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ARTICLE

Investigation of Natural Lake Pigments Prepared With a Mixture of Hemp (*Datisca cannabina* L.) and Weld (*Reseda luteola* L.)

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Abstract: In this study, lake pigments (natural pigments) were prepared by adding $KAl(SO_4)_2.12H_2O$ (alum), $FeSO_4.7H_2O$ and $SnCl_2.2H_2O$ solutions to hemp (*Datisca cannabina* L.) and weld (*Reseda luteola* L.) dye plant extracts. Reversed - phase high- performance liquid chromatography (RP-HPLC) with diode array detection (DAD) technique was utilized for the identification of natural dyes in the lake pigments. The dyes extraction from the lake pigments was carried out with a 37 % HCl/MeOH/H_2O (2:1:1; v/v/v) mixture. The performed method was able to analyze and detect natural dyes, such as luteolin (5,7,3',4' - tetrahydroxyflavone), apigenin (5,7,4'-trihydroxyflavone), datiscetin (3,5,7,2'-tetrahydroxyflavone), chrysoeriol (5,7,3'-OMe,4'-flavone or 3'-methoxy derivative of luteolin), luteolin-7-O-glucoside and luteolin-3',7-di-O-glucoside present in the lake pigments and / or the plant extracts.

Keywords: Datisca cannabina L, HPLC, Lake pigments, Natural dyes, Colour, Reseda luteola L.

Introduction

The hemp (*Datisca cannabina* L.) plant is also known as "gence" in Turkey[1]. It is a robust, glabrous perennial plant that grows up to 1-2 m high in the Black Sea region, West and South Anatolia[1-3]. This plant was used in the past as a dye plant by nomads in Turkey's northwest and is still used in carpets and plain weaves. The plant is also used to add yellow dye in the yarns in Van region in Turkey. The dyeing process was realized by using the parts above the surface of the ground of the plant[2].The plant is very rich in flavonols: datiscetin is present in the form of a rutinoside and datiscin to 10% of the weight of the fresh leaves. Kaempferol, quercetin and galangin (as flavonol compounds) are also present in the plant. Weld (*Reseda luteola* L.) is an annual or a biennial herb[3]. The branch-erected stems grow up to 150 cm tall. The leaves of the plant form in the first year and the evolution of the plant is complete in the second year. It grows in the parts of North Africa and most of the eastern Mediterranean[2]. This dye plant is one of the most important natural yellow dye sources used to produce fast yellow colours. The plant which is rich in flavonoids is known to be used in Europe since prehistoric times. Alone or together with indigo which gives blue colour it had been used to obtain yellow and green colours in the 1st century Masada textiles, 3rd century Palmyra textiles, 13th century Seljuk

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carpets and 15^{th} – 20^{th} centuries Ottoman textiles[4]. The main colouring components of the plant are luteolin and apigenin dyes giving a yellow colour[5]. The plant is known to be used in paintings, murals and icones as a pigment and in the textile dyeing since prehistoric times[2].

The precipitates are prepared by the reaction of metal salts (Al, Fe, Sn,… etc.) with natural dyes (flavonoid, anthraquinone and indigotin compounds) present in the natural dye plant extracts. These precipitates are used in several fields as dyes and pigments[6-9].

From the 14^{th} to the 19^{th} century, lake pigments were primary constituents of the artist's palette and used for artistic techniques, such as miniature, tempera, painting, oil paint and iconography[10-12].

In studies published in 2011 and 2012 by Karadag et al., weld (*Reseda luteola* L.) and hemp (*Datisca cannabina* L.) natural lake pigments were prepared and then analyzed by HPLC-DAD. Also, hemp pigments from these natural lake pigments were investigated with FTIR and FESEM-EDAX[13].

Natural lake pigments from weld (*Reseda luteola* L.) dye plant including yellow flavonoid dyes were obtained by the reaction of $KAl(SO_4)_2.12H_2O$ (alum) and $SnCI_2.2H_2O$ metal salt solutions with the weld extract[14].

In acid-hydrolyzed aluminium and tin-weld natural lake pigments, both apigenin and luteolin dyes were determined in this study. Cristea et al. have quantitatively identified the yellow coloured natural dyes present in the weld (*Reseda luteola* L.) dye plant by HPLC. In this study, three solvents, which are methanol, methanol/water and water were used. In addition, three flavonoids (luteolin, luteolin-7-glucoside and luteolin-3',7-diglucoside) were identified and investigated[15].

