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Emerald Article: The characterisation by liquid chromatography of lake pigments prepared from European buckthorn (Rhamnus cathartica L.)

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The characterisation by liquid chromatography of lake pigments prepared from European buckthorn (*Rhamnus cathartica* L.)

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Abstract

Purpose – The purpose of this paper is to prepare, analyse and measure the colour values of the lake pigments obtained from the reaction of Al3 +, Fe2 + and Sn2 + metal salts with the natural dyes present in European buckthorn (*Rhamnus cathartica* L.).

Design/methodology/approach – A reversed-phase high performance liquid chromatography (HPLC) with diode-array detection method was utilised for the identification of buckthorn lake pigments. The extraction of dyes from the lake pigments was carried out with 37% hydrochloric acid/methanol/water (2:1:1; v/v/v) solution.

Findings – According to the results of the HPLC analysis of the lake pigments, it was determined that rhamnetin, kaempferol, and emodin were present in the acid hydrolysed plant extract and in the lake pigment that was precipitated by Sn(II), quercetin-3-arabinosid, rhamnetin, and emodin were present in the non-hydrolysed plant extract, and kaempferol, rhamnetin, isorhamnetin, and emodin were found in the lake pigment that was precipitated by Al(III). Rhamnetin and emodin were present in the lake pigment that was precipitated by Fe(II).

Research limitations/implications – In the present context for the preparation of buckthorn lake pigments, a simple and practical method is presented. In addition, the analysis of the lake pigments was performed by reversed phase HPLC (RP-HPLC) with diode array detector (DAD).

Practical implications – The paper describes the preparation of lake pigments and their qualitative analysis. This method can be used to determine the origins of the dyestuffs used in historical art pieces.

Originality/value – The paper describes the development of methods for the analysis and the preparation of European buckthorn lake pigments.

Keywords Dyes, Pigments, Colours technology, Lake pigments, European buckthorn, Natural dye, Mordant, High performance liquid chromatography

Paper type Research paper

Introduction

Natural dyes are obtained from plants (buckthorn, weld, madder, hemp, etc.), insects (cochineal, Ararat kermes, etc.), and molluscs (*Hexaplex trunculus* (*Murex trunculus*), *Murex brandaris* (*Bolinus brandaris*), etc.) (Karapanagiotis *et al.*, 2006; Rosenberg, 2008; Forgacs and Cserhati, 2002; Nowik *et al.*, 2008). The buckthorn dye plant has a very important place as a natural dye source (Cardon, 2007; Karadag, 2007).

Buckthorn berries are an old Turkish dye source (Böhmer *et al.*, 2002). The lake pigments (or natural pigments) are prepared by the reaction of metals like aluminium(III) ($KAl(SO_4)_2 \cdot 12H_2O$), tin(II) ($SnCl_2 \cdot 2H_2O$) and iron(II) ($FeSO_4 \cdot 7H_2O$) with the dye components (flavonoids, anthraquinones and indigoids) present in these dye sources (Schweppe, 1979; Deveoglu *et al.*, 2009, 2010a,b,c; Karadag *et al.*, 2010; Singer *et al.*, 2011; Miliani *et al.*, 2008). High performance liquid chromatography (HPLC) using a diode array detector (DAD) is ideally suited for the identification of natural dyes present in the lake pigments and the dye sources (Karadag and Dolen, 2008; Sanyova and Reisse, 2006; Melo and Claro, 2010; Karapanagiotis *et al.*, 2008; Sanyova, 2008).

A colour is defined using the CIELab method ($L^*a^*b^*$ system) that measures the absorption intensity in the visible region. The control of these colour is generally maintained using the CIELab system (Lang, 2009; Andary *et al.*, 2008).

Here we report a study of the analysis of the lake pigments generated via metal (Al^{3+}, Fe^{2+} and Sn^{2+}) solutions with dyes present in European buckthorn (*Rhamnus cathartica* L.)

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berries according to the method presented in our previously published study (Deveoglu *et al.*, 2009).

The aim of the present study was to prepare the lake pigments and to analyse qualitatively by a reversed phase high performance liquid chromatography (RP-HPLC) method with DAD. In addition, the effect of different volumes of the metal solutions (Al^{3+}, Fe^{2+} and Sn^{2+}) on the colouring scale of the lake pigments was investigated. The present paper focuses especially on the analysis of the European buckthorn lake pigments which were prepared.

