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FLAVONOID DYES DETECTED IN HISTORICAL TEXTILES FROM ROMANIAN COLLECTIONS

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Abstract

Romanian museum collections preserve a large number of textiles which reflect the history, the geographical location - at the junction of the major trade routes transiting the Far East luxury products to Europe - and the coexistence of Romanians with other ethnic groups. A research project aiming to enrich the existing information on these textiles by dye analysis started in 1997. The first were made by liquid chromatography with diode-array detection (LC-PDA), within a joint research project between Romanian institutions and the Royal Institute for Cultural Heritage in Brussels, Belgium. Starting in 2007, an analytical protocol based on liquid chromatography with in line diode-array and (ion trap) mass spectrometric detection (LC-PDA-MS) was developed for the first time in Romania. This procedure is based on data collected on standard dyes and dyed fibres and on the progressive use of the (ion trap) mass spectrometer modes, from single stage MS to product ion scan.

The present work is an overview of the flavonoid dye sources identified in textiles from Romanian collections since 1997, with a special emphasis on their detection through the new developed analytical procedure. *Reseda luteola* L. (weld), *Genista tinctoria* L. (dyer's broom), *Serratula tinctoria* L. (sawwort), *Cotinus coggygria* Scop. (young fustic), *Rhamnus* berries (buckthorn berries), *Delphinium semibarbatum* B. (isparak) and *Datisca cannabina* L. (bastard hemp) are the flavonoid dye sources detected in various 15th-20th c. textiles preserved in Romanian collections: religious embroideries, brocaded velvets, kilim, sumak and knotted carpets from Minor Asia, Romanian ethnographical textiles.

The article proves the high capacity of the LC-PDA-MS procedure developed in the identification of the flavonoid dye sources in ancient textiles and the contribution this knowledge is bringing to better understanding the historic context in which the respective textiles have been created.

1 Introduction

Flavonoid dyes contribute to the yellow color of flowers and are important sources of dyes and pigments. They may be found in plants all over the world, in a large variety of combinations, some of them being known and used in Europe and worldwide since prehistoric times[1,2].

Reseda luteola L. (weld), maybe the oldest and most widely used flavonoid dye source, was known by the African tribes still in the Neolithic period[1], was cultivated in the Mediteranean area in the Hellenistic time and in the Roman Empire, was used by Egyptians in Coptic textiles and was mentioned in dyeing regulations during the Middle Ages[2]. This information was confirmed by dye analysis, as weld was detected in Coptic textiles from the 3rd-10th centuries[3,4], in the Hungarian Coronation Mantle (11th c.)[5], as well as in later objects.

Cotinus coggygria Scop. (young fustic), another flavonoid dye source, was appreciated for its orange hue and the large quantity of colorant that may be

obtained from each felled tree[2]. In the 11th c., it was known by Persians as "yellow wood", as mentioned by a Persian manuscript[1] and in European medieval documents as "young fustic" or "Venice sumac"[1]. It played an important economic role in European dyeing until the 19th c.[2] It was also an important source of tannin.

Genista tinctoria L. (dyer's broom) and *Serratula tinctoria* L. (sawwort) were mentioned in recipes dating from the Middle Ages. Dyer's broom has been known and used in England, as attested by the large quantities of stems found during archaeological discoveries[2]. In the 19th c., it was also known and used in Eastern Europe. In a collection of dyeing recipes written in Romania, in 1914, based on the information acquired from local peasants, dyer's broom was mentioned in 80% of the recipes[6]. The popularity of this local plant was recently confirmed by analytical results on dyes in 19th-20th c. Romanian ethnographical textiles[7].

Rhamnus (buckthorn) berries (also called Persian, Avignon, or Hungarian berries) were mentioned in German manuals during the Middle Ages[1] for being used in textiles dyeing and lakes preparation. *Rhamnus infectoria* L. was indigenous to the Near East and was used in Rome at the beginning of the Christian era[8].

