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## Pyrolysis GC-MS analysis of tars formed during the aging of wood and bamboo crude vinegars

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**Abstract** Constituents of tars formed during the aging of bamboo (*Phyllostachys pubescens*), oak (*Quercus serrata*), and pine (*Pinus densiflora*) wood crude vinegars were analyzed by pyrolysis–gas chromatography (Py-GC) and pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) to investigate their origination. The pyrolysate of tars obtained from the wood and bamboo crude vinegars were almost identical and were primarily composed of phenolic compounds and aromatic hydrocarbons. In addition, during the aging of model wood vinegar that was prepared for comparison with the wood and bamboo vinegars, a marked decrease was observed in the levels of phenolic compounds (phenol; *o*-, *p*-, and *m*-cresol; and syringol). Furthermore, the Py-GC-MS results of the tars produced during the aging of the model wood vinegar revealed that phenolic compounds were primarily responsible for the formation of tar during the aging of wood and bamboo crude vinegars. Pyrroles, which may be derived from the primary pyrolysate of amino acids, nitrogen-containing extracts, or both, were also partially involved in the formation of tar during the aging period.

**Key words** Tar · Wood and bamboo vinegar · Py-GC-MS · Pyrolysate · Pyrroles

### Introduction

Wood and bamboo vinegars are liquors with strong smoke flavors that are obtained as a by-product during the manu-

facture of charcoal from wood and bamboo. These vinegars are composed of water (80%–90%) and more than 200 species of organic compounds (10%–20%).<sup>1,2</sup> In agriculture, wood and bamboo vinegars have been used as environmentally friendly substances to stimulate plant growth, improve the quality of fruit, accelerate the speed of plant seed germination, disinfect soil, and serve as herbicides.<sup>3,4</sup> Recently, the favorable environmental effects and ecological sustainability of these vinegars has attracted increased attention.<sup>5</sup> In addition, these by-products are being used in an increasing number of products, including deodorizers, smoke flavoring, and health supplement beverages in Korea and other countries in Southeast Asia.<sup>6</sup>

Among the organic compounds found in these vinegars, tar, which is primarily composed of phenolics, has attracted attention due to its harmful influence on soil and crops when sprayed onto plants. As a result, these vinegars are used after removal of the tars through a refining process. One such refining process, known as stationing, has been widely used in the domestic wood vinegar industry due to its relatively low operating cost; however, this process requires a long time for refining. During the aging period of this process, aggregation or condensation reactions between the unstable substances in the crude vinegars result in the formation of tar. Although it is necessary to understand such tars to facilitate the refining processes, to date only a few studies regarding this topic have been published.<sup>7,8</sup> These reports have mentioned the approximate composition of the tars formed, but have not presented clear evidence of an interaction and a condensation among the wood vinegar components. In addition, a systematic and detailed study evaluating the tars formed from these vinegars has not been conducted.

Therefore, we conducted this study to identify the compounds responsible for the formation of tar during the aging of wood and bamboo vinegars. In addition to the above vinegar-related experiment, a model wood vinegar was also prepared to evaluate the compounds responsible for the formation of tar. The material was prepared using a variety of organic compounds that are the primary components of wood and bamboo vinegars.

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Pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS) is a powerful tool for the characterization of complex natural polymers, such as the lignin and polysaccharides in wood. Py-GC-MS provides detailed information regarding molecular changes from a very small amount of sample.<sup>9</sup> Accordingly, in this study the resin-like tars obtained from the wood and bamboo crude vinegars and the model wood vinegar were further characterized by Py-GC-MS.

## Experimental

### Preparation of wood and bamboo crude vinegars and tar

A pilot-scale mechanical kiln (220 × 393 × 179 cm) with a cooling device to collect wood and bamboo vinegar was used for this experiment; the kiln is located at the southern Forest Research Center in Jinju, South Korea. The carbonization was performed at 800°–1000°C. The crude vinegars of bamboo (*Phyllostachys pubescens*), oak (*Quercus serrata*), and pine (*Pinus densiflora*) were recovered from the cooling device. The recovery of the vinegars was carried out when the exhaust gas outlet temperature was 80°–150°C. The detailed carbonization condition and schedule<sup>10</sup> and the system for the vinegar recovery has been described in previous reports.<sup>11,12</sup> The wood and bamboo crude vinegars were aged in blue acid-resistant plastic cans at ambient temperature for 35 months without stirring, during which time the changes in the chemical constituents of these vinegars were investigated by GC and GC-MS as described in our previous report.<sup>13</sup> Calibration curves obtained from acetic acid and phenol were drawn prior to sample analysis to enable further quantitative measurement, and the correlation coefficient of these curves was greater than 0.99. The compounds in the vinegars were divided into three groups: phenols, organic acids, and other compounds mainly consisting of alcohols which we termed neutrals. For GC and GC-MS analysis, the crude vinegar was filtered using a disposable syringe filter (0.45 μm) to remove the tar. The tar that precipitated after 35 months of aging was then washed thoroughly with distilled deionized water, after which it was transferred to a glass Petri dish and air-dried at room temperature. The dried tars were then subjected to Py-GC-MS and Py-GC analysis.