Experimental

Materials

European buckthorn (*Rhamnus cathartica* L.) was obtained from the Laboratory for Natural Dyes, Faculty of Fine Arts, Marmara University. Standard natural dyes: rhamnetin (3,5,3′,4′-tetrahydroxy-7-methoxyflavone), kaempferol (3,5,7,4′-tetrahydroxyflavone), emodin (1,3,8-trihydroxy-6-methylanthraquinone), and isorhamnetin (3,5,7, 4′-tetrahydroxy-3′-methoxyflavone) were obtained from Carl Roth (Karlsruhe, Germany). HCl, CH_3OH, $SnCl_2 \cdot 2H_2O$, K_2CO_3, $KAl(SO_4)_2 \cdot 12H_2O$, and $FeSO_4.7H_2O$ were obtained from Merck (Darmstadt, Germany, www.merck.de). The HPLC mobile phase was prepared using Milli-Q water (Millipore, Bedford, MA, USA).

Apparatus

Heraeus D-6450 Hanau Oven, WiseStir MSH-20A Daihan Scientific Co. Stirrer, Shimadzu AEX-200G, Elga PureLab Option-Q and a Gretag-Macbeth SpectroEye Spectrophotometer were used.

HPLC equipment

Chromatographic experiments were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including a G1329A ALS autosampler, a G1315A diode array detector. Chromatograms were obtained by scanning the sample from 191 to 799 nm with a resolution of 2 nm and the chromatographic peaks were monitored at 255 and 276 nm. A G1322A vacuum degasser and a G1316A thermostatted column compartment were used. The data were analysed using Agilent Chemstation. A Nova-Pak C_{18} analytical column (3,9 · 150 mm, 4 μm, Part No. WAT 086344, Waters) protected by a guard column filled with the same material was used. Analytical and guard columns were maintained at 30°C. The HPLC gradient elution was performed using the method of Halpine, 1996 and Karapanagiotis *et al.*, 2005. Chromatographic separations of the hydrolysed samples were performed using a gradient elution program that utilizes two solvents: solvent A: H_2O – 0.1% TFA (trifluoroacetic acid) and solvent B: CH_3CN (acetonitrile) – 0.1% TFA. The flow rate was 0.5 mL/min and the applied elution program is described in Table I.

Methods

Method for the extraction of dyes from European buckthorn

European buckthorn extract was prepared in water as previously described by Deveoglu *et al.* (2009). Dried ground European buckthorn berries (30 g) were transferred into a 2,000 ml beaker. 2,000 ml of ultra pure water was then added. The mixture of buckthorn berries was heated to 100°C and mixed vigorously while heating. Then, it was maintained at 70°C-80°C for 1 h. Then, the mixture was removed from the heater. It was filtered after standing for 5-10 min.

Table I Gradient elution programme for HPLC

Time (min)	H_2O + 0.1% TFA (%)	CH_3CN + 0.1% TFA (%)
0.0	95.0	5.0
1.0	95.0	5.0
20.0	70.0	30.0
25.0	40.0	60.0
28.0	40.0	60.0
33.0	5.0	95.0
35.0	5.0	95.0
45.0	95.0	5.0

Method for the preparation of lake pigments

About 15% $KAl(SO_4)_2 \times 12H_2O$ (alum) solution and 100 ml of buckthorn extract were heated separately to 90°C and 60°C, respectively. 10 ml of alum solution at 90°C was added to buckthorn extract at 6°C. K_2CO_3 solution (0.1 M) was added to adjust the pH of the mixture to between 6 and 7. Then, the mixture was cooled to room temperature to precipitate the lake pigment. After settling, the mixture was filtered. Then, the precipitate was washed with ultra pure water and dried on a filter paper at 100°C for 30 min. The dried aluminium lake pigment precipitate was powdered. The same process was repeated by using 20, 30, 40, and 50 ml of alum solution to each part of 100 ml of European buckthorn extract. These experiments were repeated to precipitate the lake pigments by using 5% $FeSO_4.7H_2O$ and 3% $SnCl_2 \cdot 2H_2O$ solutions.