Delphinium semibarbatum B. (isparak) was one of the main sources of yellow in Central Asia before synthetic dyes became used in that part of the world[1]. It grows in Iran, Afghanistan and the north of India and was detected in 19th century ikats from Central Asia[9].

Datisca cannabina L. (bastard hemp) is originally from western Asia, Cyprus and Crete and was cultivated in India, Italy and from the beginning of the 19th century in the south of France[2]. It was used as a dye source in northern India and northern Caucasus[2]. It was also used by Turkish dyers in Western Anatolia and was identified in carpets and kilims from that area[2]. It was also identified in 16th-17th century velvets in a dyeing combination with *Cotinus coggygria* Scop. (young fustic)[10]. *Sophora japonica* L. (pagoda tree) was mentioned to produce a useful yellow colour in ancient China[2], which is confirmed by dye analysis1[1].

Identification of flavonoid dye sources in ancient textiles has always kept the attention of scientists, the methods used evolving together with the development of new analytical techniques. The first systematic approach was made by Hofenk de Graaff and Roelofs in 1978, by using thin layer chromatography[12]. Some years later, Wouters introduced high-performance liquid chromatography and diode array detection (LC-PDA) in natural dyes characterization and identification[13] and, in the next years, successfully detected various flavonoid dyes in a large variety of textiles, from all over the world[3,9,11,14,15]. Since late 1990's, when modern analytical methods became available, natural yellow dyes, and their breakdown products, have been further characterized based on mass spectrometric data, used complementary to the UV-Vis spectral information. A collection of un-aged and artificially aged laboratory dyed fibers, manufactured by using natural dye sources and following traditional recipes was used for this approach[16-21]. Liquid chromatography with in line UV-Vis and mass spectrometric detection (LC-PDA-MS) was then proved as a useful configuration for natural dyes identification19,[21-28]. Due to the increased chromatographic results that may be achieved, ultrahigh pressure liquid chromatography is now recommended as a very promising technique[29].

In the last (about 10) years, research studies on the identification of flavonoid dye sources were directed towards the development of mild extraction procedures as alternatives to the "traditional" acid hydrolysis[30]. This comes from a need to identify the glycosides, which cannot be detected after strong acid extraction, as they decompose in their parent aglycons. However, glycosides detection may be a decisive argument in the identification of biological sources containing the same aglycon but different glycosides, as for example the case of *Sophora japonica* L. (pagoda tree) and *Allium cepa* (onion skins)[30].

Romanian museum collections preserve a large number of textiles which reflect the history, the geographical location (at the junction of the major trade routes transiting the Far East, India and Central Asia luxury products to Europe) and the coexistence of Romanians with other ethnical groups. A research project aiming to enrich the existing information on these textiles by dye analysis started in 1997. The first studies (which include about 350 analysis) were made by liquid chromatography with diode-array detection (LC-PDA), within a joint research project between Romanian institutions and the Royal Institute for Cultural Heritage in Brussels, Belgium[7]. Starting in 2007, an analytical protocol based on liquid chromatography with in line diode-array and (ion trap) mass spectrometric detection (LC-PDA-MS) was developed for the first time in Romania[31]. The present work discusses the flavonoid dye sources identified in textiles from Romanian collections since 1997, with a special emphasis on their detection through the recently developed analytical protocol, based on dyes identification through the progressive use of the ion trap mass spectrometer. The paper comes as a continuation of a previous one entitled "*A discussion on the Red Anthraquinone Dyes Detected in Historic Textiles from Romanian Collections*", also published in e-Preservation Science (e-PS 2012, 9, 90-96)[32]. The article is an overview of the flavonoid dyes identified in textiles from local collections and intends to underline the variety of sources used and the contribution this knowledge is bringing to better understanding the historic context in which the respective textiles have been created.