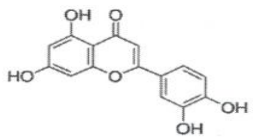
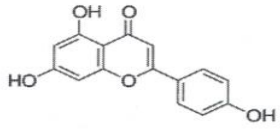
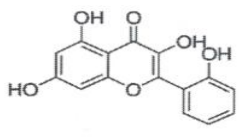
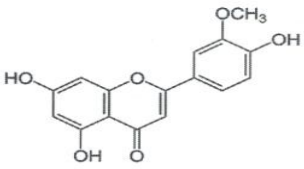
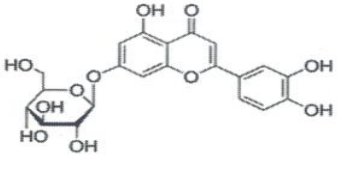
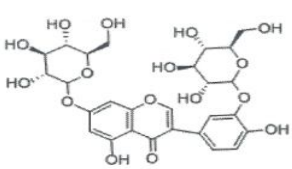
We prepared the natural pigments by using $KAl(SO_4)_2.12H_2O$ (alum) solution mixed with hemp (*Datisca cannabina* L.) and gall oak (*Quercus infectoria* Olivier) plant extracts in 2012. According to HPLC analysis results of the natural pigments, gallic acid, gallic acid derivatives, ellagic acid and datiscetin were determined[16]. CIELAB (1976) system was introduced to describe colour as a result of these factors. This system is a three - dimensional space, with coordinate axes L*, a* and b*. L* symbolizes the lightness of the colour (L*= 0: black, L*= 100: white), a* represents the green-red axis (a* negative: green, a* positive: red) and b* represents the blue-yellow axis (b* negative: blue, b* positive: yellow)[17].

High-performance liquid chromatography (HPLC) using a diode-array detection (DAD) is ideally suited for the identification of natural dyes including the lake pigments present in these materials[17-20].

In this study, we considered the chromatograms related to the non-hydrolyzed and the acid-hydrolyzed weld extracts in the study published in 2012 by Deveoglu et al.[21].

The main aim of this study is to identify the dyes present in the lake pigments prepared *via* hemp (*Datisca cannabina* L.) and weld (*Reseda luteola* L.) dye plants by RP-HPLC-DAD. Table 1 shows the chemical structures of natural dyes investigated in study.

Table 1. The chemical structures of natural dyes investigated in this study.

		
Luteolin	**Apigenin**	**Datiscetin**
		
Chrysoeriol	**Luteolin-7-*O*-glucoside**	**Luteolin-3',7-di-*O*-glucoside**

Experimental

Dye Plants and Chemicals

Hemp (*Datisca cannabina* L.) and weld (*Reseda luteola* L.) dye plants were provided from TCF / DATU (the Turkish Cultural Foundation, Cultural Heritage Preservation and Natural Dyes Laboratory, Istanbul, Turkey). Potassium-aluminium sulphate dodecahydrate ($KAl(SO_4)_2.12H_2O$), ferrous sulphate heptahydrate ($FeSO_4.7H_2O$), stannous chloride dihydride ($SnCl_2.2H_2O$), hydrochloric acid (37% fuming HCl), asetonitrile (CH_3CN, HPLC gradient grade), trifluoroacetic acid (TFA, HPLC gradient grade) and methanol (MeOH, HPLC gradient grade) were obtained from Merck (Darmstadt, Germany).

Instruments

Agilent 1200 series system, Elektro-mag M 420P Hot Air Sterilizer Laboratory Oven, WiseStir MSH-20A Daihan Scientific Co. Stirrer, Precisa XB 220A Gravimetrics AG (Dietikan, Switzerland), Elga PureLab Option-Q and Mettler Toledo S220 were used in the study.

Extraction of Dyes from Hemp and Weld

Hemp and weld extracts were prepared by water as previously performed by Deveoglu et al.[17]. 60 g of aerial parts of the weld (*Reseda luteola* L.) plant were transferred into a 5000 mL beaker. 80 g of aerial parts of the hemp (*Datisca cannabina* L.) plant were transferred into another 5000 mL beaker. 5000 mL of ultra-pure water were added and the mixtures were heated to 100 ºC by using a magnetic stirrer and then retained at 75-80 ºC for 60 minutes. Finally, the mixtures were filtered by a filter paper to obtain the hemp and weld extracts.

Procedure for the Preparation of Lake Pigments

A 15% $KAl(SO_4)_2.12H_2O$ (alum) solution, the hemp and weld extracts were separately heated to 90 °C (for the solution) and 60 °C (for the extracts), respectively. 10, 15, 20, 25 and 30 mL of alum solution at 90 ºC were separately added to each 40 mL of the hemp extract mixed with 30 mL of the weld extract at 60 °C. K_2CO_3 (0.1 M) solution was added to adjust the pH of the mixtures to 6.5 and 7.0. The mixtures were cooled to room temperature to allow the precipitation of the aluminium-hemp-weld lake pigment. After settling down, the mixtures were filtered and the precipitates were washed with ultra-pure water and dried on a filter paper at 100 ºC for 30 minutes. The dried aluminium-hemp-weld lake pigment precipitates were then powdered. The same procedure was repeated with the addition of 10, 15, 20, 25 and 30 mL of 3% $FeSO_4.7H_2O$ and 3% $SnCl_2.2H_2O$ solutions to each 40 mL of the hemp extract mixed with 30 mL of the weld extract.

