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Case report

Discrimination of cultivated silk and wild silk by conventional instrumental analyses

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ABSTRACT

In Japan, recent trends have seen wild silk preferred over cultivated silk because of its texture. Some cases of fraud have occurred where cultivated silk garments are sold as wild silk. Samples from these cases, morphological observation using light microscope and polarized microscope have been conducted in forensic science laboratories. Sometimes scanning electron microscopy was also carried out. However, the morphology of silk shows quite wide variation, which makes it difficult to discriminate wild and cultivated silks by this method. In this report, silk discrimination was investigated using conventional instrumental analyses commonly available in forensic laboratories, such as Fourier-transfer infrared spectrometry (FT-IR), pyrolysis-gas chromatography/mass spectrometry (pyr-GC/MS) and differential thermal analysis (DTA). By FT-IR, cultivated and wild silk gave similar infrared spectra, but wild silk had a characteristic peak at 965 cm^{-1} from the deformation vibration of the carbon–carbon double bond of the indole ring. Comparison of the pyrograms of cultivated and wild silk showed that wild silk had large indole and skatole peaks that cultivated silk did not, and these peaks might arise from tryptophan. The results of thermogravimetry/DTA showed that the endothermic peak was about 40 °C higher for wild silk than for cultivated silk. Using a combination of these results, cultivated and wild silk could be discriminated by common forensic instrumental techniques.

1. Introduction

Silk is a popular but expensive fiber that is used in formal Japanese garments and high-end fashion. Generally, the quality of cultivated silk is higher than that of wild silk, and there are many silkworm farms in Japan. However, recent trends have seen wild silk preferred over cultivated silk because of its texture. Consequently, wild silk garments are more expensive than those made of cultivated silk, and this has led to several cases of fraud. In these cases, samples have been analyzed to determine if the silk is cultivated or wild [1,2]. Cultivated and wild silk can be discriminated by morphological observation by light microscope and polarized microscope, and sometimes scanning electron microscope observation [3], and recently, discrimination methods by a cross section of the sample and amino acid analysis were reported [4]. In addition, endothermic analysis [5], elemental analysis by scanning electron microscopy with an energy dispersive micro analyzer [6] and UV–vis spectrometry with infra-red spectrometry [7] have been used. Pyrolysis gas chromatography/mass spectrometry (pyr-GC/MS) has been used with artificial leathers, and pyrolyzed products and protein components of silk have been assigned [8]. However, forensic science laboratories are typically equipped with instruments such as Fourier transfer-infrared (FT-IR) spectrometers, pyr-GC/MS, and thermo gravimetry/differential thermal analyzers (TG/DTA). Recently, analysis of silk by FT-IR and TG/DTA were reported [9,10]. Consequently, these devices are more convenient and familiar to forensic scientists than the above instruments used in earlier studies. In addition, combination of the data obtained by these instrumental analyses would presumably provide more accurate results for discrimination of cultivated and wild silk than the methods used previously. In this report, cultivated (*Bombyx mori*) and wild silk (*Antheraea peruyi* and *yamamai*) reference samples were analyzed by the above instrumental methods, and results were compared with those of fibers retrieved from suspicious garment.

2. Materials and methods

2.1. Materials

Reference samples of untreated cultivated and wild silk utilized in this were from our fiber collection. Cultivated silk was from