2 Experimental

2.1 Samples

Samples (consisting of small fibers, less than 0.5 cm long), in most cases remains which could not be integrated into the objects after restoration, were provided by restorers. They all belong to historical textiles in Romanian collections. Samples were heated at 105 °C with 250 μL solution consisting of hydrochloric acid (37%) / methanol / water (2:1:1, v/v/v), for 10 min. The resulted extract was evaporated to dryness under nitrogen flow at 60 °C and the residue was taken up in 200 μL methanol/water mixture 1:1 (v/v), centrifuged and the supernatant was transferred into an injection vial. A library of references was used for data evaluation. This includes the UV-Vis, single stage and tandem MS data for the dye components discussed (Table 1).

More details on the extraction procedure as well as on the single stage and tandem MS data of dyes in the database can be found in an earlier publication[31].

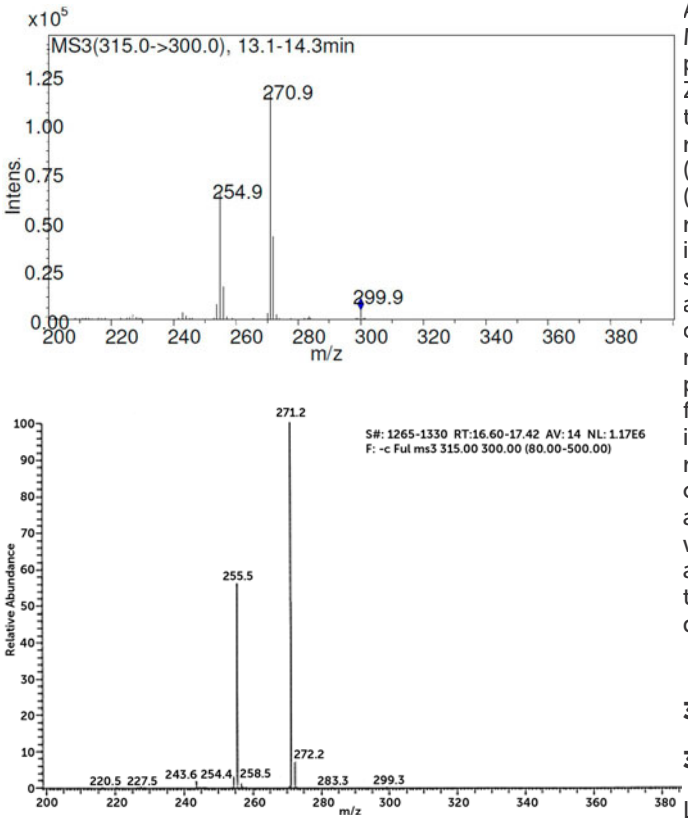

Figure 1. Identification of 3 methyl quercetin (together with luteolin and apigenin) in a sample from "kilim Basarabia"; MS3 315 300 of the unknown compound (top) as compared with MS3 315 300 of 3 methyl quercetin in Seratula tinctoria (sawwort) from Peggie 2006.[22]

2.2 Instrumentation

An Agilent 1100 LC system, equipped with diode array (G1315 A) and MS/MS ion trap (model G2445D-SL) detectors and using an ESI ion source, operated under negative mode, was used for the LC-MS experiments. Agilent ChemStation software LC incorporating the MSD trap control was used for data acquisition and processing. LC-MS separation was achieved on a Zorbax C18 column, 150 mm L x 4.6 mm i.d., 5 µm particle diameter. Gradient elution was applied to the mobile phase consisting of a mixture of aqueous 0.2% (v/v) formic acid (solvent A) and methanol/acetonitrile (1:1 v/v, as solvent B). The flow rate was set at 0.8 mL/min. An automated injector was used, 5 µL being injected from a total of about 200 µL resulted from the sample preparation. The diode array (PDA) detector and the MS ion source were placed in series and in that order after the column. MS detection was made in the negative ion mode with the following ESI operational parameters: drying gas temperature 350 °C; drying gas flow rate 12 L/min; nebulising gas pressure 65 psi; capillary high voltage 2484 V. The ion trap used a maximum accumulation time of 300 ms and an ion charge control (ICC) of 30000. The multiplier voltage was set at 2000 V and the dynode potential at 7 kV. When working in the MS/MS mode, the spectral width was 4 a.m.u. and the collisional induced dissociation amplitude 1.6 V. More details on the chromatographic and detection conditions can be found elsewhere[31].

