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ANALYSIS OF PROTOBERBERINES IN HISTORICAL TEXTILES: DETERMINING THE PROVENANCE OF EAST ASIAN TEXTILES BY ANALYSIS OF PHELLODENDRON

Yoshiko Sasaki*[1], Ken Sasaki*[2]

Abstract

Species of Phellodendron (Amur cork tree and its relatives) have been used as a source of traditional yellow dyes in East Asia. HPLC analyses of the dye has shown that the relative ratios of palmatine and jatrorrhizine to berberine, (the J/B and P/B ratios) in it, strongly reflect the differences between the species, Phellodendron amurense in Japan and Phellodendron chinense in China, respectively. The provenance can be easily determined by using a scatter diagram of J/B and P/B ratios. This methodology was applied to weaving and embroidery threads from Chinese and Japanese style historical textiles. The results of weaving samples showed that the provenance and the style were accorded, except for one Chinese style textile: the 14th Century Kasaya. It clearly appeared in the Japanese region of the diagrams, leading to the conclusion that it originated in Japan. Regarding the embroidery threads in historical textiles, most results reflected each style, but the result of one Japanese style textile appeared in the Chinese region, indicating a trading of dye material or dyed thread from China to Japan in ancient times. Thus, our methodology will be useful for gaining historical information about the techniques and trading of textiles in East Asia.

1 Introduction

Plant materials that contain protoberberine alkaloids have been used since ancient times in East Asia for dyeing, as well as for medicinal purposes. Typical plants were phellodendron (Amur cork tree and its relatives, *Phellodendron amurense* in Japan and *Phellodendron chinense* in China),[1,2,3] goldthread (*Coptis japonica* in Japan and *Coptis chinensis* in China),[2,3] Japanese barberry (*Berberis thunbergii*),[4] and huangteng (*Fibraurea tinctoria*).[5,6] The use of Amur cork tree and goldthread were described in old Japanese law sources (*Yoro-rei*, Chap.10, Article 1, A.C.757) where these materials were said to be one of tax materials, together with other dye plants such as safflower and madder.[3]

Major protoberberine alkaloids are berberine (B), palmatine (P), jatrorrhizine (J) and coptisine (C), which have a common cationic protoberberine backbone (Fig. 1). Since the protoberber-

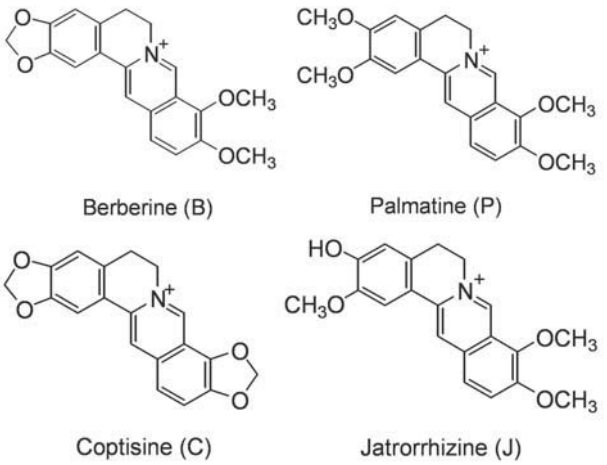

Figure 1: Typical protoberberine alkaloids in dye plants materials.

ines have characteristic spectroscopic properties, including their unique fluorescent nature, it has been possible to develop non-destructive methods for the detection of protoberberine dyes in historical textiles.[7,8]

In this paper, we describe a methodology for discrimination between various dye plants containing protoberberine alkaloids, based on quantitative analysis of the four major protoberberines.[9] More specifically, we focus on the determination of the origin of phellodendron (Amur cork tree and its relatives). This determination is based on the differences in relative amounts of palmatine and jatrorrhizine in the dyed textiles and was developed to distinguish between historical textiles originating in Japan and China.[10] The knowledge would be useful in providing historical information concerning the techniques used for textile production and the history of dye trading in East Asia.

2 Materials and methods

2.1 Instrumentation

High performance liquid chromatographic analyses (HPLC) were carried out using the Hitachi F-7000 elution system (Hitachi, Tokyo, Japan) equipped with a JASCO MCD2010 photo-diode-array (PDA) detector (Jasco, Tokyo, Japan). Separations were achieved on a Cosmosil 5C18ArII column (4.6 mm I.D. x 250 mm) (Nacalai Tesque, Kyoto, Japan) eluted with 5% SDS-acetonitrile/H_2O (1/1) at a flow rate of 1 mL/min [11] (Condition 1); or on a Cosmosil 5Ph column (4.6 mm I.D. x 250 mm; Nacalai Tesque, Kyoto, Japan) eluted with 0.01% TFA-H_2O/methanol (1/1) at a flow rate of 1 mL/min and combined with LC-MS detection (Condition 2). Electrospray Ionization Ion Trap Mass Spectrometric analyses (ESI-IT-MS) were carried out with a Bruker Amazon SL instrument (Bruker, Massachusetts, USA) (ionization voltage 4 KeV, ion source temperature 220 °C) in the positive ion mode. High Resolution Mass Spectrometric analysis (HRMS) was made using a JEOL JMS-700 (Jeol, Tokyo, Japan). ^{1}H-NMR spectra were measured on a Bruker AV-600 spectrometer (Bruker, Massachusetts, USA) with CD_3OD as solvent at 300 K. UV-VIS absorption and reflection absorption spectra were obtained with a Shimadzu UV-3101 spectrophotometer with integrating spheres (Shimadzu, Kyoto, Japan); or on an Ocean Optics USB-4000 optical fiber spectrometer (Ocean Optics, Florida, USA). Fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer (Hitachi, Tokyo, Japan).