Method of extraction for HPLC analysis

Dye extraction was done using the previously described method (Wouters, 1985; Wouters and Rosario-Chirinos, 1992; Wouters and Verhecken, 1989). The samples were prepared as follows:

- Lake pigment samples (each one approximate 3 mg) were hydrolysed by using H_2O: MeOH: 37% HCl (1:1:2; v/v/v; 400 μl) in conical glass tubes for precisely 8 min in a water-bath at 100°C to extract organic dyes. After rapid cooling under running cold water, the solution was evaporated just to dryness in a water-bath at 50°C-65°C under a gentle stream of nitrogen. The dry pigment residues were dissolved in 200 μl of the mixture of MeOH: H_2O (2:1; v/v).
- 1 ml of the European buckthorn extract was evaporated in a porcelain crucible on a water-bath at 100°C. The dry residue was hydrolysed according to above procedure.

The hydrolysates of the dry pigment residues and of the dry European buckthorn extract residues were dissolved in 200 μl of the mixture of MeOH: H_2O (2:1; v/v) and was centrifuged at 2,500 rpm for 10 min. Then 5 μl and/or 50 μl of the supernatant liquid were injected into the HPLC apparatus.

Colour measurements for lake pigments

L^*, a^* and b^* values of the lake pigments were measured with Gretag-Macbeth SpectroEye Spectrophotometer.

Results and discussion

Preparation of lake pigments

The complexes of dyes present in the European buckthorn (*Rhamnus cathartica* L.) extract with aluminium(III), iron(II) and tin(II) were prepared as lake pigments.

Analysis of natural dyes from lake pigments

To identify the natural dyes present in lake pigments, the lake pigments were analysed qualitatively by a RP-HPLC.

Identification of dyes from European buckthorn (Rhamnus cathartica L.) by HPLC-DAD chromatogram and spectrum

The dye extractions for HPLC analysis were done by using the previously described method (Wouters, 1985; Wouters and Verhecken, 1989). The chemical composition of the precipitated dyestuff was identified based on the absorption spectra acquired with standard reference dye compounds.

UV-Vis maxima and the retention times of the HPLC-DAD chromatograms (nm) relating to the dye components present in the buckthorn extracts and the lake pigments are given in Table II.

The HPLC-DAD chromatograms obtained from the analysis of the non-acid hydrolysed and the acid hydrolysed European buckthorn (*Rhamnus cathartica* L.) extracts are shown in Figure 1.

The photodiode array (PDA) spectra corresponding to the peaks from the chromatograms of non-hydrolysed and acid hydrolysed European buckthorn (*Rhamnus cathartica* L.) extracts are shown in Figures 2 and 3.

Three compounds in the chromatogram indicated as (a) in Figure 1 were identified based on the comparison of retention times and spectra with standards (Figure 2), namely quercetin-3-arabinosid, rhamnetin and emodin standards. In addition, several other unknown compounds were found in the non-hydrolysed plant extract but they could not be identified. Probably, the unidentifed peaks (15.1, 18.0 and 23.5; t_r (min) values) belong to the quercetin glycosides. Also, another unknown compound (25.1 min) was found, however, it could not be identified and therefore, it is not discussed here.

Rhamnetin, kaempferol and emodin in the chromatogram labelled (b) in Figure 1 were identified based on the absorption spectra acquired with standard reference dyestuff compounds (Figure 3). Rhamnetin from these dyes was the main flavonoid component of the acid hydrolysed plant extract.

Identification of dyes from lake pigments

Natural dye compounds (flavonoids, anthraquinones, etc.) are metal chelates. The natural dyes present in Buckthorn extract were precipitated by the various mordant metals (Sn(II), Fe(II) and Al(III)). According to the results of HPLC analysis of the lake pigments, it was determined that rhamnetin,

Table II The retention times and the UV-Vis spectra (maxima, nm) of dyes present in the buckthorn extracts and the lake pigments

