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Chemical Constituents of Three *Launea* and One *Crepis* Species

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Abstract. This article describes the results of phytochemical investigations of three *Launea* and one *Crepis* species, belonging to the tribe *Lactuceae*. The triterpenoids lupeol and taraxasterol were identified from *Launea spinosa*, *L. resedifolia*, and *L. intybacea*, whereas their acetates were identified from *L. intybacea* and *Crepis bulbosa*. The sterols β-sitosterol and stigmasterol were isolated from *L. intybacea* and *C. bulbosa*, while their β-D-glucopyranosides were isolated from *L. spinosa* and *C. bulbosa*. Additionally, *L. spinosa* afforded two coumarin glycosides, aesculin and cichoriin. The isolated compounds were identified on the basis of spectral data.

Introduction

A study of natural products at the family, tribal or generic level is of great interest to chemotaxonomists, even in cases in which the compounds isolated are not highly specific, because it may help to indicate what the chemical pattern is within the taxa under study and thus contribute to a better understanding of the relationships and differences which exist between plants. This article describes the results of phytochemical investigations of three *Launea* and one *Crepis* species, belonging to the tribe *Lactuceae,* which is more familiar as *Cichorieae.* Generally, this tribe is considered as an independent subfamily (*Liguliflorae*) of the family *Compositae*[1]. Its members contain latex, but rarely essential oils[1].

Some medicinal plants of *Cichorieae* are known, for instance *Cichorium intybus* L. is tonic, depurative, diuretic, laxative, chologogue, febrifuge, used for

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digestive troubles and to stimulate bile secretion[2]. *Crepis rueppellii,* a traditional medicinal plant of Yemen was proved to possess hepatoprotective properties[3] as well as heptobiliary properties[4]. Some *Cichorieae* plants are used as green leafy vegetables of good nutritive value[5].

Gonzalez[1] stated that *Cichorieae* has so far been little studied chemically. Common chemical constituents are sesquiterpenes (especially guaianolides), triterpenoids, flavonoids, coumarins and acetylenic compounds, while alkaloids were detected only in eighteen species of *Cichorieae,* but not further identified[1]. From the four species under investigation, only *Launea spinosa* and *L. resedifolia* were studied for flavonoids[6].

Experimental

General

GC/MS spectra were taken on a QP-7000 Shimadzu, with fused silica capillary column (30 m × 0.25 mm ID), film (5% phenyl, 95% methylsilicon) thickness of 0.25 μ, and the output of an IBM computer with software Class 500 and NIST library for comparison; ^{1}H-NMR spectra were recorded on Bruker FT-400 MHz; Merck silica gel with 100-120 mesh was used for CC.

Processing of the plant materials

Launea spinosa (Forssk.)

Air-dried aerial parts (400 g), were collected from Dahab-Sharm ElSheikh road, Sinai, Egypt in April 1987, identified by Dr. I. Mashaly, Botany Department, Faculty of Science, Mansoura, Egypt and directly processed after collection. It was extracted by soaking at room temp. in a mixture of MeOH/ether/pet.ether (1:1:1) for 24 hr. The filtrate was evaporated under vacuum using rotatory evaporator and the residue was defatted by dissolving in least amount of MeOH and leaving in the refrigerator freezer for overnight, followed by quick filtration through a piece of cloth material. The defatted extract, after evaporation, (4.5 g) was separated by silica gel CC. The fractions eluted by pet.ether/ether 3:1 (200 mg), 1:1 (350 mg) afforded a mixture, 2:1 of lupeol **1** and taraxasterol **3.** The fraction eluted with ether (550 mg) contained unsaturated fatty acids. The fraction eluted with ether/MeOH, 9:1 (1.4 g) gave a mixture, 2:3 of coumarin glycosides **5** and **6** as well as β-sitosteryl-β-D-glucopyranoside and stigmasteryl-β-D-glucopyranoside (2:1).

