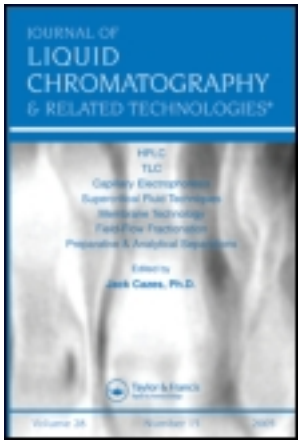

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IDENTIFICATION BY RP-HPLC-DAD OF NATURAL DYESTUFFS FROM LAKE PIGMENTS PREPARED WITH A MIXTURE OF WELD AND DYER'S OAK DYE PLANTS

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□ *The lake pigments by means of the weld (Reseda luteola) and dyer's oak (Quercus infectoria) dye plants were prepared by using $KAl(SO_4)_2 \cdot 12H_2O$ (alum), $FeSO_4 \cdot 7H_2O$ and $SnCl_2 \cdot 2H_2O$ mordants. A reversed-phase high performance liquid chromatography (RP-HPLC) with diode array detection (DAD) method was utilized for the identification of dyestuffs present in the lake pigments. The dyestuff extractions from the pigments were carried out with a solution mixture of 37% HCl:MeOH:H_2O (2:1:1, v/v/v). The performed method is able to analyze and detect natural dyestuffs such as luteolin, apigenin, gallic acid, and ellagic acid present in the lake pigments.*

Keywords dyer's oak, lake pigment, luteolin, natural dyestuff, *Reseda Luteda*, RP-HPLC

INTRODUCTION

The dyer's oak (*Quercus infectoria* Olivier) is a semi-deciduous little tree that grows to 12 m height and skirts along Asia Minor and the Mediterranean countries as well as southeastern Europe. The leaves are 1 to 4 inches long with unevenly scalloped edges. The acorn-caps are about an inch long and enclose two-thirds of the acorn.[1–3] The gallnuts also known in English as Levant galls or Turkish galls, *Aleppogallen* in German, *noci di galla* in Italian, and *agallas* in Spanish.[3] The gallnuts have been

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used for various scopes such as dye and leather as well as ink manufacture from Sumerians to today.[1] It was the main source of black dye for silk.[3] The gallnuts collected in Turkey are boiled with wool. The obtained color is between soiled yellow and brown. This dyeing type is known as "tetre dyeing" by local community in Turkey. (*Tetre* is apparently an old process, as the pale yellow in many called historical rugs.) The black color for the *tetre* dyed wool was achieved with mordanting by means of the iron mordant. This form was used for the black dyeing in Turkish carpets and rugs. But, this type of dyeing suffers from spilling and abrasion. On the other hand, in Iran, black color is obtained by using a mixture of madder, indigo, and plants providing yellow color. Corrosion is formed in the black dyed colours with gallnuts and iron over time. However, the corrosion is not formed in the black colour obtained by using a mixture of the plants (madder, indigo, and plants providing yellow colour) for ages.[1] The gallnuts contains as much as 50–70% of gallotannins.[3] Ellagic acid related to *Quercus infectoria* was identified by Karadag et al.[4] in some natural dyestuffs from the fifteenth to the seventeenth century ottoman silk textiles.

Weld (*Reseda luteola* L.) is an annual or biennial herb.[3] The branched erect stems grow up to 150 cm tall. The leaves of the plant are formed in the first year and the plant evolution is complete in the second year. It grows in parts of North Africa and most of the eastern Mediterranean Region.[2] The whole plant was used for dyeing of wool and silk. The yellow dyestuffs that are used for the coloring matters are concentrated mainly in the leaves, inflorescences, and fruits.[3] The flavonoids are known as yellow dyestuffs.[5,6] Luteolin and apigenin flavonoids are effective dyestuffs present in the weld plant.[7] Luteolin from these dyestuffs is known to possess antibacterial and anti-inflammatory properties.[8]

