J Wood Sci (2007) 53:529–532
DOI 10.1007/s10086-007-0900-1

NOTE

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The composition of volatiles from tatami mats containing hinoki (*Chamaecyparis obtusa*) wood-wool and its decline over the long term

Received: November 1, 2006 / Accepted: April 6, 2007 / Published online: July 8, 2007

Abstract Volatiles inside tatami mats containing hinoki (*Chamaecyparis obtusa*) wood-wool as padding were analyzed. Volatiles were collected with solid-phase microextraction (SPME) fibers in a small chamber prepared in tatami mats and assayed by gas chromatography. Most of the detected compounds are typically found in hinoki extractives. Monoterpenes rapidly decreased at the beginning of the experiment, while the dispersion of sesquiterpenes that contain hydroxyl groups was observed to last more than 1 year. These sesquiterpenes, T-cadinols, and α-cadinols may play a role in the suppression of house dust mites.

Key words Volatiles · *Chamaecyparis obtusa* · Tatami mat · Cadinol

Introduction

Hinoki (*Chamaecyparis obtusa*) is one of the most popular wood species in Japan. Many studies have reported that hinoki extractives with their characteristic odor (volatile components) show typical antifungal and insecticide activities.[1,2] Attempts have been made to bring the biological efficiency of hinoki extractives closer into our daily lives. For example, tatami mats, an essential flooring element of Japanese-style rooms, were manufactured with embedded hinoki veneers in an attempt to utilize its properties. Volatiles from the veneers were effective in suppressing the activity of house dust mites (*Dermatophagoides pteronyssins*) in the mats.[3] Hinoki volatiles have enough potency to repel house dust mites that often live inside tatami mats.

Recently, more advanced tatami mats have been manufactured using hinoki wood-wool as padding in place of the traditional rice straw. Our previous study[4] reported that these novel tatamis showed excellent potential to suppress the activity of house dust mites, at least for 1 year. This suppression is considered to have occurred because of volatiles emitted from hinoki wood-wool as demonstrated previously.[5]

Among the many kinds of compounds found in hinoki extractives, cadinols are the most likely source of these suppressive functions because of their strong ability to kill mites,[6] their inhibition of the growth of *Streptococcus mutans*, which is one of the causes of dental cavities,[7] and other antifungal properties.[8] As a result of these studies, much interest has arisen in the contribution of cadinols to the mite suppression activity of hinoki tatami; however, it is difficult to analyze the volatiles in the very small cavities in tatami mats. To resolve this problem, solid-phase microextraction (SPME) was employed in this study. Developed within the past 15 years, SPME has been utilized in the field of headspace and indoor air analysis.[9] Volatiles in the air are extracted and concentrated in a fine fused silica fiber coated with a polymeric organic liquid. The analysis of adsorbed substances can be easily conducted by thermal desorption using a conventional gas chromatograph.

The aim of this study is to clarify the relationship between the amount of cadinols and their effectiveness in repelling house dust mites. The volatile components in tatami mats made from hinoki wood-wool were analyzed by the SPME technique, using the same experimental procedure used in the suppression test of house dust mites.[4]

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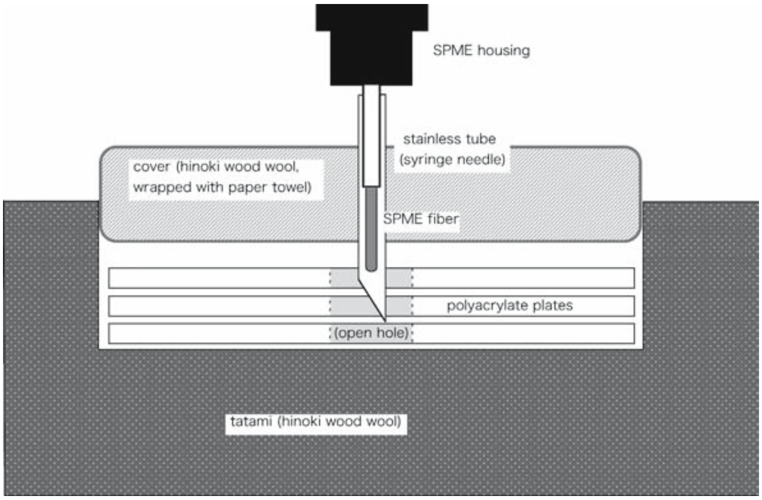
Part of this report was presented at the 55th Annual Meeting of the Japan Wood Research Society in Kyoto, March 2005

Fig. 1. Extraction of volatiles using solid-phase microextraction (*SPME*) fiber from hinoki tatami mat



Materials and methods

Tatami mats

The preparation of tatami mats containing hinoki wood-wool (Hinoki Tatami, Hida Forest, Gifu, Japan) is described in a previous report in detail.[4] Briefly, wood-wool was prepared from hinoki (*Chamaecyparis obtusa*) logwood having dimensions of 5 mm in width, 0.1–0.3 mm in thickness, and 50–400 mm in length. The hinoki wood-wool was then dried to 10% moisture content in a drying oven (40°C) for 10 h. Tatami mats (400 × 400 mm, 60 mm thick) were made from hinoki wood-wool, lauan veneers, hemp clothes, and vinylon strings by roll pressing and sawing. A control tatami mat was prepared by immersing it in 75% ethanol for 5 days and air-dried, then this extraction was repeated.