2.2 Reagents

Berberine chloride was commercially available (Tokyo Chemical Industry Co., Tokyo, Japan) and recrystallized twice from methanol. Coptisine chloride was purchased from Wako Pure Chemical Industries (Tokyo, Japan) and used as received.

Palmatine chloride was extracted from Colombo root (*Jateorhiza columba,* from Yoshimi Pharmaceutical Co., Osaka, Japan) and purified by a published procedure.[12, I]

Jatrorrhizine was extracted from Chinese goldthread (*Coptis chinensis*, Kara Ohren, from Takasago Pharmaceutical Co., Osaka, Japan) and was purified as the iodide by a reported procedure.[13, II]

2.3 Dye Plants

Modern phellodendron (Amur cork tree and its relatives; M-J1~J3, M-C1~C2) ,[III] goldthread, and Japanese barberry were obtained from drug stores in Japan. Phellodendron (M-C3~C11), [c] and huangteng were purchased in China and Taipei, Taiwan. Some samples of Japanese Amur cork tree (*P. amurense;* M-J4~J10) [c] were donated by Ms. Hisako Sumi, NGO Earth Network, Sapporo Japan.

2.4 Preparation and Extraction of Standards

1 g of plant material was extracted in 150 mL water at 70 °C for 1 h; after filtration, silk cloth (2 x 3 cm) was dyed in this extract at 70 °C for 1 h. The dye ingredients were extracted with 3% formic acid in methanol (300 μL) at room temperature and 10 μL of the extract was subjected to HPLC analysis.

2.5 Sampling of Historical Textiles

Weaving threads were obtained from Chinese and Japanese style textile fragments stored at the Kyoto Institute of Technology (W-C1~C11 and W-J1~J6), [c] from a Japanese style kimono garment of the Matsuzakaya Collection (W-J7 and J8), [c] and from a *kasaya* [IV] of the *Donke-in* temple in Kyoto (W-C12). [c] Embroidery threads were obtained from Chinese and Japanese style textile fragments stored in the Kyoto Institute of Technology (E-C1~C8 and E-J6~J16), [c] and from Japanese style textile fragments in a private collection (E-J1~J5) .[c]

2.6 Extraction of Dyes from Historical Textiles

Dyes were extracted from threads (0.3 mg) with 3% formic acid in methanol (300 μL) at room temperature and 10 μL of the dye extract was subjected to HPLC analysis.

3 Results and Discussion

3.1 Methodology for the Analysis of Protoberberines in Standards

Identification of dye plants considered in this paper was made possible by HPLC separation and relative quantification of the four major protoberberines in extracts of dyed standards. Analyses were carried out under Condition 1. The results (Fig. 2) show characteristic distributions of protoberberines. Both Japanese and Chinese goldthreads were marked by the presence of coptisine. Huangteng was distinguished by the absence of berberine. Phellodendron (Amur cork tree and its relatives) and Japanese barberry included small amounts of palmatine and jatrorrhizine relative to berberine. But discrimination was possible by observ-

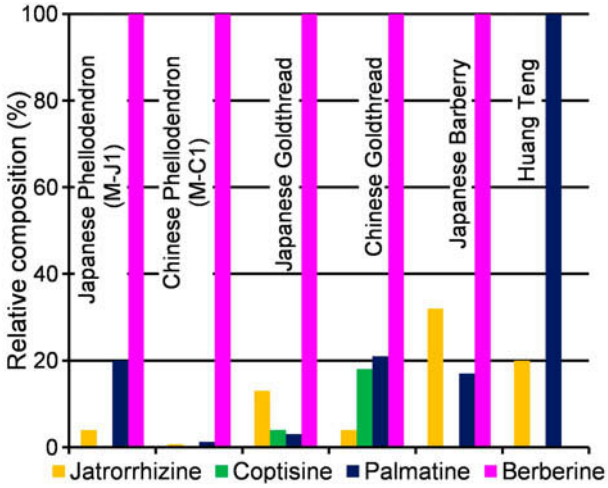

Figure 2: Composition of protoberberines relative to berberine in extracts from dyed standards by HPLC monitored at 350 nm.

ing the relatively smaller amount of jatrorrhizine in phellodendron.

Interestingly, Japanese phellodendron showed a relatively higher content of palmatine as compared with the Chinese type. Similar differences between Japanese and Chinese phellodendron have been reported in the analyses of extracts of medicinal herbs.[14,15] Also goldthreads could be identified as either Japanese or Chinese, based on differences of relative amounts of palmatine. Thus, determination of amounts of palmatine relative to berberine would be effective for determining whether the dye plants considered originated in Japan or China.

