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Journal of the Korean Society
of Clothing and Textiles
Vol. 31, No. 6 (2007) p.859~868

Analysis of the Degradation Products of Turmeric using GC-MS

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GC-MS법을 이용한 울금의 퇴화물 분석

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(2007. 1. 18. 접수)

Abstract

Degradation products of the dye extracted from turmeric and the turmeric dyed textiles were examined by using GC-MS after 100 oven (OV) and H_2O_2/UV/O_2 (PER) treatments for up to 28 days. Throughout the OV degradation times, 2-propenoic acid, 3-(2-hydroxyphenyl)- was found consistently, while isovanillin, and vanillic acid were newly detected. In 28 day PER degradation sample, feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, benzoic acid, and vanillic acid were detected as well as isovanillin. Feruloylmethane, and 2-propenoic acid, 3-(2-hydroxyphenyl)- were detected from the degraded fabric samples. With the absence of curcuminoids in the GC-MS result, the decreasing pattern of 2-propenoic acid, 3-(2-hydroxyphenyl)- reflect the degradation of curcuminoids in turmeric extraction with the progression of OV degradation times. It is suggested that isovanillin, feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, and vanillic acid are the probable fingerprint products for determining the turmeric dye from the badly faded archaeological textiles.

Key words: Turmeric, Curcumin, Degradation product, GC-MS, Archaeological Textiles; 울금, 커큐민, 퇴화물, 가스크로마토그라피 질량분석, 출토직물

I. Introduction

Color fading is probably the most often observed damage in the exhumed textiles, since these historic relics are the products of natural dyeing which generally have poor colorfastness. Often the textiles have completely lost their original hue, and show indiscriminantly tan to brown color. Since the severe color fading in an exhumed textile is the result of chemical degradation of the dye, the remains of the dye in the textile cannot be compared with a fresh standard dye chemical. Hence, there is a need for identifying the degradation products of each natural dye, which can then be part of the data pool for the comparative standards in dye identification.

Among the different natural colorant used in the past turmeric is one of the representative plant source for yellow dye. Turmeric is the common name for *Curcuma longa* L. which is a tropical herb of the *Zingiberaceae* family indigenous to southern Asia. The powdered rhizome of turmeric is well known as the ingredient for Indian spice curry more so than the source for dyeing cloth yellow. Turmeric is also long been known as an excellent natural antibiotic and recently as an anti-carcinogen. Such medicinal prop-

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This work was supported by the Korea Research Foundation Grant funded by the Korean Government(MOEHRD, Basic Research Promotion Fund) (KRF-2005-202-C00361).

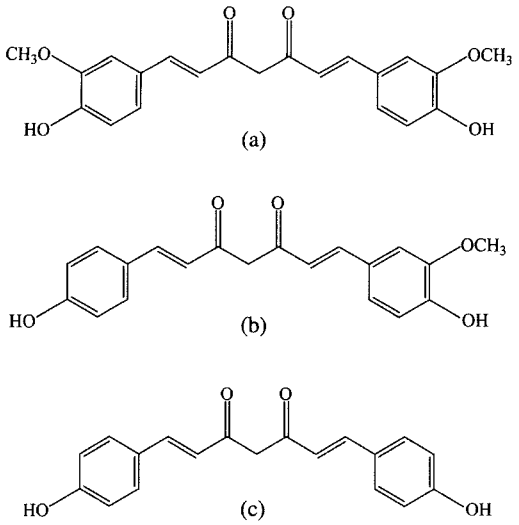


Fig. 1. Structure of the Curcuminoids- (a) Curcumin, (b) Demethoxycurcumin, (c) Bisdemethoxycurcumin.

erties of turmeric is attributable to the antioxidant characteristics of its major components(Wang et al., 1997). Three major substances isolated from turmeric via different instrumental methods are curcumin(or diferuloylmethane), demethoxycurcumin, and bisdemethoxycurcumin and these comprise about 3-5% of the raw plant(He et al., 1998) (Fig. 1). The three components are generally called the curcuminoids and these give turmeric its distictive yellow color(He et al., 1998). The purpose of the present research was to examine the degradation products of the dye extracted from the rhizome of turmeric after selective degradation treatments.

