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Triterpenoids and Flavonoid from *Scorzonera undulata* ssp. alexandrina

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Abstract

A phytochemical investigation of EtOAc extract of *Scorzonera undulata* ssp. *alexandrina* (Boiss.) Maire yielded five compounds including four triterpenoids called lupeol **1**, 24-methylenecycloartanol **2**, 3-*O*-(6-*O*-acetyl-β-D-glucopyranosyl) β-sitosterol **3** and daucosterol **4** and one flavonoid named apigenin **5**. Their structures were determined using spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, DEPT, HMBC, HSQC, COSY, NOESY), ESI-MS and EI-MS, values of optical rotation and chemical correlations with known compounds that have been described in the literature.

Key words: *Scorzonera undulata* ssp. *alexandrina*, Asteraceae, Triterpenoids, Flavonoid.

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1. Introduction

Scorzonera genus is a member of the family Asteraceae, one of the largest families of flowering plants which is a source of numerous classes of secondary metabolites [1, 2]. This genus includes more than 170 species in the world [3], with eight found in the flora of Algeria [4]. Plants of this genus which afforded different types of compounds as stilbene derivatives [5, 6], dihydroisocoumarin derivatives [7, 8], lignans [9, 10], neolignans [11], sesquiterpenes [12, 13], triterpenes [14, 15] and flavonoids [1], have been widely used in food as well for medicine [3, 6]. *Scorzonera undulata* ssp. *alexandrina* known in Algeria with the traditional name *"Guiz"*, is used in folk medicine for the treatment of snake bites [16]. The species *Scorzonera undulata* ssp. *deliciosa* has been studied previously and allowed the isolation of triterpenoids, flavonoid, coumarin and phenylethanoid [17]. However, no reports have been found about the chemical constituents from *Scorzonera undulata* ssp. *alexandrina* (Boiss.) Maire.

2. Material and Methods

2.1. Plant material

Scorzonera undulata ssp. *alexandrina* was collected in June 2009 at Aïn Touta of Batna vicinity (Algeria). The plant was identified by Pr. Bachir Oudjehih, Agronomic Institute of the University of Batna, where a voucher specimen, with the identification number 657/LCCE, was preserved.

2.2. Chromatographic and instrument methods

The isolated compounds were established by IR spectra (Shimadzu model IR-470 spectrometer), positive and negative ESI-MS (ion trap Bruker Esquire), EI-MS (Bruker Micromass Q-TOF), optical rotation (Perkin-Elmer model 241 polarimeter) and extensive 1D and 2D NMR analysis (COSY, HSQC, HMBC, NOESY, Bruker Avance Spectrometer, ^{1}H 500 MHz, ^{13}C 125 MHz). CC was conducted on silica gel (Kieselgel 60, 320-400 mesh) and Sephadex LH-20. TLCs were carried on silica gel (Kieselgel 60 F_{254}, Merck) plates.

2.3. Extraction and isolation

1 Kg of powdered plant of *S. undulata* ssp. *alexandrina* was extracted with 5 L of petroleum ether three times for 72 h at room temperature. Filtration and evaporation to dryness gave 16 g of petroleum ether extract. The residue was extracted with ethyl acetate (5 L × 3) at room temperature during 72 h. The solvent was evaporated under reduced pressure to yield 27 g of the EtOAc extract. 6 g of this extract were subjected to silica gel vacuum liquid chromatography (VLC) using a gradient of petroleum ether/ethyl acetate (100:0 to 0:100), then ethyl acetate/methanol (100:0 to 0:100). The fractions presented similarities in their constitution were combined to give 13 fractions (F-1 to F-13). The fraction F-3 was further applied to silica gel column chromatography using petroleum ether/ethyl acetate (100:0, 99:1, 98:2, 96:4) as eluent, to obtain six fractions (F-3-1 to F-3-6). Fraction F-3-5 was subjected to preparative TLC (eluent: chloroform/methanol

