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Examination of Berberine Dye using GC-MS after Selective Degradation Treatments

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GC-MS를 이용한 Berberine 염료의 퇴화 거동 연구

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Abstract

The degradation behavior of berberine is examined using GC-MS to select the fingerprint products that can be used to identify berberine dye in badly faded archaeological textiles. A total of 100°C thermal and H_2O_2/UV/O_2 degradation systems were used to degrade berberine chloride 0.1% solution up to 408 hours. The samples were analyzed using the GC-MS. Dihydroberberine, 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]-, and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide were detected as the major products of thermal degradation and identified as the fingerprint products for berberine dye at the early stage of degradation. Isobenzofuran-1,3-dione,4,5-dimethoxy-, 9H-fluorene,3,6-bis(2-hydroxyethyl)-, 1,3-dioxolo[4,5-g]isoquinolin-5(6H)-one,7,8-dihydro-, and 3-tert-butyl-4-hydroxyanisole were detected as the major products generated by the H_2O_2/UV/O_2 degradation and identified as the fingerprint products for berberine dye under severe degradation conditions.

Key words: Berberine, Degradation, Amur cork tree, GC-MS, Natural dye; 베르베린, 퇴화, 황벽, GC-MS, 천연염료

I. Introduction

During the past decade, there has been a growing interest in the restoration and exhibition of the textile relics unearthed from the burial sites across the country. While most uncovered textiles are in tact in terms of form, most or all the textiles exhibit severe case of colorfading which makes it impossible to identify the original hue. Colorfading of the exhumed textiles are the result of complex environmental conditions. Interaction of soil microbes with the fiber, dye, or textile stain, contamination of the textile by humic substance in soil (Walton & Taylor, 1991), or the sudden exposure to sunlight and atmosphere during excavation process, all attribute to the complex mechanism of the fading of dye in archaeological textiles. In any case, the fading of the textile relics presents limitations in the restoration and exhibition by museum curators since the lack of information on the original hue makes it impossible to carry out an accurate documentation of the textile piece.

Nonetheless, dye identification of a textile which

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completely lacks information on the original hue is a difficult or even an impossible task. Most often, dye identification of museum textiles are carried out by comparing the dye component of textiles with the standard dye. However, in case of badly faded archaeological textiles using such comparative method is practically impossible because due to the lack of original hue it is impossible to select one or a number of standard dyes for the comparative analysis. Moreover, since the dye chemistry has changed, it is difficult to compare the remains of the dye in the textile with the chemically fresh standard dye. As an alternative method, it is possible to deliberately degrade each possible dyestuff in a controlled environment, and use instrumental analysis to identify the chemical structure of degradation products. The data from such experiment can then be used as the pool of comparative standards for investigation the dye in archaeological textiles.

Under such premise, previous researches on alizarin and curcumin have been successfully carried out (Ahn & Obendorf, 2004, 2007). And as part of the continuing effort for the identification of dye in archaeological textiles, the purpose of the present research was to examine the degradation behavior of berberine using gas chromatography mass spectrometry (GC-MS). Berberine ($[C_{20}H_{18}NO_4]^+$, 5,6-dihydro-9,10-dimethoxybenzo[g]-1,3-benzodioxolo[5,6-a] quinolizinium) is a strong yellow dye which is found in the stems of the amur cork tree (*Phellodendron ammurense* R.) and the roots of Rhizome Coptidis (Fig. 1). It is the only cationic dye among the natural plant dyes which is part of the chemical group of isoquinoline akaloids. Amur cork tree is a deciduous tree in the family of Rutaceae and native to east and northeast Asia. Amur cork tree is called Huang Bai in China and it has long been used in Chinese herbalism and also as source of yellow dye.