The precipitates were prepared by the reaction of the mordant metals (Al, Fe, Sn, etc.) with dyestuffs (flavonoid, anthraquinone, and indigotin compounds) present in the dye plants or insects and used as organic pigments.[8–12]

From the fourteenth to the nineteenth centuries, lake pigments were primary constituents of the artist's palette and used for artistic techniques such as miniature, tempera, painting, oil paint, and iconography.[13–15] High performance liquid chromatography (HPLC) using a diode-array detection (DAD) is ideally suited for identification of natural dyestuffs including lakes present in these materials.[16–19]

The goal of the present study was to perform natural dyestuff analysis using HPLC-DAD in samples extracted from lake pigments prepared with a mixture of weld (*Reseda luteola* L.) and dyer's oak (*Quercus infectoria* Olivier) dye plants.

EXPERIMENTAL

Materials

Weld (*Reseda luteola* L.) dye plant and dyer's oak (*Quercus infectoria* Olivier) dye plants were provided from TCF, Research and Development Laboratory for Natural Dyes, Istanbul, Turkey. The following standard dyestuffs were used as references: apigenin from Carl Roth (Karlsrube, Germany); and gallic acid and ellagic acid from Merck (Darmstadt, Germany). Potassium-aluminum sulfate (alum), ferrous sulfate, stannous chloride, potassium carbonate, hydrochloric acid (37% fuming HCl), acetonitrile (MeCN, HPLC gradient grade), trifluoroacetic acid (TFA, HPLC gradient grade), and methanol (MeOH, HPLC gradient grade) were obtained from Merck (Darmstadt, Germany).

Instruments

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

Methods

Extraction of Dyes from Weld and Dyer's Oak

Weld and dyer's oak extracts were prepared by water as previously described by Deveoglu et al.,[16–19] in which 40 g of the highly granulated dyer's oak (*Quercus infectoria* Olivier) plant were transferred into a 5000 mL beaker (0.8%). A quantity of 60 g of the aerial parts of weld (*Reseda luteola* L.) plant were transferred into another 5000-mL beaker (1.2%). A total of 5000 mL ultra-pure water were added and the mixtures were heated to 100°C by using a magnetic stirrer and then retained at 75–80°C for 1 hr. Finally, the mixtures were filtered by a filter paper to obtain the weld and the dyer's oak extracts.

Procedure for the Preparation of Lake Pigments

Potassium aluminum sulfate (alum) solution 15%, weld, and dyer's oak extracts were heated at 90°C (solution) and 60°C (extracts), respectively. The alum solutions of 5, 10, 15, 20, and 25 mL at 90°C were each added to a solution containing a mixture of 50 mL weld extract and 10 mL dyer's oak 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.[16–19] The mixtures were cooled to room

temperature to allow the precipitation of the aluminum-weld-dyer's oak lake pigments. After settling down, the mixtures were filtered and the precipitates were washed with ultra-pure water and dried on a filter paper at 100°C for 0.5 hr. The dried aluminum-weld-dyer's oak lake pigment precipitates were then powdered. The same process was repeated to precipitate the lake pigments by using 3% ferrous sulfate and 3% stannous chloride solutions.[19,20]

Sample Preparation for the HPLC Analysis

The dyestuff extraction from the dye plants and the lake pigments were done by using the previously performed method.[16–23]

For the dyestuff extraction from weld (*Reseda luteola* L.) and dyer's oak (*Quercus ithaburensis* Decaisne) plant and lake pigments, three procedures (1°, 2° and 3°) were performed.