Liquid dye and the dye component extracted from the turmeric dyed textiles were both analyzed using the gas chromatography mass spectrometry(denoted 'GC-MS' in the following). Thermal treatment in 100°C oven and H_2O_2/UV/O_2 (denoted 'PER' in the following) treatments were utilized for the degradation experiment. The thermal series were chosen on the basis of the research on soil microclimate(Child, 1995; Rieger, 1983) and past researches simulating natural ageing of dyed textiles via accelerated thermal treatment(Brushwood, 1988; Needles & Nowak, 1989). The PER 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), and the assumption that such oxidation process with H_2O_2/UV occurs in nature from the reduction of humic substances in soil(Scheck & Frimmel, 1995).

The chromatographic analysis is efficiently used in the chemical field for the separation 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 are generally small in their molecular weight can be successfully singled out by gas chromatography whereas they can be overlooked in other chromatographic analyses such as thin layer or liquid chromatographies. 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). By utilizing the two degradation treatments and the GC-MS analysis, the result of this study will become part of the cumulative collection of analytical data which can then be used as the fingerprint for the identification of turmeric dye in badly faded archaeological textiles. An example of such approach can be found in the previous research by the author which identified alizarin from the exhumed textile(Ahn, 2003).

II. Experimental

1. Materials

Dried rhizomes of turmeric were purchased from Korean traditional medicinal market. Methanol(HPLC grade) was purchased from Acros Organics(NJ), 30% H_2O_2(ACS reagent grade) was purchased from J.T. Baker(Phillipsburg, NJ). Reagent grade HCl was purchased from EM Science(Darmstadt, NJ). Potassium aluminum sulfate was purchased from Shinyo Pure Chemicals(Osaka, Japan). Silk fabric used for dyeing was standard silk fabric(KS K0905) purchased from Korea Apparel Testing & Research

Institute. A 0.45 μm glass fiber enhanced syringe filter(Alltech, Deerfield, IL) was used for filtering samples for GC-MS analysis. Deionized distilled water from Corning Megapure System(MP-1) was used throughout the experiment.

2. Methods

The extraction of dye from turmeric was carried out using the method developed in the previous research which investigated the most effective extraction procedure for examining the chromophoric substance of turmeric(Ahn & Obendorf, 2006). Dried rhizomes of turmeric were purchased from Korean traditional medicinal market and ground in a mill(Thomas Scientific Model 3383-L10). 20g of ground turmeric was pre-extracted with 200ml methanol in 250ml erlenmeyer flask for 1 hour using a shakerbath(140rpm, 30°C). The liquor was decanted and the second extraction was carried out with fresh 200ml of HPLC grade methanol for 12 hours in the shakerbath(140rpm, 30°C), covered with aluminum foil to block light. The extraction was filtered using a büchner funnel with glassfiber filter. The second extraction was used for the liquid degradation experiment and for dyeing the fabric. Four different flasks of turmeric dye were prepared in this manner, two flasks for the liquid degradation and two flasks for dyeing the fabric.

Two vials of 15ml aliquots were placed in different times of 100°C oven and H_2O_2/UV/O_2 degradation systems. Degradation times for the 100 thermal treatment were control, 1, 2, 7, 14, 21, and 28 days. The control denotes the sample without thermal treatment in oven. Samples for the PER degradation were prepared by mixing the extraction with 30% H_2O_2 in 1:1 v/v ratio. Aliquots of 10ml of PER specimen were placed under the UV lamp(365nm, 8Watt, UVL-18, UVP, Upland CA) radiation for the same degradation times as the OV samples. A specimen with mixture of liquid dye and 30% H_2O_2 but without the uv radiation was also prepared and labeled as the '0 day' sample. Samples were completely evaporated and the residues were dissolved with HPLC grade methanol, filtered for GC-MS analysis using a 0.45 μm glass fiber enhanced syringe filter.

Approximately 2g each of two pieces of silk fabric were mordanted with 10% o.w.f. concentration of potassium aluminum sulfate in 200m*l* water for 30 minutes at 80°C in separate erlenmeyer flasks. The fabrics were thoroughly washed, and then dyed with the second turmeric extraction for 1 hour at 50°C, again in separate flasks. Second mordanting and dyeing were followed consecutively and the dyed fabric was used for the degradation samples. The two pieces of dyed fabric were separately used to prepare the OV and PER degradation samples. Dyed fabrics were cut into approximately 3cm×5cm sized samples. Each sample was labeled for different degradation treatment and time. The thermal degradation samples were placed in a 100°C oven for the thermal treatment for 2, 7, 14, 21, and 28 days. Control sample without the oven treatment was also prepared. The PER degradation sample were immersed in different glass vials each filled with 15m*l* of 1:1 v/v ratio of 30% H_2O_2:water. The vials were placed under the UV lamp(365nm) at room temperature. The degradation times for the thermal and the PER treatments were 2, 7, 14, 21, 28 days and two samples were allotted for each degradation time. Control sample without the immersion in the 30% H_2O_2: water, and also without the UV radiation was also prepared. The control samples for OV and PER degradation treatments were prepared from separate piece of dyed fabrics.