3 Results and Discussion

3.1 Identification of flavonoid dye sources

Luteolin, the main dye component in many biological sources, was detected in a large number of samples, based on the presence of its molecular ion (m/z=285,[M-H]$^-$). In most cases it was accompanied by apigenin (m/z=269,[M-H]$^-$). This data was obtained

Biological source		Dyes detected	Retention time (min)	Spectral maxima (nm)	Molecular ion (m/z) (MS)	Product ions (m/z) (MS/MS)
Latin name	Common name					
Reseda luteola L.	weld	luteolin	12.7	208,254,266,348	285	241,175,257,217,199,151,133
		apigenin	13.7	210,268,336	269	225,149,241,201,183,117
		chrysoeriol	13.9	208,250,266,346	299	284
Genista tinctoria L.	dyer's broom	luteolin	12.7	208,254,266,348	285	241,175,257,217,199,151,133
		genistein	13.4	208.26	269	225,181,251,241,213,201,157
		apigenin	13.7	210,268,336	269	225,149,241,201,183,117
Serratula tinctoria L.	sawwort	luteolin	12.7	208,254,266,348	285	241,175,257,217,199,151,133
		apigenin	13.7	210,268,336	269	225,149,241,201,183,117
		3 methyl quercetin	13.4	255.359	315	300
Cotinus coggygria Scop.	young fustic	fisetin	11.3	206,248,320,360	285	163,135,257,241,213,153,121
		sulphuretin	12.2	256,290,394	269	225,133,241,201
Rhamnus berries	buckthorn berries (Persian, Avignon, or Hungarian berries)	quercetin	12.7	210,256,370	301	179.151
		kampferol	13.7	204,266,366	285	257,151,241,229,213,185,169
		rhamnetin	14.9	204,256,370	315	165,193,300,287, 256193,165
Delphinium semibarbatum B.	isparak	quercetin	12.7	210,256,370	301	179.151
		isorhamnetin	13.9	204,254,370	315	300
Datisca cannabina L.	bastard hemp	datiscetin	13.7		285	213,257,151,143

Table 1. Flavonoid based biological sources detected in textiles from Romanian collections; retention, UV-Vis and mass spectrometric data (MS and MS/MS) of the dye components.

from the chromatograms collected with the mass spectrometer working in Full Scan Mode (FS) followed by extraction of chromatograms (IEC) corresponding to dyes in the database. In the cases where both dyes (present in a certain source) were detected, it was not necessary to confirm their identification by further fragmentation. However, that may be achieved by new injections (from the same solution) with the mass spectrometer in the product ion scan mode and comparison with data collected on standards. The combination between luteolin and apigenin suggests the use of *Reseda luteola* L. (weld), *Genista tinctoria* L. (dyer's broom), *Serratula tinctoria* L. (sawwort) or other biological sources. In order to establish with certainty if one of the sources mentioned above was used, other dyes should be detected, together with luteolin and apigenin. *Reseda luteola* L. (weld)[17,22,23] is undoubtedly identified if chrysoeriol is present (together with luteolin and apigenin). Chrysoeriol is a minor compound with a molecular ion of m/z=299, which produces through fragmentation a fragment of m/z=284 (Table 1). Based on the detection of the three dyes, weld was identified in brocaded velvets (15th-18th c.), religious embroideries (15th-19th c.), knotted carpets (15th-17th c.), textiles from Minor Asia (19th c.) and Romanian ethnographical textiles (19th-20th c.). This information is in very good correspondence with results obtained by other researchers who detected the presence of weld in 14th-16th c. Florentine borders[14], 16th-19th c. textiles from Mount Athos[26] and 14th-16th c. Ottoman carpets[33].

