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THE FATTY ACIDS FROM PLANTS OF THE GENUS *ACHILLEA*

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Abstract. *The content and composition of fatty acids of three species of* Achillea *L.:* A. lingulata *W. et K.,* A. nobilis *L. and* A. crithmifolia *W. et K. have been analyzed by GC. It was found that unsaturated acids were prevailing compounds (average U/S was 1.6) and the major components are: palmitic, linoleic and linolenic acids. The ratio of linolenic and linoleic acid were:* A. lingulata *1.1,* A. nobilis *0.8 and* A. crithmifolia *0.2.*

Key words: Achillea*, fatty acids, palmitic, linoleic and linolenic acids.*

1. INTRODUCTION

The Genus *Achillea* L. includes about 100 species, spread mostly across the Euro-Asian Continent (the moderate climate zone). In Serbia there are 19 species [1]. They have been used in traditional medicine for centuries. Chemical studies of these species have been concerned with essential oils [2-8], sesquiterpenes [9-11], alkamides [12], flavonoids [13] and alkanes [14].

The present paper reports the content and composition of fatty acids of three species of the *Achillea* genus: *A. lingulata*, *A. nobilis* and *A. crithmifolia* (subcarpathian, subpontiac and Pannonia-balkanic element of flora, respectively) because the value of fatty acid patterns is becoming increasingly apparent in deducing systematic relationships among plants [15].

2. EXPERIMENTAL

Plant material. Plant material was collected in the blooming phase of vegetation. *A. crithmifolia* was collected near Niš (location Selicevica), *A. lingulata* near Vranje (location Besna kobila) and *A. nobilis* near Niš (location Kovanlučka Čuka Oblačina), all in Serbia. Specimens were deposited in Herbarium Moesicum Doljevac [HMD]. Leaves, flowers and green parts of stems were air-dried for ten days at room temperature and kept in a cold and dark place until extracted.

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Extraction. The dried plant material (100 g) was extracted with 500 mL $CHCl_3$-MeOH (2 : 1) at room temperature for 24 hours. After separation of solvent, the residue was extracted three times more in the same way. The extracts were combined and evaporated under reduced pressure till a constant weight was achieved. The remain solid phase of *A. crithmifolia* was 11.4 g, *A. lingulata* 7.3 g and *A. nobilis* 11.0 g, respectively.

Saponification. Extracts were refluxed with tenfold amount of 12% ethanolic solution of NaOH for 2 hours on the steam bath. Water (50 mL) was added to the reaction mixture and cooled to room temperature. The part of the extract, which failed to react, was separated by extraction with petroleum. The water-ethanolic solution of soaps was acidified with HCl (1:1) to pH 5-6 and extracted four times with petroleum. The combined organic phases were washed with a 10% sodium chloride solution. The evaporation of the solvent under reduced pressure afforded 1.1 g, 0.5 g and 0.6 g of fatty acids for *A. crithmifolia*, *A. lingulata* and *A. nobilis*, respectively.

Esterification. The fatty acids were esterifed by handredfold amount of 1% methanolic solution of H_2SO_4 on the steam bath for 1.5 hours. The reaction mixture was evaporated under reduced pressure. Water (50 mL) was added to the residue and reaction mixture was extracted three times with petroleum. The combined petroleum extracts were washed two times with 2% $NaHCO_3$ solution, than with water till pH 7 was achieved. The organic phase was dried over anhydrous sodium sulfate and concentrated to 5 mL under reduced pressure.

Identification. The methyl esters of fatty acids analyzed on a Varian model 3700 Gas Chromatograph, equipped with a 60 m × 0.25 mm capillary column, with a 0.25 μm film thickness of Supelcowax 10 and FID was used for GC measurements. The operating conditions were: oven temperature program 200-230°C at 2°C/min.; an injector temperature of 250°C; detector temperature of 300°C; carrier gas was H_2 (2 mL/min.).

The identification of compounds was carried out by coinjection of an authentic compounds and retention times. Area percent was obtained electronically from the GC-FID response without the use of internal standard or correction factors.

3. RESULTS AND DISCUSSION

Fatty acids composition of total lipids in aerial parts of *A. crithmifolia, A. lingulata* and *A. nobilis* is presented in Table 1.

Table 1. The fatty acids composition (%) of *A. lingulata, A. nobilis* and *A. crithmifolia*

Acid	*A. lingulata*	*A. nobilis*	*A. crithmifolia*
Miristic	4.8	2.2	2.5
Palmitic	28.4	26.1	30.9
Stearic	2.9	3.7	2.9
Oleic	6.6	6.3	15.4
Linoleic	24.3	21.6	41.3
Linolenic	25.9	16.8	7.4
U/S*	1.6	1.4	1.8
Linolenic/ Linoleic	1.1	0.8	0.2

*U/S - unsaturated/saturated

The palmitic acid was the most abundant in *A. lingulata* (28.4 %) and *A. nobilis* (26.1%). For *A. crithmifolia* it was linoleic acid (41.3%). The ratio of unsaturated and saturated fatty acids (U/S) was: *A. crithmifolia* 1.8, *A. lingulata* 1.6 and *A. nobilis* 1.4. The average U/S value was 1.6 which is similar to those reported for *Micromeria* [16] and *Satureja* [17] genus (2.4 and 1.5, respectively). The U/S index for nutlet lipids of previous examined genus ranged from 10.0 to 22.8 for genus *Satureja* L.; from 11.7 to 19.4 for genus *Micromeria* Bentham; from 8.4 to 14.4 for genus *Acinos* Miller and from 6.1 to 15.1 for genus *Mentha* L. [18]. As it can be seen, U/S index of aerial plant material was significantly smaller than in nutlet lipids.

The linolenate/linoleate ratio was: 0.2, 1.1 and 0.8 for *A. crithmifolia A. lingulata* and *A. nobilis*, respectively. These values are lower than those reported for *Micromeria* [16] and *Satureja* [17] genus (2.6-3.0 and 2.0-2.4, respectively). The average ratio linolenate/linoleate for nutlet lipids for genus *Satureja* was 4.4; for genus *Micromeria* Bentham 3.4; for *Acinos* Miller 3.9; for genus *Mentha* L 1.6 [18]. The difference between the linolenate/linoleate ratio in nutlet lipids and aerial parts of plant are not so great as for U/S ratio.

The saturated fatty acid composition of examined species showed low intraspecific variability while it was significant in unsaturated fatty acid composition.

The results suggest that U/S ratio of aerial plant material can be used as a taxonomic marker as well as this parameters for nutlet lipids, but the ratio linolenate/linoleate of aerial plant material was in wide range (0.2-1.1) thus is reducing its importance as a possible taxonomic marker.

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MASNE KISELINE IZ BILJAKA RODA *ACHILLEA*

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Određen je sastav masnih kiselina iz nadzemnog dela biljaka roda Achillea L.: A. lingulata, A. nobilis i A. crithmifolia gasnom hromatografijom. Palmitinska kiselina je najzastupljenija kod A. lingulata (28.4%) i A. nobilis (26.1%). Linolna kiselina je dominantna kod A. crithmifolia (41.3%). Odnos nezasićenih i zasićenih kiselina (U/S) je: 1,6 (A. lingulata), 1,4 (A. nobilis) i 1,8 (A. crithmifolia). Odnos linolenske i linolne kiseline je: 1,1 (A. lingulata), 0,8 (A. nobilis) i 0,2 (A. crithmifolia).