3.2 Determination of Phellodendron Provenance through Analysis of Standards

Standards dyed by modern Japanese and Chinese phellodendron were prepared from all available sources (10 from Japan, 11 from China). Non-destructive spectroscopic analyses, providing visible absorption and fluorescence excitation-emission matrix (EEM) spectra were applied. Typical results for one Japanese (M-J1) and one Chinese (M-C1) phellodendron standard are shown in Fig. 3. Obviously, close to inconspicuous differences in both spectrometric analyses were unable to distinguish between Chinese and Japanese phellodendron species. However, due to counter-peaks at 520 nm/350 nm and 520 nm/460 nm characteristic for protoberberine fluorescence spectra, this non-destructive analytical approach can be used to reveal the presence of protoberberine containing dyes on dyed cloths.

Micro-destructive HPLC analyses (under Condition 2) of extracts from dyed standards (2 mg) were carried out to determine the composition of protoberberines in phellodendron of different origins. Fig. 4 shows typical HPLC chromatograms monitored at 350 nm and normalized to the berberine peak. Berberine (B), palmatine (P) and jatrorrhizine (J) were identified by their characteristic absorption spectra, by comparison of the retention times with authentic pure products, and by the ESI mass spectra (*m/z* 336 for B, 338 for J, and 352 for P).

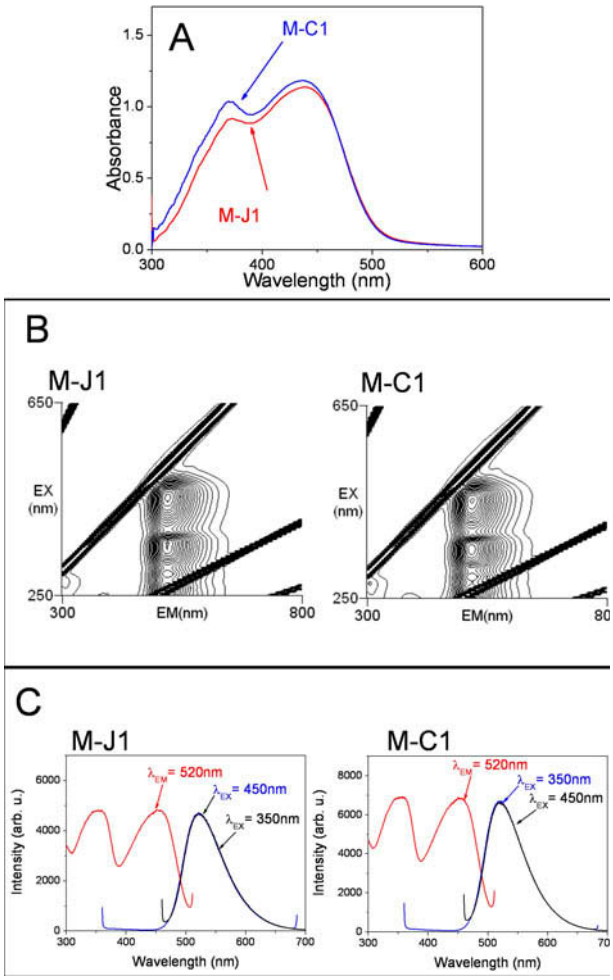

Figure 3: Visible absorption and fluorescence spectra of standards dyed by one Japanese (M-J1) and one Chinese (M-C1) phellodendron; A: visible absorption spectra, red line: Japanese, blue line: Chinese; B: EEM fluorescence spectra; C: Fluorescence emission (black and blue line, λ_{EX} =350, 450 nm) and excitation spectra (red line, λ_{EM} = 520 nm).

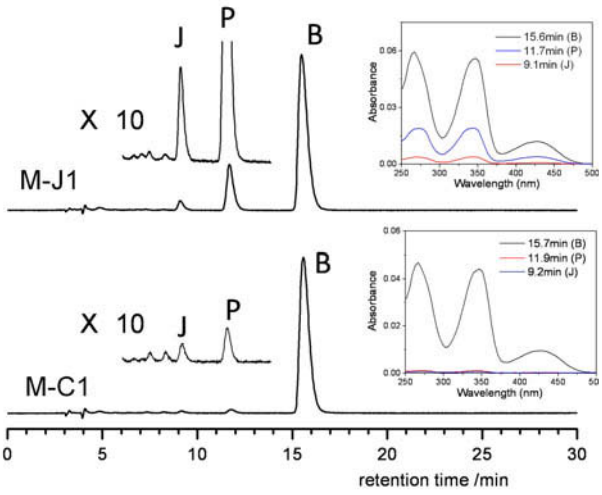

Figure 4: HPLC chromatograms of extracts from standards dyed by Japanese (M-J1) and Chinese (M-C1) phellodendron, monitored at 350 nm; B: berberine; P: palmatine; J: jatrorrhizine.