99:1), then submitted to purification by a silica gel CC eluting with cyclohexane/dichloromethane (100:0, 99:1, 97:3, 95:5, 90:10, 80:20), leading to lupeol **1** (5 mg) and 24-methylenecycloartanol **2** (4 mg). Fraction F-8 was subjected to silica gel CC eluting with chloroform/methanol (100:0, 99:1, 97:3, 95:5, 93:7, 90:10, 80:20), to give 10 fractions (F-8-1 to F-8-10). Fraction F-8-7 was purified using Sephadex CC and elution with chloroform/methanol (100:0, 99:1, 97:3, 95:5, 93:7), to provide five fractions. Apigenin **5** (9 mg) was obtained from the last fraction after precipitation in chloroform. Fractions F-9 and F-10 were grouped and submitted to Sephadex CC eluting with chloroform/methanol (100:0, 99:1), to afford 7 fractions (A-1 to A-7). Fraction A-4 was precipitated in methanol to provide 3-*O*-(6-*O*-acetyl-β-D-glucopyranosyl) β-sitosterol **3** (6 mg). Fraction F-11 was applied to Sephadex CC eluting with chloroform/methanol (100:0, 97:3, 95:5, 93:7), to give 6 fractions (F-11-1 to F-11-6). Precipitation of the first fraction in methanol yielded 12 mg of daucosterol **4**.

3. Results and Discussion

In continuation of our studies on the secondary metabolites of Algerian medicinal plants, we have isolated five known compounds (Fig. 1.) from *Scorzonera undulata* ssp. *alexandrina* (Boiss.) Maire, namely lupeol **1** [18], 24-methylenecycloartanol **2** [19], 3-*O*-(6-*O*-acetyl-β-D-glucopyranosyl) β-sitosterol **3** [20], daucosterol **4** [21] and apigenin **5** [22]. The structures of these compounds have been elucidated especially on the basis of comparison of their NMR and mass spectra and values of optical rotation with literature data.

