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TWO FLAVONE GLUCOSIDES FROM *SIDERITIS LEUCANTHA*

FRANCISCO TOMAS and FEDERICO FERRERES

Centro de Edafología y Biología Aplicada del Segura, C.S.I.C., Apdo. 195, Murcia, Spain

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Key Word Index—*Sideritis leucantha*; Labiatae; 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone 7-glucoside; 5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone 7-glucoside.

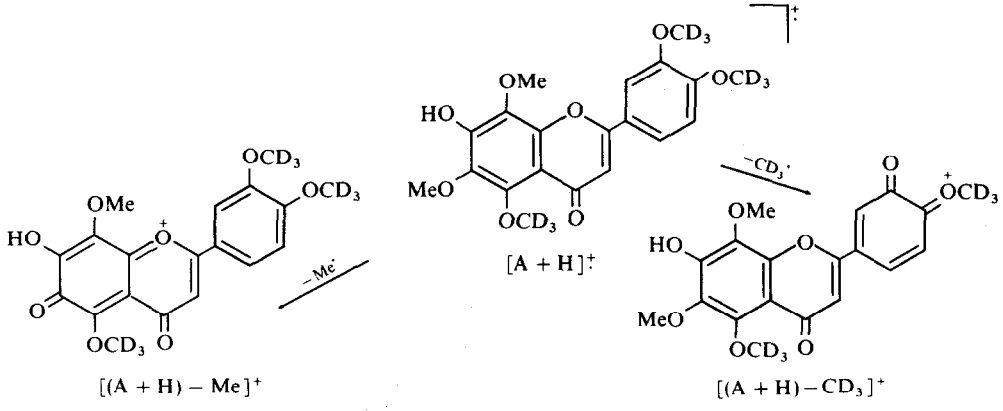
In continuation of our work from *Sideritis leucantha* Cavanilles [1], two new flavone glucosides, 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone 7-glucoside (**1**) and 5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone 7-glucoside (**2**), have been identified.

UV data [2] indicated that there were free hydroxyls at the 5-, 3′- and 4′-positions in **1** and also that the 6- and/or 8-hydroxyls were substituted [3]. Similarly, free 5- and 4′-hydroxyls were confirmed in **2** as well as substituents in the 6- and/or 8-positions and two or more substituents in the B-ring of the flavone nucleus. Both substances gave glucose on acid hydrolysis. Permethylation of the aglycones of both **1** and **2** gave nobiletin (5,6,7,8,3′,4′-hexamethoxyflavone) identified by co-TLC with an authentic marker. Alkaline degradation of **2** gave vanillic acid, identified by TLC with an authentic sample. The permethylated derivatives of both glucosides showed identical R_f on TLC. The MS spectra of PM and PDM derivatives suggest that peaks of *m/e* (A + H) − Me may correspond to the quinonoidal structures formed by the loss of Me from positions 6, 8 or 3′. Thus, the peak corresponding to the ion of *m/e* (A + H) − CD_3 seen on the PDM spectrum of **1** (which is not present in the PDM spectrum of **2**) indicates a different type of substitution at the 3′-position of each derivative.

The determination of structures and the elucidation of the substitution pattern were carried out by standard spectroscopic and analytical methods [4–6]. From these data **1** was identified as 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone 7-glucoside and **2** as 5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone 7-glucoside. Chhabra *et al.* [7] have identified 5,7,3′,4′-tetrahydroxy-6,8-dimethoxyflavone from the gums of *Gardenia lucida* and *G. gummifera* and Horie *et al.* [8] have characterized 5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone from unripe fruit of *Citrus sudachi*. However, the 7-glucosides of both these substances have not been reported previously.

EXPERIMENTAL

The MeOH extract [1] was successively chromatographed (Whatman No. 1) in the following solvent systems: 15% HOAc (R_fs: **1** and **2**, 0.15), HOAc–HCO_2H–H_2O (10:2:3) (R_fs: **1** and **2**, 0.76), 50% HOAc (R_fs: **1** and **2**, 0.74) and *n*-BuOH–EtOH–H_2O (4:1:2.2) (R_f **1**: 0.72; R_f **2**: 0.55). Mp **1** 192–195°; mp **2** 185–187°. R_f PM **1** = R_f PM **2**, TLC (Si gel) EtOAc (R_f: 0.72), $CHCl_3$–EtOAc–Me_2CO (5:4:1) (R_f: 0.68). UV **1** λ_{max}nm: MeOH, 344, 278, 258; NaOMe, 406, 274; $AlCl_3$, 434, 366, 310 sh, 288; $AlCl_3$/HCl, 362, 310 sh, 282, 266: NaOAc, 410, 270; NaOAc/H_3BO_3, 366, 270. UV **2** λ_{max}nm: MeOH, 344, 272, 254; NaOMe, 408, 266; $AlCl_3$, 390 sh, 360, 300 sh, 278; $AlCl_3$/HCl, 390 sh, 360, 300 sh, 278; NaOAc, 410, 268. MS (70 eV direct inlet) *m/e*: PM **1** = PM **2**, 606 (M^+, 11), 388 (A + H = m, 100), 373 (m − 15, 82), 255 (a_1 − 2, 9), 197 [(a_1 − 2) − CO, 31], 182 (14), 167 (16), 165 (b_1, 16), 162 (b_2, 14), 218 (T_1, 15), 187 (T_2, 37), 155 (T_3, 39), 101 (175). MS (70 eV, direct inlet) *m/e*: PDM **1**, 627 (M^+, 7), 397 (A + H = m, 100), 382 (m − 15, 45), 379 (m − 18, 71), 288 (a_1 − 2, 22), 200 [(a_1 − 2) − CO, 47], 185 (16), 171 (b_1, 22), 168 (b_2, 27), 230 (T_1, 27), 196 (T_2, 62), 161 (T_3, 52), 107 (142). MS (70 eV, direct inlet) *m/e*: PDM **2**, 624 (M^+, 7), 394 (A + H = m, 100), 379 (m − 15, 45), 368 (17), 339 (14), 313 (21), 285 (13), 264 (13), 257 (12), 239 (23), 236 (19), 213 [(a_1 − 2) − 15, 17], 211 (20), 200 [(a_1 − 2) − CO, 23], 185 (31), 171 (33), 168 (b_1, 29), 165 (b_2, 26), 196 (T_2, 43), 161 (T_3, 57), 107 (238).



