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FLAVONOIDS OF *Smyrnium olusatrum* FROM ALGERIA

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The genus *Smyrnium* is not well documented. Previous reports have shown sesquiterpene lactones to be the main constituents in the studied species [1–5]. The species *Smyrnium olusatrum* L., the subject of the present work, is traditionally also used as antiscorbutic [6]. To our best knowledge, flavonoids have never been reported from the genus.

Smyrnium olusatrum L. (Apiaceae) was collected in May 2006 at Constantine (eastern Algeria). The plant was gathered by Mr. Kamel Kabouche and authenticated by Prof. Gerard De Belair (Annaba University, Algeria). A voucher specimen (ZKLOST So05/06) was deposited at the Herbarium of the Laboratory of Therapeutic Substances (LOST), Faculty of Sciences, Mentouri-University, Constantine, Algeria.

Air-dried and powdered aerial parts (1 kg) of *Smyrnium olusatrum* L. [7] were macerated in a methanolic solution (70%). The extract was successively concentrated to dryness (under low pressure); the residue was dissolved in boiling water and extracted with ethyl acetate and *n*-butanol, successively.

The combined ethylacetate and butanolic extracts were column chromatographed on polyamid SC6 and eluted with toluene–methanol with increasing polarity. The major fractions were subjected to preparative TLC plates on cellulose with 15% AcOH and purification by flash chromatography on Sephadex LH20 eluted with MeOH–H_2O with increasing polarity, leading to four compounds **1–4** which were identified by using UV, ^{1}H NMR, ^{13}C NMR, and MS analysis [8–10].

Acid Hydrolysis. The pure compounds were treated with 2M HCl at 100°C for 1 h. The hydrolysates were extracted with EtOAc, and the aglycones were identified by their UV spectra in methanol and by comparison of their R_f with authentic samples.

Sugars were identified in the aqueous residue by comparison with authentic samples on silica gel TLC impregnated with 0.2 M NaH_2PO_4, solvent Me_2CO–H_2O (9:1), and revealed with aniline malonate.

Compound 1. $C_{21}H_{20}O_{12}$, mp 218–212°C. UV (MeOH, λ_{max}, nm): 257, 353; + NaOH: 272, 331, 404; + $AlCl_3$: 273, 300 sh, 434; $AlCl_3$/HCl: 269, 359 sh; 396. Acid hydrolysis of **1** produced quercetin and D-glucose. Compound **1** was identified as quercetin 3-*O*-glucoside [8–10].

Compound 2. $C_{22}H_{22}O_{12}$, mp 154–155°C. UV (MeOH, λ_{max}, nm): 255, 267 sh, 300 sh; +NaOH: 272, 329, 417; +$AlCl_3$: 267, 300, 361, 398 sh; +HCl: 267, 300 sh, 359, 400; +NaOAc: 274, 320, 382; +H_3BO_3: 255, 267 sh, 305 sh, 358. FAB$^+$-MS *m/z* 479 [M + H]$^+$. Acid hydrolysis of **2** produced isorhamnetin and D-glucose. Compound **1** was identified as isorhamnetin-3-*O*-glucoside [8–10].

Compound 3. $C_{24}H_{22}O_{15}$. UV (MeOH, λ_{max}, nm): 257, 267 sh, 300 sh, 358; + NaOH: 271, 320, 410; + $AlCl_3$: 273, 300 sh, 326 sh, 434; +HCl: 270, 296 sh, 359 sh; 400; +NaOAc: 269, 312 sh, 400; +H_3BO_3: 260, 267 sh, 305 sh, 379. ES$^+$-MS *m/z* 550 [M]$^+$. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm, J/Hz): 7.55 (1H, d, J = 2.1, H-2′), 7.47 (1H, dd, J = 2.1, 8.5, H-6′), 6.85 (1H, d, J = 8.5, H-5′), 6.65 (1H, d, J = 2.1, H-8), 6.40 (1H, d, J = 2.1, H-6), 5.35 (1H, d, J = 7.0, H-1″ glucose), 4.20 (1H, br.d, J = 11.2, H-6″a), 3.95 (1H, dd, J = 11.2, 5.7, H-6″b), 3.16 (1H, s, H-2‴malonyl). Acid hydrolysis of **3** produced quercetin and D-glucose. Compound **3** was identified as quercetin 3-(6″-malonylglucoside) [11].

Compound 4. $C_{25}H_{24}O_{15}$. UV (MeOH, λ_{max}, nm): 257, 266 sh, 300 sh, 358; +NaOH: 272, 322, 415; +$AlCl_3$: 272, 300 sh, 358; +HCl: 268, 298 sh, 360 sh, 400; +NaOAc: 270, 315 sh, 383; +H_3BO_3: 260 sh, 305 sh, 357. ES$^+$-MS *m/z* 565 [M]$^+$.

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^{1}H NMR (250 MHz, CD_3OD, δ, ppm, J/Hz): 7.80 (1H, d, J = 2.1, H-2′), 7.61 (1H, dd, J = 8.6, J = 2, H-6′), 6.87 (1H, d, J = 8.6, H-5′), 6.34 (1H, d, J = 2.1, H-8), 6.18 (1H, d, J = 2.1, H-6), 5.36 (1H, d, J = 7.3, H-1″glucose), 4.21 (1H, br.d, J = 11.6, H-6″a), 3.97 (1H, dd, J = 11.6, 6.1, H-6″b), 3.90 (3H, s, 3′-OMe), 3.18 (1H, s, H-2‴malonyl). Acid hydrolysis of **4** produced isorhamnetin and D-glucose. Compound **3** was identified as isorhamnetin 3-(6″-malonylglucoside) [12].

Four flavonoids **1–4** are reported for the first time from the algerian species *Smyrnium olusatrum* L. and from the genus *Smyrnium* (Apiaceae).

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