All three protoberberines were detected in, both, the Japanese and the Chinese dye, but at significantly different relative amounts. The amount of palmatine relative to berberine (P/B ratio) was much higher in the Japanese dye M-J1 (22%) than in the Chinese dye M-C1 (1.2%). The amount of jatrorrhizine relative to

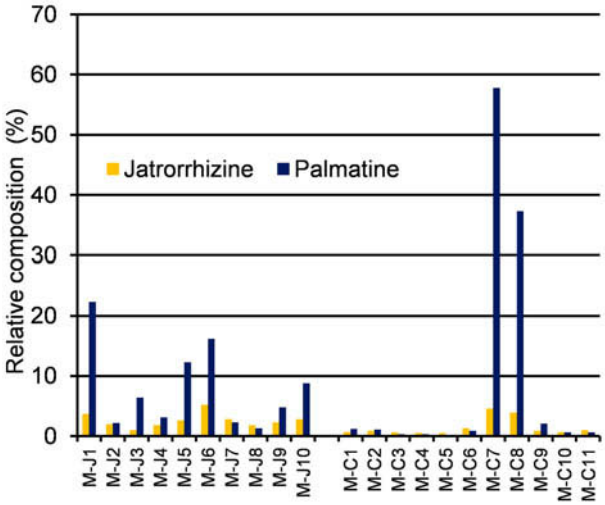

Figure 5: Composition of protoberberines, relative to berberine, in extracts from standards dyed by phellodendrons, determined by HPLC monitored at 350 nm.

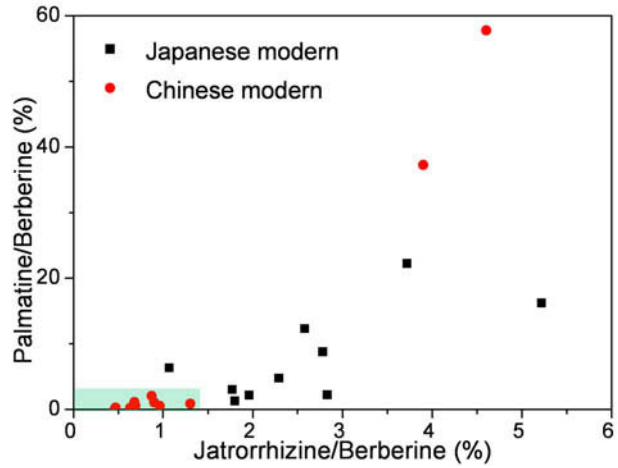

Figure 6: A plot of the relative amount of palmatine to berberine vs. jatrorrhizine to berberine, based on HPLC analyses of extracts from standards dyed by Japanese and Chinese phellodendrons.

berberine (J/B ratio) also showed a difference between the Japanese (3.7%) and the Chinese dye (0.7%). Further investigations were made by analyzing all available phellodendron of different origins. Fig. 5 shows P/B and J/B ratios in the extracts from dyed standards. The P/B ratios of Japanese dyes were between 1 and 22%, while those of the Chinese dyes were either less than 2% or more than 35%. The J/B ratios showed a tendency to be the higher in the Japanese dyes, with the exception of the two Chinese samples with the very high P/B ratios. All calculated results are depicted in the scatter diagram of Fig. 6, showing P/B ratios plotted against J/B ratios.

The characteristic distribution was within the range 2.3% for P/B and 1.3% for J/B when their origin was Chinese, except for M-C7and M-C8 (see also Fig. 5). Large P/B and J/B values in M-C7 and M-C8 are characteristic for *P. amurense* originating in Northeast China. But this plant has a lower total protoberberine content.[16] The inferior protoberberine dye quality of Chinese *P. amurense* (Northeast China) compared to *P. chinense* (Central and Southern China), may have caused the latter to have been the preferred dye to use for a precious textile. The wide range of P/B values as found for the Japanese dyes (1 to 25%) was observed previously,[14,16] and may result from the fact that the palmatine content in *P. amurense* varies depending on which part of the tree it is obtained from.[17,18]

3.3 An Application of the Modern Phellodendron Data to Historical Textiles; Weaving Threads

Analyses were conducted on weaving threads taken from historical textiles with Japanese (Momoyama, 16th C to Edo, 18th C) and Chinese (Yuan, 14th C, to Qing, 20th C) styles (Tab 1), and on which preliminary EEM matrix spectra suggested the presence of a berberine containing dye (Fig. 7).

textile code	date (century)	sample code	color
AN.406	17	W-J1	yellow
		W-J2	green
AN.513	18	W-J3	red
AN.529-5	18	W-J4	green
AN.529-12	16	W-J5	yellow
		W-J6	pale green
M Ka	18	W-J7	yellow
		W-J8	pale green
AN.324	18	W-C1	yellow
AN.374	16	W-C2	red
AN.433	17	W-C3	red
AN.460	18	W-C4	red
AN.461	20	W-C5	red
AN.461	20	W-C6	pale green
		W-C7	yellow
AN.466	19	W-C8	green
		W-C9	red
		W-C10	red
AN.470	18	W-C11	pale green
Donke-in	14	W-C12	pale green

Table 1: Weaving threads from historical textiles.