1°) The first procedure for the dyestuff extraction from weld (2.7 mg) and dyer's oak (9.9 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°) As the second procedure, weld (2.5 mg) and dyer's oak (6.5 mg) dye plants were hydrolyzed in 400 μL of a solution mixture of 37% HCl/MeOH/H_2O (2:1:1, v/v/v) in conical glass tubes exactly 10 min in a water-bath at 100°C to extract organic dyestuffs. After rapid cooling under running cold water, the solution was evaporated just to dryness in a water-bath at 55–65°C under a gentle stream of nitrogen. Subsequently, the dry residues were dissolved in 400 μL of the mixture MeOH:H_2O (2:1, v/v) and were centrifuged at 2500 rpm for 10 min; 10 μL and/or 15 μL of the supernatant was injected into the HPLC equipment.
3°) The sample preparation for the extraction of dye components from lake pigments is based on the commonly used hydrolysis procedure with hydrochloric acid.[24] For the extracts, this treatment is necessary to isolate the organic dyestuff from its mordant metal. The acid hydrolysis of aluminum-weld-dyer's oak, iron-weld-dyer's oak, and tin-weld-dyer's oak lake pigments (7.1–10.8 mg) was achieved according to the procedure presented in 2° step. Then, 20 μL and/or 50 μL of the supernatant were injected into the HPLC equipment.

HPLC Equipment

Chromatographic experiments 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. 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

TABLE 1 Gradient Elution Program 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

255 and 268 nm. A G1322A vacuum degasser and a G1316A thermostated column compartment were used. The data were evaluated using Agilent Chemstation. A Nova-Pak C_{18} analytical column (3.9 mm × 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 previously reported method.[21,22] Chromatographic separations of the hydrolyzed samples were performed using a gradient elution program that utilizes two solvents: solvent A: H_2O - 0.1% TFA (trifluoro-acetic acid) and solvent B: CH_3CN (acetonitrile) - 0.1% TFA. The solvent selection originated from previous publications.[21] The flow rate was 0.5 mL/min and the applied elution program is described in Table 1.

RESULTS AND DISCUSSION

In the present study, the complexes formed with adding aluminum(III), iron(II), and tin(II) solutions to weld (*Reseda luteola* L.) and dyer's oak (*Quercus infectoria* Olivier) extracts were obtained as lake pigments. In Figure 1, retention times (R_t) and corresponding spectral characteristics of the main coloring components of dyer's oak and weld, detected in Table 2, are presented. The main coloring components (gallic acid, ellagic acid, luteolin, and apigenin) of dyer's oak and weld can be fully separated, detected, and identified by their UV-Vis spectra. Detection of these components in extracts originating from lake pigments allows univocal identification of dyer's oak and weld.

The standard dyestuffs used in the present study, such as gallic acid, ellagic acid, and apigenin were also chromatographically and spectrophotometrically (UV-Vis) characterized. Absorbance maxima (nm) and retention time (min) related to luteolin standard dyestuff were evaluated according to the present literature[4] because of the corresponding standard dyestuffs were not exactly available. Absorbance maxima in Figure 1, which correspond to the two dyer's oak components, appear to be similar and in good

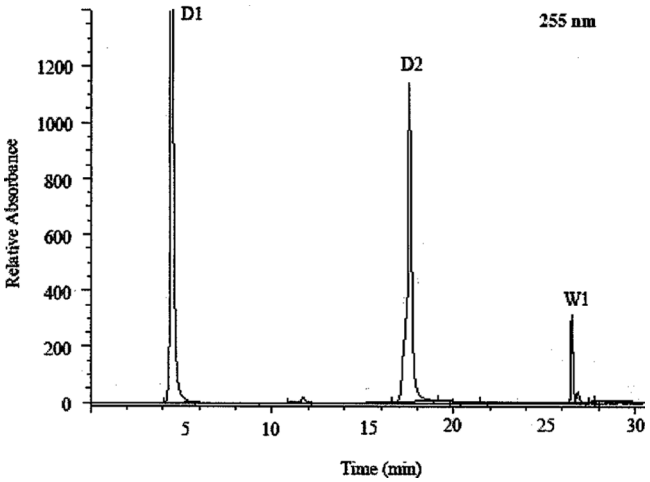


FIGURE 1 Chromatogram of standard sample mixture. D1: gallic acid (R_t: 4.4 min, λ_{max}: 215, 271 nm; D2: ellagic acid (R_t: 17.5 min, λ_{max}: 253, 307, 369 nm; and W1: apigenin; R_t: 26.5 min, λ_{max}: 267, 293, 337 nm).