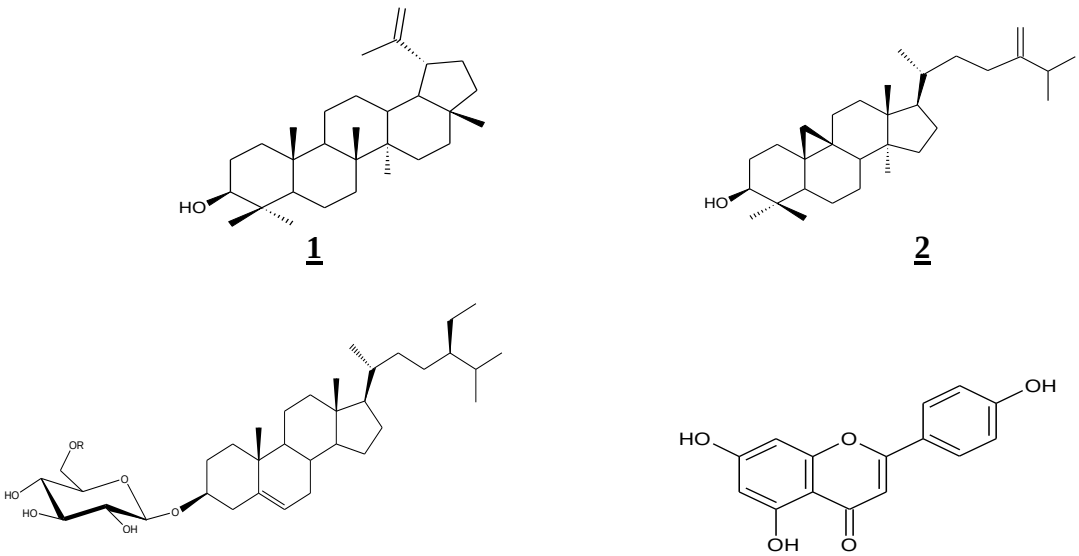
3.1. Compound 2

Compound **2** was isolated as a white powder. EI mass spectrum indicated molecular ion peak at *m/z* 440.4111 $[M]^{+\cdot}$ corresponding to the formula $C_{31}H_{52}O$ which was supported by HR-EI-MS (440.4018). The IR spectrum showed the presence of hydroxyl group at 3396 cm^{-1} and double bond at 1640 cm^{-1}. The ^1H NMR spectrum of **2** exhibited a pair of the particularly high field doublets signals of the cyclopropane ring [19] bearing two non equivalent protons at δ_H 0.38 (1H, *d*, *J* = 4.1 Hz, H-19 *exo*) and 0.60 (1H, *d*, *J* = 4.1 Hz, H-19 *endo*) and a doublet of doublets signal at δ_H 3.33 (1H, *dd*, *J* = 11.2, 4.3 Hz) attributed to oxymethine proton H-3α. The spectrum displayed also seven methyl signals at δ_H 0.95 (3H, *s*, H_3-30), 0.93 (3H, *d*, *J* = 6.2 Hz, H_3-21), 0.86 (3H, *s*, H_3-29), 1.01 (3H, *s*, H_3-28), 1.01 (3H, *s*, H_3-18), 1.07 (3H, *d*, *J* = 6.8 Hz, H_3-27) and 1.08 (3H, *d*, *J* = 6.8 Hz, H_3-26) and an exocyclic methylene group attached to a quaternary carbon C-24 at δ_H 4.76 (1H, *brs*, H-31a) and 4.71 (1H, *brs*, H-31b). The *J*-modulated ^{13}C NMR spectrum (Table I) showed signals including seven methyl, twelve methylene, six methine and six quaternary carbon atoms. A total of 31 carbon resonances were observed, which confirmed its triterpenic nature. COSY, HSQC and HMBC experiments allowed identification of all the protons of this compound and the corresponding carbons. The stereochemistry of **2** was deduced from the NOESY spectrum. Indeed the NOE effects between the protons H_3-28 and H-3α, H-5α and H-6α indicated the equatorial position of methyl Me-28. This spectrum showed also correlations of H-19 *endo*, H-2β and H_3-29 as well as between the protons H-19 *exo* and H-11β and H_3-18 confirming the β-axial position of both methyl Me-29 and Me-18. These spectral data and the value of $[\alpha]_D$ = + 40.2° (*c* = 1.01 g/100 ml) allowed then, unambiguously, the following structure 24-methylenecycloartanol. This compound was previously isolated from numerous *Euphorbia* species [19, 23, 24].

