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Sterols and Triterpenes from *Gundelia tournefortii* L. var Armata

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ABSTRACT

Chemical investigation of the dichloromethane extract of the the edible young stems of Gundelia tournefortii *L. var Armata yielded β-sitosteryl-3β-glucopyranoside-6′-O-fatty acid esters (**1**); mixtures of β-sitosterol (**2a**) and stigmasterol (**2b**) in a 1:2 ratio; phytyl fatty acid esters (**3a**), α-amyrin fatty acid esters (**3b**); lupeol fatty acid esters (**3c**) and β-amyrin fatty acid esters (**3d**) in a 3:2:2:1 ratio; α-amyrin (**4a**) and β-amyrin (**4b**) in a 1:3 ratio; oleic acid (**5a**) and linoleic acid (**5b**) in a 1:2 ratio; and long-chain fatty alcohols (**6**). The structures of **1**-**6** were identified by comparison of their NMR data with literature data.*

Keywords: *Gundelia tournefortii* L. var Armata, Asteraceae, Compositae, β-sitosteryl-3β-glucopyranoside-6′-*O*-fatty acid esters, β-sitosterol, stigmasterol, phytyl fatty acid esters, α-amyrin fatty acid esters, lupeol fatty acid esters, β-amyrin fatty acid esters, α-amyrin, β-amyrin, oleic acid, linoleic acid, long-chain fatty alcohols

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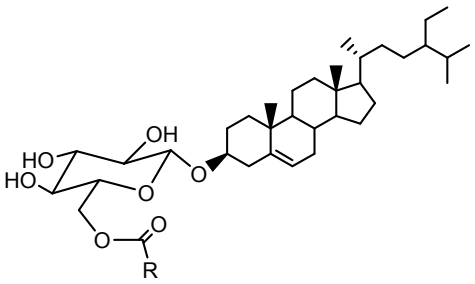
INTRODUCTION

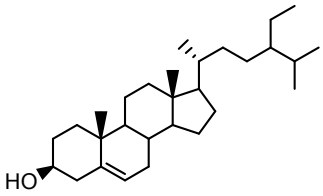
Gundelia tournefortii L., also known as tumble thistle, is found in the semi-desert areas of Lebanon, Syria, Palestine, Israel, Jordan, Iraq, Iran, Azerbaijan, Armenia, and Turkey (Anatolia). The leaves, stems, roots, and undeveloped flower buds of *G. tournefortii* are edible and utilized as a medicinal plant that dates back to more than 2000 years [1]. The plant is traditionally used for the treatment of liver diseases, diabetes, angina pectoris, stroke, gastric ailments, skin diseases, pain, diarrhea and respiratory diseases [2,3,4]. The genus *Gundelia* has been considered monospecific with *Gundelia tournefortii* L. of Irano-Turanian origin in most recent floras with all other names declared as synonymous [4]. *G. tournefortii* L. belongs to the family Asteraceae (Compositae) and is reportedly composed of three varieties, namely: var. *armata* Freyn and Sint., var. *tenuisecta* Boiss. and var. *tournefortii* [5]. The *armata* is the only native variety reportedly present in Iran [6].

Several studies were conducted on the chemical constituents of *G. tournefortii*. Chemical investigation of the aerial parts of plant has led to the isolation of scopoletin, isoscopoletin, esculin, and a mixture of *β*-sitosterol and stigmasterol. The major components of the volatile oil of *G. tournefortii* was determined by GC-MS as α-terpinyl acetate (36.21%), methyl eugenol (12.57%), eugenol (6.7%), *β*.-caryophellene (5.94%), and zingiberene (5.84%)

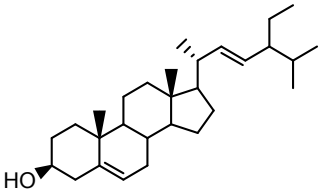
[2]. The oil of the flower buds of *G. tournefortii* yielded linoleic (57.8%), oleic (28.5%), palmitic (8.1%), stearic, vacsenic and arachidic acids. The total sterol of the oil was 3.7666 g/kg which included β-sitosterol (51.76%), stigmasterol (18.52%), 5-avenasterol (9.82%), campesterol (6.02%), 7-stigmastenol (3.68%) and 7-avenasterol (2.63%). The total content of vitamin E was 51.9 mg/100 g with α-tocopherol (48.9 mg/100 g) and γ-tocopherol (1.0 mg/100 g) as the major constituents [7]. Another study reported the isolation of caffeic acid and caffeic acid derivatives, neochlorogenic acid, cryptochlorogenic acid, and chlorogenic acid from *G. tournefortii* [8].



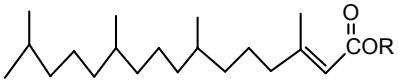
1 R = long-chain fatty acid alkyls



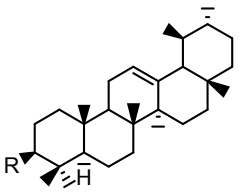
2a



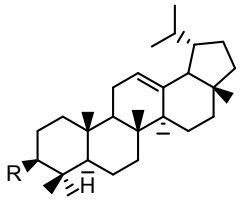
2b



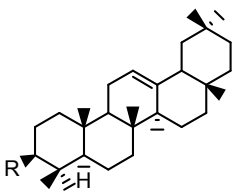
3a R = long-chain fatty acid alkyls



3b R = long-chain fatty acid esters
4a R = OH



3c R = long-chain fatty acid esters



3d R = long-chain fatty acid esters
4b R = OH

Furthermore, the roots of *G. tournefortii* afforded oleanolic acid 3-*O*-(2-[α-L-arabinopyranosyl(1→3)-β-D-gentiotriosyl(1→6)-β-D-glucopyranosyl]gb-D-xylopyranoside), oleanolic acid 3-*O*-(2 -[α-L-arabinopyranosyl]