Thermal and $H_2O_2/UV/O_2$ radiation systems were utilized for the degradation of berberine. Following the previous method of analysis (Ahn & Obendorf, 2004, 2007), the thermal degradation in 100°C oven temperature was chosen based on the researches simulating natural ageing of dyed textiles via accelerated thermal treatment (Brushwood, 1988; Needles et al., 1986; Needles & Nowak, 1989). Needles et al. (1986) examined burial-induced color and strength changes in wool and silk fabrics and found that alizarin dyed fabrics became extremely dark and changed shade toward purple. $H_2O_2/UV/O_2$ treatment was chosen on the basis of the advanced oxidation process (Colonna et al., 1999) which was developed to reproduce the microbial decomposition of dye wastewater (Jarosz-Wilkolazka et al., 2002) in the laboratory situation, and the assumption that such oxidation process with $H_2O_2/UV/O_2$ occurs in nature through the formation of a superoxide ion-radical (O_2^-) from the reduction of humic substances in soil (Scheck & Frimmel, 1995).

Chromatographic analyses such as high performance liquid chromatography (HPLC), gas chromatography (GC), or thin layer chromatography (TLC) is often used for separating the complex mixtures into smaller compounds. Among different chromatographic analyses the gas chromatography is often used for analyzing the degradation products since it offers the most sensitive separation of mixtures (Bauer et al., 1978). The degradation products which generally have small molecular weight can be separated by gas chromatography whereas they can be overlooked in other

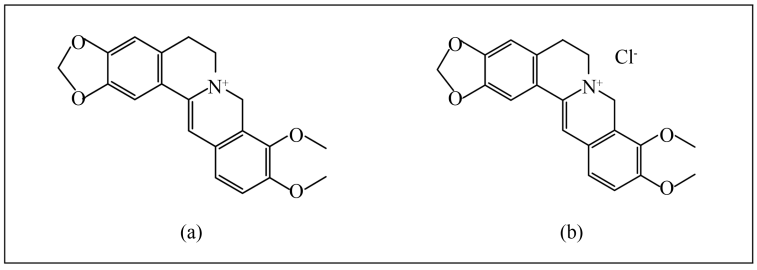


Fig. 1. The chemical structure of berberine (a) and commercial form berberine chloride (b).

chromatographic analyses such as thin layer chromatography. When gas chromatography (GC) is coupled with mass spectrometry (MS), the instrument becomes a powerful tool for separating and identifying the degradation products (Zhang & Lemley, 2006). In this study, thermal and H_2O_2/UV/O_2 degradation treatments were used to deliberately degrade berberine dye and GC-MS analysis was used to analyze the degradation products with the purpose of establishing the data pool of degradation products of berberine dye.

II. Experimental

Berberine sold commercially as berberine chloride was purchased from Sigma Aldrich and dissolved in HPLC grade methanol to make 0.1% dye solution (Fig. 1). 2 vials of 1ml aliquots were placed in different times of thermal and H_2O_2/UV/O_2 degradation systems. An oven heated to 100°C was used for the thermal degradation system (denoted as OV in the following) and the samples were heated in oven up to 408 hours. Samples for the H_2O_2/UV/O_2 (denoted as PER in the following) degradation were prepared by mixing the dye solution with 30% H_2O_2 in 4:1 v/v ratio. Aliquots of 1ml of PER specimen were placed under the UV lamp (365nm, 8Watt) for up to 336 hours.

Samples were completely evaporated in oven (OV samples) and hotplate (PER samples) respectively and the residues were dissolved with 1ml of HPLC grade methanol, filtered for GC-MS analysis using a 0.45μm glass fiber enhanced syringe filter.

Samples were analyzed on the Hewlett-Packard GC 6890 Series coupled to the Agilent Technologies 5973N MSD system. Products were separated on a Hewlett Packard 19091s-433 capillary column (HP-5MS, 30cm×250i.d., 0.25μm nominal film thickness). The instrument parameter for running the GC-MS was selected based upon the experimental result obtained from the previous study on the separation of berberine dye from the amur cork tree (Ahn, 2009). Column temperature was initially 50°C, gradually increased to 210°C at a 23°C/min rate, finally increased to 305°C at 30°C/min rate, and held for 14 minutes with the total run time 24.12 min. The initial temperature of the MSD system was 310°C and the mass spectra were recorded at scan range of 75~400m/z. The assignment of possible degradation products was based on the match with standard mass spectrum available in the GC-MS library database.