agreement with the spectral characteristics of gallic acid and ellagic acid, the main coloring components of the dyer's oak, that can be found in the literature.[2,3] Table 3 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.[10] We analyzed at 255 nm and 268 nm dyestuffs present in the lake pigments and the plant extracts in this study.

In samples derived from the hydrolyzed and non-hydrolyzed weld extracts a minor peak, shown as peak A in Figure 2a and 2b, respectively, has been recorded just "in behind" of the main peak that corresponds to

TABLE 2 Chromatographic Characteristics of the Plants and Lake Pigments

Dyestuff Source	Colouring Component	Observation Peaks
Dyer's oak	Gallic acid	K, D
	Gallic acid derivative	H, M, R
	Ellagic acid	P, T
	Ellagic acid derivative	I, L
Weld	Luteolin-3′-7-di-*O*-glucoside	E
	Luteolin-7-*O*-glucoside	F
	Luteolin	C, N
	Apigenin	A
	Possible apigenin derivative	V
	Chrysoeriol	B

TABLE 3 Chromatographic and Spectral Characteristics of the Plants and Lake Pigments

Sample Number	Sample Extract	Colouring Components Detected	Characteristics of the Detected Colouring Components		
			Rt (min)	Peak	Absorbance Maxima (nm)
S.1	Non-hydrolyzed weld	Luteolin-3′-7-di-*O*-glucoside	18.4	Fig. 2	241, 267, 341
		Luteolin-7-*O*-glucoside	19.9	Fig. 2	253, 265, 349
		Luteolin	25.5	Fig. 2	253, 267, 291, 347
		Apigenin	26.8	Fig. 2	267, 293, 337
		Chrysoeriol	27.0	Fig. 2	251, 267, 289, 347
S.2	Acid hydrolyzed weld	Luteolin	25.5	Fig. 2	253, 267, 291, 347
		Apigenin	26.8	Fig. 2	267, 293, 337
		Chrysoeriol	27.1	Fig. 2	251, 267, 289, 347
S.3	Non-hydrolyzed dyer's oak	Gallic acid	4.0	Fig. 3	269
		Ellagic acid derivative	14.2	Fig. 3	251, 297, 359
		Gallic acid derivative	14.9	Fig. 3	235, 275
		Ellagic acid	16.9	Fig. 3	251, 301, 367
S.4	Acid hydrolyzed dyer's oak	Gallic acid	3.9	Fig. 3	229, 243, 271
		Gallic acid derivative	9.3	Fig. 3	229, 235, 243, 271
		Ellagic acid derivative	10.0	Fig. 3	255, 373
		Ellagic acid	17.2	Fig. 3	251, 307, 369
S.5	Al-weld-dyer's oak pigment	Gallic acid	3.9	Fig. 4	271
		Gallic acid derivative	9.2	Fig. 4	273
		Ellagic acid	17.2	Fig. 4	253, 307, 371
		Luteolin	23.1	Fig. 4	229, 259, 345
S.6	Fe-weld-dyer's oak pigment	Ellagic acid	16.1	Fig. 4	261, 305, 367
		Luteolin	23.2	Fig. 4	253, 263, 349
S.7	Sn-weld-dyer's oak pigment	Gallic acid	4.0	Fig. 4	273
		Luteolin	23.3	Fig. 4	257, 295, 349
		Apigenin	25.5	Fig. 4	263, 293, 337
		Possible apigenin derivative	25.9	Fig. 4	261, 295, 347

pure apigenin. Luteolin (peak N) was identified in the non-hydrolyzed (S.1) and hydrolyzed weld (S.2) extracts as a major component. As shown in Figure 2a, the main peak (peak F) was determined as luteolin-7-*O*-glucoside by the corresponding reference.[25] Nevertheless, in the chromatogram related to the same extract, peak E was identified as luteolin-3′,7-di-*O*-glucoside. As shown in Figure 2a and 2b, peak B may likely be chrysoeriol according to the present literatures.[26,27]