The use of *Genista tinctoria* L. (dyer's broom) is confirmed when genistein (m/z=269,[M-H]$^-$) is detected, together with luteolin or luteolin and apigenin[12,17,31]. The combination of genistein, luteolin and apigenin was detected in most of the visual yellow/brown/green samples from Romanian ethnographical textiles (19th-20th c.), which suggests the use of dyer's broom. This is in perfect correspondence with literature and earlier results obtained in the same group[7]. Dyer's broom was also identified in religious embroideries (15th-19th c.) and in a 18th c. brocaded velvet. This well corresponds to data obtained by other researchers who identified dyer's broom in textiles from the same period, such as the costume of the Albertinian Elector August of Saxony and in Frederik's III "Polish" Costume (~1650) preserved at Rosenberg Castle in Copenhagen[34,35]. Dyer's broom was also detected in a sample from a 19th c. kilim, which in the evidence of the National Museum of Art of Romania is registered as "kilim Basarabia" (geographic region in Eastern Europe). In two other samples from the same object ("kilim Basarabia") luteolin and apigenin were identified, accompanied by a compound having a molecular ion m/z=315,[M-H]$^-$. Such a compound was not present in the database built for dye analysis, as it was not available, neither as standard, nor in one of the standard dyed fibres considered. Further fragmentation of the molecular ion, MS3 315 300 allowed the dye identification as 3 methyl quercetin, based on the perfect correspondence of the fragmentation spectra with data available in literature, obtained on similar instrumentation[22], Figure 1. According to the same source, as well as with other literature data[2], 3 methyl quercetin could be found together with luteolin and apigenin in *Serratula tinctoria* L. (sawwort). Accordingly, sawwort was used to dye the fibre in the object registered as "kilim Basarabia". Later on, this source was also identified in two other samples from a 19th c. Romanian ethnographical textile. Sawwort is common in all parts of Europe except Scandinavia and much of the Mediteranian region but was never detected in historical textiles[2].

The combination of fisetin (m/z=285,[M-H]$^-$) and sulphuretin (m/z=285,[M-H]$^-$) was detected several times in 15th-16th c. religious embroideries, as well as in later embroideries and in 15th-18th c. brocaded velvets. This dye source was also identified in 19th-20th c. Romanian ethnographical textiles. This is in perfect correspondence with literature which mentions the detection of young fustic in 14th-16th c. Florentine borders[14], in Ottoman lampas and velvets[10], in 15th-18th c. historical garments from the Holy Mount of Athos[20] and in 16th c. tapestries manufactured in Brussels[22].

Quercetin (m/z=301,[M-H]$^-$), in a dyeing combination with rhamnetin (m/z=315,[M-H]$^-$) and sometimes also with kaempferol (m/z=285,[M-H]$^-$), suggests the use of *Rhamnus* berries (buckthorn), or an equivalent source. As both quercetin and rhamnetin may be found in various combinations in different biological sources, it was important to confirm their individual detection by further fragmentation. This comes as a need to unambiguously detect each of the two dyes and suggest the biological source responsible for dyeing.