### Preparation of model wood vinegar and tar

Model wood vinegar was prepared by mixing acetic acid (3.0%), propionic acid (0.4%), formic acid (0.2%), methanol (0.4%), phenol (0.3%), cresols (*o*-, *m*-, *p*-cresols; 0.1% each) and syringol (0.1%). Acetonitrile was added as an internal standard. The model wood vinegar was put in 10-ml clear screw-top vials with phenolic caps (PTFE/silicone septa, Supelco) and aged at ambient temperature for 26 months. The vinegar was analyzed by GC after 5 months, at which time its color was light brown. After 1 year, a resin-like tar had formed in the vinegar. This residue was sepa-

rated by decantation and was then washed with distilled deionized water and air-dried thoroughly, after which it was subjected to Py-GC-MS and Py-GC analysis.

### Pyrolysis–gas chromatography–mass spectrometry

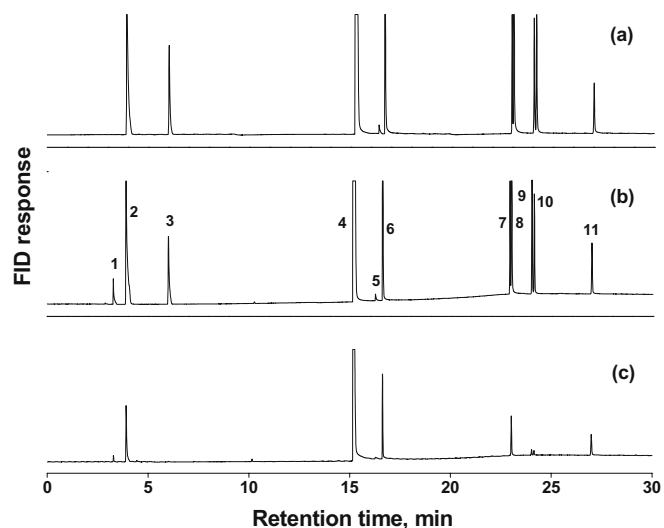
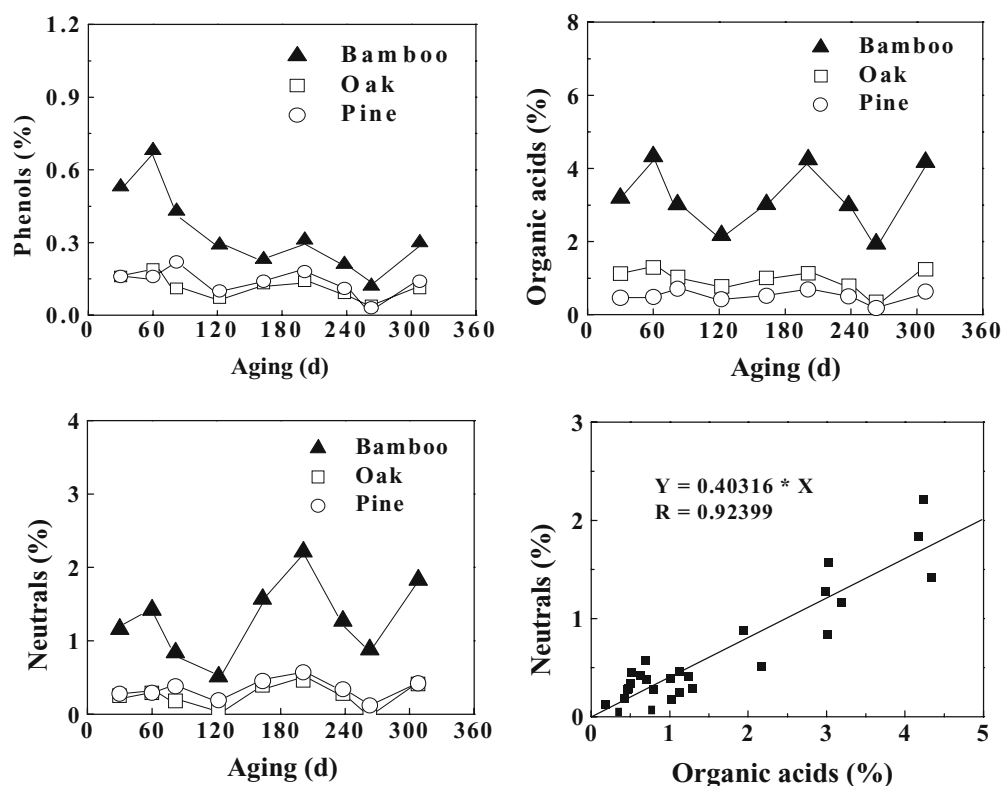
Approximately 1 mg of the finely ground tars was loaded into a platinum bottle and then introduced into a quartz tube in a Shimadzu Pyr-4A (preset at 650°C). The pyrolysates of each tar were then analyzed using a Shimadzu QP5050 GC-MS. A CBP 20 silica fused capillary column (25 m × 0.22 mm inside diameter, 0.25 μm film thickness) was used to separate the pyrolysates. The detailed GC-MS parameters are now described. The oven temperature was maintained at 50°C for 2 min and then elevated from 50°C to 220°C at a rate of 2°C/min. The temperature was then maintained at 220°C for 5 min. The flow rate of He gas was held at 0.8 ml/min, the split ratio was adjusted to 38, the MS was operated in electron ionization (EI) mode at 70 eV, and the interface temperature was maintained at 230°C. The compounds were then identified by comparing the results with previously reported values<sup>14,15</sup> and with values in the Wiley 139 computer library. A Shimadzu GC-17A combined with a flame ionization detector (FID) was used for the Py-GC analysis of tar. The GC parameters and the column used were as described above.