3.2. Compound 3

Compound **3** was also obtained as a white powder. The molecular formula of compound **3** was determined as $C_{37}H_{62}O_7$ (*m/z* 657 $[M+K]^+$, ESI-MS). Its IR spectrum displayed absorption bands at 3424 cm^{-1} (hydroxyl group), 1648 cm^{-1} (double bond) and 1708 cm^{-1} (carbonyl group). The ^1H and ^{13}C NMR data of **3** (Table I) presented similarities with those of daucosterol **4** [21], is isolated previously from *Myrica rubra* [20]. Indeed, the ^1H and ^{13}C NMR and COSY spectra of **3** exhibited signals of six methyl groups at δ_H 0.67 (3H, *s*, H_3-18), 1 (3H, *s*, H_3-19), 0.81 (3H, *d*, *J* = 6.8 Hz, H_3-26), 0.83 (3H, *d*, *J* = 6.8 Hz, H_3-27), 0.87 (3H, *t*, *J* = 7.7 Hz, H_3-29), 0.92 (3H, *d*, *J* = 6.2 Hz, H_3-21) attributed to sitosterol skeleton, sugar moiety at δ_H 3.26 (1H, *t*, *J* = 7.7 Hz, H-2′), 3.30 (1H, *brs*, H-5′), 3.42 (1H, *t*, *J* = 7.6 Hz, H-4′), 3.45 (1H, *t*, *J* = 7.8 Hz, H-3′), 4.25 (1H, *dd*, *J* = 11.7; 4.8 Hz, H-6′b), 4.42 (1H, *d*, *J* = 7.7 Hz, H-1′), 4.51 (1H, *dd*, *J* = 11.7; 2.8 Hz, H-6′a) characteristic of β-D-glucopyranoside and signal of carbonyl at δ_C 171.5. The difference between **3** and **4** was that **3** showed a methyl group with signal of protons at δ_H 2.11 (3H, *s*, H_3-2″), which correlated on the HSQC spectrum with the carbon resonating at 21.5 ppm (C-2″). The deshielded chemical shifts of protons H_2-6′ indicated that glucopyranosyl moiety was substituted at C-6′ by an acetyl group. The oxymethylene protons CH_2O-6′ correlated in the HMBC spectrum with carbonyl carbon at 171.5 ppm confirming this substitution. From these data and the value of $[\alpha]_D$ = –11.9° (*c* = 0.14 g/100 ml), compound **3** was elucidated as 3-*O*-(6-*O*-acetyl-β-D-glucopyranosyl) β-sitosterol. To the best of our knowledge, this compound has been isolated for the first time from *Scorzonera* genus. Compounds **1**, **2** and **3** ($CDCl_3$, 500 MHz) and compound **4** ($CDCl_3$+CD_3OD, 500 MHz). **lupeol 1:** White powder; EI-MS: *m/z* 426 $[M]^{+\cdot}$ for formula $C_{30}H_{50}O$; $[\alpha]_D$ = +26.2° (*c* = 0.83, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.73 (1H, *dd*, *J* = 10.0; 2.5 Hz, H-5), 0.81 (1H, *s*, H-24), 0.84 (1H, *s*, H-28), 0.86 (1H, *s*, H-25), 0.92 (1H, *m*, H-1b), 1 (1H, *s*, H-27), 1.02 (1H, *s*, H-23), 1.06 (1H, *m*, H-2b), 1.06 (1H, *m*, H-15b), 1.07 (1H, *s*, H-26), 1.12 (1H, *m*, H-12b), 1.25 (1H, *m*, H-11b), 1.25 (1H, *m*, H-22b), 1.31 (1H, *m*, H-21b), 1.35 (1H, *m*, H-9), 1.41 (1H, *m*, H-18), 1.43 (1H, *m*, H-7), 1.43 (1H, *m*, H-22a), 1.45 (1H, *m*, H-6b), 1.48 (1H, *m*, H-11a), 1.51 (1H, *m*, H-16), 1.55 (1H, *m*, H-6a), 1.61 (1H, *m*, H-2a), 1.61 (1H, *m*, H-15a), 1.69 (1H, *m*, H-1a), 1.7 (1H, *m*, H-13), 1.72 (1H, *m*, H-12a), 1.72 (1H, *s*, H-30), 1.97 (1H, *m*, H-21a), 2.42 (1H, *td*, *J* =10.0; 5.0 Hz, H-19), 3.35 (1H, *dd*, *J* =12.5; 5.0 Hz, H-3), 4.62 (1H, *d*, *J* = 0.3 Hz, H-29b), 4.75 (1H, *d*, *J* = 0.3 Hz, H-29a). **24-methylenecycloartanol 2:** White powder; EI-MS: *m/z* 440.4111 $[M]^{+\cdot}$ for formula $C_{31}H_{52}O$; $[\alpha]_D$ = +39.9° (*c* = 0.99, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.36 (1H, *sl*, H-19 *exo*), 0.58 (1H, *sl*, H-19 *endo*), 0.83 (1H, *m*, H-6b), 0.84 (1H, *s*, H-29), 0.9 (1H, *d*, H-21), 0.93 (1H, *s*, H-30), 0.99 (1H, *s*, H-28), 1.02 (1H, *s*, H-18), 1.05 (1H, *d*, H-26), 1.05 (1H, *d*, H-27), 1.15 (1H, *m*, H-7a), 1.15 (1H, *m*, H-22b), 1.16 (1H, *m*, H-11b), 1.28 (1H, *m*, H-