Plant extract/lake pigment	Retention time (min)	λ_{max} (nm)	Dye compound
Non-hydrolysed extract	15.1	256, 268, 292, 355	Possible quercetin derivative
	16.9	265, 292, 347	Not identified
	18.0	255, 267, 292, 355	Possible quercetin derivative
	18.5	255, 350	Not identified
	21.6	255, 266, 295, 356	Quercetin-3-arabinosid
	22.9	266, 295, 348	Not identified
	23.5	255, 266, 295, 355	Possible quercetin derivative
	25.1	257, 265, 299, 350	Not identified
	28.0	255, 269, 295, 374	Rhamnetin
	31.8	253, 267, 287, 440	Emodin
Acid hydrolysed extract	12.2	229, 282	Not identified
	29.3	261, 294, 321, 367	Kaempferol
Al-European buckthorn	29.6	255, 299, 371	Rhamnetin
	31.5	263, 287, 440	Emodin
	12.1	267, 297, 355, 412	Not identified
	15.5	267, 299, 357, 412	Not identified
	24.4	255, 299, 371	Possible rhamnetin derivative
	26.6	261, 293, 321, 367	Possible kaempferol derivative
	27.9	255, 297, 371	Isorhamnetin
	29.3	263, 293, 321, 367	Kaempferol
	29.5	255, 298, 371	Rhamnetin
	31.5	263, 287, 440	Emodin
Sn-European buckthorn	26.7	263, 293, 323, 367	Possible kaempferol derivative
	29.6	255, 298, 371	Rhamnetin
	31.5	265, 287, 440	Emodin
	8.1/12.6/15.8/21.0	260, 293/260, 292/ 260, 294/261, 295	Possible flavonoid derivatives
	11.0/20.0	255/256	Possible flavonoid derivatives
Fe-European buckthorn	26.3	293, 340	Not identified
	29.6	255, 298, 370	Rhamnetin
	31.5	263, 287, 440	Emodin

Figure 1 HPLC chromatograms of the acid hydrolysed (a) and the non-hydrolysed (b) *Rhamnus cathartica* L. extracts

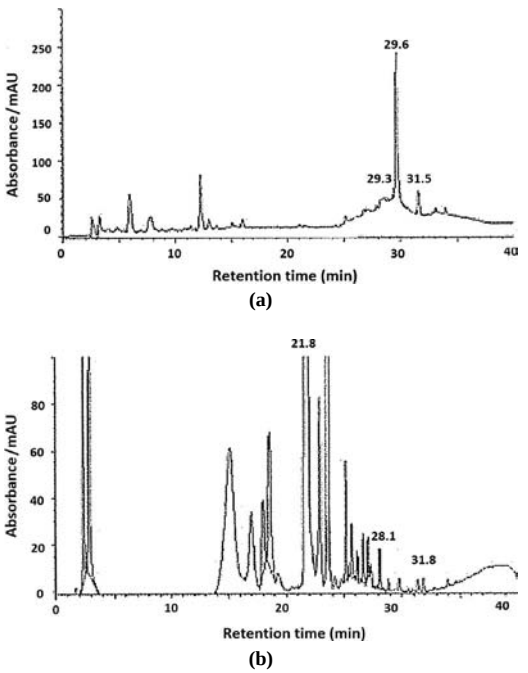


Figure 2 PDA spectra of peaks at (1) 29.3 min, (3) 29.6 min, (6) 31.5 min from chromatogram in Figure 1(a); (2) kaempferol standard compound, (4) rhamnetin standard compound and (5) emodin standard compound