As shown in Figure 3c, gallic acid (peak K) was identified as a minor component. Ellagic acid (peak T) was determined in the non-hydrolyzed dyer's oak extract (S.3). And the peak L was attributed to an ellagic acid derivative. Peak M discloses existing gallic acid derivative. Gallic acid was determined as a main component in the chromatogram of the acid hydrolyzed dyer's oak extract (S.4) as shown in Figure 3d. Ellagic acid was also identified. Nevertheless, in the chromatogram related to the same extract, peaks H and I were identified as gallic acid and ellagic acid derivatives.

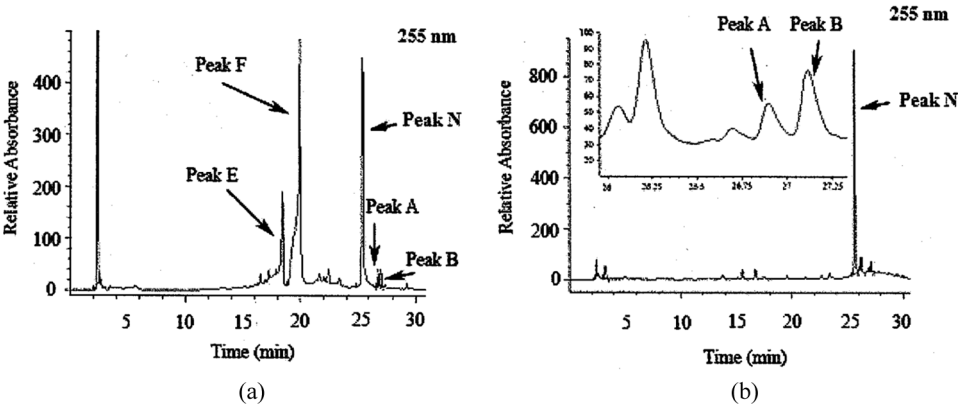


FIGURE 2 Chromatograms of non-hydrolyzed (a) and acid hydrolyzed; and (b) weld extracts (peak E: luteolin-3′-7-di-*O*-glucoside; peak F: luteolin-7-*O*-glucoside; peak N: luteolin; peak A: apigenin; peak B: chrysoeriol).

Chromatographic peaks are presented in Figure 4a, 4b, and 4c) for the samples extracted from lake pigments (S.5, S.6, and S.7, respectively). Peak A was not recorded for the extracts of lake pigments (S.5 and S.6), and the acquired absorption spectra corresponding to peak A. Comparison of these with Table 3 results in the identification of the detected dyestuffs, which can be summarized as follows. Luteolin, the main component of weld, was recorded for the sample extracted from the acid hydrolyzed weld extract (S.2). No other yellow dyestuffs (gallic acid and ellagic acid) were detected with respect to Figure 1. The main dyestuff component, gallic