## Results and discussion

### Changes in wood and bamboo crude vinegars during the aging period

In this study, the physicochemical changes in wood and bamboo crude vinegars during a prolonged aging period were investigated. Figure 1 shows the quantitative changes in the chemical constituents of these vinegars. The amount of organic acids and neutral compounds in the vinegars increased or decreased periodically every 3 months. In addition, a good linear relationship (correlation coefficient of around 0.92) was observed between the amount of organic acids and the amount of neutral compounds following such changes. This may have resulted from reversible reactions, such as slow esterification and hydrolysis reactions of the esters. In the model wood vinegar experiment, the appearance of methyl acetate is evidence of the esterification of acetic acid with methanol (Fig. 2). Although the amount of phenolic compounds increased or decreased periodically, the total amount decreased over the entire aging period. Furthermore, the decrease in phenolic components in the bamboo vinegar was more marked than those observed in oak and pine wood vinegars. It is assumed that this decrease in phenolic components was associated with condensation reactions,<sup>16,17</sup> aggregation among the phenolic compounds, or both. Precipitation of tar in crude and refined vinegars has been observed as a natural phenomenon, which likely occurs due to the association of unstable substances. However, there is no direct evidence to support the forma-

**Fig. 1.** Changes in the chemical constituents of wood and bamboo crude vinegars during the aging period



**Fig. 2.** Changes in the compounds of model wood vinegar at **a** 0 months, **b** 5 months, and **c** 26 months during the aging period. 1, methyl acetate; 2, methanol; 3, acetonitrile (internal standard); 4, acetic acid; 5, formic acid; 6, propionic acid; 7, *o*-Cresol; 8, phenol; 9, *p*-cresol; 10, *m*-cresol; 11, syringol. FID, flame ionization detector

tion of tar in wood and bamboo vinegars. Accordingly, these results are expected to be applied as crucial information in future vinegar tar studies.

#### Changes in model wood vinegar during the aging period

A variety of organic acids and neutral and phenolic compounds were mixed to provide a model wood vinegar as

similar to wood and bamboo crude vinegars as possible. The concentrations of these compounds were determined based on the contents of bamboo vinegar, which contains higher concentrations of the major compounds than oak and pine wood vinegars (Fig. 1). This model vinegar was then maintained at ambient temperature during the analysis period. The model wood vinegar was a clear colorless solution at the beginning of the study; however, it became light brown after 5 months. After 26 months, the color was much darker and tar-like materials were attached to the wall and bottom of the glass bottle that was used for the experiment. Figure 2 shows the changes in the amounts of the compounds in the model vinegar over the aging period. The amounts of all compounds in the model vinegar were decreased very slightly after 5 months. Methyl acetate (peak no. 1) was newly formed after 5 months of aging. This shows evidence of the esterification of acetic acid with methanol, as expected from the long-term aging of wood and bamboo vinegars. However, after 26 months, most of the compounds in the model wood vinegar had decreased or disappeared. Acetonitrile, which was used as an internal standard, was no longer present after 26 months. A significant decrease was observed in the amounts of phenolic compounds including phenol, cresols (*o*-, *m*-, and *p*-), and syringol, which was likely caused by self-condensation, strong aggregation among these compounds, or both (Table 1). The decreasing percentage of the phenolic compounds occurred in the following order: cresols (*o*-, *m*-, *p*-cresols; 100.0%) > phenol (90.3%) > syringol (66.7%). From this result, we can conclude that if these compounds in the model wood vinegar were not released from the storage bottle during long-term aging, they could be con-

