].

An examination of the spectroscopic and physical data reported for the coumarin designated as **7**, isolated from *P. balansae* and *P. lanatum*, matched very well with those we obtained for **5** [5-(2,3-dihydroxy-3-methylbutyloxy)-6,7-methylenedioxcoumarin], which was first published as sabandinol [2]. Therefore, the previously reported structure **7** [5] must also have structure **5**. Consequently, coumarin **8** must be revised to structure **9**. It seems that care should be taken in the structural identification of tri- and tetraoxxygenated coumarins and that several previously reported com-

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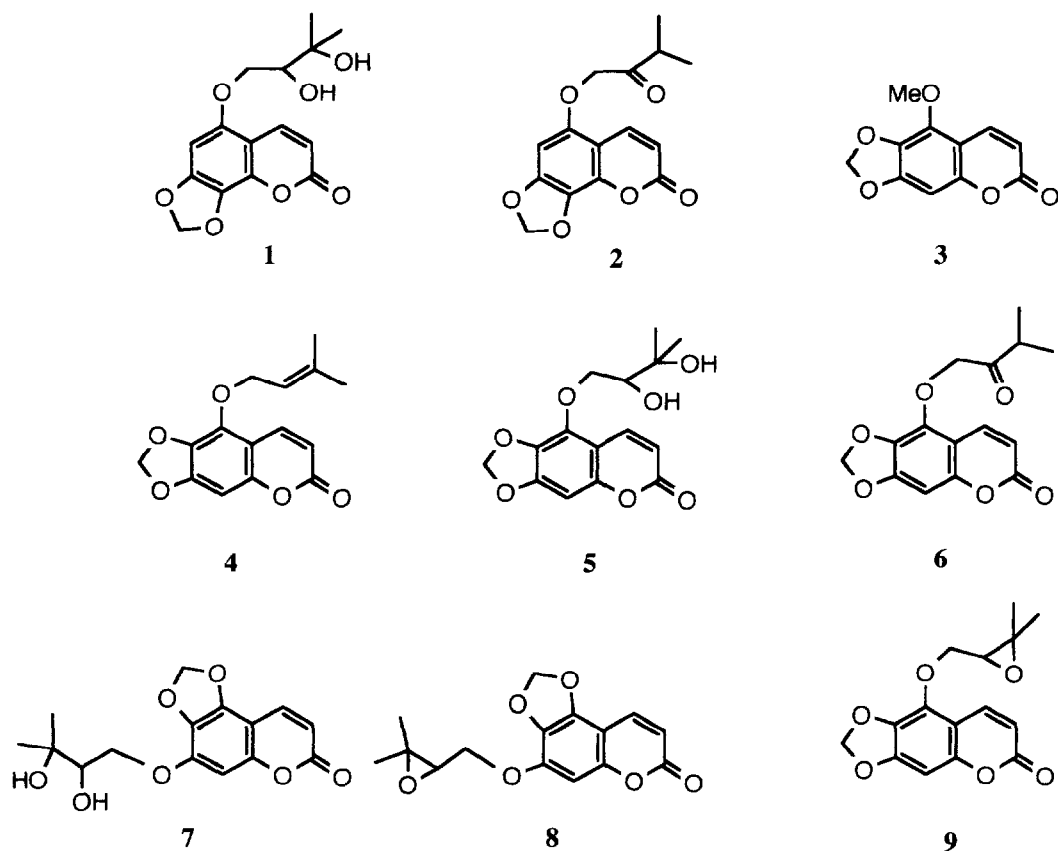


Table 1. ^1H NMR spectral data of coumarins **1** (now assigned structure **5**), **2** (now assigned structure **6**) and **4** (500 MHz, CDCl_3 , TMS as internal standard)

H	4	5 (newly assigned)*	6 (newly assigned)†
3	6.20 (<i>d</i> , $J = 9.8$ Hz)	6.23 (<i>d</i> , $J = 9.7$ Hz)	6.25 (<i>d</i> , $J = 9.7$ Hz)
4	7.95 (<i>d</i> , $J = 9.8$ Hz)	7.96 (<i>d</i> , $J = 9.7$ Hz)	8.07 (<i>d</i> , $J = 9.7$ Hz)
8	6.53 (<i>s</i>)	6.57 (<i>s</i>)	6.55 (<i>s</i>)
O-CH ₂ -O	6.02 (<i>s</i>)	6.06 (<i>s</i>)	5.95 (<i>s</i>)
1'	4.85 (<i>d</i> , $J = 7.4$ Hz)	4.37 (<i>dd</i> , $J = 10.4, 8.1$ Hz) 4.51 (<i>dd</i> , $J = 10.4, 2.9$ Hz)	5.08 (<i>s</i>)
2'	5.48 (<i>br, d</i> , $J = 7.4$ Hz)	3.82 (<i>dd</i> , $J = 8.1, 2.9$ Hz)	—
3'	—	—	2.77 (<i>m</i>)
4'	1.73 (<i>s</i>)	1.27 (<i>s</i>)	1.17 (<i>s</i>)
3'-CH ₃	1.83 (<i>s</i>)	1.33 (<i>s</i>)	1.17 (<i>s</i>)

* Originally assigned as **1**.

† Originally assigned as **2**.

Table 2. ^{13}C NMR spectral data of coumarins **1** (now assigned structure **5**), **2** (now assigned structure **6**) and **4** (20 MHz, CDCl_3)

C	4	5 (newly assigned)*	6 (newly assigned)†
2	161.25 (s)	161.18 (s)	161.22 (s)
3	111.63 (d)	112.14 (d)	112.12 (d)
4	139.04 (d)	138.58 (d)	138.88 (d)
4a	107.39 (s)	106.97 (s)	106.56 (s)
5	137.28 (s)	136.77 (s)	136.51 (s)
6	132.37 (s)	132.23 (s)	131.19 (s)
7	151.64 (s)‡	151.52 (s)‡	151.71 (s)‡
8	92.40 (d)	93.14 (d)	92.93 (d)
8a	152.55 (s)‡	152.43 (s)‡	152.31 (s)‡
O-CH ₂ -O	101.92 (t)	102.06 (t)	101.88 (t)
1'	68.90 (t)	73.76 (t)	73.74 (t)
2'	119.55 (d)	71.61 (d)	208.44 (s)
3'	139.70 (s)	76.46 (s)	32.12 (d)
4'	25.75 (q)	26.72 (q)	18.02 (q)
3'-CH ₃	18.15 (q)	24.82 (q)	18.02 (q)

* Originally assigned as **1**.

† Originally assigned as **2**.

‡ May be interchanged.

pounds of this type might have isomeric structures. Several incorrect structures have been reported in the

recent literature, as proven by structural revisions, e.g. obtusifol [8].

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