Dye Extraction Procedure for HPLC Analysis

Dye extraction from the dye plant and the lake pigments was completed as described in earlier reports[17-25]. The samples were prepared as follows:

For the dye extraction from hemp (*Datisca cannabina* L.), weld (*Reseda luteola* L.) plants and lake pigments, three procedures (1, 2 and 3) were performed.

1) In the first procedure, the dye extraction from the hemp (10.2 mg) and the weld (2.7 mg) dye plants was achieved in 400 µL of the mixture of MeOH: H_2O (2:1; v/v) in a conical glass tube without heating.

2) In the second procedure, organic dyes were extracted from hemp (7.3 mg) and weld (2.5 mg) dye plants and hydrolyzed by heating in 400 µL of the mixture of 37% HCl: MeOH: H_2O (2:1:1; v/v/v) in conical glass tubes for 8 min in a water bath at 100 ºC. After rapid cooling under running cold water, the solution was evaporated to dryness in a water bath at 55-65 ºC under a gentle stream of nitrogen. The dry residues were dissolved in 400 µL of the mixture of MeOH: H_2O (2:1; v/v) and centrifuged at 2500 rpm for 10 min. 25 µl and 50 µL of the supernatant were injected into the HPLC apparatus.

3) Acid hydrolysis of aluminium and tin–hemp-weld lake pigments (5.3 - 8.9 mg) was utilized according to the procedure presented in the second step. Then, 15 µL and/or 70 µL of the supernatant were injected into the HPLC apparatus.

HPLC Equipment

Chromatographic separations were carried out using an Agilent 1200 series system (Agilent Technologies, Hewlett-Packard, Germany) including a G1329A ALS autosampler and a G1315A diode-array detector. A G1322A vacuum degaser and a G1316A thermostatted column compartment were used. The chromatograms were obtained by scanning the

sample from 191 nm to 799 nm with a resolution of 2 nm, where eluted peaks were monitored at 255 nm and 350 nm. The data was analyzed using an Agilent Chemstation. A Nova-Pak C18 analytical column (3.9 mm x 150 mm, 4 µm particle size, Part No. WAT 086344, Waters) protected by a guard column filled with the same material was used. The analytical and guard columns were maintained at 30°C. HPLC gradient elution was performed using the previously described method [26,27].

The chromatographic separations of the hydrolyzed 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 solvent selection originated from a previous publication[26]. The flow rate was 0.5 mL/min and the elution program was as described earlier[17-22].

Colour Measurements for Lake Pigments

L*, a* and b* values of lake pigments were measured with a GretagMacbeth SpectroEye Spectrophotometer. Table 2 presents colour measurements of the prepared lake pigments.

Table 2. Colour measurements of the prepared lake pigments.

Lake pigment	Used metal solution volume (mL)	L*	a*	b*
Al-hemp-weld	10	57.84	10.65	47.57
	15	66.47	7.19	48.68
	20	69.50	5.65	46.64
	25	72.86	4.70	39.92
	30	74.81	3.92	34.02
Sn- hemp-weld	10	61.53	9.93	43.17
	15	65.47	8.40	42.38
	20	70.45	6.79	42.21
	25	69.29	7.74	42.26
	30	74.37	5.90	41.71

Results and Discussion

HPLC Analysis

In recent years, lake pigments were obtained by the reaction of metal salts with extracts of *Helichrysum arenarium*, *Quercus infectoria* Olivier and *Thymus serpyllum*. Flavonoid and tannin compounds were identified in these lake pigments [28-30]

In the present study, lake pigments were obtained as the complexes formed with adding aluminium(III), iron(II) and tin(II) solutions to the hemp (*Datisca cannabina* L.) and weld (*Reseda luteola* L.) extracts. In Table 3, the detected retention times (t_R) and the corresponding spectral characteristics of the main colouring components of hemp and weld plants are presented. The main colouring components (datiscetin, luteolin and apigenin) of hemp and weld can be fully separated, detected and identified by HPLC UV-Vis Absorption spectra.Generally, the detection of characteristic absorptions of natural dyes allows the identification of lake pigments and natural colourants present in the dye plants.

Table 3. Chromatographic and spectral characteristics of the investigated standard dyes.

Dye	Colouring component	t_R (min)	Absorbance maxima (nm)	Corresponding peak in Figs. 1 and 2
Hemp	Datiscetin	26.4	257, 305, 347	H1
Weld	Apigenin	26.5	267, 293, 337	W1
Weld	Luteolin	22.7	217, 253, 259, 291, 349	W2

