FLAVONOIDS FROM *LACTUCA QUERCINA* AND *L. TATARICA*

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ABSTRACT

From aerial parts of *Lactuca quercina* L. and *Lactuca tatarica* C. A. Meyer six flavonoids were isolated using different chromatographic techniques. Of these, three compounds, apigenin, luteolin and quercetin-3-O- β -glucopyranoside, were found in both species, two compounds, apigenin-7-O- β -glucopyranoside and kaempferol-3-O- β -glucopyranoside, originated from the latter, and one compound, luteolin-7-O- β -glucopyranoside, from the former.

KEY WORDS: *Lactuca quercina*, *Lactuca tatarica*, Asteraceae, Lactuceae, flavonoid compounds, flavones, flavonols, glycosides.

INTRODUCTION

Wild *Lactuca* species (Asteraceae, tribe Lactuceae), e.g. *L. virosa* L. and *L. saligna* L. are being used in breeding programs for the introduction of virus resistance into commercial lettuce (*L. sativa* L.) (Tamaki et al. 1995). We have recently studied sesquiterpene lactone compositions in roots of the two above mentioned species (Kisiel and Barszcz 1997, Kisiel and Gromek 1993), as well as in *L. quercina* L. (Kisiel and Szneler 1998) and *L. tatarica* C. A. Meyer (Kisiel et al. 1997). We have also observed that aerial parts of *L. quercina* and *L. tatarica* contain no sesquiterpene lactones but flavonoids as characteristic secondary metabolites. The compounds are important constituents of the human diet that are found in fruits and vegetables. They exhibit antioxidant and free-radical scavenging activities, and currently are of particular interest as protective agents against cardiovascular disease and cancer (Robak and Gryglewski 1996). The purpose of the present study was to characterize the flavonoid compositions in both species and to compare them with that reported for *L. sativa* (Ferrerres et al. 1997).

MATERIAL AND METHODS

Plant material

Aerial parts of *L. tatarica* were collected in July 1994 from plants at the flowering stage. Aerial parts (=leaves) of *L. quercina* were collected in September 1995 from plants in the first year of vegetation. The plants were cultivated in the Garden of Medicinal Plants of the Institute of Pharmacology, Polish Academy of Sciences, in Kraków.

Extraction and isolation of flavonoid compounds 1-6

Fresh aerial parts of *L. quercina* (225 g) and *L. tatarica* (401 g) cut into small pieces were exhaustively extracted with ethanol at room temperature with shaking and the solvents were evaporated under reduced pressure to give 15.0 g and 28.8 g of residues, respectively. In each case, the residue was chromatographed on a silica gel (Merck, Art. 7754) column using hexane-ethyl acetate (up to 100% ethyl acetate), followed by ethyl acetate-methanol (up to 20% methanol) gradient solvent systems. Less polar fractions eluted with hexane-ethyl acetate (1:1) and more polar fractions eluted with ethyl acetate and ethyl acetate-methanol (97:3, 95:5) mixtures containing flavonoid aglycones and glycosides, respectively, were further separated and purified by preparative TLC (Merck, Art. 5553) and PC (Whatman 3MM), as described below.

L. quercina

The less polar fractions afforded **1** (2.3 mg) and **2** (28.7 mg), after separation by preparative TLC (chloroform-methanol, 9:1). The more polar fractions were subjected to preparative TLC (chloroform-methanol, 7:3) to give a crude mixture of **4** and **6** (619 mg), a portion of which was processed by preparative PC (15% acetic acid) yielding **4** (13.6 mg) and **6** (10.5 mg).

L. tatarica

Similar separation procedures were used. The less polar fractions afforded after precipitation a mixture (212 mg) of two compounds, a portion of which was subjected to preparative TLC giving **1** (14.0 mg) and **2** (11.0 mg). The more polar fractions were combined according to their contents and were further separated by preparative TLC (chloroform-meth-

anol, 8:2 or 7:3) to yield **5** (9.0 mg), a mixture of **3** and **5**, and **6** (16.0 mg). Preparative PC (15% acetic acid) of the mixture allowed isolation of additional amounts of **5** (40.2 mg) and **3** (21.8 mg).

Identification of flavonoid compounds 1-6

The isolated flavonoids were identified by comparison of their spectral data (500.13 MHz ^1H NMR, EIMS or ESIMS) with those reported in the literature (Markham and Geiger 1996) and by co-chromatography with standard samples.

RESULTS AND DISCUSSION

The ethanol extracts of the fresh aerial parts of *L. quercina* and *L. tatarica* were separately chromatographed on silica gel columns to give fractions which contained flavonoid compounds. The fractions, after further separation and purification by preparative TLC and PC, yielded a total of six compounds (Fig. 1), of which three were common to both species. They were identified as apigenin (**1**), luteolin (**2**) and quercetin-3-O- β -glucopyranoside (isoquercitrin) (**6**). The remaining three compounds were characterized as luteolin-7-O- β -glucopyranoside (**4**), originating from *L. quercina*, and apigenin-7-O- β -glucopyranoside (cosmosiin) (**3**) and kaempferol-3-O- β -glucopyranoside (astragalin) (**5**), originating from *L. tatarica*. The compounds belonging to the flavone (**1-4**) and flavonol (**5** and **6**) classes of flavonoids are known plant constituents. They were isolated from the above mentioned plant species for the first time.

Fig. 1. Chemical structures of flavonoids (Glc = O- β -glucopyranosyl) isolated from *Lactuca quercina*: compounds **1**, **2**, **4**, **6** and *Lactuca tatarica*: compounds **1**, **2**, **3**, **5**, **6**.

Up to now, only quercetin-3-O- β -glucopyranoside (**6**) along with three other quercetin glycosides and no free aglycone have been reported from leaves of commercially grown lettuce (*L. sativa*) (Ferrerres et al. 1997). Varietal differences in the content of quercetin estimated after hydrolysis of its glycosides in the lettuce extracts have also been studied (Crozier et al. 1997 and references cited herein).

The results indicate that flavonoid compositions of *L. quercina* and *L. tatarica* differ from that reported for *L. sativa*.

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FLAWONOIDY *LACTUCA QUERCINA* I *LACTUCA TATARICA*

STRESZCZENIE

Z nadziemnych części *Lactuca quercina* L. i *Lactuca tatarica* C.A. Meyer wyodrębniono sześć flawonoidów, stosując różne techniki chromatograficzne. Trzy związki występujące w obydwu gatunkach zidentyfikowano jako apigeninę, luteolinę i 3-O- β -glukopiranozyd kwercetyny. Ponadto scharakteryzowano 7-O- β -glukopiranozyd luteoliny występujący w *Lactuca quercina* i dwa związki, 7-O- β -glukopiranozyd apigeniny i 3-O- β -glukopiranozyd kemferolu, wyodrębnione z *Lactuca tatarica*.

SŁOWA KLUCZOWE: *Lactuca quercina*, *Lactuca tatarica*, Asteraceae, Lactuceae, związki flawonoidowe, flawony, flawonole, glikozydy.