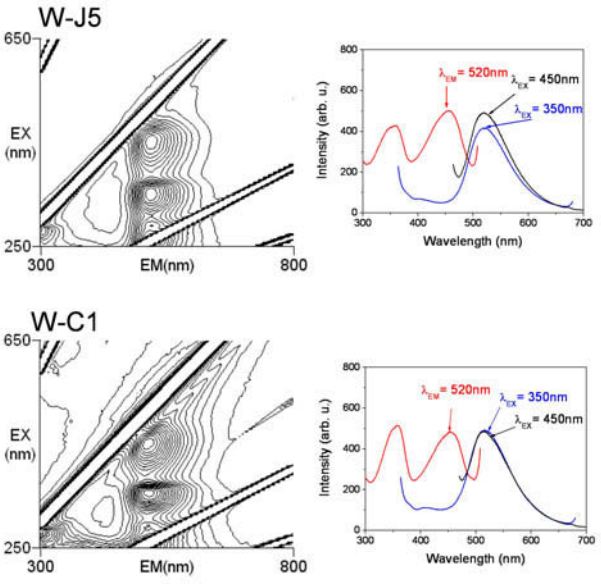

Figure 7: Fluorescence spectra of typical yellow colored woven textiles with Japanese style (W-J5) and Chinese style (W-C1).

The analysis was made by HPLC, using Condition 2. Fig. 8 shows typical HPLC chromatograms, with monitoring at 350 nm, of the dye extracts of Japanese (W-J5) and Chinese (W-C1) style textile fragments. Palmatine and jatrorrhizine were detected, along with the major component, berberine, in both cases. The resultant P/B and J/B ratios for all the samples given in Tab 1 are shown in Fig. 9, and this data was combined with data plots of standards (Fig. 10). Because there were no data from historical samples in the region of the Chinese *P. amurense* standards, data plots from the latter were omitted from Fig. 10.

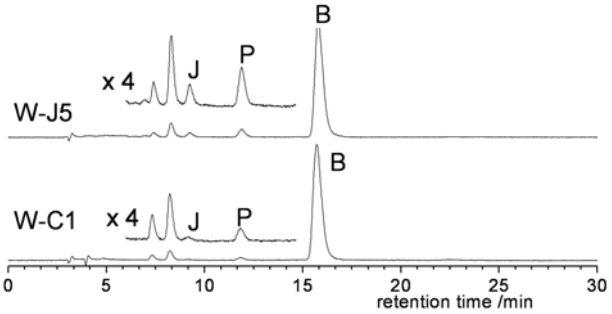

Figure 8: HPLC chromatograms of extracts from historical woven textiles with Japanese style (W-J5) and Chinese style (W-C1) monitored at 350 nm. B: berberine, P: palmatine, J: jatrorrhizine.

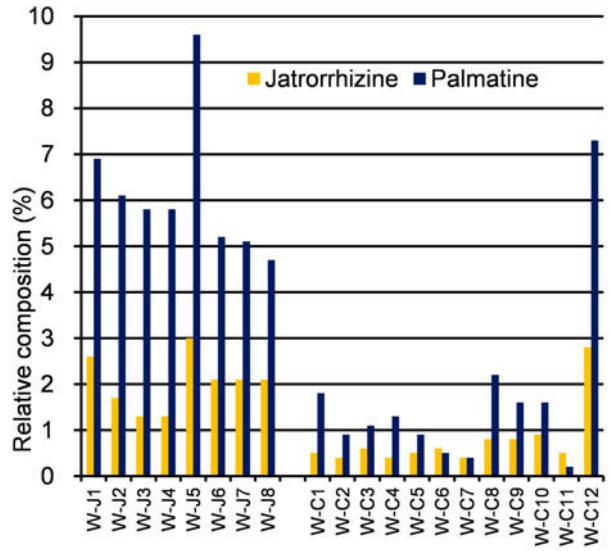

Figure 9: Composition of protoberberines relative to berberine in extracts from weaving threads of historical textiles shown in Tab 1, determined by HPLC, monitored at 350 nm.

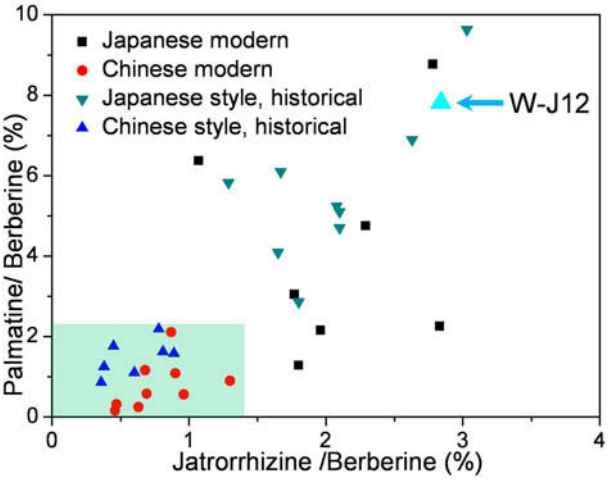

Figure 10: A plot of relative amounts of palmatine to berberine vs. jatrorrhizine to berberine based on HPLC analyses of extracts from weaving threads of historical textiles shown in Tab. 1.