Extraction of dye from turmeric dyed fabrics were carried out following Kharbade and Agrawal(1985). Approximately 0.02g of dyed fabric was treated in simmering 10% HCl for 30min, the solvent evaporated and the residue was dissolved in methanol for GC-MS analysis.

3. Instrumentation

Samples were analyzed on the Hewlett-Packard GC 6890 Series coupled to the Agilent Technologies 5973N MSD system. Front inlet was kept at splitless mode with initial temperature at 250°C. Products were separated on a Hewlett Packard 190915-433 capillary column(30cm x 250 i.d., 0.25 nominal film

thickness). 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. The mass spectra were recorded at scan range of 75-400 m/z. The assignment of possible degradation products was based on the match with standard mass spectrum available in the GC-MS library database(Agilent Technologies, 2000).

III. Results and Discussion

1. Experimental Results

When the liquid control sample of turmeric extraction was analyzed using the GC-MS analysis, five major peaks were identified to represent either the fragments or degradation products of curcumin(Table 1).

Table 1. Major products detected from control and degraded samples of turmeric dye

R.T. (min)	*No.*	Assigned Product	liquid control	OV Degradation						PER Degradation						
				1d	2d	7d	14d	21d	28d	0d	1d	2d	7d	14d	21d	28d
6.75	*1*	Curcumene	◎													
5.90	*2*	Isovanillin		◎	◎		◎	◎	◎	◎	◎					◎
6.42	*3*	phenol, 2,4-bis(1,1-dimethylethyl)-			◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎	◎
6.81	*4*	zingiberene	◎													
6.98	*5*	cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene	◎													
7.25	*6*	dihydrocurcumene	◎													
7.59	*7*	benzene, 1-(3-cyclopentylpropyl)-2,4		◎												
8.06	*8*	feruloylmethane														◎
8.14	*9*	2-propenoic acid, 3-(2-hydroxyphenyl)-	◎	◎	◎	◎	◎	◎	◎	◎						
4.70	*10*	benzoic acid														◎
6.93	*11*	vanillic acid								◎						◎

Table 2. Assignment of the detected products

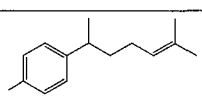
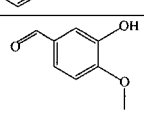
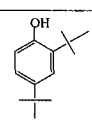
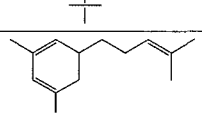
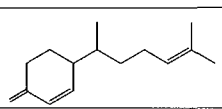
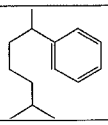
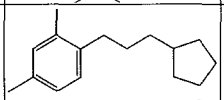
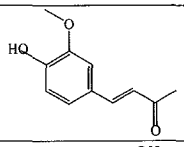
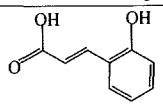
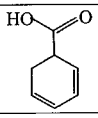
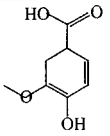
Retention time (min)	*No.*	Assigned product	Chemical structure	Major ion fragments (*m/z*)	Relative abundance library	Relative abundance experimental
6.75	*1*	curcumene		119 105 132	100 47.5 74.3	100 49.6 88.0
5.90	*2*	isovanillin		151 152 81	100 86.3 45.0	100 93.3 20.9
6.42	*3*	phenol, 2,4-bis(1,1-dimethylethyl)-		191 192 206	100 14.9 16.4	100 14.0 15.4
6.81	*4*	zingiberene		93 91 119	100 25.9 78.5	85.1 40.0 100
6.98	*5*	cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene		69 91 93	100 27.6 46.0	100 81.1