1b), 1.31 (1H, *m*, H-15), 1.31 (1H, *m*, H-16b), 1.32 (1H, *m*, H-5), 1.35 (1H, *m*, H-7b), 1.41 (1H, *m*, H-20), 1.53 (1H, *dd*, *J* = 12.6; 4.4 Hz, H-8), 1.58 (1H, *m*, H-2b), 1.59 (1H, *m*, H-1a), 1.59 (1H, *m*, H-22a), 1.60 (1H, *m*, H-6a), 1.62 (1H, *m*, H-17), 1.64 (1H, *m*, H-12), 1.77 (1H, *m*, H-2a), 1.89 (1H, *m*, H23b), 1.93 (1H, *m*, H-16a), 1.99 (1H, *m*, H-11a), 2.13 (1H, *m*, H-23a), 2.24 (1H, *sept*, *J* = 6.9 Hz, H-25), 3.32 (1H, *dd*, *J* = 11.0; 4.1 Hz, H-3), 4.69 (1H, *sl*, H-31b), 4.74 (1H, *sl*, H-31a). **3-O-(6-O-acetyl-β-D-glucopyranosyl) β-sitosterol 3:** Lacquer; ESI-MS: *m/z* 641 $[M+Na]^+$, *m/z* 657 $[M+K]^+$ for formula $C_{37}H_{62}O_7$; $[\alpha]_D = -11.8°$ (*c* = 0.13 $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.67 (1H, *s*, H-18), 0.81 (1H, *d*, *J* = 6.8 Hz, H-26), 0.83 (1H, *d*, *J* = 6.8 Hz, H-27), 0.87 (1H, *t*, *J* = 7.7 Hz, H-29), 0.92 (1H, *d*, *J* = 6 Hz, H-21), 1 (1H, *s*, H-19), 1.02 (1H, *m*, H-9), 1.05 (1H, *m*, H-24), 1.08 (1H, *m*, H-14), 1.11 (1H, *m*, H-22b), 1.16 (1H, *m*, H-1b), 1.17 (1H, *m*, H-15b), 1.19 (1H, *m*, H-23), 1.22 (1H, *m*, H-17), 1.24 (1H, *m*, H-12b), 1.30 (1H, *m*, H-28b), 1.35 (1H, *m*, H 28a), 1.42 (1H, *m*, H-22a), 1.43 (1H, *m*, H-2b), 1.43 (1H, *m*, H-20), 1.52 (1H, *m*, H-8), 1.55 (1H, *m*, H-11b), 1.60 (1H,*m*, H-11a), 1.63 (1H, *m*, H-7b), 1.66 (1H, *m*, H-15a), 1.74 (1H, *m*, H-25), 1.92 (1H, *m*, H-16), 1.93 (1H, *m*, H-1a), 1.98 (1H, *m*, H-2a), 2.03 (1H, *m*, H-7a), 2.11 (1H, *s*, H-2”), 2.17 (1H, *m*, H-12a), 2.36 (1H, *t*, *J* = 10 Hz, H-4b), 2.44 (1H, *dd*, *J* = 15; 5 Hz, H-4a), 3.26 (1H, *t*, *J* = 7.7 Hz, H-2′), 3.30 (1H, *m*, H-5′), 3.42 (1H, *t*, *J* = 7.6 Hz, H-4′), 3.45 (1H, *t*, *J* = 7.8 Hz, H-3′), 3.60 (1H, *m*, H-3), 4.25 (1H, *dd*, *J* = 11.7; 4.8 Hz, H-6′b), 4.42 (1H, *d*, *J* = 7.7 Hz, H-1′), 4.51 (1H, *dd*, *J* = 11.7; 2.8 Hz, H-6′a), 5.37 (1H, *dl*, *J* = 5 Hz, H-6). **daucosterol 4:** White powder; ESI-MS: *m/z* 599 $[M+Na]^+$, *m/z* 575 $[M–H]^-$ for formula $C_{35}H_{60}O_6$; $[\alpha]_D = -43°$ (*c* = 1.9 $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$ + CD_3OD): δ (ppm) = 0.61 (1H, *m*, H 18), 0.75 (1H, *d*, *J* = 6.7 Hz, H-26), 0.76 (1H, *d*, *J* = 6.7 Hz, H-27), 0.80 (1H, *t*, *J* = 7.5 Hz, H-29), 0.85 (1H, *d*, J = 6 Hz, H-21), 0.95 (1H, *m*, H-9), 0.95 (1H, *s*, H-19), 0.98 (1H, *m*, H-24), 1.01 (1H, *m*, H-14), 1.04 (1H, *m*, H-22b), 1.09 (1H, *m*, H-1b), 1.10 (1H, *m*, H-15b), 1.12 (1H, *m*, H-23), 1.15 (1H, *m*, H-17), 1.17 (1H, *m*, H-12b), 1.23 (1H, *m*, H-28b), 1.28 (1H, *m*, H-28a), 1.35 (1H, *m*, H 22a), 1.36 (1H, *m*, H-2b), 1.36 (1H, *m*, H-20), 1.45 (1H, *m*, H-8), 1.48 (1H, *m*, H-11b), 1.53 (1H, *m*, H-11a), 1.56 (1H, *m*, H-7b), 1.59 (1H, *m*, H-15a), 1.67 (1H, *m*, H-25), 1.85 (1H, *m*, H-16), 1.86 (1H, *m*, H-1a), 1.91 (1H, *m*, H-2a), 1.96 (1H, *m*, H-7a), 2.1 (1H, *m*, H-12a), 2.29 (1H, *t*, *J* = 10 Hz, H-4b), 2.37 (1H, *dd*, *J* = 15; 5 Hz, H-4a), 3.19 (1H, *t*, *J* = 7.8 Hz, H-2′), 3.23 (1H, *m*, H-5′), 3.35 (1H, *t*, *J* = 7.7 Hz, H-4′), 3.38 (1H, *t*, *J* = 7.9 Hz, H-3′), 3.53 (1H, *m*, H-3), 3.70 (1H, *dd*, *J* = 11.9; 4.9 Hz, H-6′b), 3.81 (1H, *dd*, *J* = 11.9; 2.9 Hz, H-6′a), 4.35 (1H, *d*, *J* = 7.8 Hz, H-1′), 5.30 (1H, *dl*, *J* = 5 Hz, H-6). **apigenin 5:** Yellow powder; UV ($AlCl_3$+MeOH): λmax (log ε): 341 (0.78), 271 (2.66); ESI-MS: *m/z* 309.1 $[M+K]^+$ for formula $C_{15}H_{10}O_5$; ^1H NMR (500 MHz, CD_3OD): δ (ppm) = 6.21 (1H, *s*, H-6), 6.49 (1H, *s*, H-8), 6.59 (1H, *s*, H-3), 6.90 (1H, *d*, *J* = 8.8 Hz, H-3′), 6.90 (1H, *d*, *J* = 8.8 Hz, H-5′), 7.40 (1H, *d*, *J* = 8.8 Hz, H-2′), 7.40 (1H, *d*, *J* = 8.8 Hz, H-6′).