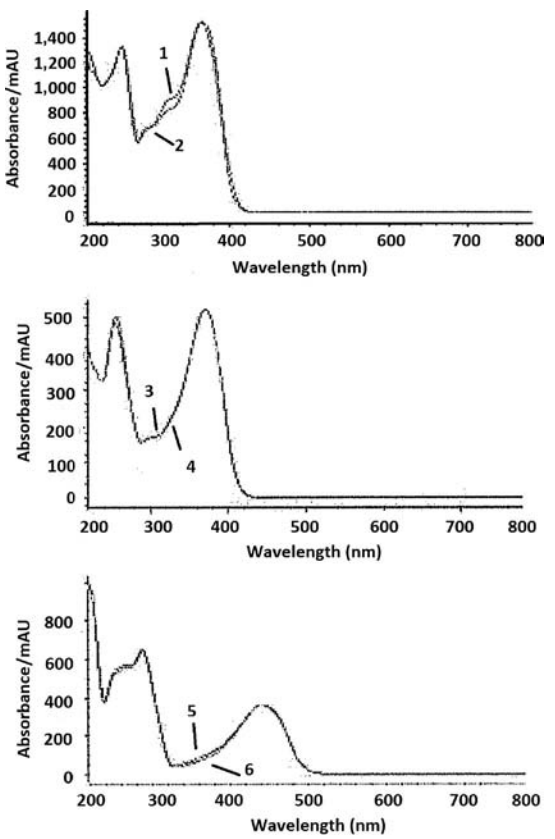
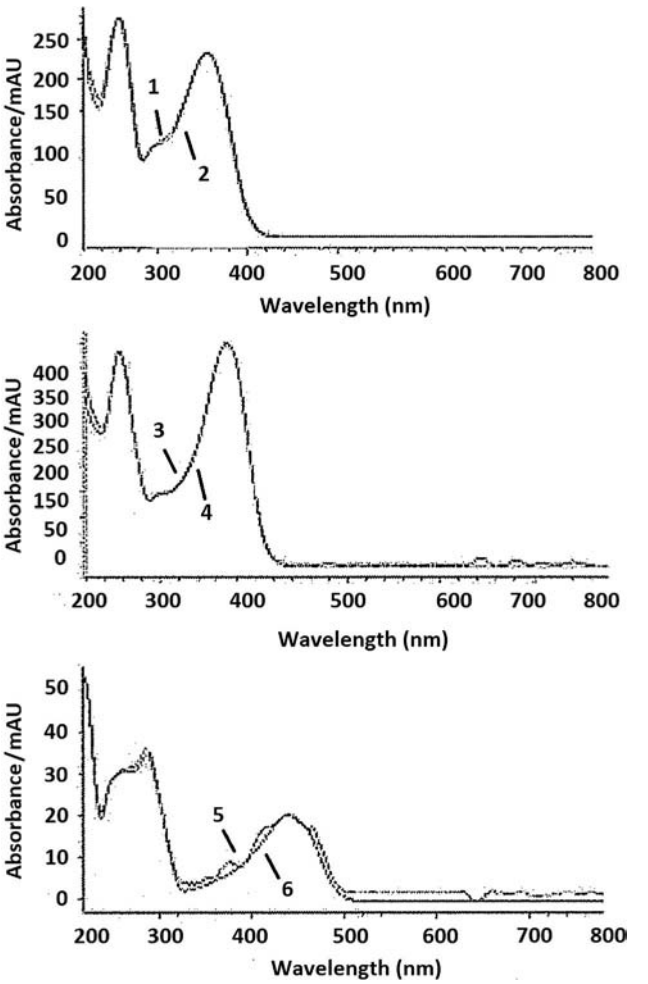


Figure 3 PDA spectra of peaks at (2) 21.8 min, (4) 28.1 min, (5) 31.8 min from chromatogram in Figure 1(b); (1) quercetin-3-arabinosid standard compound, (3) rhamnetin standard compound and (6) emodin standard compound