Table 2. Continued

Retention time (min)	*No.*	Assigned product	Chemical structure	Major ion fragments (*m/z*)	Relative abundance library	Relative abundance experimental
7.25	*6*	dihydrocurcumene		119 120	100 10.7	100 11.1
7.59	*7*	benzene, 1-(3-cyclopentylpropyl)-2,4		119 120 216	100 16.8 17.8	100 14.5 40.4
8.06	*8*	feruloylmethane		145 177 192	100 88.2 79.7	76.7 93.6 100
8.14	*9*	2-propenoic acid, 3-(2-hydroxyphenyl)-		91 119 120	100 26.5 87.0	42.9 26.1 100
4.70	*10*	benzoic acid		105 122	100 78.5	100 90.1
6.93	*11*	vanillic acid		153 168 97	100 95.7 66.0	74.4 100 31.3

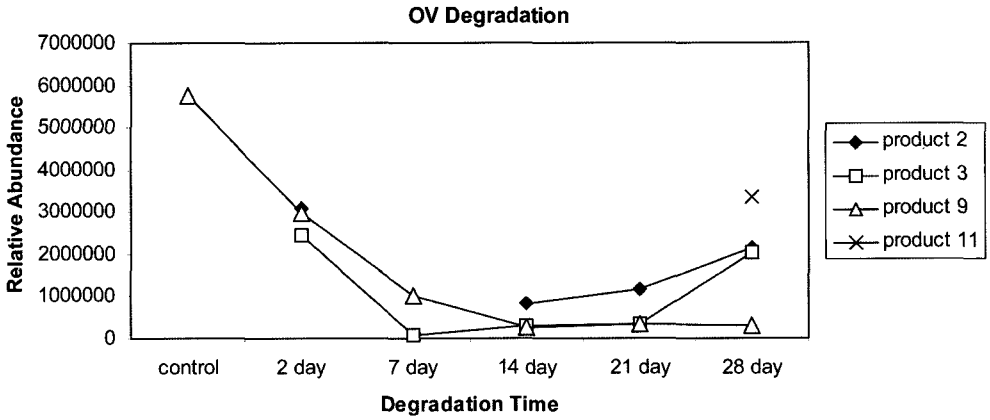


Fig. 2. Change of relative abundance of ov degradation products in turmeric dye with degradation pro-gression-product *2*: Isovanillin, Product *3*: Phenol,2,4-bis(1,1-dimethylethyl)-, Product *9*: 2-Propenoic acid,3-(2-hydroxyphenyl)-, Product *11*: Vanillic acid.

They were curcumene(6.75min), zingiberene(6.81min), cyclohexene, 3-(1,5-dimethyl-4-he-xenyl)-6-methylene (6.98min), dihydrocurcumene(7.25min), and 2-propenoic acid, 3-(2-hydroxyphenyl)- (8.14min). The assignment of the products was carried out by comparing the relative abundance of the experimental result to the relative abundance of the NIST MS library for the major ion fragments of each product(Table 2)(Agilent

Technologies, 2000). Curcumin, the main chromophoric substance of turmeric, was not detected from the standard extraction.

When the samples were degraded in 100°C oven many of the products identified from the standard turmeric extraction were not detected from the degraded samples while several new products appeared. The only products identified from the standard turmeric extraction which was consistently found throughout the OV degradation times is 2-propenoic acid, 3-(2-hydroxyphenyl)- (Table 1). The other products were either none existent or very sparingly detected. The newly detected products were isovanillin(5.90min), phenol, 2,4-bis(1,1-dimethylethyl)- (6.42 min), and vanillic acid(6.93min)(Table 2). Vanillic acid was detected in 28 day OV degraded sample only.

<Fig. 2> illustrates the change in the relative abundance of the OV degradation products with degradation progression. 2-propenoic acid, 3-(2-hydroxyphenyl)- showed a dramatic decrease with degradation progression up to 7 days after which its decreasing rate slowed and reached equilibrium. On the other hand, isovanillin showed a decreasing pattern during the initial stage of degradation, and then it showed a steady increase with further progression of degradation times. Same pattern was observed with phenol, 2,4-bis(1,1-dimethylethyl)-.