Processing of coumarin fraction

One-half of the coumarin fraction was refluxed with 5% ethanolic HCl for 1 hr. After cooling, the reaction mixture was diluted with water and treated with

NaOH soln. (5%) till basic to litmus, then it was exhaustively extracted with $CHCl_3$ to get rid of fats and sterols. The aqueous basic layer was acidified with HCl and extracted with $CHCl_3$ giving the coumarin solution, which was dried over anhydrous Na_2SO4 and prepared, a sample of which, to ^{1}H-NMR.

Launea resedifolia (L.)

Air-dried aerial parts (280 g), were collected from Dahab-Sharm ElSheikh road, Sinai, Egypt in April 1987, identified by Dr. I. Mashaly, Botany Department, Faculty of Science, Mansoura, Egypt and directly processed after collection. It was extracted by soaking at room temp. in a mixture of MeOH/ether/pet.ether (1:1:1) for 24 hr. The filtrate was evaporated under vacuum using rotatory evaporator and the residue as defatted by dissolving in least amount of MeOH and leaving in the refrigerator freezer for overnight, followed by quick filtration through a piece of cloth material. The defatted extract (2.8 g) was extracted with $CHCl_3$ (180 mg) and then with MeOH (2 g). The $CHCl_3$-extract contained lupeol **1** and taraxasterol **3** (1:1). The MeOH-extract was indicated by ^{1}H-NMR to be a glycosidic material, so that it was acetylated by refluxing with Ac_2O for 30 min. The acetylated material, obtained after evaporating Ac_2O, was fractiona ed with pet.ether (120 mg) then with ether (500 mg) and finally with $CHCl_3$ (620 mg). The pet.ether-extract afforded a mixture, 1:1 of lupeyl acetate **2** and taraxasteryl acetate **4.** The ether and the $CHCl_3$ extracts contained unresolved mixture of sesquiterpene glycosides with C-13 methylene group like picriside A.

Launea intybacea (Jacq.) Beauv.

Air-dried whole-plant (500 g), were collected in March 1998 from the campus of King Abdulaziz University, Jeddah, K.S.A., and identified by Prof. Dr. Abdulaziz Faied, Botany Department, Faculty of Science, King Abdulaziz University. The plant material was extracted and the extract was defatted as described under *L. spinosa.* The defatted extract (4 g) was separated by silica gel CC into five fractions. Fraction I (420 mg, eluted with pet.ether/ether 9:1) afforded a mixture, 1:3 of **2** and **4.** Fraction II (550 mg, eluted with pet.ether/ether 3:1) gave, as fraction I, **2** and **4** (1:3). Fraction III (370 mg, eluted with pet. ether/ether 1:1) afforded a mixture, 1:1 of **1** and **3.** Fraction IV (1.1 g, eluted with ether) gave a mixture, 3:1 of β-sitosterol and stimasterol. Fraction V (800 mg, eluted with ether/MeOH 9:1) contained fatty acids.

Crepis bulbosa (L.) Tausch = *Aetheorhiza bulbosa* (L.) Cass.

The air-dried underground tubers (200 g) were collected from the Mediterranean coastal strip at Baltim, Egypt, in January 1992, identified by Dr. I. Mashaly, Botany Department, Faculty of Science, Mansoura, Egypt and directly

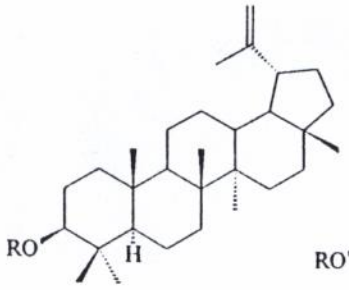
processed after collection. It was extracted by soaking at room temp. in a mixture of MeOH/ether/pet.ether (1:1:1) for 24 hr. The filtrate was evaporated under vacuum using rotatory evaporator and the residue was defatted by dissolving in least amount of MeOH and leaving in the refrigerator freezer for overnight, followed by quick filtration through a piece of cloth material. The tubers comprise about 80% glycolanes (polysaccharides), which are insoluble in organic solvents. The defatted extract (2.5 g) was separated by silica gel CC. The fraction eluted with pet.ether/ether, 3:1 (90 mg) gave a mixture, 2:1 of lupeyl acetate **2** and taraxasteryl acetate **4.** The second fraction (820 mg, eluted with pet.ether/ether 1:1) afforded a mixture, 1:2 of β-sitosterol and stigmasterol. The third fraction (440 mg, eluted with ether) contained a mixture of unsaturated fatty acid glycerides. The forth fraction (610 mg, eluted with ether/ MeOH 9:1) gave a mixture, 1:1 of β-sitosteryl-β-D-glucopyranoside and stigmasteryl-β-D-glucopyranoside.