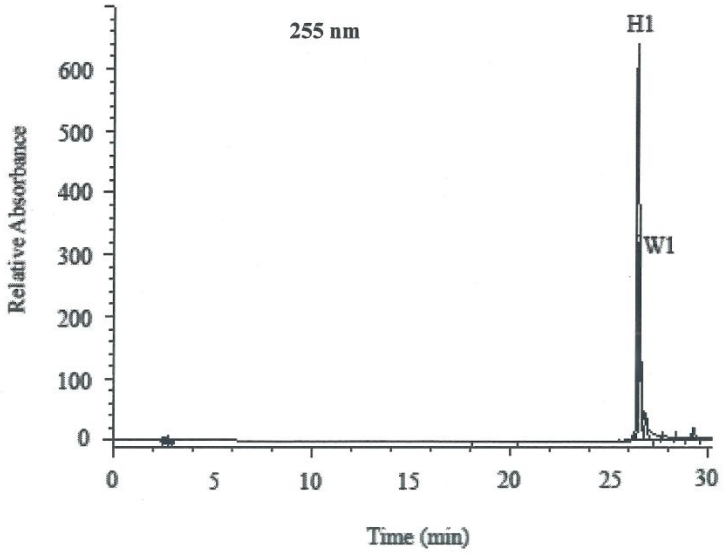


Figure 1. Chromatograms of datiscetin and apigenin standard dyes.

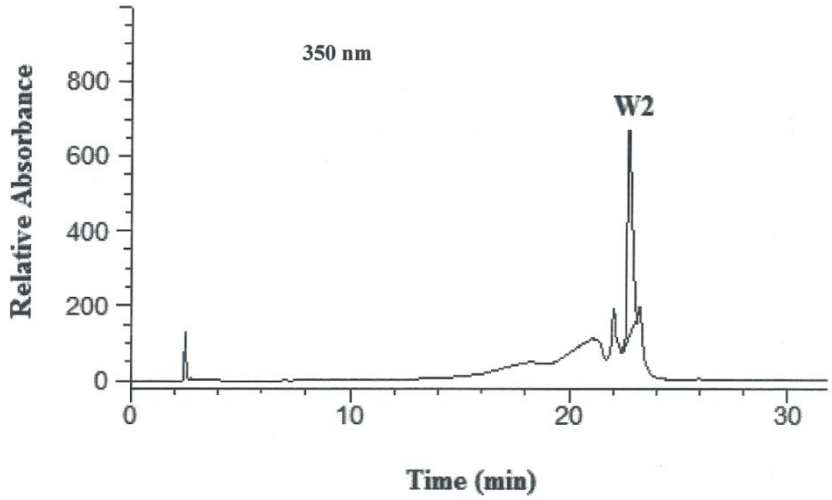


Figure 2. Chromatogram of luteolin standard dye.

The standard dyes used in the present study, such as datiscetin and apigenin, were also chromatographically and spectrophotometrically (UV-Vis) characterized. Absorbance maxima (nm) and retention times (min) related to luteolin, apigenin and datiscetin were evaluated according to standard dyes. Absorbance maxima in Table 4, which correspond to one weld component, appear to be similar and in good agreement with the spectral characteristics of luteolin and apigenin standard dyes and luteolin and apigenin - the main colouring components of the weld, that can be found in literature[15].

Besides, the datiscetin dye present in the hemp (*Datisca cannabina* L.) plant was determined with evaluating the absorbans maxima and the retention time (t_R) relating to the standard datiscetin dye. Table 4 provides the results of HPLC-DAD analysis of the sample extracts, including retention times and corresponding absorbance maxima. The detection wavelength was selected according to the chemical nature of peaks present. In general, animal dyes were best analyzed at 275 nm, whereas 255 nm was the optimal detection wavelength for vegetal mordant dyes and 288 nm for indigoids[7]. In this study, we analyzed dyes present in lake pigments and plant extracts at 255 nm and 350 nm, respectively.

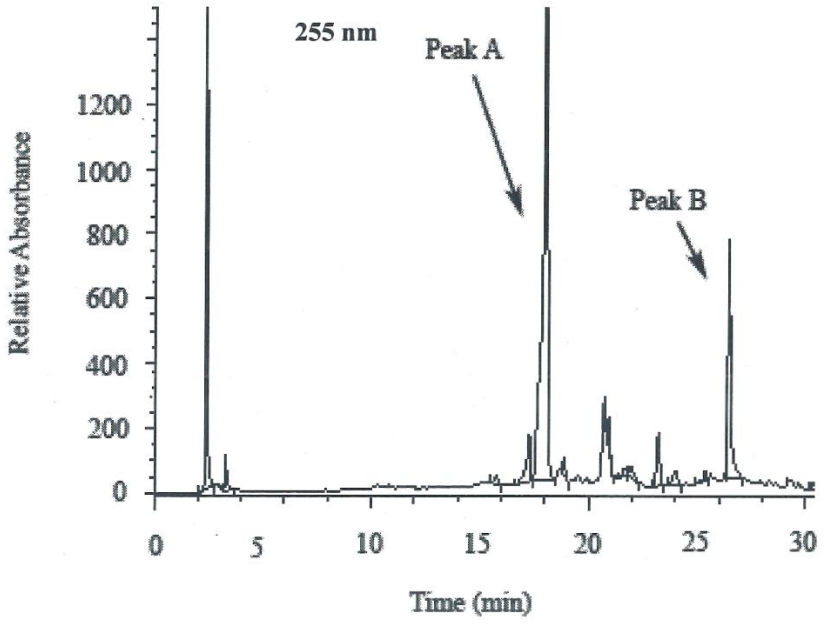


Figure 3. Chromatogram of non-hydrolyzed hemp extract.