In PER degradation, even less products were detected during the experimental progression. Isovanillin and phenol, 2,4-bis(1,1-dimethylethyl)- were detected when the sample was mixed with H_2O_2 but with no uv radiation. While phenol, 2,4-bis(1,1-dim-

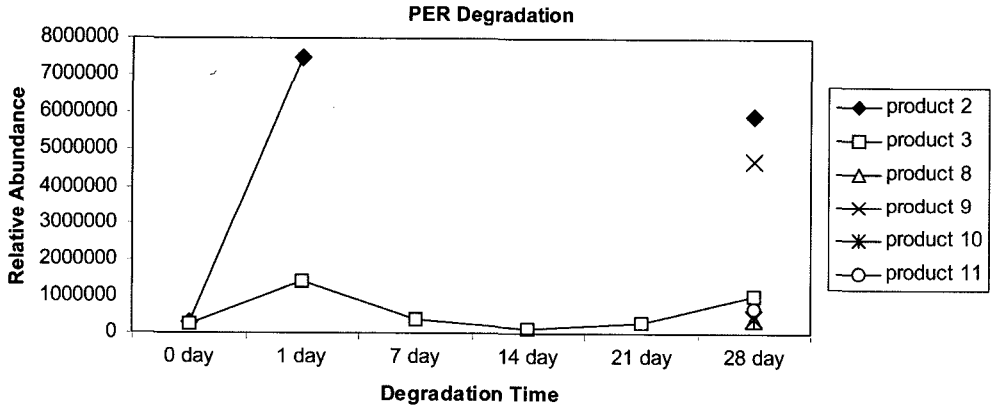


Fig. 3. Change of relative abundance of per degradation products in turmeric dye with degradation pro-gression- Product *2*: Isovanillin, Product *3*: Phenol,2,4-bis(1,1-dimethylethyl)-, Product *8*: Feruloyl-methane, Product *9*: 2-Propenoic acid,3-(2-hydroxyphenyl)-, Product *10*: Benzoic acid, Product *11*: Vanillic acid.

Table 3. Detection of products in turmeric dyed textiles after oven degradation

Retention Time, minutes	Product No.	Assigned products	Presence/Absence of Products						
			liquid control	control textile	2 day textile	7 day textile	14 day textile	21 day textile	28 day textile
6.75	1	curcumene	◎	X	X	X	X	X	X
6.42	*3*	phenol, 2,4-bis(1,1-dimethylethyl)-	◎	◎	◎	◎	◎	◎	◎
6.81	*4*	zingiberene	◎	X	X	X	X	X	X
6.98	*5*	cyclohexene, 3-(1,5-dimethyl-4-hexe-nyl)-6-methylene	◎	X	X	X	X	X	X
7.25	*6*	dihydrocurcumene	◎	X	X	X	X	X	X
8.06	*8*	feruloylmethane	X	X	X	◎	◎	X	X
8.14	*9*	2-propenoic acid, 3-(2-hydroxyphenyl)-	◎	X	X	◎	◎	X	◎

Table 4. Detection of products in turmeric dyed textiles after H_2O_2/UV degradation

Retention Time, minutes	Product No.	Assigned Products	Presence/Absence of Products		
			liquid control	control textile	2 day textile
6.42	*3*	phenol, 2,4-bis(1,1-dimethylethyl)-	X	◎	◎
8.04	*9*	2-propanoic acid, 3-(2-hydroxyphenyl)-	◎	◎	X

ethylethyl)- was detected throughout the degradation times, isovanillin was detected in only 1 day degradation sample. Interestingly enough, in 28 day sample several products were detected including iso-vanillin and phenol, 2,4-bis(1,1-dimethylethyl)-. They were feruloylmethane(8.06min), 2-propenoic acid, 3-(2-hydroxyphenyl)- (8.14min), benzoic acid(4.70min), and vanillic acid(6.93min)(Table 2). Among the degradation products of PER system, isovanillin was the most abundantly found although its presence was limited to the initial degradation and 28 days samples (Fig. 3).

The result of OV degradation experiment on the turmeric dyed textile samples is shown in <Table 3>. The fabric samples which were dyed with the turmeric extract only showed phenol 2,4-bis(1,1-dimethylethyl)-(6.42 min) as the main product and the rest of the peaks were very unstable. Feruloylmethane was detected at 8.06min but it was not detected in the control, and only detected in 7, 14 day degraded samples. 2-propenoic acid, 3-(2-hydroxyphenyl)- was detected after 8.14 min and this was detected in 7, 14, 28 day samples. When the turmeric dyed textile samples were treated in the PER degradation system, the samples lost color and disintegrated after about 2 days of uv radiation. And thus the full range of data was not obtainable with the PER textile degradation. From the obtainable data, the PER degradation experiment showed very little products and the GC-MS spectrum was very unstable. In the PER degraded samples only 2,4-bis(1,1-dimethylethyl)- (6.42min), and 2-propenoic acid, 3-(2-hydroxyphenyl)- (8.06min) were detected, and even these were present only in the control and 2 day degraded samples(Table 4).