3 **R** = $COCH_3$
4 **R** = H
5

Fig. 1. Structures of the isolated compounds 1-5

Table 1: ^{13}C NMR data of compounds 1-4

	δ_C			
Position	**1**	**2**	**3**	**4**
1	38.6	31.9	39.5	37.5
2	27.3	30.3	31.8	29.8
3	78.9	78.8	81.3	79.3
4	38.8	40.4	40.3	38.3
5	55.2	47.1	144	140.8
6	18.2	21.1	125	122.3
7	34.2	26	34.1	32.1
8	43	48	34.1	32.2
9	50.3	20	52.4	50.4
10	37.1	26	38.9	36.9
11	20.8	26.4	23.2	21.2
12	25	32.8	42	40
13	38	45.3	44.5	42.5
14	42.7	48.8	59	57
15	27.3	35.5	26.5	24.5
16	35.5	28.1	30.4	28.4
17	42.9	52.2	58.3	56.3
18	48.2	18	14	12
19	47.9	29.9	22	19.4
20	151	36.1	38.3	36.3
21	29.8	18.3	21.2	18.9
22	39.9	34.9	36.1	34.1
23	27.9	31.3	28.3	26.3
24	15.3	156.9	48.1	46.1
25	16.1	33.8	31.3	29.3
26	15.9	21.8	21.1	19.1
27	14.5	22	22.4	19.9
28	17.9	25.4	25.2	23.2
29	109.3	14	15	12.1
30	19.8	19.3	-	-
31	-	105.9	-	-
1′	-	-	105	101.3
2′	-	-	76	73.8
3′	-	-	79.1	76.7
4′	-	-	73.3	70.5
5′	-	-	79	76.1
6′	-	-	65	62
1″	-	-	171.5	-
2″	-	-	21.5	-

Conclusion

This work reports the isolation of one flavonoid aglycone identified as apigenin **5** which was previously isolated from other *Scorzonera* species such as *S. columnae* [25], *S. laciniata* [26] and *S. divaricata* [3] and four triterpenoids like lupeol **1**, 24-methylenecycloartanol **2**, 3-*O*-(6-*O*-acetyl-β-D-glucopyranosyl) β-sitosterol **3** and daucosterol **4**. The compounds **1** and **4** have been previously isolated from some *Scorzonera* species as *S. columnae* [25], *S. hispanica* [11] and *S. aristata* [25]. These compounds have not been found in *Scorzonera undulata* ssp. *deliciosa* [17]. It is interesting to note that triterpenoids **2** and **3** are detected for the first time in *Scorzonera* plants. In our point of view, the results obtained from this investigation are in good agreement with the works done previously on *Scorzonera* species. This study that completes our knowledge of the phytochemical constituents of *Scorzonera undulata* indicates that triterpenoids are the major components of the two ssp. *deliciosa* and *alexandrina*.

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