HPLC-MS ANALYSIS OF FLAVONOIDS OBTAINED FROM *SOLIDAGO* SP. (ASTERACEAE)

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Abstract

The goal of our study was to differentiate among the medicinal species of Solidago virgaurea L., from the ornamental species of S. canadensis Ait. and S. gigantea L. using HPLC-MS of the flavonoid content. HPLC qualitative and quantitative analysis allowed us a detaliled determination of the flavonoid compounds. For each analized species the number and identity of separate fractions were confirmed through MS.Through HPLC analysis we observed that each species of Solidago is characterized by a main flavonoid: rutoside for S. virgaurea and S. canadensis and quercitrine for S. gigantea. Other flavonisids present in various ratios are, hiperozide and isoquercitrine, whereas for S. canadensis free quercetol is identified.

Key words: *Solidago species*, *Flavonoids, HPLC-MS*

INTRODUCTION

The studied species *Solidago virgaurea* L. is spontaneously growing allower in our country, at plain or in the mountains, next to the rivers, in the bushes, or forests, whereas Solidago gigantea Ait. and Solidago canadensis were introduced in Europe as ornamental flowers and later became almost spontaneous (Tămaş M., 1999).

Solidago virgaurea L. (golden-rod) is known since ancient times, and it's product Virgaureae herba, has diuretic, natriuretic, antiinflammatory and antispastic actions (Dobjanschi L., 2006). Recently new actions were described for this species, namely, antitumoral, antimicrobial, sedative and hypotensive actions (Dobjanschi L., 2006).

Phytotherapy also mentiones, *Solidaginis giganteae* herba (early golden-rod herb) as a product known for it's diuretic and natriuretic properties, but the presence of some saponnins with high hemolytic index (above 20.000) has a negative impact on it's use, as is the case with *S. canadensis* sp. There is a tendency to replace the well known *S. virgaurea* sp. with the other two species which are more accessible for harvesting. That is why it is necessary to have some well established phytochemical criteria to identify the two species and recognize their pharmacological properties. Our purpose was to differentiate among the medicinal species of *S. virgaurea* and *S. canadensis* and *S. gigantea*, analysing their content in flavonids, using HPLC-SM.

MATERIAL AND METHODS

We studied the upper part of the local species of *Solidago* sp. harvested from the garden of the Botanic Pharmaceutical Department of the University of Pharmacy in Cluj-Napoca, Romania.

For analysis of flavonoid content we used the HPLC method published in the speciality literature, which was modified according to references mentioned bellow (Vlase L. et all; Fodorea Cristina-Ştefania et all.,2003, 2005). The HPLC technique allowed us to perform a detailed qualitative and quantitative analysis of the flavonoid components. For each analized species the number of separated fractions was identified and some of their identities was confirmed with MS (Vlase L. et all; Fodorea Cristina-Ştefania et all.,2003, 2005).

HPLC Equipment:

HPLC system coupled with mass spectrometry, and equipped with: HP 1100 Series binary pump, Autosampler HP 1100 Series, HP Termostat 1100 Series, UV Detector HP 1100 Series and Mass Spectometer Agilent Ion Trap 1100 VL.

RESULTS AND DISCUSSIONS

HPLC analysis revealed that each species of *Solidago* plant has a main, characteristic flavonoid: rutozide for *S. virgaurea* and *S. Canadensis* and quercitrine for *S. gigantea*. Other flavonoids present in different ratios, are hiperozide and isoquercitrine, whereas for *S. canadensis* free quercetole is also identified.

The HPLC chromatogram and the components identified in the extract of *Solidago virgaurea* are shown in Figure 1 and Table 1.

The HPLC chromatogram and the components identified in the extract of *Solidago virgaurea* are shown in Figure 2 and Table 2

The HPLC chromatogram and the components identified in the extract of *Solidago canadensis* are shown in Figure 3 and Table 3.

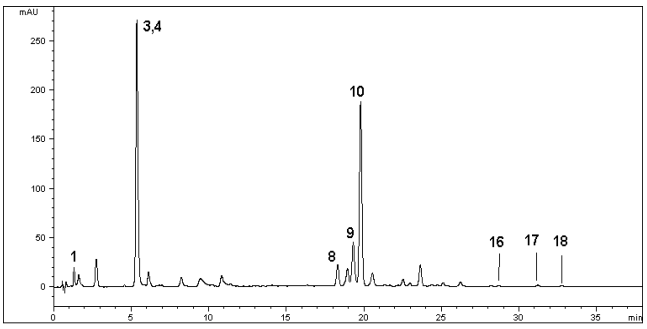

Fig. 1. HPLC chromatogram of unhydrolized *Solidago virgaurea* extract identified by UV. Numbering of components is according to Table 1.

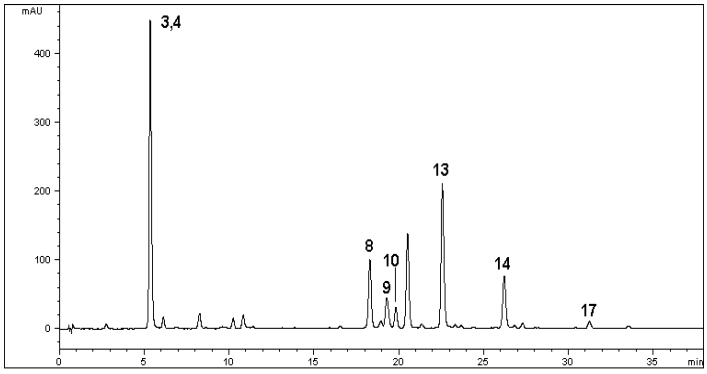

Figure 2. Chromatogram of *Solidago gigantea* extract, unhidrolized by UV. Numbering of components, according to Table 2.