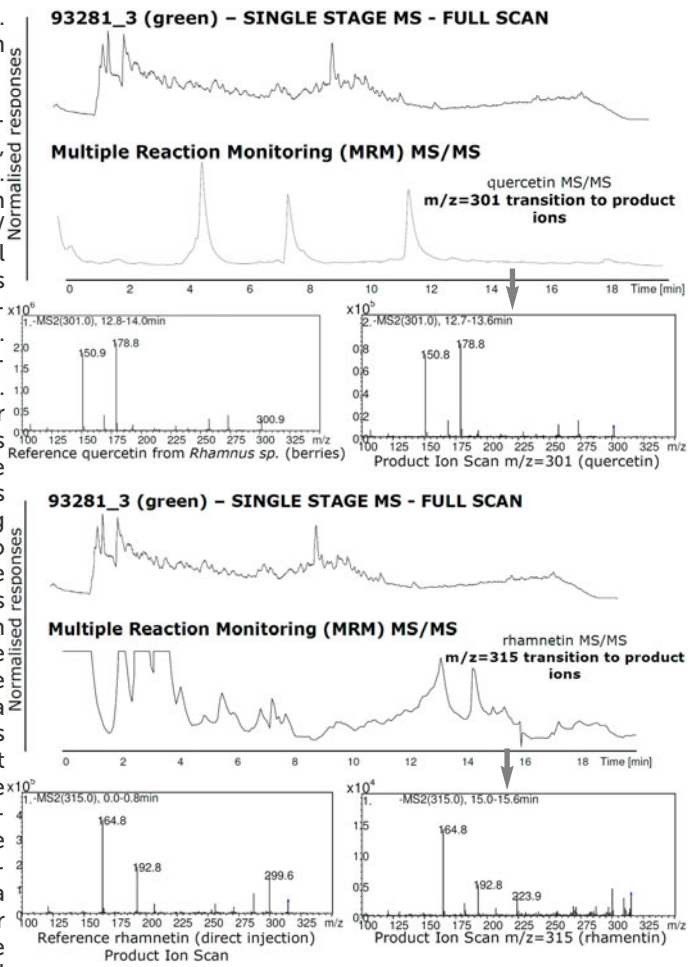

Figure 2. Detection of quercetin (top) and rhamnetin (bottom) in a sample from a 19th c. kilim suggesting the use of Rhamnus berries (buckthorn) or an equivalent.
For quercetin, in the absence of a pure reference of the dye, the MS/MS spectra (Product Ion Scan) was collected from a Rhamnus berries standard dyed wool, identified as compared with data available in literature, obtained on similar instrumentation[17].

Fragmentation was achieved by new injections (from the same solution), with the mass spectrometer in the product ion scan mode (Figure 2). Buckthorn berries were detected in various textiles from Romanian collections: 15th-19th c. religious embroideries, 19th-20th c. ethnographical textiles and 19th c. kilims from Minor Asia. These results are in perfect agreement with literature where this source is mentioned as detected in 12th c. textiles from the Imperial workshop at Sicily "Nobiles Officinae" Coronation Robes[36], in bandiera di San Giorgio (13th c.), Italy[37], in 14th-16th c. Florentine borders[14] and in the 17th c. Frederik's III "Polish" Costume preserved at Rosenberg Castle in Copenhagen[34].

The combination between quercetin (m/z=301,[M-H]$^-$) and isorhamnetin (m/z=315,[M-H]$^-$) is an indication that *Delphinium semibarbatum* L. (isparak) was used for dyeing. The two dyes were detected in some samples based on the presence of their molecular ions and confirmed by further fragmentation (of the molecular ions) with the mass spectrometer in the product ion scan mode (Figure 3). Isparak was thus detected in 19th c textiles from Minor Asia worked in the sumak and kilim techniques as well as in 19th c. Romanian ethnographical textiles. According to literature data, in the 19th c., isparak was the main dye used by the nomadic people of Persia, Caucasus and Turkestan[38]. It was also detected in a prayer rug preserved in Topkapy Museum, Istanbul[38].