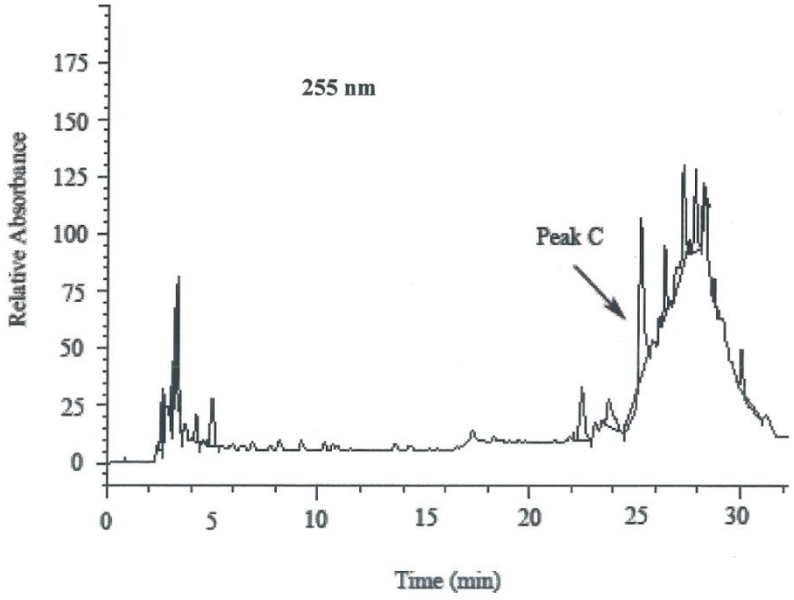


Figure 4. Chromatogram of hydrolyzed hemp extract.

In a sample derived from the non-hydrolyzed hemp extract, as shown in Figure 3, the peak A may likely be datiscetin-3-*O*-[rhamnosyl(1-6)glucoside] according to λmax (258, 304 and 332 nm) present in a book published by Campos and Markham in 2007[31]. The peak B present in the chromatogram related to the same extract was identified as a datiscetin compound. In the chromatogram of the acid hydrolyzed hemp extract, as shown in Figure 4, the peak C was identified as a datiscetin compound.

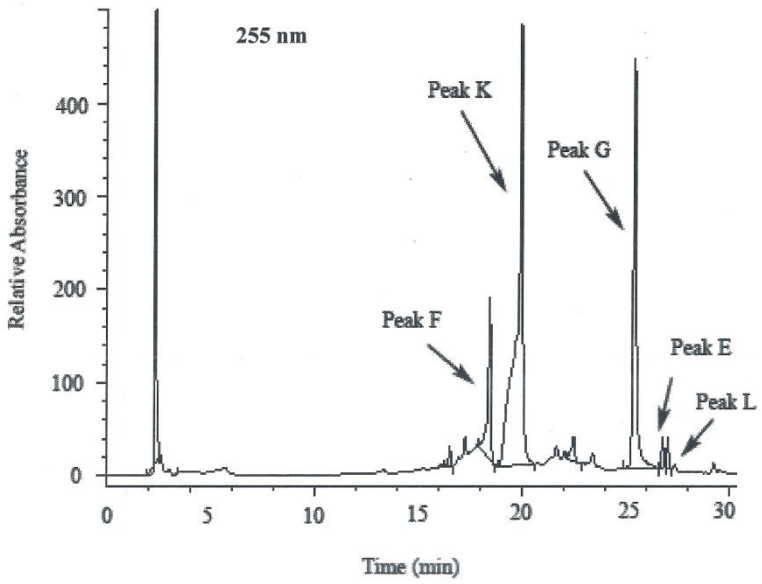


Figure 5. Chromatogram of non-hydrolyzed weld extract.