All Japanese style historical textiles showed a distribution of 2 to 10% for P/B and/or 1.3 to 3% for J/B values, whereas it was found that almost all of the Chinese style historic textiles were concentrated in the region of less than 2% for P/B and less than 1% for J/B values. Obviously, data plots of historical samples coincided very well with those of modern samples, with W-C12 as an exception. Thus, provenance of the phellodendron dye and, hence that of historical woven textiles could easily be determined using simple HPLC analysis, combined with plotting of the resultant J/B and P/B values in a scatter diagram. Apparently, even the ageing of the phellodendron dye and/or its mixing with other dyes did not affect the interpretation of results.

The exception, W-C12, is a 14th Century *Kasaya* stored in the *Donke-in* temple at Kyoto. It has the typical Chinese (Yuan) style, as was found by previous research on its design, but the specific weaving technique is found only in Japan in the 15th Century.[19] Radiocarbon dating of this *Kasaya* places it between 1300 and 1420 AD.[20] This dating was supported by an old document recording its donation to the temple in 1382.[21] Thus, one can conclude that the *Kasaya* was a Japanese product, in spite of its typical Chinese style of textile design. The blue dye was determined to be indigoid. This means that the green color was made by multi-dyeing with the Japanese Amur cork tree and an indigoid dye source.

3.4 An Application of the Modern Phellodendron Data to Historical Textiles; Embroidery Threads

We also investigated threads found in the embroidery of historical textiles. Analyses were conducted on samples taken from both Japanese and Chinese style textile fragments (Kyoto Institute of Technology), Japanese style Yuzen dyed fragments (private collec-

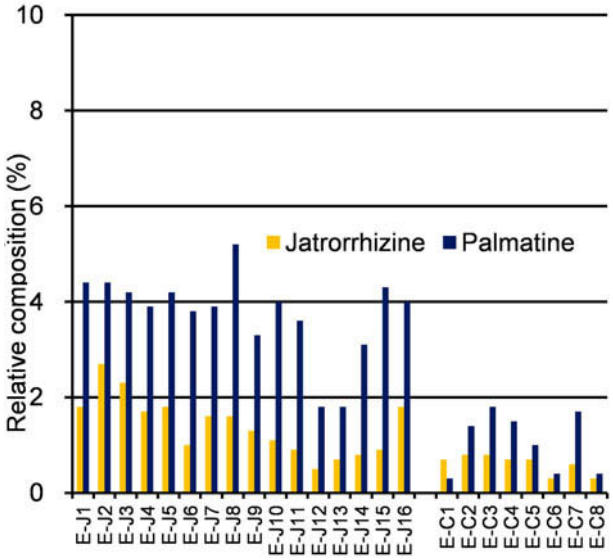

Figure 11: Composition of protoberberines relative to berberine, in extracts from embroidery threads of historical textiles shown in Tab 2, determined by HPLC monitored at 350 nm.

tion), and also from a *Kimono* garment (Matsuzakaya collection). All samples are shown in Tab 2. Again, threads were first selected using the non-destructive detection of characteristic protoberberine fluorescence.

The results of calculations resulting from HPLC analyses (Fig. 11) are shown in a scatter diagram, which also contains data sets of phellodendron standards (Fig. 12). As explained higher, data sets of Chinese *P. amurense* standards were omitted.

textile code	date (century)	sample code	color
Y2	18	W-J1	red
Y3	19	W-J2	yellow
		W-J3	green
		W-J4	red
Y6	19	W-J5	pale green
M1	19	W-J6	green
		W-J7	pale green
		W-J8	red
M2	19	W-J9	green
		W-J10	green
		W-J11	red
M3	19	W-J12	green
		W-J13	red
M5	19	W-J14	green
M6	19	W-J15	green
		W-J16	pale green
AN.410	18	W-C1	pale green
AN.469	19	W-C2	red
AN.505	19	W-C3	pale green
AN.566-2-7	16	W-C4	yellow
		W-C5	pale green
AN.1808	18	W-C6	pale green
		W-C7	green
		W-C8	red

Table 2: Embroidery threads from historical textiles.

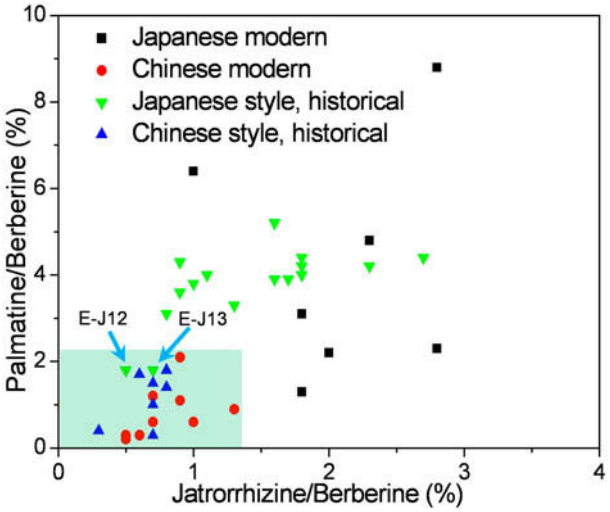

Figure 12: A plot of relative amounts of palmatine to berberine vs. jatrorrhizine to berberine based on HPLC analyses of extracts from embroidery threads of historical textiles shown in Tab 2.