III. Results and Discussion

A number of prominent peaks were identified in the repeated GC-MS analyses of the berberine control (berberine dye before the degradation treatment) and the result is shown in <Fig. 2>. Among the peaks identified, the products represented as the peaks in retention times 15.03 minutes (min), 16.35 min, and 13.45 min exhibited the highest relative abundance in the GC chromatogram. When the products of those peaks were analyzed in terms of their ion fragmenta-

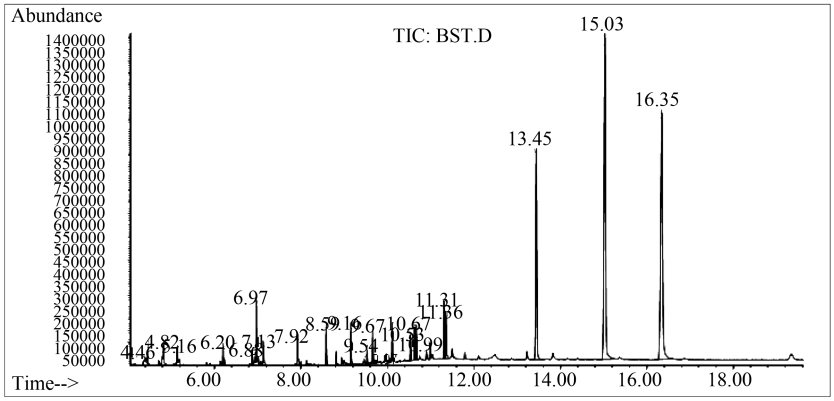


Fig. 2. Gas chromatogram of berberine control.

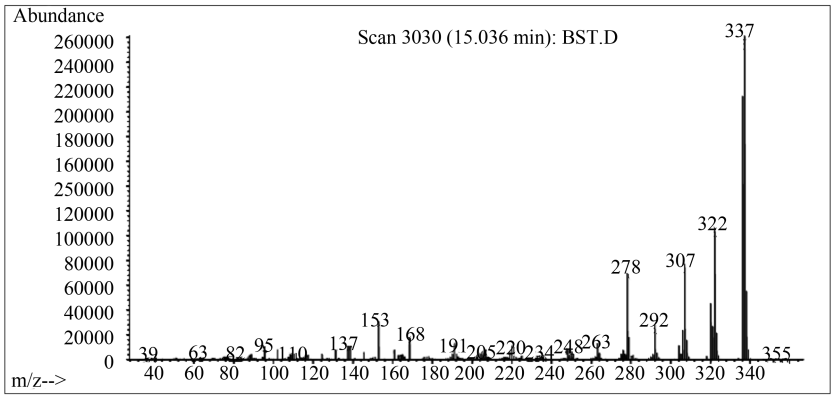


Fig. 3. Mass spectrum of dihydroberberine.

tion pattern of the mass spectrum they were assigned as dihydroberberine (CAS No.: 483-15-8) <Fig. 3> at 15.03 min, 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]- (CAS No.: 36972-94-8) at 16.35 min, and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide (CAS No.: not available) at 13.45 min. The product assignment was carried out by comparing the ion fragmentation patterns of the experimental data obtained in this study and those of the NIST library database provided in the Agilent Technologies MSD software. The result of the product assignment is shown in <Table 1>. A few other peaks detected repeatedly at 4.45 min, 4.82 min, and 6.97 min also showed well match with the library database and they were assigned as benzoic acid, methyl ester (CAS No.: 93-58-3), benzoic acid (CAS No.: 65-85-0), and 2,4-di-tert-butyl phenol (CAS No.: 96-76-4) respectively (Table 1).