verted to some other compounds or condensed with other compounds in the model vinegar. On the GC chromatogram, however, no new peaks appeared except for methyl acetate, which was formed by esterification of acetic acid with methanol. Therefore, it is thought that the phenolic compounds contributed to the precipitated tar-like materials during 26 months of aging.

### Pyrolysis of tar

The tars were pyrolyzed at 650°C under a He atmosphere. The tar from model wood vinegar that had been aged for 1 year was compared to tars formed by wood and bamboo crude vinegars. The pyrolysates of the tars were identified by comparing the results to previously reported mass patterns fragmented at 70 eV and to the Wiley 139 library. As shown in Table 2, various phenolic isomers with the same MS fragments were identified based on comparison of their retention times (RT) with previously reported RT<sup>18</sup> and the

RT of standard compounds. The pyrograms and the main pyrolysates present in these tars are shown in Fig. 3 and Table 2, respectively. Approximately 100 compounds were detected from the pyrolysates.

The pyrolysates of the tars originating from wood and bamboo vinegars were almost identical and were primarily composed of phenolic compounds and aromatic hydrocarbons. There were also a variety of compounds, such as acetic acid, pyrroles, benzofuran, and naphthalene present in these tars.

As shown in Table 2, phenolic compounds such as phenol, cresols, xylenols, ethylphenols, trimethylphenols, and 2-ethyl-4-methylphenol corresponded to the phenolic compounds identified in the wood and bamboo vinegars.<sup>13,19</sup> Therefore, these results demonstrate that the phenolic compounds present in crude vinegars lead to the occurrence of tar during the aging process. Aromatic hydrocarbons such as toluene, xylene, styrene, and 1-propenylbenzene are common products that usually occur during the high-temperature pyrolysis of woody biomass<sup>20,21</sup> as a result of dehydration of a hydroxyl group and cleavage of a C–C bond in resin-like condensed phenolic compounds.<sup>22,23</sup> It is believed that the acetic acid in the samples evaluated in this study originated from the pyrolytic cleavage of certain types of ester linkages that exist in the tar. In addition, the pyrroles likely originated from the primary pyrolysate of amino acids, nitrogen-containing extracts, or both.<sup>22</sup> Although pyrrole is an extremely weak base, it possesses strong proton-donating acids that form protonated coordinate covalent compounds. The protonated ion of pyrrole is highly unstable and undergoes polymerization readily.<sup>24,25</sup> Therefore, the presence of pyrroles as pyrolysates occurs during polymerization of these vinegars under acidic condi-

**Table 1.** Changes in the phenolic compounds in model wood vinegar during the 26-month aging period

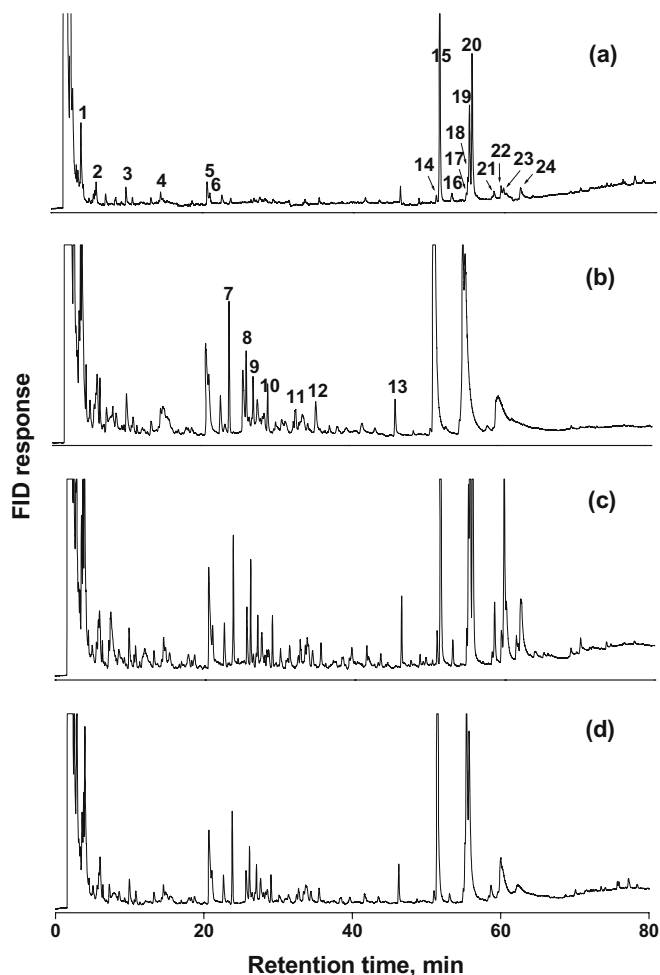
Peak label	Compound	Month			Percentage decrease
		0	5	26	
7	<i>o</i> -Cresol	0.10 <sup>a</sup>	0.08	0.00 <sup>b</sup>	100.0
8	Phenol	0.31	0.26	0.03	90.3
9	<i>p</i> -Cresol	0.09	0.08	0.00	100.0
10	<i>m</i> -Cresol	0.09	0.06	0.00	100.0
11	Syringol	0.09	0.07	0.03	66.7