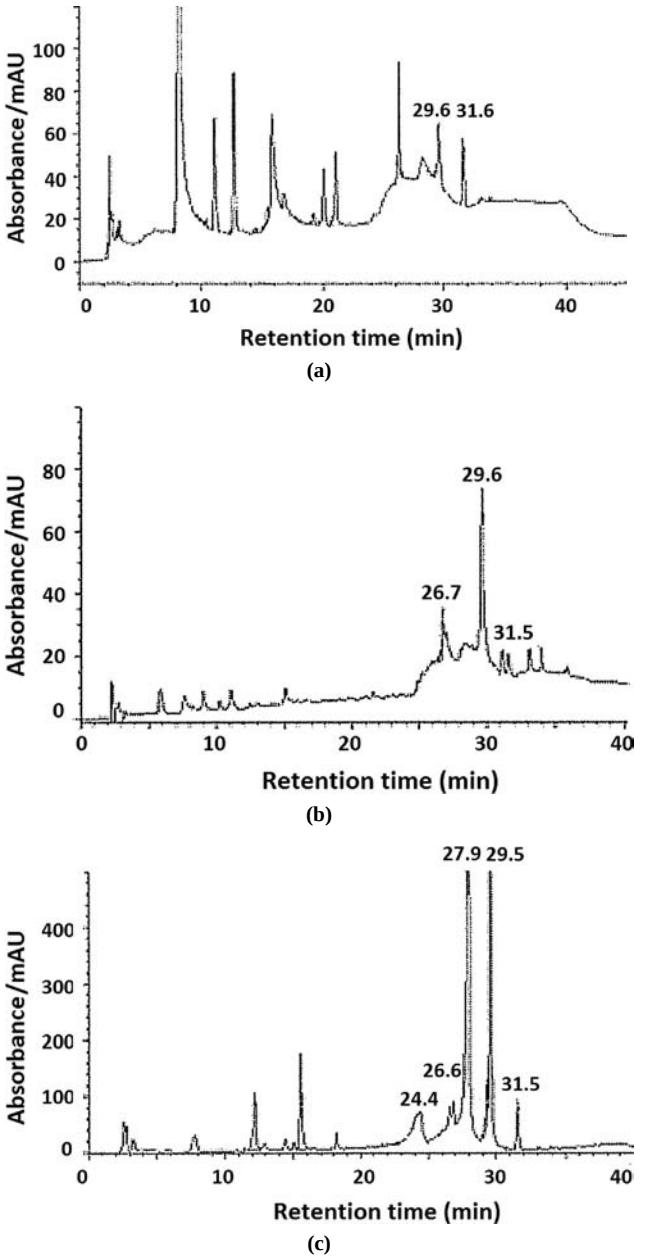
kaempferol, and emodin was precipitated with Sn(II), kaempferol, rhamnetin, isorhamnetin, and emodin in the lake pigment that precipitated by Al(III). Rhamnetin and emodin were precipitated with Fe(II). HPLC chromatograms of the acid hydrolysed lake pigments are shown in Figure 4.

The dyes obtained were identified from the PDA spectra by relating the peaks from the chromatograms of standard dye compounds. The PDA spectra are shown in Figures 5, 6 and 7.

The PDA spectra of the some unidentified peaks present in the chromatograms relating to the lake pigments precipitated by Al (III) and Fe (II) are shown in Figure 8. The PDA spectra of the peaks relating to the retention times of 11.0 and 20.0 min with 8.1, 12.6, 15.8 and 21.0 min determined in the lake pigment precipitated by Fe (II) with 12.6 and 15.5 min determined in the lake pigment precipitated by Al (III) show nearly the same spectra. The compounds related to these peaks are derived from each other.

The main dye component present in the lake pigment precipitated by Sn(II) belongs to the rhamnetin dye compound. The two main dye components also present in the lake pigment precipitated by Al(III) are related to the rhamnetin and isorhamnetin dye compounds. The other dyes

Figure 4 HPLC chromatograms of acid hydrolysed iron-*rhamnus cathartica* L. (a) tin-*rhamnus cathartica* L. (b) and aluminium-*rhamnus cathartica* L. (c) lake pigments



(quercetin, quercetin-3-arabinosid, etc.) did not form complexes with the metals that were used in the study. Strong complexes were formed between tin and isorhamnetin and between aluminium and rhamnetin and isorhamnetin.

Determination of colour values of the lake pigments

CIELab colour values of the lake pigments prepared by using the varied metal solutions (Al^{3+}, Fe^{2+} and Sn^{2+}) are given in Table III. According to the results in Table III, the best brightness (L-value) of aluminium, iron, and tin-buckthorn lake pigments were observed in samples that have been prepared with 50, 40, and 10 ml of the solution of metal salts, respectively. When yellow and blue colour values of

Figure 5 PDA spectra of peaks at (2) 29.6 min, (4) 31.6 min from chromatogram in Figure 4(a); (1) rhamnetin standard compound and (3) emodin standard compound