2. Discussion of the Results

Curcumin, the major chromophoric substance of turmeric was not detected in either the control or degraded samples of the turmeric extraction and the turmeric dyed textiles. The result was consistent with the previous research on the degradation of commercial curcumin using GC-MS(Ahn & Obendorf, 2007). Such result is likely due to the chemical instability of curcumin due to its ability to scavenge reactive oxygen and nitrogen free radicals(Priyadarsini, 1997). The review of literature on the different results derived from either HPLC or GC-MS analyses of curcumin or turmeric is fully discussed in author's previous work on the degradation of curcumin(Ahn & Obendorf, 2007). For the summary of the readings, in studies which used the GC-MS analysis, curcumin was not detected whether the sample analyzed was the natural rhisome of turmeric or commercial curcumin purchased from the chemical stock. It is highly likely that such result was due to the nature of the GC-MS analysis, since in GC-MS analysis the sample dissolved in a volatile solvent immediately turns into gaseous phase as it is injected into the GC port. And due to the chemical instability of curcumin (Priyadarsini, 1997; Wang et al., 1997), it is highly probable that the degradation of curcumin took place as it enters the GC injection port, and thus producing the fragments of curcumin or its degradation products. Our previous work which investigated the different extraction procedures of turmeric using the GC-MS analysis also found curcumene, zingiberene, feruloylmethane instead of curcumin and this verifies the above premise(Ahn & Obendorf, 2007). The same products were detected from the control or degraded samples of turmeric extraction in the present analysis.

Hiserodt et al.(1996) used both HPLC and GC-MS to identify a number of major and minor components of commercial turmeric powder as well as its fragmentation pattern. The HPLC analysis identified the three curcuminoids- curcumin, demethoxycurcumin,

and bisdemethoxycurcumin from commercial turmeric powder. However, when GC-MS with flame ionization detector was used, they detected a number of products with curcumene backbone which have the most common ion at m/z 119, but not the curcuminoids themselves. Among the identified products were zingiberene and dihydrocurcumene as well as curcumene. The absence of curcuminoids in Hiserodt et al.'s GC-MS result is again consistent with the already mentioned instability of curcumin in the GC-MS instrumental technique. It is obvious that Hiserodt et al.'s products with the curcumene backbone are the fragmentation of the curcuminoids which occurred in the GC column and thus it is safe to say that they are the fingerprint products of turmeric when using GC-MS analysis.

The result of the present investigation coincides with that of Hiserodt et al.(1996). Among the products detected in this research in either the control or degraded samples, zingiberene, dihydrocurcumene, benzene, 1-(3-cyclopentylpropyl)-2,4, and 2-propenoic acid, 3-(2-hydroxyphenyl)-, not to mention curcumene itself, all have the base structure resembling or identical to curcumene backbone with the most common ion fragment occurring at m/z 119(Table 2). Therefore, it is safe to say that these six products are the fragmentation of curcuminoids in turmeric extract in the present investigation. Except for 2-propenoic acid, 3-(2-hydroxyphenyl)-, four products mentioned above were mainly detected in the control sample or at the initial stage of OV degradation experiment. 2-Propenoic acid, 3-(2-hydroxyphenyl)- however, was found throughout the OV degradation times, relative abundance of which decreased substantially with degradation progression. With the absence of curcuminoids in the GC-MS result, the decreasing pattern of 2-propenoic acid, 3-(2-hydroxyphenyl)- reflect the degradation of curcuminoids in turmeric extraction with the progression of OV degradation times.

Vanillin and vanillic acid were reported as the major degradation products of curcumin in different research efforts(Grosjean et al., 1988; Masuda et al., 1999; Wang et al., 1997). In this research, isovanillin, which differs from vanillin only in that -H and -CH_3 positions are switched, has been detected consistently as the degradation product in the OV degradation system, and also in the later stage of the PER degradation system. Vanillic acid was also detected in the 28 day samples of both OV and PER degradation. Phenol, 2,4-bis(1,1-dimethylethyl)- is another product which was consistently detected throughout the degradation times in both OV and PER degradation system and also in the degraded textiles. However, it is not likely that phenol, 2,4-bis(1,1-dimethylethyl)- is the fingerprint product for turmeric since this product was also consistently detected in the previous research on alizarin degradation(Ahn & Obendorf, 2004). This product seems to be the degradation product of phenolic compound in general, which is the structural framework for all natural dyes.