All embroidery threads from Chinese style textiles showed very low values of P/B and J/B ratios as was also seen in weaving threads. The points on the scatter diagram for the Chinese style embroideries almost completely overlapped the region corresponding to modern Chinese phellodendron. These results indicated that the dyes used for the Chinese style embroidery were of Chinese origin, more specifically, *P. chinense*. Analyses of the embroidery threads from Japanese style textiles showed relatively large P/B and J/B values. The distribution of historical data sets on the scatter diagram once again almost completely overlapped the dispersed region seen for modern Japanese phellodendron. This indicates that the dyes used were *P. amurense*, and therefore of Japanese origin. However, exceptional results were observed for plots of E-J12 and E-J13, a green and a red embroidery thread, respectively. They were taken from a typical Japanese style *Kimono* garment, M3, but analysis suggests that this embroidery thread was dyed with a dye that originated in China. This leads to the hypothesis of import or trading of the yellow dye or dyed thread from China to Japan.

There are large numbers of old shipment records at Nagasaki, where was the only official international-trading port during the Edo period in Japan.[22] Research on these records revealed that shipments of dyed silk threads or dye materials were imported from China to Japan regularly until 1820. However, there were no records of similar shipments from Japan to China. Generally, it was recognized that, in ancient times, Chinese silk products were superior to Japanese ones in terms of, both, quality and quantity. Therefore, *P. amurense* could be found only in Japanese style embroideries, whereas *P. chinense* could appear not only in Chinese style embroideries, but also in Japanese ones. The latter referring to threads dyed with dyes that originated in China.

The results found for the yellow dye in the green and red threads from the Japanese style *Kimono* garment would be the first direct evidence, based on chemical analysis, to support the old Japanese shipment records.

4 Conclusion

We have described here a method for determining the provenance of historical textiles, based on the composition of protoberberines in the yellow phellodendron dye, more specifically on the calculation of the ratio of palmatine to berberine (P/B), and of jatrorrhizine to berberine (J/B). This research revealed a significant difference between Japanese phellodendron (*P. amurense*) and Chinese phellodendron (*P. amurense* and *P. chinense*). This methodology is the first scientific basis for specifying the precise origin of historical textiles in East Asia, more specifically in Japan and China. It must be regarded a practical and very effective approach, especially when combined with preliminary non-destructive fluorescence analysis screening for better sample selection.

5 Acknowledgement

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6 References

1. L. Grycová, J. Dostál, R. Marek, *Quaternary Protoberberine alkaloids*, Phytochemistry, 2007, **68**, 150-175.

2. T. Kyo, Y. Yamamoto, *Phellodendri cortex*, in Tochimototenkaido Ed., *60th year Memorial Book of Tochimototenkaido*, Osaka, 2010, 148-159.

3. S. Yamazaki, Ed., *The Illastrated book of Dye Plants*, Bijutsu shuppan, Tokyo, 1985, 46.

4. S. Goto, R. Yamakawa, Eds., *Senryo Shokubutu-fu (History of Dye Plants)*, Senshoku bunka sha, Osaka, 1937, 209-210.

5. X. Zhang, K. Corrigan, B. MacLaren, M. Leveque, R. A. Laursen, *Characterization of Yellow Dyes in Nineteenth-Century Chinese Textiles*, Studies in Conservation, 2007, **52**, 211-220.

6. Shanghai Science & Technical Publishers Ed., *Dictionary of Chinese Herbal Medicine*, Shogakukan, Tokyo, 1985, **1**, 155.

7. Y. Matsuda, *Non-destructive Analysis of Yellow Natural Dyestuffs by Three-Dimensional Fluorescence Spectroscopy*, Bunkazai Hozon Shufuku Gakkaishi, 1997, **41**, 54-63.

8. Y. Sasaki, K. Fujii, K. Sasaki, *Non-destructive analysis for 17thC traditional Japanese textile, "White ground satin with design of snow, crests, and chrysanthemums*, Bunkazai Hozon Shufuku Gakkaishi, 2008, **53**, 35-53.

9. Y. Sasaki, K. Sasaki, *Determination of Dye Plant Materials Including Protoberberines by Component Analysis Using HPLC and ESI-Mass Spectrometry*, Archeology and Natural Science, 2012, **63**, 53-69.

10. Y. Sasaki, K. Fujii, K. Sasaki, *Provenance Study of Historical Textiles Based on Quantitative Analysis of Protoberberines in Amur Cork Tree: Discrimination between Textiles of Japanese and Chinese Products*, Archeology and Natural Science, 2012, **63**, 71-88.

11. T. Misaki, K. Sagara, M. Ojima, S. Kakizawa, T. Oshima, H. Yoshizawa, *Simultaneous determination of Berberine, Palmatine, and Coptisine in crude drugs and oriental pharmaceutical preparations by ion-pair high-performance liquid chromatography*, Chem. Pharm. Bull., 1982, **30**, 354-357.