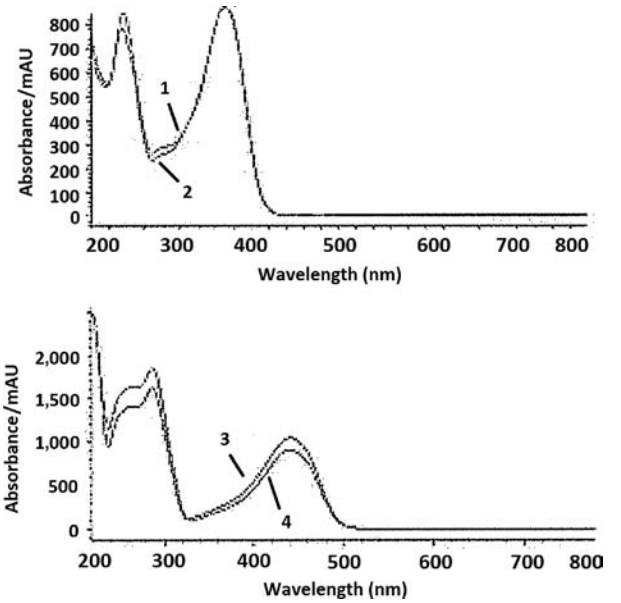


Figure 6 PDA spectra of peaks at (2) 26.7 min, (3) 29.6 min, (6) 31.5 min from chromatogram in Figure 4(b); (1) kaempferol standard compound, (4) rhamnetin standard compound and (5) emodin standard compound

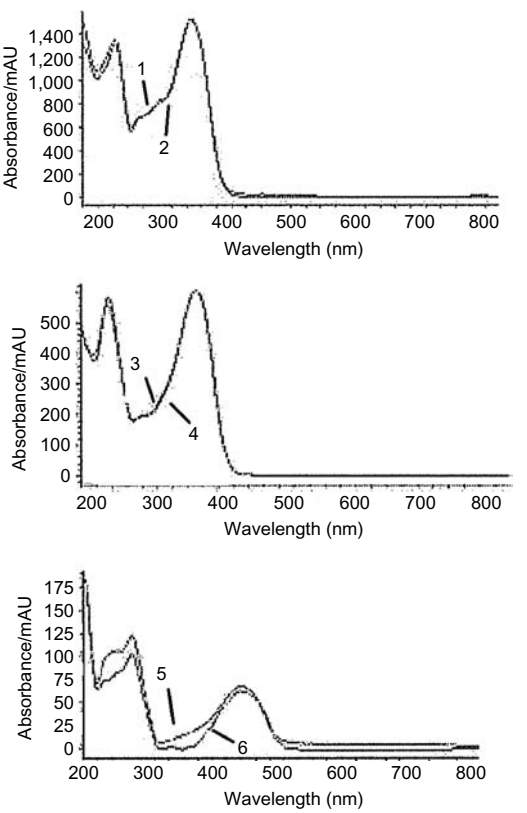


Figure 7 PDA spectra of peaks at (1) 26.6 min, (4) 27.9 min, (6) 29.5 min, (8) 31.5 min from chromatogram in Figure 4(c); (2) kaempferol standard compound, (3) isorhamnetin standard compound, (5) rhamnetin standard compound and (7) emodin standard compound