When berberine was thermally degraded, the same products identified in the control sample of berberine dye were detected continuously in the samples of different degradation times. <Table 2> which shows the result on the detection of products after thermal treatment indicates that except for benzoic acid, all five products were detected after the dye was degraded from 24 hours to 408 hours. The trace of benzoic acid disappeared beginning with the 240 hour degradation sample.

The changing pattern of the relative abundance of each product is illustrated in <Fig. 4>. Regardless of degradation time, dihydroberberine showed the highest relative abundance among the six products, followed by 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]- and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide. The three products showed an increase at the beginning of the degradation treatment and then they showed a notable decrease in the relative abundance after 96 hour degradation samples, the lowest relative abundance occurring in the 336 hour sample.

In H_2O_2/UV/O_2 degradation samples there were some major changes to the products detected by GC-MS <Table 3>, the most prominent being the disappearance of dihydroberberine and 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]- after the 24 hour degradation sample (Table 2). <Fig. 5> illustrates the dramatic decrease in the relative abundance of the two products and their disappearance after 6 hours of H_2O_2/UV/O_2 degradation. The disappearance of benzoic acid and benzoic acid methylester after 96 hours and 240 hours respectively and the dramatic decrease of 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide and its disappearance after 240 hours is observed in <Table 3> and <Fig. 5>.

Another phenomenon which is clear in H_2O_2/UV/O_2 degradation samples is the detection of new products after the initiation of the degradation treatment. The new products with which the product assignment was successfully carried out were isobenzofuran-1,3-dione,4,5-dimethoxy- (CAS No.: 1567-56-2) at 8.38 min, 9H-fluorene,3,6-bis(2-hydroxyethyl)- (CAS No.: not available) at 8.65 min, 1,3-dioxolo[4,5-g]iso-

Table 1. Assignment of products by GC-MS analysis of berberine dye

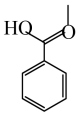
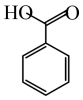
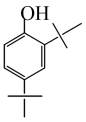
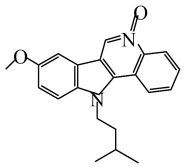
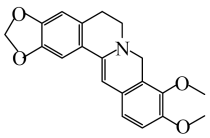
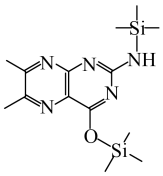
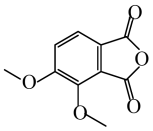
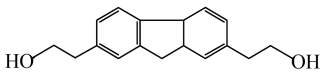
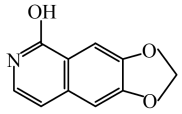
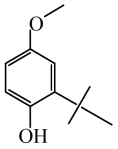
No.	R.T. (min)	Product assignment		Major ion (m/z)	Relative abundance	
					Library	Sample
1	4.45	benzoic acid, methylester		77 105 136	62.4 100 38.5	54.1 100 38.8
2	4.82	benzoic acid		77 105 122	75.2 100 80.8	63.0 100 88.9
3	6.97	2,4-di-tert-butylphenol		57 191 206	26.8 100 14.9	18.5 100 15.1
4	13.45	8-methoxy-11-[3-methylbutyl] -11H-indolo[3,2-c] quinoline,5-oxide		318 334 335	50.7 100 20.8	24.2 100 72.4
5	15.03	[berbine,13,13a-didehydro -9,10-dimethoxy-2,3- (methylenedioxy)-] dihydroberberine		336 337 338	54.3 100 20.3	81.3 100 21.0
6	16.35	2-pteridinamine, 6,7-dimethyl-N- [(trimethylsilyl)oxy]-		320 335 336	100 49.2 14.0	90.4 100 22.3
7	8.38	isobenzofuran-1,3-dione, 4,5-dimethoxy-		78 163 208	90.0 33.2 100	59.3 50.1 100
8	8.65	9H-fluorene,3,6-bis (2-hydroxyethyl)-		178 223 254	51.4 100 98.3	2.1 100 41.1
9	9.41	1,3-dioxolo[4,5-g]isoquinolin-5 (6H)-one,7,8-dihydro-		134 162 191	100 72.1 80.9	94.7 73.8 100
10	9.17	3-tert-butyl-4-hydroxyanisole		137 165 180	73.1 100 45.6	59.6 64.7 100