The tatami mats had six cavities for the exposure test of house dust mites, as described previously.[4] In this experiment, to prepare the same environment for tests using mites, open polyacrylate chambers were set in three of the cavities in tatami mats. Each cavity was covered with hinoki wood-wool wrapped in a paper towel. Whole tatami mats were conditioned to 25°C and 70%–80% relative humidity in desiccators.

Extraction of volatiles from hinoki tatami mats by SPME

A disposable syringe needle (Terumo, 1.20 × 38 mm) was used as a guide tube to avoid damaging the SPME fiber in the tatami cavities (Fig. 1). The needle was inserted beforehand into the vacant space of the polyacrylate chamber through the cover of a cavity. A SPME fiber (Supelco, polydimethylsiloxane coating 100 μm thick) was then exposed in the needle tube and left for 2 h to collect volatiles in the cavity. This procedure was carried out in the three cavities simultaneously, for four consecutive days in the 6th, 17th, 33rd, and 55th weeks after the preparation of the tatami mats.

Table 1. Volatile compounds detected in tatami made of hinoki wood wool in the sixth week after tatami production

Retention time[a]	Compound	Chromatogram peak area (%)
0.433	α-Pinene	0.8
0.690	Terpinene-4-ol	0.4
0.702	α-Terpineol	0.4
0.849	γ-Terpineol	2.4
0.892	β-Elemene	1.6
0.950	α-Humulene	0.7
0.966	γ-Muulolene	9.4
0.979	β-Selinene	2.9
0.985	Elemophiladiene	13.8
0.990	allo-Aromadendrene	1.1
1.000	γ-Cadinene	27.0
1.003	cis-Calamenene	5.0
1.016	α-Cadinene	2.3
1.021	β-Calacorene	1.2
1.079	Cubenol	2.0
1.088	α-Cedrene	2.9
1.099	*T*-Cadinol	12.7
1.109	α-Cadinol	9.9
1.117	γ-Calacorene	1.0
1.124	Cadalene	2.3

[a] Relative to γ-cadinene

Analysis of volatiles

The volatiles collected in the SPME fibers were introduced into a gas chromatograph [Shimadzu GC17A; column: Supelco Equity 5, from 40°C (hold 5 min) to 250°C (10 min) by 4°C/min] by thermal desorption at the injection port (250°C). Each detected peak area was evaluated according to the calibration curve of α-pinene. The peaks were identified using gas chromatography-mass spectrometry (GC-MS) (Agilent 6890-5973), and a library search was carried out using the NIST Library and the Baser Library of Essential Oil Constituents.

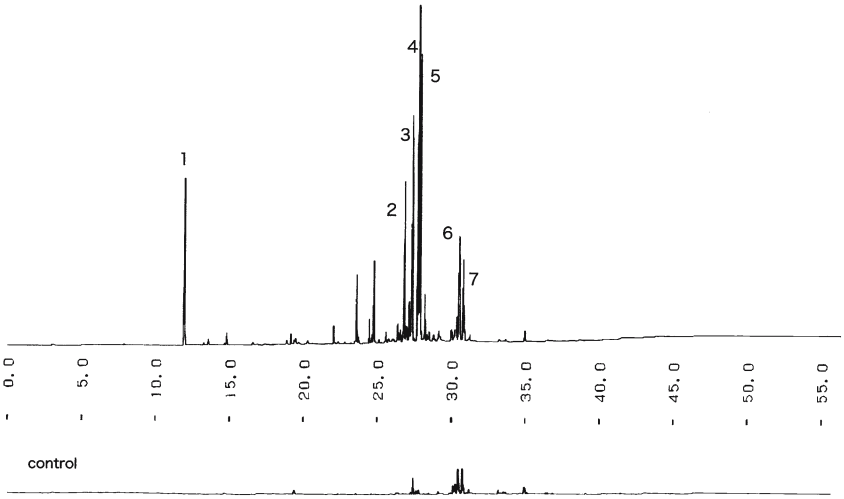


Fig. 2. Gas chromatogram of volatiles from hinoki tatami mat. *1*, α-Pinene; *2*, γ-muulolene; *3*, elemophiladiene; *4*, γ-cadinene; *5*, calamenene; *6*, *T*-cadinol; *7*, α-cadinol