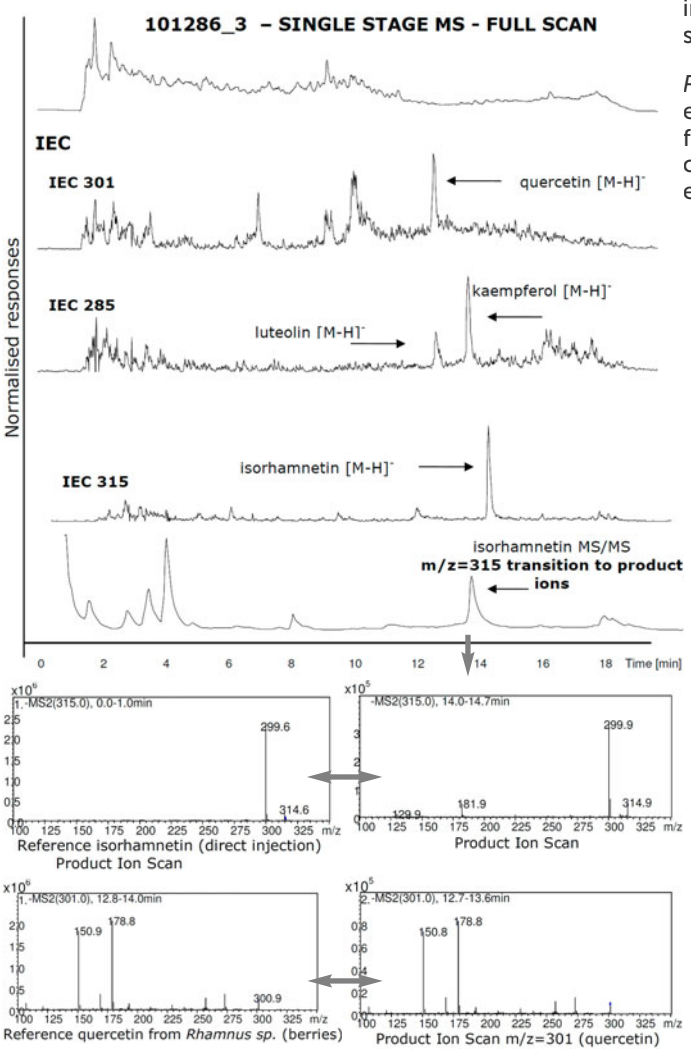

Figure 3. Detection of quercetin and isorhamnetin in a sample from a 19th c. kilim suggesting the use of Delphinium semibarbatum L. (isparak). For quercetin reference, see comment in Figure 2.

Datiscetin, detected based on the molecular ion (m/z=285,[M-H]$^-$) and confirmed by the fragmentation pattern (obtained with the mass spectrometer in the product ion scan mode) was identified in 15th-18th c. religious embroideries suggesting the use of *Datisca canabina* L. (bastard hemp). This dye source was known and used in Asia and also used by Turkish dyers in Western Anatolia[2,38]. It was also detected in Ottoman lampas and velvets from the same period[10].

3.2 Flavonoid Dye Sources Detected According to the Textiles Technique and Period

All the flavonoid dyes detected in textiles from Romanian collections, both by LC-PDA and LC-PDA-MS, are presented in Table 2. It illustrates the number of detections for each biological source according to the group of textiles (religious embroideries, brocaded velvets, knotted carpets, kilims and sumak from Minor Asia, Romanian ethnographical textiles) and period. For each group, the number of samples analysed depends on the number of objects under restoration and the possibilities of sampling. However, some important observations regarding the use of each source may be observed.

Reseda luteola L. (weld) was identified in religious embroideries from the 15th-19th c., brocaded velvets from the 15th-18th c., 15th-17th c. knotted carpets, 19th c. kilims from Minor Asia and 19th-20th c. Romanian ethnographical textiles. This also includes the analysis

Table 2. Flavonoid based biological sources detected in textiles from Romanian collections. Number of detections according to textile (manufacturing) technique and period.

	Religious embroideries 15th-16th c.	Religious embroideries 17th-18th c.	Religious embroideries 19thc.	Brocaded velvets 15th-16th c.	Brocaded velvets 18th c.	Knotted carpets 15th-17th c.	Knotted carpets 19th c.	Sumak Minor Asia 19th c.	Kilim Minor Asia 19th c.	Kilim Basarabia 19th c.	Romanian ethnographical textiles 19th-20th c.
Reseda luteola L. (weld) sau eq.	29	7	4	7	1	5	-	-	4	-	23
Genista tinctoria L. (dyer's broom)	8	4	1	-	1	-	-	-	-	1	40
Serratula tinctoria L. (sawwort)	-	-	-	-	-	-	-	-	-	2	2
Cotinus coggygria Scop. (young fustic)	24	2	3	3	2	-	-	-	-	-	3
Rhamnus sp. berries (buckthorn berries)	1	4	2	-	-	-	-	-	4	-	4
Delphinium semibarbatum B. (isparak)	-	-	-	-	-	-	-	1	1	-	3
Datisca cannabina L. (bastard hemp)	1	4	-	-	-	-	-	-	-	-	-