Table 2. Detection of products after thermal treatment

No.	Product	0 hour	24 hour	96 hour	240 hour	336 hour	408 hour
1	benzoic acid, methylester	○	○	○	○	○	○
2	benzoic acid	○	○	○	×	×	×
3	2,4-di-tert-butylphenol	○	○	○	○	○	○
4	8-methoxy-11-[3-methylbutyl]-11H -indolo[3,2-c]quinoline,5-oxide	○	○	○	○	○	○
5	dihydroberberine	○	○	○	○	○	○
6	2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]-	○	○	○	○	○	○

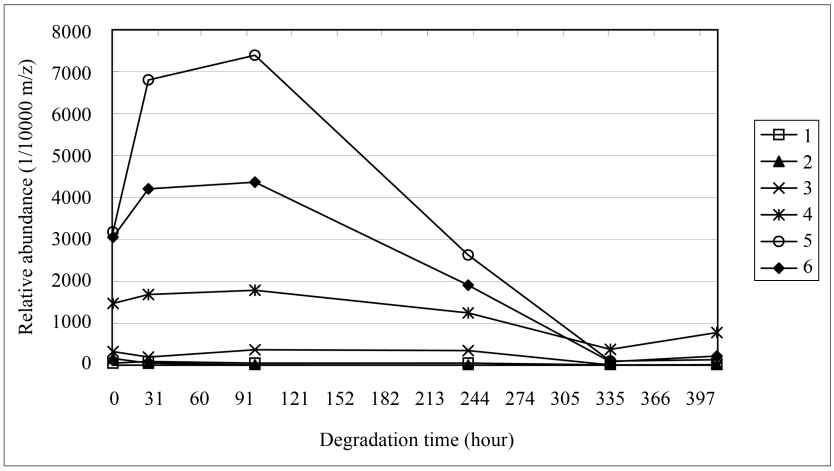


Fig. 4. Change of relative abundance of the products in thermal degradation after 0, 24, 96, 240, 336, and 408 hours of degradation treatment.

Table 3. Detection of products after H_2O_2/UV/O_2 treatment

No.	Product	Control	6 hour	24 hour	48 hour	96 hour	240 hour	336 hour
1	benzoic acid, methylester	○	○	○	○	○	×	×
2	benzoic acid	○	○	○	○	×	×	×
3	2,4-di-tert-butylphenol	○	○	○	○	○	○	○
4	8-methoxy-11-[3-methylbutyl]-11H -indolo[3,2-c]quinoline,5-oxide	○	○	○	○	○	×	×
5	dihydroberberine	○	○	×	×	×	×	×
6	2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]-	○	○	×	×	×	×	×
7	isobenzofuran-1,3-dione,4,5-dimethoxy-	×	○	○	○	○	○	○
8	9H-fluorene,3,6-bis(2-hydroxyethyl)-	×	○	○	○	○	○	○
9	1,3-dioxolo[4,5-g]isoquinolin-5(6H)-one, 7,8-dihydro-	×	○	○	○	○	○	○
10	3-tert-butyl-4-hydroxyanisole	×	×	×	○	○	○	×