12. K. Yamagishi, M. Mori, *Studies on the Standardization of crude Drugs Produced in Hokkaido (Part 10) Studies on the Quantitative Analysis of Berberine Alkaloids in Pellodendri Cortex*, Annual Report of Hokkaido Institute of Public Health, 1976, **26**, 26-31.

13. C. Tani, N. Takao, *On the Phenolic bases from Coptis japonica, Journal of the Pharmaceutical Society of Japan*, 1957, **77**, 805-806.

14. K. Sagara, Y. Ito, M. Ojima, T. Oshima, T. Yoshida, H. Itokawa, *Determination of berberine-type alkaloids in Coptidis Rhizoma, Phellodendri Cortex and their oriental pharmaceutical preparations by ion pair high performance liquid chromatography*, Bunseki Kagaku, 1986, **35**, 326-329.

15. G. Yoneda, E. Yamagata, H. Longjin, M. Mizuno, *Studies on Resources of Crude Drugs (II) Morphological Studies and Constituents of Berberine Type Alkaloids of Chinese Coptis Rhizome*, Shoyakugaku Zasshi, 1988, **42**, 116-121.

16. M. Anetai, T. Hayashi, T. Yamagishi, *Determination of Berberine Alkaloids in Phellodendri Cortex*, Annual Report of Hokkaido Institute of Public Health, 1987, **37**, 18-21.

17. T. Tosa, S. Ishihara, Y.Nose, T. Ushikawa, S. Yoshida, Y. Nakazawa, T. Tomimatu, *Studies on quality control of crude drugs. (I) Analysis and distribution of alkaloids in Phellodendron amurense RUPRECHT*, Shoyakugaku Zasshi, 1989 **43**, 28-34.

18. A. Zhang, C. Mouri, M. Mikage and R. Laursen, *Identification of Sources of Protoberberine Alkaloids used as Yellow Dyes in Asian Objects of Historical Interest*, Studies in Conservation, 2010, **55**, 177-185.

19. M. Bethe, *Kenmonsha, or patterned three-end Gauze, within an East Asian Context*, in Kyoto National Museum Ed., *Transmitting Robes, Linking Mind, The World of Buddhist Kasaya*, Kyoto, 2010, 26-27.

20. A.Yamakawa, *List of works No.113 Nine Panel Kasaya, Associated with Shun'oku Myoha, Presented to Chisen Sintsu*, in Kyoto National Museum Ed., *Transmitting Robes, Linking Mind, The World of Buddhist Kasaya*, Kyoto, 2010, 266-267.

21. P. Fister and M. Bethe, *Donkein Imperial Convent*, in Medieval Japanese Studies Institute Ed., *Amamonzeki, A Hidden Heritage, Treasures of the Japanese Imperial Convents*, Kyoto, 2009, 76-82.

22. Y. Nagazumi, *List of the item names and their quantities of international trade with Chinese ship from 1637 through 1833*, Sobun sha, Tokyo, 1987, 36-328.

7 Endnotes

I. Palmatine Chloride: HRMS (FAB, *m*-NBA) Calcd. for $C_{21}H_{22}NO_4$, 352.1549, Found 352.1549, ^{1}HNMR (MeOH-d_4) d 9.79 (s, 1H, H8), 8.84 (s, 1H, H-13), 8.14 (d, *J* = 9 Hz, 1H, H-11), 8.04 (d, *J* = 9 Hz, 1H, H-12), 7.70 (s, 1H, H-1), 7.08 (s, 1H, H-4), 4.96 (t, *J* = 6.6 Hz, 2H, H-6), 4.24 (s, 3H, 9- or 10-OCH_3), 4.14 (s, 3H, 9- or 10-OCH_3), 4.02 (s, 3H, 2-OCH_3), 3.97 (s, 3H, 3-OCH_3), 3.31 (t, *J* = 6.6 Hz, 2H, H-5)

II. Jatrorrhizine Iodide: HRMS (FAB, *m*-NBA), Calcd. for $C_{20}H_{20}NO_4$: 338.1392, Found: 338.1398, ^{1}HNMR (MeOH-d_4) d 9.75 (s, 1H, H-8), 8.79 (s, 1H, H-13), 8.13 (d, *J* = 9 Hz, 1H, H-11), 8.02 (d, *J* = 9 Hz, 1H, H-12), 7.68 (s, 1H, H-1), 7.05 (s, 1H, H-4), 4.93 (t, *J* = 6.6 Hz, 2H, H-6), 4.23 (s, 3H, 9- or 10-OCH_3), 4.13 (s, 3H, 9- or 10-OCH_3), 4.04 (s, 3H, 2-OCH_3), 3.31 (t, *J* = 6.6 Hz, 2H, H-5)

III. Abbreviations: M: modern; J: purchased as Japanese Phellodendron or Japanese style; C: purchased as Chinese Phellodendron or Chinese style; W: weaving thread; E: embroidery thread.

IV. Kasaya: an oblong piece of ornamental cloth worn over the robe by a Buddhist priest.