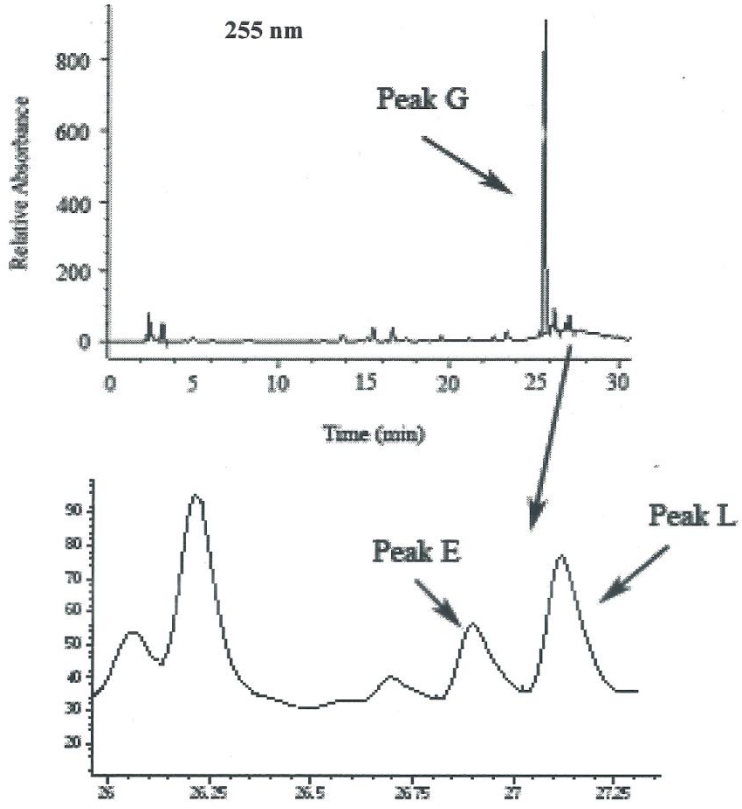


Figure 6. Chromatogram of hydrolyzed weld extract.

In the samples derived from acid hydrolyzed and non-hydrolyzed weld (*Reseda luteola* L.) extracts, a minor peak, is shown as peak E in Figures 5 and 6. This minor peak is related to apigenin colourant. When the corresponding retention time and the absorption maxima of the sample together with the standard apigenin dye are evaluated, we determined this compound as apigenin. As shown in Figure 5, the main peak (peak K) (λmax = 253, 265 and 349 nm) corresponds with luteolin-7-*O*-glucoside (λmax = 255 and 348 nm) determined as a probable compound in a study published in 2009 by Marques et al.[32].

Nevertheless, in the chromatogram related to the same extract, peak F was identified as luteolin-3',7-di-*O*-glucoside[32,33]. As shown in Figures 5 and 6, the peak L may likely be chrysoeriol according to literature[34,35]. Peak G present in the chromatograms related to hydrolyzed and non-hydrolyzed weld extracts was identified as luteolin. Datiscetin-3-*O*-[rhamnosyl (1-6) glucoside], luteolin-3'-7-di-*O*-glucoside and luteolin-7-*O*-glucoside could be converted into datiscetin and luteolin dyes as an aglycon in the hydrolyzed weld and hemp extracts. In Table 5, the pH measurements of the sample extracts are given.

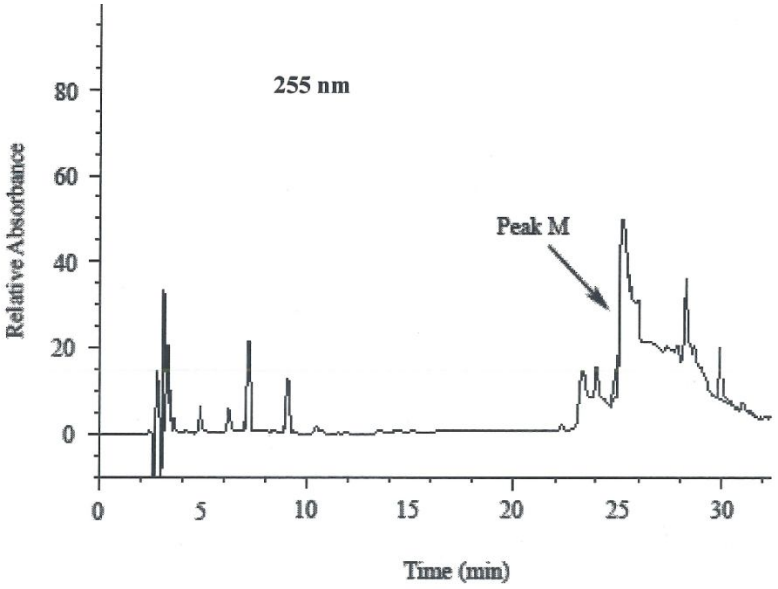


Figure 7. Chromatogram of tin-hemp-weld lake pigment (prepared with 10 mL tin solution).

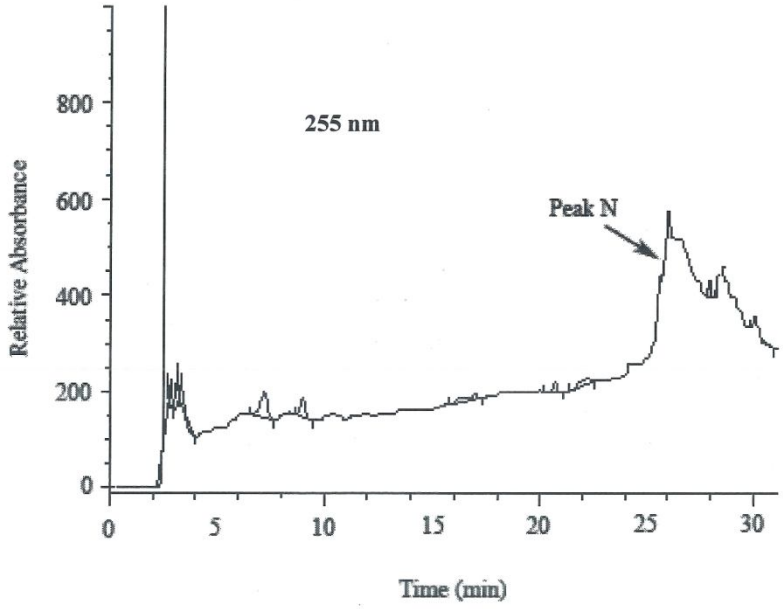


Figure 8. Chromatogram of tin-hemp-weld lake pigment (prepared with 15 mL tin solution).