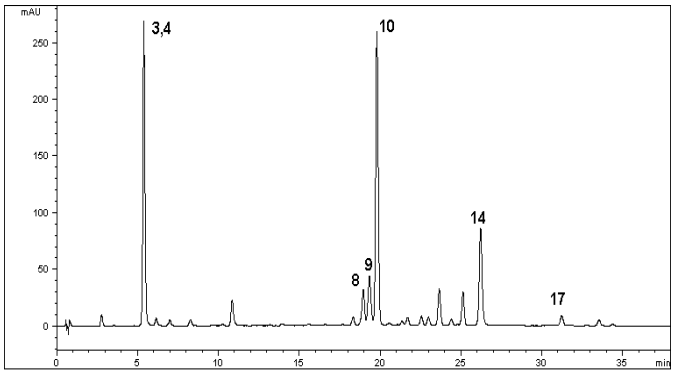

Figure 3. Chromatogram of Solidago canadensis extract, unhydrolized by UV. Numbering of components, according to Table 3.

Table 1

Poliphenols identified in the extract of unhydrolized *Solidago virgaurea*

Components	**No.**	**Identified by UV**	**Confirmed by MS**	**Extract concentration (µg/ml)**
Caftaric acid	1	NO	YES	-
Cafeic acid	3	NO	YES	-
Clorogenic acid	4	NO	YES	-
Hyperozide	8	YES	YES	24.160
Isoquercitrine	9	YES	YES	69.100
Rutozide	10	YES	YES	291.300
Luteoline	16	YES	YES	0.800
Kaempferol	17	YES	YES	1.450
Apigenine	18	YES	YES	1.230

Table 2

Poliphenols identified in the extract of unhydrolized *Solidago gigantea*

Components	**No.**	**Identified by UV**	**Confirmed by MS**	**Concentration in extract (µg/ml)**
Gentisic acid	2	NO	YES	-
Cafeic acid	3	NO	YES	-
Clorogenic acid	4	NO	YES	-
Hyperozide	8	YES	YES	120.000
Isoquercitrine	9	YES	YES	82.490
Rutozide	10	YES	YES	45.540
Quercitrine	13	YES	YES	450.560
Kaempferol	17	YES	YES	8.520

Table 3

Poliphenols identified in the extract of unhydrolized Solidago canadensis

Component	No.	Identified by UV	Confirmed by SM	Concentration in extract (µg/ml)
Gentisic acid	2	NO	YES	-
Cafeic acid	3	NO	YES	-
Chlorogenic acid	4	NO	YES	-
Hyperozide	8	YES	YES	7.704
Isoquercitrine	9	YES	YES	67.754
Rutozide	10	YES	YES	400.890
Quercetol	14	YES	YES	60.250
Kaempferol	17	YES	YES	7.626

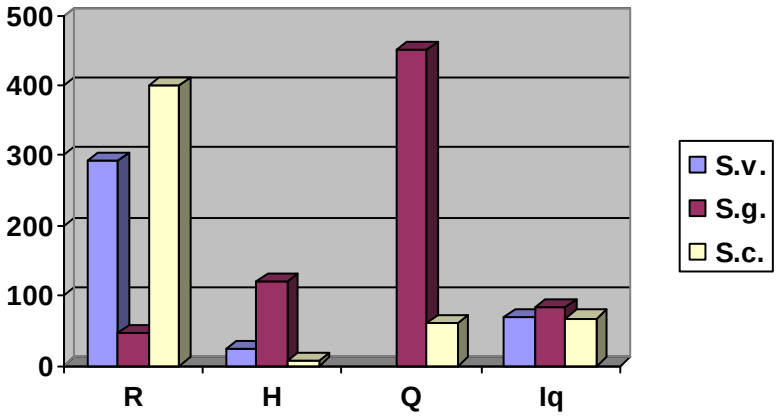

Figure 5. Content in flavonoidic components for the 3 species of Solidago, from the unhydrolized extract(R-rutoside, H-hyperozide, Q-quercitrine, Iq-isoquercitrine)

CONCLUSIONS

HPLC and mass spectrometry of the extracts obtained from the Solidago species we draw the following results:

- In the *Solidago virgaurea* extract, the major flavonoidic component is rutozide (291,3 μg/ml) followed by isoquercitrine (69,1 μg/ml) and hiperozide (24,16 μg/ml).
- In the extract of *Solidago gigantea* flavonoidic hetherozides are represented by quercitrine as the major percetage (450,56 μg/ml) followed by hiperozide (120,0 μg/ml), izoquercitrine (82,49 μg/ml) and rutozide (45,54 μg/ml).
- In the extract of *Solidago canadensis* the major hetherozide flavonoidic component is rutozide (400,89 μg/ml) followed by isoquercitrine (67,75 μg/ml) and hiperozide (7,7 μg/ml) (fig.5).

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