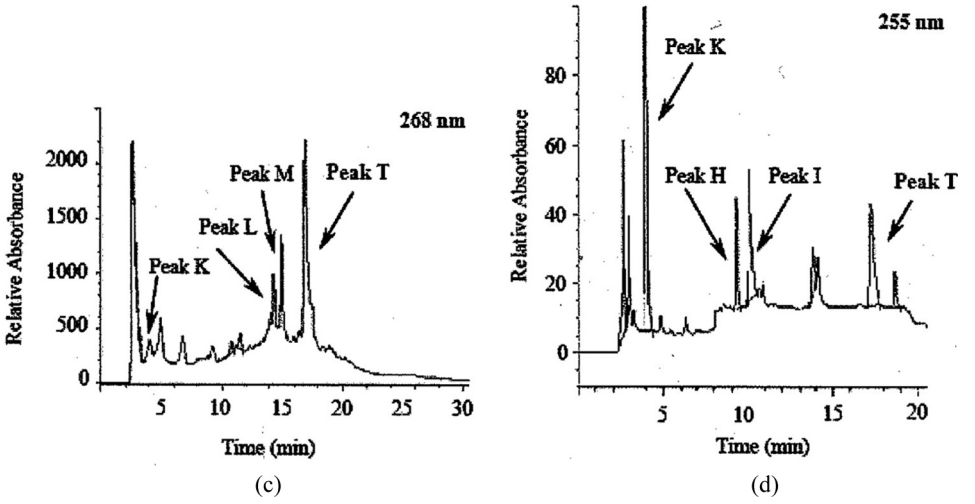


FIGURE 3 Chromatograms of non-hydrolyzed (c) and acid hydrolyzed (d) dyer's oak extracts (peak K: gallic acid; peaks H-M: gallic acid derivatives; peaks I-L: ellagic acid derivatives; peak T: ellagic acid).

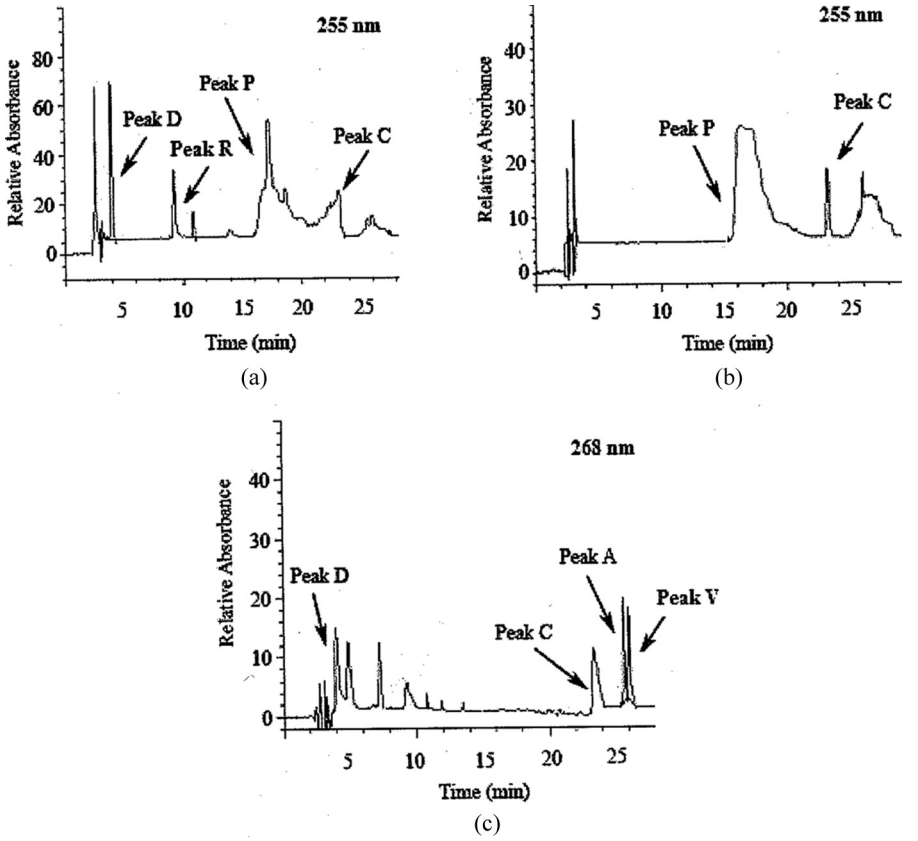
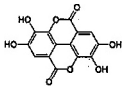
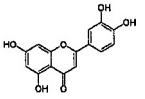
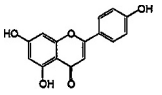
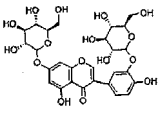
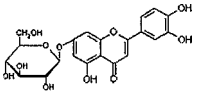
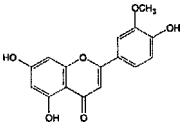