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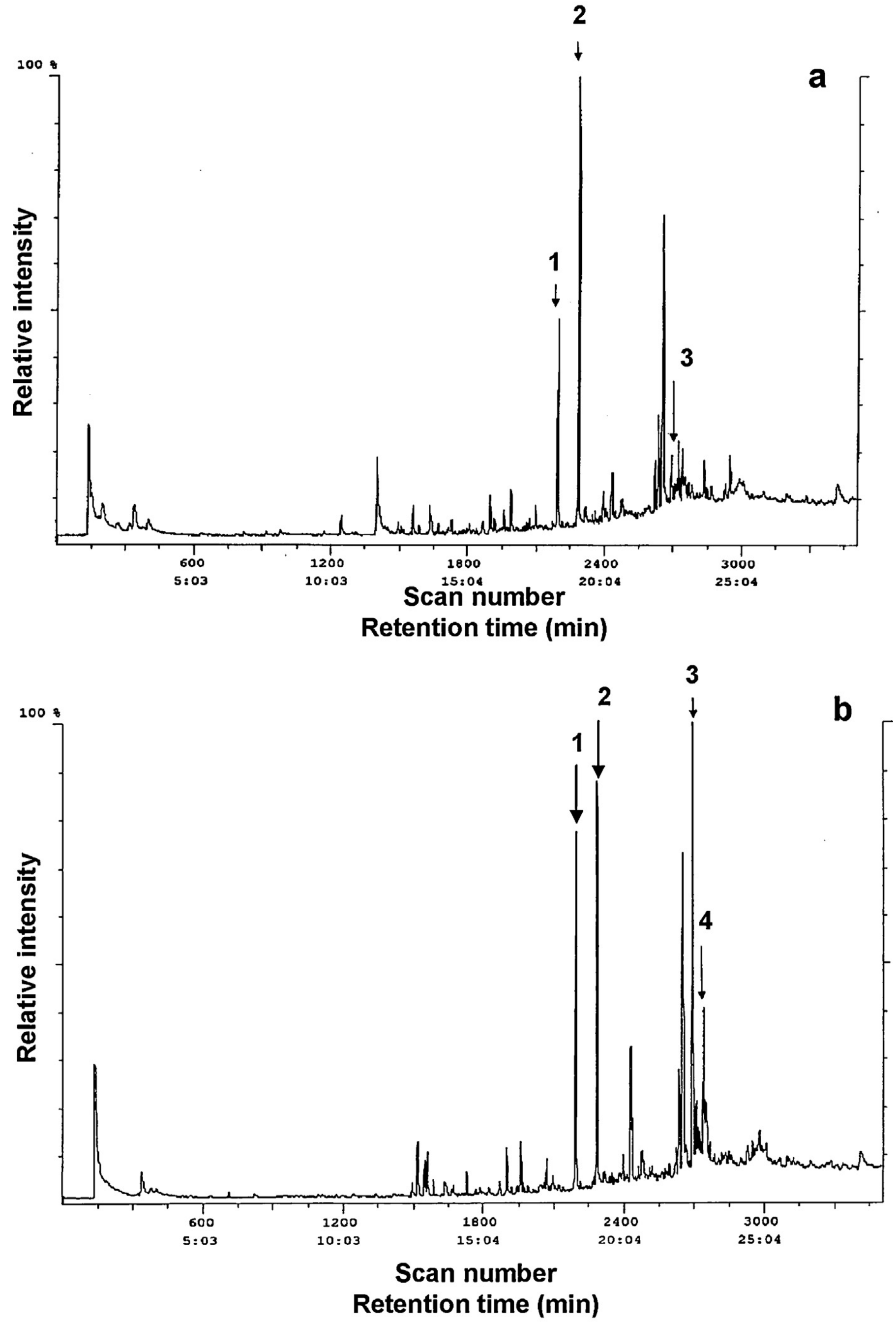

Fig. 1. Pyrograms of cultivated silk (a) and wild silk (b). Peak 1: phenol, peak 2: *p*-cresol, peak 3: indole, and peak 4: skatole.

Bombyx mori (only this description was written) and two wild silks were from *A. peruyi* and *Antheraea yamamai* and suspected single fibers retrieved suspicious silk garment. Reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan). For the blind test, cultivated and wild silk were kindly supplied from the manufacturer.

2.2. Instrumental analyses

The silk samples were pyrolyzed using a JHP 3S type Curie point pyrolyzer (Japan Analytical Industry, Tokyo, Japan) for pyr-GC/MS. Each sample (approximately 10 mm of two single fibers) was wrapped in pyro-foil from Japan Analytical Industry and pressed. The samples were pyrolyzed at 590 °C for 5 s. GC/MS was performed using a Finnigan MAT GCQ (ThermoFisher Scientific Japan, Yokohama, Japan) GC/MS system and a DB-WAX column,30 m × 0.25 mm I.D., 0.25-μm film thickness (Agilent Technologies Japan, Tokyo, Japan). The column temperature was programmed from 50 °C (5 min hold) to 230 °C at 10 °C/min). The injection temperature was 250 °C. The samples were ionized by electron ionization at 90 eV. The TG/DTA was conducted by on a TG/DTA 320 type thermo analyzer (SII NanoTechnology, Tokyo, Japan) using approximately 10 mm of 20 single fibers of each silk sample. The temperature was increased from 50 °C to 550 °C at 10 °C/min. The carrier gas was nitrogen at a flow rate of 50 mL/min. A single fiber was analyzed by FT-IR making a small pellet by KBR, and IR spectra were obtained by using a Magna-550 FT-IR with a microspectrometer-system (ThermoFisher Scientific, Yokohama, Japan). Spectra were obtained using a HgCdTr detector in the range from 650 cm^{-1} to 4000 cm^{-1}. The resolution was 4 cm^{-1}.