Scheme 1. MS partial fragmentation of PDM of **1**.

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FLAVONOIDS FROM *ABRUS PRECATORIUS*

D. K. BHARDWAJ, M. S. BISHT and C. K. MEHTA

Department of Chemistry, University of Delhi, Delhi-110007, India

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Abrus precatorius, having medicinal properties [1], has been examined for its chemical components [2–6]. This communication describes the isolation of a new flavone, abrectorin and a known glycoside, desmethoxycentaureidin 7-*O*-rutinoside.

A. precatorius seed kernels (2 kg) were defatted using petrol and then extracted exhaustively with EtOH. Solvent-free EtOH extract was repeatedly extracted with Et_2O and then EtOAc to separate non-glycosidic and glycosidic components. Combined Et_2O and EtOAc extracts containing non-glycosidic components were concentrated. The solvent-free concentrate was chromatographed on a Si gel column; elutions with C_6H_6–EtOAc (3:1) gave a mixture which was separated into two compounds by preparative TLC (Si gel; C_6H_6–EtOAc; 1:1). One of these was characterized as luteolin by direct comparison with an authentic sample whereas the second compound (**1**) was a new flavone, here named abrectorin. Et_2O- and EtOAc-insoluble fractions containing glycosidic components were combined, concentrated and the resulting solvent-free concentrate was chromatographed on a Si gel column, which was eluted with EtOAc–MeOH (3:1) to give a mixture of three compounds which on preparative-PC using *n*-BuOH–HOAc–H_2O (4:1:5; upper layer) yielded orientin, isoorientin and a flavone glycoside (**2**).

Abrectorin (**1**)

Colour reactions and spectral data indicated **1** to be a polyhydroxyflavone. Methylation of **1** yielded a dimethyl ether identical with 6,7,3′,4′-tetramethoxyflavone (**1a**) [Bhardwaj, D. K. *et al.*, unpublished results] showing that **1** was a 6,7,3′,4′-dihydroxydimethoxyflavone. It gave a negative Quastel test [7] showing the absence of an *ortho*-dihydroxyl in the molecule. On alkali fission **1** yielded isovanillic acid, fixing an OH and an OMe at C-3′ and C-4′ respectively. The solubility of **1** in aqueous Na_2CO_3 (10%) indicated another OH at C-7, so that the other OMe was therefore at C-6. Abrectorin is thus 6,4′-dimethoxy-7,3′-dihydroxyflavone (**1**). This was confirmed by the identity of its diethyl ether with synthetic 6,4′-dimethoxy-7,3′-diethoxyflavone (**1b**) [8].

Desmethoxycentaureidin-7-O-rutinoside (**2**)

Colour reactions and spectral data indicated **2** to be a polyhydroxyflavone glycoside. On hydrolysis it yielded an aglycone (**2a**) and two free sugars identified as rhamnose and glucose by PC (*n*-BuOH–Py–H_2O, 6:4:3). Methylation of **2a** yielded a trimethyl ether identical with 5,6,7,3′,4′-pentamethoxyflavone (**2b**) [9] indicating that **2a** was a 5,6,7,3′,4′-trihydroxydimethoxyflavone. On alkali fission **2a** yielded isovanillic acid showing a OH and a OMe at C-3′ and C-4′ respectively. **2a** did not give the Bargellini test) for a 5,6,7-trihydroxy system or the Quastel test [7] characteristic for an *ortho*-dihydroxy system. Consequently, the remaining OMe and OH were at C-6 and C-7 respectively. Bathochromic shifts in UV spectrum of **2a** with $AlCl_3$ confirmed the chelated OH at C-5 and its solubility in aqueous Na_2CO_3 (10%) supported another OH at C-7. The absence of the usual bathochromic shifts in