FIGURE 4 Chromatograms of aluminum (a), iron (b), and tin-weld-dyer's oak (c) pigments (peak D: gallic acid; peak R: gallic acid derivative; peak P: ellagic acid; peak C: luteolin; peak A: apigenin; peak V: possible apigenin derivative).

acid, related to the aluminum-weld-dyer's oak lake pigment (S.5), was identified as shown in Figure 4a. It should be noted here, that both standard dyestuffs and sample extracts from the plants and the lake pigments, were treated by exactly the same 1° and 2° procedures, described in the paragraph on sample preparation for the HPLC analysis. Gallic acid (peak D) was also identified in both lake pigments (S.5 and S.7). Ellagic acid (peak P), which is a gallic acid dimer, was determined as a major coloring component in both lake pigments (S.5 and S.6). Peak C was identified as luteolin and it was a minor coloring component. Otherwise, luteolin was also identified as a major component as shown in Figure 4b. Peaks A, C, and D relating to gallic acid, luteolin, and apigenin in the tin-weld-dyer's oak lake pigment (S.7) were identified according to increasingly retention times (min), respectively, as shown in Figure 4c. Peak V may likely be an apigenin derivative. Peak A from these peaks appears apigenin that a major

TABLE 4 Identified Dyestuff in the Plants and Lake Pigments

Identified Dyestuff	Non-Hydrolyzed Weld Extract	Acid Hydrolyzed Weld Extract	Non-Hydrolyzed Dyer's oak	Acid Hydrolyzed Dyer's oak	Aluminium Weld-Dyer's Oak Pigment	Iron Weld-Dyer's Oak Pigment	Tin Weld-Dyer's Oak Pigment
Gallic acid 	−	−	+	+	+	−	+
Gallic acid derivative	−	−	+	+	+	−	−
Ellagic acid 	−	−	+	+	+	+	−
Ellagic acid derivative	−	−	+	+	−	−	−
Luteolin 	+	+	−	−	+	+	+
Apigenin 	+	+	−	−	−	−	+
Possible apigenin derivative	−	−	−	−	−	−	+
Luteolin-3′,7-di-*O*-glucoside 	+	−	−	−	−	−	−
Luteolin-7-*O*-glucoside 	+	−	−	−	−	−	−
Chrysoeriol 	+	+	−	−	−	−	−

component. Ellagic acid was not recorded in the lake pigment (S.7). However, our qualitative analytical technique allows great sensitivity in the detection of flavonoids and tannins from organic lake pigments and, thus, allows distinction between possible plant sources for dyestuffs in weld and dyer's oak lake pigments on the basis of their coloring components.

CONCLUSION

In this study, the reaction of the dyestuff present in weld and dyer's oak extracts with aluminum(III), iron(II), and tin(II) has been used to prepare lake pigments. RP-HPLC-DAD was used to analyze the organic colorants of samples extracted from lake pigments, which were generated by a mixture of weld and dyer's oak extracts with aluminum(III), iron(II), and tin(II). Even several dyestuffs (gallic acid and ellagic acids for dyer's oak and luteolin; apigenin and chrysoeriol for weld) were detected in the acid hydrolyzed extracts of the biological sources discussed and only some of them are present in the lakes prepared. The experiments showed that either ellagic or gallic acid were detected, no matter which mordant was used in the lake pigment preparation. On the other hand, luteolin was the only dyestuff obtained from weld plant extract, except for the tin weld dyer's oak pigment where apigenin was also present. The dyestuffs identified as present in the plant and lake pigments are given in Table 4.

ACKNOWLEDGMENTS

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