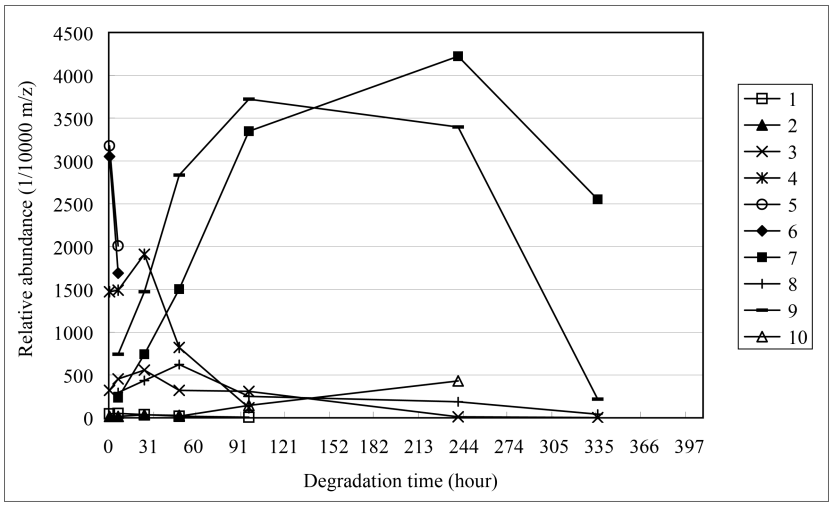


Fig. 5. Change of relative abundance of the products in H_2O_2/UV/O_2 degradation after 0, 6, 24, 48, 96, and 336 hours of degradation treatment.

quinolin-5(6H)-one,7,8-dihydro- (CAS No.: 21796-14-5) at 9.41 min, and 3-tert-butyl-4-hydroxyanisole (CAS No.: 121-00-6) at 9.17 min retention times. It should be noted that isobenzofuran-1,3-dione,4,5-dimethoxy- and 1,3-dioxolo[4,5-g]isoquinolin-5(6H)-one,7,8-dihydro- showed a dramatic increase in the relative abundance up to 96~240 hours after which they showed a downfall.

Berberine <Fig. 1> was not detected in the control nor any of the degraded samples. Instead, the control sample of berberine dye showed a prominent peak at 15.03 min, followed by 16,35 min and 13.45 min in the repeated analyses, and the products were successfully assigned as dihydroberberine, 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]-, and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide respectively by the analysis of NIST library database. This phenomenon coincided with the result of the previous investigation on the GC-MS analysis of dye extracted from the amur cork tree (Ahn, 2009). And as explained in Ahn (2009) with the theoretical base on Turner et al. (2008a, 2008b), Song et al. (2002), and Choi (2005), it can be said that dihydroberberine is a fingerprint product for identifying the presence of berberine dye. And to a lesser degree, 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]- and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide may also act as a supplementary fingerprint for the trace of berberine dye.

The result of change of relative abundance in the present study provides further support for the above assumption. The strong relative abundance of dihydroberberine and to a lesser degree, 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]- and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide in the control dye and the samples of initial degradation treatment, along with its disappearance after continued degradation highly suggest that these products are the fingerprint products of 'fresh' berberine dye and that they can act as the traces of berberine dye when initial degradation occurs. As for the initial increase of the relative abundance of the three main products at the early stage of thermal degradation, it is highly probable that it is due to the volatilization of small molecules which cause the increase in the relative concentration of the main products (Ahn & Obendorf, 2004).

Between the thermal and H_2O_2/UV/O_2 degradation treatment, H_2O_2/UV/O_2 treatment is intended to induce a stronger oxidative environment than the thermal treatment by the production and reaction of hydroxyl radicals from H_2O_2 (Ahn & Obendorf, 2007). The present data which showed that dihydroberberine was detected only in the 6 hour sample of H_2O_2/UV/O_2

degradation while it was detected throughout the thermal degradation times clearly reflects the difference in the magnitude of oxidative strength between the two degradation conditions. By the same token, it should be aware that $H_2O_2/UV/O_2$ treatment generated products such as isobenzofuran-1,3-dione,4,5-dimethoxy-, 9H-fluorene,3,6-bis(2-hydroxyethyl)-, 1,3-dioxolo [4,5-g]isoquinolin-5(6H)-one,7,8-dihydro-, and 3-tert-butyl-4-hydroxyanisole with the initiation of degradation and that their relative abundance increased as degradation progressed.