Results and Discussion

The defatted extracts were separated by silica gel column chromatography and the separated compounds were identified from their ^{1}H-NMR spectra. The proposed structures were confirmed by comparing with authentic ^{1}H-NMR or MS spectra and/or literature spectral data.

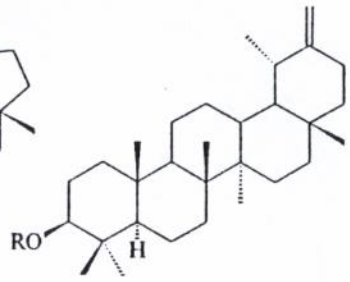
Lupeol **1**[7] and taraxasterol **3**[7] were isolated from *L. spinosa, L. resedifolia* and the aerial parts of *L. intybacea.* Lupeyl acetate **2**[7] and taraxasteryl acetate **4** [7] were isolated from the underground parts of *L. intybacea* and *Crepis bulbosa.* β-sitosterol[7] and stigmasterol[7] were isolated from *L. intybacea* (both aerial and underground parts) and *C. bulbosa.* β-sitosteryl-β-D-glucopyrano-side[8] and stimasteryl-β-glucopyranoside[8] were isolated from *L. spinosa* and *C. bulbosa.*

The two coumarins **5** and **6** (separated from *L. spinosa*) gave the characteristic ^{1}H-NMR signals of H-3, H-4 [at δ 6.10 d (9.5 Hz), δ 7.53 d (9.5 Hz) for **5** and at δ 6.20 d (9.5 Hz), δ 7.56 d (9.5 Hz) for **6**] and those of H-5, H-8 (at δ 6.79 br s, δ 6.71 br s for **5** and at δ 7.02 br s, δ 6.88 br s for **6**). The anomeric proton of the glucose moiety appeared at δ 4.19 as a doublet with coupling of 8 Hz in the spectrum of **5** and at δ 4.77 as a doublet with coupling of 7 Hz in the spectrum of **6.** The rest of the sugar protons absorbed from δ 3.9 to δ 3.1 ppm. These data were found by comparison to be in good agreement with aesculetin-6-glucoside **5,** known as aesculin[9] and aesculetin-7-glucoside **6,** known as cichoriin[9,10]. Acid-hydrolysis, followed by extraction of coumarins (*c.f.* experimental) afforded aesculetin which gave ^{1}H-NMR spectrum in agreement with the literature data[11]. Coumarins are interesting chemotaxonomic markers, which have been reported in fifty-five species from *Compositae* including thirty five from *Cichorieae*[11].



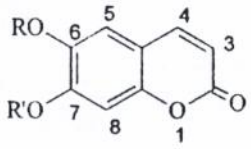
1; R= H

2; R= Ac



3; R= H

4; R= Ac



5; R= gluc, R'= H

6; R= H, R'= gluc

For chemotaxonomic purposes, the identified constituents were placed together in Table 1.

TABLE 1. Chemical constituents of *Launea spinosa, L. resedifolia, L. intybacea* and *Crepis bulbosa.*

Constituent	*L. spinosa*	*L. resedifolia*	*L. intybaceae*	*C. bulbosa*
Lupeol	+	+	+	–
Lupeyl acetate	–	–	+	+
Taraxasterol	+	+	+	–
Taraxasteryl acetate	–	–	+	+
Stigmasterol	–	–	+	+
β-Sitosterol	–	–	+	+
β-Sitosteryl-β-D-glucopyranoside	+	–	–	+
Stigmasteryl-β-D-glucopyranoside	+	–	–	+
Aesculetin	+	–	–	–
Cichoriin	+	–	–	–

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