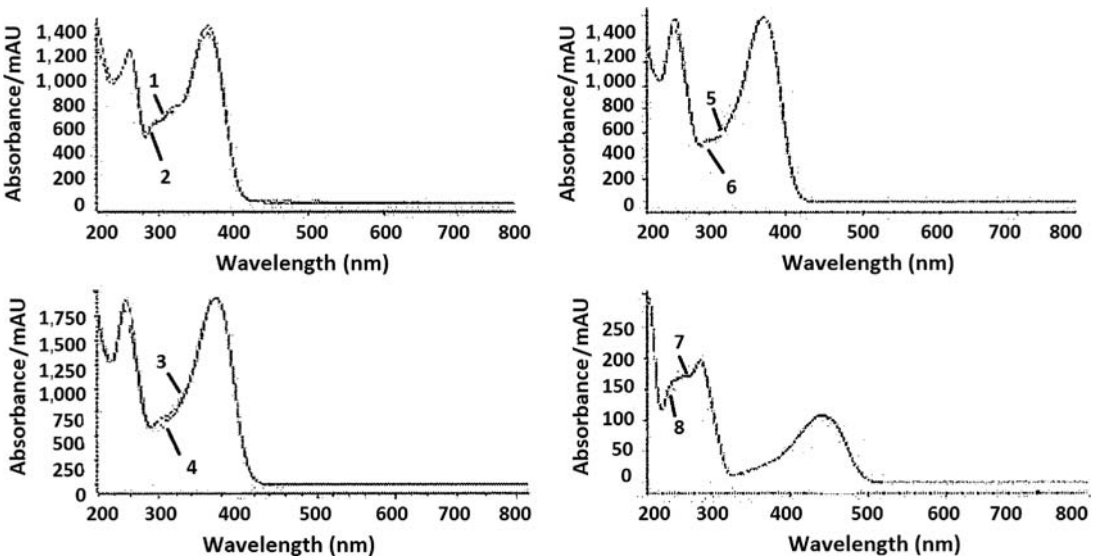


Figure 8 PDA spectra of unidentified peaks at (12.1 min and 15.5 min) (c) from chromatogram in Figure 4(c) with (8.1 min, 12.6 min, 15.8 min, 21.0 min) (a) and (11.0 min and 20.0 min) (b) from chromatogram in Figure 4(a)

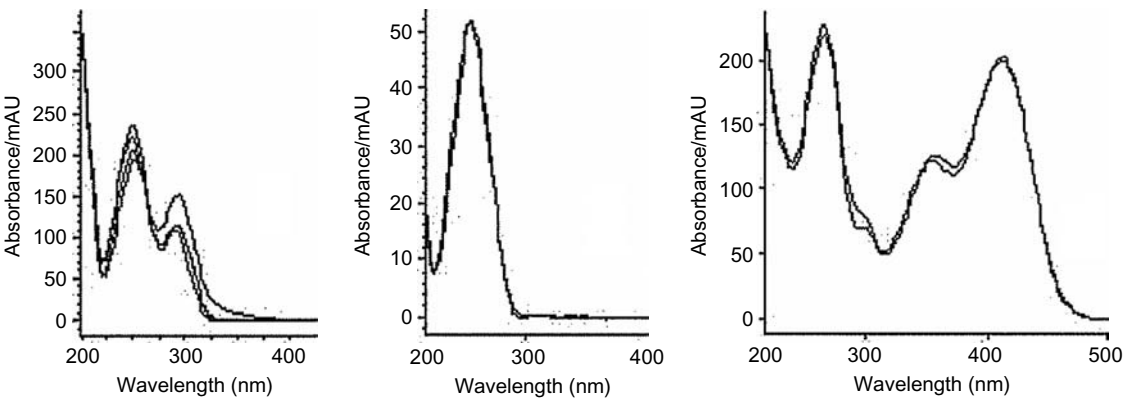


Table III The colour measurements of the prepared lake pigments

Lake pigment	Used metal solution volume (ml)	L*	a*	b*
Al-European buckthorn	10	24.33	0.34	18.38
	20	23.09	0.10	12.10
	30	33.59	−0.22	15.09
	40	31.35	−1.00	24.57
	50	50.34	−2.81	32.10
Fe-European buckthorn	10	15.84	−0.20	2.15
	20	16.12	−0.38	3.06
	30	16.98	−0.36	3.11
	40	17.16	−0.47	3.73
	50	17.08	0.10	7.01
Sn-European buckthorn	10	64.11	9.28	4.21
	20	28.00	1.61	18.46
	30	39.71	0.62	31.32
	40	45.32	0.78	34.67
	50	50.09	−0.12	32.80

aluminium, iron, and tin-buckthorn lake pigments were investigated, it was observed that the best yellow and blue colour values were obtained from the lake pigments that generated by using 50, 50, and 40 ml solutions for aluminium, iron and tin-buckthorn lake pigments, respectively.

Conclusions

Simple and practical methods for the analyses and preparations of natural lake pigments (aluminium, iron, and tin-European buckthorn), by the reaction of mordant metals (Al^{3+}, Fe^{2+}, and Sn^{2+}) with the main constituent dyes (mostly flavonoids) present in European buckthorn, were developed. The natural dyes present in the prepared lake pigments could be characterised based on the absorption spectra acquired with standard reference dyes by a RP-HPLC with DAD. The effects of different volumes of metal solutions on the colouring scale of the lake pigments were investigated. The best ideal values of L^* (brightness) and b^* (yellow/blue) were found for the lake pigments prepared by using 50 ml metal solutions.

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