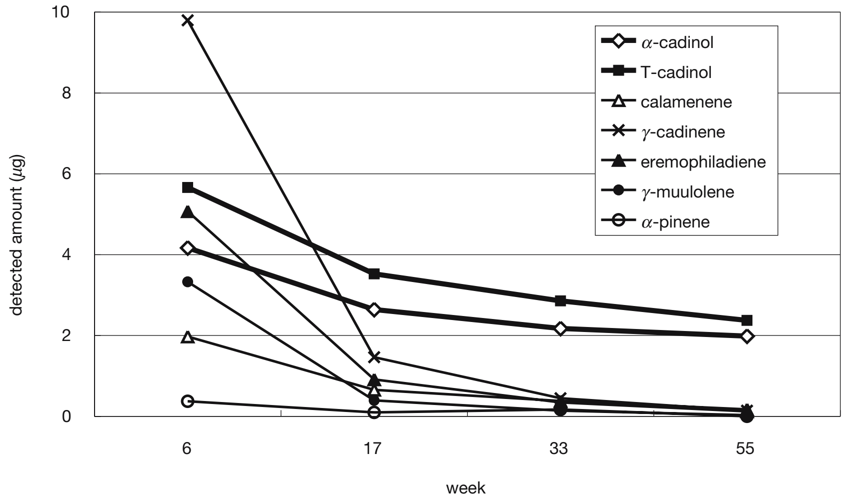


Fig. 3. Change of the constitution of volatiles over time for tatami made of hinoki wood-wool

Results and discussion

The volatile components arising from the hinoki tatami mats were extracted by SPME fiber and analyzed by gas chromatography. The chromatogram profile at the beginning of this experiment is shown in Fig. 2, and compounds identified in the profile of the 6th week are summarized in Table 1. These volatiles are typical terpenoids found in hinoki extractives.[10]

There are several reports concerning the absorption characteristics of SPME fibers showing that SPME tends to be more effective for analyzing substances that have higher molecular mass.[11,12] This tendency might have affected the results obtained in this study, because most of the components shown in Table 1 are sesquiterpenes, and the proportion of monoterpenes is relatively small. However, there is no deficiency in detecting cadinols, and this method is useful for evaluating the long-term dependent change of each component of hinoki volatiles.

Volatiles originating from other components of the hinoki tatami mats, such as lauan veneer, hemp cloth, and vinylon strings, were not detected as major components in this profile (Table 1). This result shows that most volatiles detected in the tatami mats originate from the hinoki wood-wool.

A comparison of the new tatami mats and the control (ethanol-extracted) tatami shows a clear difference in the amount of volatiles (Fig. 2); the control tatami mat showed less than 5% of the volatiles contained in the hinoki tatamis.

Changes in the major components of the volatiles from hinoki tatamis are summarized in Fig. 3. At the very beginning of the experiment, α-pinene was very noticeable (Fig. 2), but it disappeared almost completely within 6 weeks, possibly because of its high volatility. Some sesquiterpenes (γ-cadinene, elemophiladiene, γ-muurolene, and calamenene) were observed to be most plentiful in the 6th week, but their quantities quickly dropped off by the 17th week (Fig. 3).

In contrast, α-cadinols and T-cadinols exhibited much slower decline during this experiment. Even after 1 year (55 weeks), almost half of the initial dispersion of cadinols remained. In general, compounds that contain hydroxyl group have a higher boiling point, that is, lower volatility, than other substances of similar molecular weights because of the formation of hydrogen bonds. Therefore, the volatility of α-cadinols and T-cadinols is lower than that of other sesquiterpenes with no hydroxyl group (cadinenes, etc.), and the rate of dispersion is considered to be much slower. As a result, cadinols kept dispersing for 1 year with only a slight decrease, and accounted for the majority of the volatile constituents in the 55th week.

Tatami mats are an integral part of the traditional Japanese lifestyle, so the effects of these tatami-derived volatiles have drawn much attention. Normal rice-straw tatami mats tend to be easily invaded by house dust mites. Dead mites and mite excrement are known to be allergens, and they even cause several human diseases.[13,14] Hiramatsu et al.[4] surveyed the effect of the inner environment of tatami mats on mites using the same hinoki tatami mat employed here. In that study, the mite suppression effect lasted at least 1 year after the tatamis were produced (exposure to the mats for 5 days immobilized 62% of the mites). In the present study, the volatile components from hinoki tatamis at 1 year after production were mostly α-cadinols and T-cadinols. This suggests that these cadinols are largely responsible for the long-term mite-suppressing activity of hinoki tatami mats.

Hiramatsu et al.[4] also reported very strong mite suppressing activity (100% of immobilized mites) just after the production of new hinoki tatami mats. This means that some components must work very strongly in the beginning. However, there was not a dramatic decrease in the amount of cadinols between the start and end of this experiment, so they would not have had a major role in this early activity. Thus, there must be other components that have strong suppressive activity against mites. Such components would have high volatility, and disperse too quickly after the production of tatami mats to be involved with the mite-suppressing activity over 1 year. It is not possible to determine what substances are responsible for this instant suppression from the results of the present study. However, tatami mats are generally used for several years in Japanese homes. The slowly dispersing cadinols should be regarded as playing an important role in mite suppression when considering the actual, long-term usage of tatami mats made of hinoki wood-wool.

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