It should be noted that from the 28 day PER degraded sample, isovanillin, feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, benzoic acid, and vanillic acid were detected. Considering that the PER degradation system provides a more severe degradation environment than the OV system via oxidation of dye by both hydroxyl radical or oxygen (Kurbus et al., 2002), it is suggested that the extent of degradation in the PER system can somewhat simulate the degradation of dye in the archaeological textile. Therefore, when the dye component of archaeological textile is examined using GC-MS, and when the certain textile was dyed with turmeric, it is likely that isovanillin, feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, benzoic acid, and vanillic acid will serve as the fingerprint products for the presence of turmeric dye in the textile. The fact that feruloylmethane, and 2-propenoic acid, 3-(2-hydroxyphenyl)- were detected from the OV and PER degraded textile samples verifies above premise. The mechanism for the degradation of curcumin dye in H_2O_2/UV system has been explored in a number of studies. The initial step of photo degradation under H_2O_2/UV system is the production of hydroxyl radicals(·OH) in the excited H_2O_2 aqueous, which subsequently reacts with H_2O_2 to produce oxygen(Kurbus et al., 2002). Both hydroxyl radical and the oxygen species could react with the dye to form oxidized products. Curcumin, which has a symmetrical diketone structure with the CH_2 at the center of the backbone(Fig.

1) can be easily attacked by hydroxyl radical or oxygen species to break its symmetrical diketone structure. And it is believed that the degradation products identified from the present investigation are the result of such chemical attack.

IV. Conclusions

The findings of the present investigation are as follows. Curcumene, zingiberene, cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-methylene, dihydrocurcumene, and 2-propenoic acid, 3-(2-hydroxyphenyl)- were detected from the control sample of turmeric extraction and not the curcuminoids. 2-Propenoic acid, 3-(2-hydroxyphenyl)- was consistently detected in different OV degradation times showing a dramatic decrease with degradation progression up to 7 days after which its decreasing rate slowed and reached equilibrium. Isovanillin, and vanillic acid were newly detected from the OV degraded turmeric extraction. In the 28 day PER degradation sample, feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, benzoic acid, and vanillic acid were detected as well as isovanillin. From the turmeric dyed textiles, feruloylmethane and 2-propenoic acid, 3-(2-hydroxyphenyl)- were detected from several degradation samples.

Considering that PER degradation induces strong oxidative environment for the dye, it is suggested that PER degradation somewhat simulates the degradation environment of the archaeological textiles, and thus isovanillin, feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, and vanillic acid are the probable fingerprint products for determining the turmeric dye from the badly faded archaeological textiles.

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요 약

퇴색된 출토복식의 염료를 판정하기 위한 장기적인 프로젝트의 일환으로서 본 연구에서는 울금뿌리로부터 추출한 염료와 추출염료로 염색한 직물을 실험실 조건에서 28일간 퇴화시킨 후 그로부터 생성되는 퇴화 화합물을 가스 크로마토그라피 질량분석법(GC-MS)을 이용해 분석하였다. 2-propenoic acid, 3-(2-hydroxyphenyl)-는 오븐 퇴화시킨 울금추출액 전체에서 지속적으로 검출되었으며, 그 양은 7일 퇴화시료까지 급격히 감소하다가 그 후 28일까지는 서서히 평형을 유지하였다. 울금추출액의 오븐 퇴화 결과 위의 다섯 개 화합물 외에 isovanillin과 vanillic acid가 새롭게 검출되었다. 28일간 퇴화시킨 PER 시료에서는 isovanillin과 그 외에 feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, benzoic acid, and vanillic acid가 검출되었다. 울금추출액으로 염색한 직물로부터는 feruloylmethane과 2-propenoic acid, 3-(2-hydroxyphenyl)-가 퇴화물로 검출되었다. PER 방법에서 검출된 isovanillin과 feruloylmethane, 2-propenoic acid, 3-(2-hydroxyphenyl)-, benzoic acid, vanillic acid 등은 출토복식 중 울금으로 염색된 직물을 확인하는 데 주요한 대조구 화합물로 사용될 수 있을 것으로 사료된다.