(1→3)-β-D-gentiobiosyl(1→6)-β-D-glucopyranosyl-β-D-xylopyranoside which possess potent molluscicidal activity against the schistosomiasis transmitting snail *Biomphalaria glabrata [9]*. The essential oil of *G. tournefortii* yielded as major components, palmitic acid (12.48 %), lauric acid (10.59 %), alpha ionene (6.68 %), myristic acid (4.45 %), 1-hexadecanol, 2-methyl (3.61 %), phytol (3.6 %), and beta turmerone (3.4 %) [10]. Moreover, the seed oil content and saponification value of *G. tournifortii* oil were 22.8% and 166.05, respectively. The oil contains oleic (27.99%) and linoleic acid (54.59%), while the main unsaponifiable compounds were β-sitosterol and stigmasterol [11].

In this study, the edible young stems of *G. tournefortii* L. var Armata yielded β-sitosteryl-3β-glucopyranoside-6′-*O*-fatty acid esters (**1**); mixtures of β-sitosterol (**2a**) and stigmasterol (**2b**) in a 1:2 ratio; phytyl fatty acid esters (**3a**), α-amyrin fatty acid esters (**3b**); lupeol fatty acid esters (**3c**) and β-amyrin fatty acid esters (**3d**) in a 3:2:2:1 ratio; α-amyrin (**4a**) and β-amyrin (**4b**) in a 1:3 ratio; oleic acid (**5a**) and linoleic acid (**5b**) in a 1:2 ratio; and long-chain fatty alcohols (**6**). To the best of our knowledge, this is the first report on the isolation of **1**, **3a**-**3d** and **6** from *G. tournefortii*.

MATERIALS AND METHODS

General Experimental Procedure

^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were acquired in $CDCl_3$ on a 500 MHz Agilent DD2 NMR spectrometer with referencing to solvent signals (δ 7.26 and 77.0 ppm). Column chromatography was performed with silica gel 60 (70-230 mesh). Thin layer chromatography was performed with plastic backed plates coated with silica gel F_{254} and the plates were visualized by spraying with vanillin/H_2SO_4 solution followed by warming.

General Isolation Procedure

A glass column 18 inches in height and 1.0 inch internal diameter was packed with silica gel. The crude extracts were fractionated by silica gel chromatography using increasing proportions of acetone in CH_2Cl_2 (10%increment) as eluents. Fifty milliliter fractions were collected. All fractions were monitored by thin layer chromatography. Fractions with spots of the same R_f values were combined and rechromatographed in appropriate solvent systems until TLC pure isolates were obtained. A glass column 12 inches in height and 0.5 inch internal diameter was used for the rechromatography. Two milliliter fractions were collected. Final purifications were conducted using Pasteur pipettes as columns. One milliliter fractions were collected.

Sample Collection

Gundelia tournefortii L. young plants were harvested during early spring on the slopes of the Zagros at elevations 2,000 meters above sea level around Yasuj, capital city of Kohgoluyeh Vah Boyer-ahmad province, Iran. Taxonomic identification was confirmed by comparing the collected voucher specimen with that of known identity in the Iranian Research Institute of Plant Protection, Tehran, Iran, with the guidance of a resident plant taxonomist.

Isolation of the Chemical Constituents of Gundelia tournefortii L.

The freeze-dried stems of *G. tournefortii L. var Armata young plant* (30.7 g) were ground in a blender, soaked in CH_2Cl_2 for 3 days and then filtered. The solvent was evaporated under vacuum to afford a crude extract (0.4394 g) which was chromatographed using increasing proportions of acetone in CH_2Cl_2 at 10% increments by volume. The CH_2Cl_2 and 10% acetone in CH_2Cl_2 fractions were combined and rechromatographed using 2.5% EtOAc in petroleum ether to yield a mixture of **3a-3d** (5 mg) after washing with petroleum ether. The 20% acetone in CH_2Cl_2 fraction was rechromatographed using 20% EtOAc in petroleum ether to afford **6** (3 mg) and a mixture of **4a** and **4b** (3 mg) after washing with petroleum ether. The 30% acetone in CH_2Cl_2 fraction was rechromatographed using CH_3CN:Et_2O:CH_2Cl_2 (1:1:8, v/v) to yield a mixture of **5a** and **5b** (4 mg) and another mixture of **2a** and **2b** (6 mg) after washing with petroleum ether. The 40% acetone in CH_2Cl_2 fraction was rechromatographed using CH_3CN:Et_2O:CH_2Cl_2 (2.5:2.5:5, v/v) to yield **1** (3 mg) after trituration with petroleum ether.

RESULTS AND DISCUSSION

The NMR spectra of **1** are in accordance with data reported in the literature for β-sitosteryl-3β-glucopyranoside-6′-*O*-fatty acid esters [12]; **2a** for β-sitosterol [13]; **2b** for stigmasterol [13]; **3a** for phytyl fatty acid esters [14], **3b** for α-amyrin fatty acid esters [15]; **3c** for lupeol fatty acid esters [16]; **3d** for β-amyrin fatty acid esters [16]; **4a** for α-amyrin [18] and **4b** for β-amyrin [18]; **5a** for oleic acid [19]; **5b** for linoleic acid [20], and long-chain fatty alcohols (**6**) [21].

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