Going back to the archaeological textiles, since most exhumed textiles were buried for several hundreds of years in the burial environment at the least, the extent of degradation is enough to cause a chemical change of the dye. And such degradation environment can be simulated by the $H_2O_2/UV/O_2$ degradation system based on the theory of advanced oxidation process (Colonna et al., 1999). Since badly faded archaeolgocial textiles are chemically degraded to the extent that the original chemical structure of the dye is lost, and that the $H_2O_2/UV/O_2$ degradation system is apt to simulate the under soil degradation through the formation of a superoxide ion-radical (O_2^-) from the reduction of humic substances in soil (Scheck & Frimmel, 1995) it can be postulated that the newly detected products of the $H_2O_2/UV/O_2$ degradation are the fingerprint of berberine dye when it is exposed to a severe degradation environment.

IV. Conclusions

The purpose of the present research was to examine the degradation behavior of berberine using GC-MS for the ultimate goal of identifying the berberine dye in badly faded archaeological textiles. Dihydroberberine (15.03 min), 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]- (16.35 min), and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide (13.45 min) were identified as the major products of berberine control and the thermally degraded samples and the products were designated as the fingerprint product for identifying berberine dye at the early stage of degradation. Isobenzofuran-1,3-dione,4,5-dimethoxy- (8.38 min), 9H-fluorene,3,6-bis(2-hydroxyethyl)- (8.65 min), 1,3-dioxolo[4,5-g]isoquinolin-5(6H)-one,7,8-dihydro- (9.41 min), and 3-tert-butyl-4-hydroxyanisole (9.17 min) were detected as the major products generated by the $H_2O_2/UV/O_2$ degradation treatment and were identified as the fingerprint products of berberine after severe degradation condition. Since the burial context induces severe case of degradation caused by the microbial environment of the soil, it is suggested that the products such as isobenzofuran-1,3-dione,4,5-dimethoxy-, 9H-fluorene,3,6-bis(2-hydroxyethyl)-, 1,3-dioxolo[4,5-g]isoquinolin-5(6H)-one,7,8-dihydro-, and 3-tert-butyl-4-hydroxyanisole can act as the fingerprint product for singling out berberine dye when attempting to identify dye of badly faded archeological textiles.

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요 약

본 연구는 가스크로마토그라피 질량분석기(GC-MS)를 이용하여 황벽의 주 염료성분인 berberine의 퇴화 거동을 조사하는데 목적을 두며 궁극적으로는 심하게 퇴색된 출토직물의 염료성분을 판정하기 위해 각 천연염료별 퇴화물 자료를 수집하고자 한다. Berberine chloride 0.1% 수용액을 100°C 오븐법과 H_2O_2/UV/O_2법을 이용해 최고 408시간까지 퇴화시키고 GC-MS를 이용해 시료를 분석하였다. 연구결과 오븐 퇴화에 의해 dihydroberberine, 2-pteridinamine, 6,7-dimethyl-N-[(trimethylsilyl)oxy]-, and 8-methoxy-11-[3-methylbutyl]-11H-indolo[3,2-c]-quinoline, 5-oxide의 3개 화합물이 주로 검출되었으며 이들은 berberine 염료의 초기 퇴화 과정에서 나타나는 화합물로 판정되었다. 반면 H_2O_2/UV/O_2법으로 퇴화시킨 시료에서는 isobenzofuran-1,3-dione,4,5-dimethoxy-, 9H-fluorene,3,6-bis(2-hydroxyethyl)-, 1,3-dioxolo[4,5-g]isoquinolin-5(6H)-one,7,8-dihydro-, and 3-tert-butyl-4-hydroxyanisole의 4개 화합물이 퇴화 시작과 더불어 새로 생산되었는데 이들은 berberine 염료가 극심한 퇴화 조건에 놓이게 될 때 검출될 수 있는 화합물로 판정되었다. H_2O_2/UV/O_2법은 매우 강한 산화작용으로 염료를 퇴화시키는 방법임을 감안할 때 H_2O_2/UV/O_2법으로 생성된 화합물은 심하게 퇴색된 출토직물 중 berberine 염료가 사용된 직물을 확인하는데 사용될 수 있을 것으로 사료된다.