where luteolin alone or the combination of luteolin and apigenin was detected, when an equivalent source cannot be excluded. *Genista tinctoria* L. (dyer's broom) was also identified in religious embroideries but less frequently as compared to weld. It was detected only once in a brocaded velvet. It was the main dye source in 19th-20th c. Romanian ethnographical textiles. *Cotinus coggygria* Scop. (young fustic) was detected in religious embroideries and brocaded velvets but never in textiles from Minor Asia (kilims, knotted carpets, sumak). *Rhamnus* berries and *Datisca cannabina* L. (bastard hemp) were detected in religious embroideries but not in brocaded velvets, textiles from Minor Asia or in Romanian ethnographical textiles. *Delphinium semibarbatum* L. (isparak) was only identified in textiles from Minor Asia (kilim and sumak) and in Romanian ethnographical textiles.

Detection of biological sources used in Oriental textiles but never detected in textiles from Western Europe, such as *Datisca cannabina* L. (bastard hemp) in religious embroideries from the 15th-18th c., suggest that at least part of the materials used in the manufacture of these pieces have an Oriental origin. The variety of biological sources detected in 19th-20th c. ethnographical textiles, including local plants (dyer's broom, sawwort, *Rhamnus* berries) and also plants not growing in Romania, suggest that in the period considered peasants also used dyes or dyed fibers commercially available.

4 Conclusion

The LC-PDA-MS procedure, with the progressive use of the (ion trap) mass spectrometer, from single scan MS mode to product ion scan, was proved as a valuable tool in the detection of flavonoid dyes and their biological sources. It should be underlined that the procedure is based on data collected on standards of dyes and dyed fibers (fibers dyed in the laboratory by following traditional recipes)[31,33].

Reseda luteola L. (weld), *Genista tinctoria* L. (dyer's broom), *Serratula tinctoria* L. (sawwort), *Cotinus coggygria* Scop. (young fustic), *Rhamnus* berries (buckthorn berries), *Delphinium semibarbatum* B. (isparak) and *Datisca cannabina* L. (bastard hemp) are the flavonoid dye sources detected in various categories of 15th-20th c. textiles from Romanian collections. All the dye sources identified were also detected by other researchers in textiles from Western Europe or Asia Minor, from the same period. In what the use of the flavonoid dye sources in textiles from Romanian collections is concerned, a preference for certain sources according to the textiles (manufacturing) technique, origin and function was observed. Weld was identified in almost all the categories of textiles studied while dyer's broom was considerably less used in most of them (religious embroideries, brocaded velvets and textiles from Minor Asia) but was the main flavonoid dye source in Romanian ethnographical textiles. This last observation is not surprising, if we consider that, while weld (*Reseda luteola* L.) may not be found in Romania, dyer's broom is a local plant. The former should not be confused with its wild relative, *Reseda lutea* L. which is growing in Romania but do not contain any dye (or have them in very low quantity)[2].

Another important conclusion which is supported by dye analysis is that, considering that bastard hemp was never detected in textiles from Western Europe but was present in pieces from Minor Asia[2,10,33], at least part of the materials used in religious embroideries are of Oriental origin.

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References 34-37 are based on information in the OCW-RCE (Amsterdam, The Netherlands) archives, access being provided by the ARCHLAB facility within CHARISMA program. The authors are grateful to the European 7th Framework Programme CHARISMA who financed the EURODYE project as well as to dr. Ineke Joosten, dr. Maarten van Bommel and colleagues from the OCW-RCE library for their kind help and implication in the EURODYE project.

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