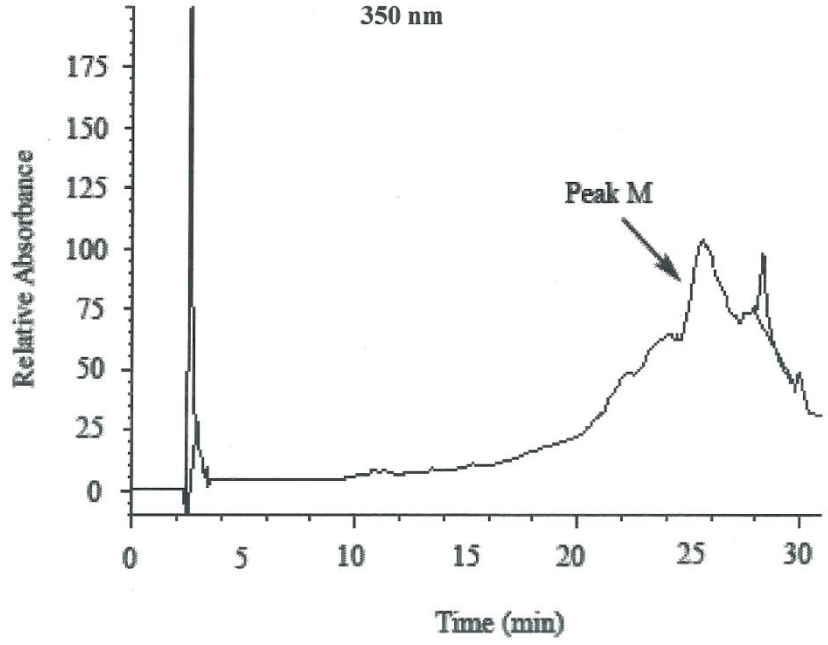


Figure 9. Chromatogram of aluminium-hemp-weld lake pigment (prepared with 20 mL alum solution).

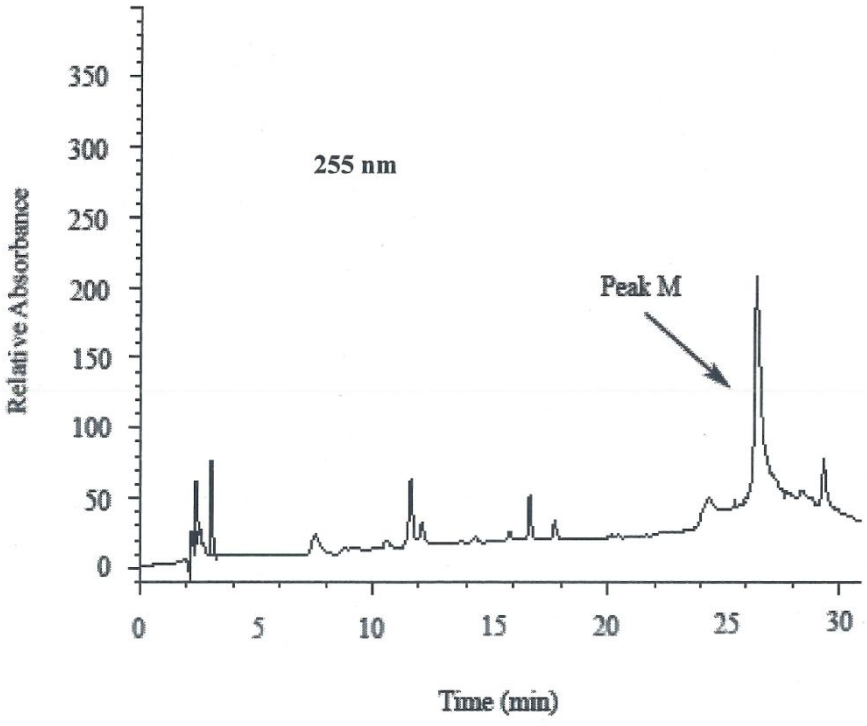


Figure 10. Chromatogram of aluminium-hemp-weld lake pigment (prepared with 15 mL alum solution).

As shown in Figures 7, 9 and 10, peak M was identified based on the absorption spectra acquired with standard datiscetin reference dye compound in the hydrolyzed tin-hemp-weld and aluminium-hemp-weld lake pigments. On the other hand, peak N was identified as luteolin, as shown in Figure 8. Comparison of these results with those shown in Table 3 results in the identification of the detected dyes, which can be summarized as follows.

Table 4. Chromatographic and spectral characteristics of the investigated sample extracts.

Sample number	Sample extract	Colouring components detected	Characteristics of the detected colouring components: t_R (min)	Peak	Absorbance maxima (nm)
S.1	Non-hydrolyzed hemp extract	Possible datiscetin-3-*O*-[rhamnosyl (1-6)glucoside]	18.0	Fig. 3	257, 305, 329
		Datiscetin	26.4	Fig. 3	257, 305, 347
S.2	Hydrolyzed hemp extract	Datiscetin	25.2	Fig. 4	255, 305, 347
S.3	Non-hydrolyzed weld extract	Luteolin-3',7-di-*O*-glucoside	18.4	Fig. 5	241, 267, 341
		Luteolin-7-*O*-glucoside	19.9	Fig. 5	253, 265, 349
		Luteolin	25.4	Fig. 5	253, 267, 291, 347
		Apigenin	26.7	Fig. 5	267, 291, 337
		Chrysoeriol	27.0	Fig. 5	251, 267, 289, 347
S.4	Hydrolyzed weld extract	Luteolin	25.5	Fig. 6	253, 267, 291, 347
		Apigenin	26.8	Fig. 6	267, 293, 337
		Chrysoeriol	27.1	Fig. 6	251, 267, 289, 347
S.5	Tin-hemp-weld lake (prepared with 10 mL tin solution)	Datiscetin	25.2	Fig. 7	255, 305, 345
S.6	Tin-hemp-weld lake (prepared with 15 mL tin solution)	Luteolin	26.0	Fig. 8	257, 265, 295, 347
S.7	Aluminium-hemp-weld lake (prepared with 20 mL alum solution)	Datiscetin	25.5	Fig. 9	255,305,351
S.8	Aluminium-hemp-weld lake (prepared with 15 mL alum solution)	Datiscetin	26.4	Fig. 10	257,307,347

Table 5. pH measurements of the investigated sample extracts and solutions.

Sample extract	pH
Weld extract	5.44
Hemp extract	5.37
30 mL weld extract + 40 mL hemp extract	5.43
15 % $KAl(SO_4)_2.12H_2O$ solution	3.29
3 % $SnCl_2.2H_2O$ solution	1.80
10 mL Al + 30 mL weld extract + 40 mL hemp extract	3.13
15 mL Al + 30 mL weld extract + 40 mL hemp extract	3.11
20 mL Al + 30 mL weld extract + 40 mL hemp extract	3.10
25 mL Al + 30 mL weld extract + 40 mL hemp extract	3.09
30 mL Al + 30 mL weld extract + 40 mL hemp extract	3.09
10 mL Sn + 30 mL weld extract + 40 mL hemp extract	2.56
15 mL Sn + 30 mL weld extract + 40 mL hemp extract	2.49
20 mL Sn + 30 mL weld extract + 40 mL hemp extract	2.37
25 mL Sn + 30 mL weld extract + 40 mL hemp extract	2.31
30 mL Sn + 30 mL weld extract + 40 mL hemp extract	2.26

- All measurements were performed at room temperature.

Colour Analysis

The brightness and colour values of aluminium and tin-hemp-weld lakes were determined by CIELAB colour space system. The highest brightness values (L*) for aluminium -and tin-hemp-weld lake pigments were observed in samples that have been prepared with 30 mL of the solution of metal salts. When the yellow and blue colour values (b*) for aluminium and the tin – hemp - weld lake pigments were examined, it was observed that the best yellow and blue colour were obtained from lake pigments formed by using 15 and 10 mL of alum and tin solutions. We determined that the brightness values increased with increasing volumes of metal solutions (except for 25 ml of tin solution) used in the aluminium- and tin-hemp-weld lake pigments. The maximum red and green value (a*) was determined in the aluminium-hemp-weld obtained using 10 ml alum solution. The lowest red and green value is related to the aluminium-hemp-weld lake pigment obtained with 30 ml alum solution. The lowest yellow and blue (b*) value was provided from the aluminium-hemp-weld obtained using 30 ml alum solution. The lowest brightness value (L*) is related to the aluminium-hemp-weld prepared with 10 ml alum solution.

Conclusion

In this study, the reaction of dyes present in hemp and the weld plants with aluminium (III), iron (II) and tin (II) has been used to prepare lake pigments. The dyes present in the lake pigments were analyzed qualitatively by a reversed -phase high- performance liquid chromatography (HPLC) with diode array detection (DAD) in comparison with standard dyes. The effect of different amounts of metals on the colouring scale of the lake pigments, except for the iron-hemp-weld pigment, was investigated. This pigment was not considered because of non-identification of peaks in chromatogram. So, the colour measurements of this pigment were not realized. We believe that lake pigments obtained from dye plants as a result of colour measurements will be used in conservation and restoration works, especially for wall paintings and historical manuscripts.

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