All compounds are expressed as peak area percentage  
Percentage decrease is calculated as  $((a - b)/a) \times 100$

**Table 2.** Major pyrolysates of tars obtained from wood and bamboo crude vinegars and model wood vinegar

Peak label	Compound	MS fragments	Model vinegar	Bamboo vinegar	Oak vinegar	Pine vinegar
1	Toluene	91, 92	○	○	○	○
2	Xylene	77, 91, 106	○	○	○	○
3	Styrene	78, 104	○	○	○	○
4	1-Propenylbenzene	91, 103, 117, 118	○	○	○	○
5	Acetic acid	43, 45, 60	○	○	○	○
6	Benzofuran	89, 90, 118	○	○	○	○
7	Pyrrole	41, 67	–	○	○	○
8	2-Methylpyrrole	53, 80, 81	–	○	○	○
9	3-Methylpyrrole	53, 80, 81	–	○	○	○
10	2,5-Dimethylpyrrole	80, 94, 95	–	○	○	○
11	2,3,5-Trimethylpyrrole	94, 108, 109	–	○	○	○
12	Naphthalene	86, 102, 128	○	○	○	○
13	2,6-Xylenol	77, 91, 107, 122	○	○	○	○
14	2,3,6-Trimethylphenol	77, 91, 121, 136	○	○	○	○
15	Phenol <sup>a</sup> + <i>o</i> -cresol <sup>b</sup>	<sup>a</sup> 66, 94, <sup>b</sup> 77, 108	○	○	○	○
16	2,4,6-Trimethylphenol	77, 91, 121, 136	○	○	○	○
17	<i>o</i> -Ethylphenol	77, 91, 107, 122	○	○	○	○
18	2,5-Xylenol	77, 91, 107, 122	○	○	○	○
19	<i>p</i> -Cresol	77, 90, 107, 108	○	○	○	○
20	<i>m</i> -Cresol	77, 79, 107, 108	○	○	○	○
21	2,3-Xylenol	77, 91, 107, 122	○	○	○	○
22	2-Ethyl-4-methylphenol	91, 121, 136	○	○	○	○
23	<i>p</i> -Ethylphenol	77, 91, 107, 122	○	○	○	○
24	3,4-Xylenol	77, 91, 107, 122	○	○	○	○

MS, mass spectrometry



**Fig. 3.** Pyrograms of tars obtained from model wood vinegar and wood and bamboo crude vinegars after 35 months of aging: **a** model wood vinegar, **b** bamboo vinegar, **c** oak wood vinegar, **d** pine wood vinegar. The numbered compounds are defined in Table 2

tions (pH 2.5–3.5) due to the presence of the unshared electron pairs of pyrroles.

The tar components of the model wood vinegar showed similar results to those of wood and bamboo crude vinegars (Fig. 3 and Table 2). The pyrolysates of the model wood vinegar tar contained almost all of the primary compounds, with the exception of pyrroles such as pyrrole, 2- and 3-methylpyrrole, 2,5-dimethylpyrrole, and 2,3,5-trimethylpyrrole. Therefore, it can be assumed that the compounds used for the preparation of the model wood vinegar (acetic acid, propionic acid, formic acid, methanol, phenol, cresols, and syringol) play a significant role in the formation of tar in wood and bamboo vinegars, which is supported by the pyrolysis results observed in the model wood vinegar. In addition, the pyrolysates of the tars obtained from the wood and bamboo crude vinegars and the model wood vinegar primarily consisted of phenolic compounds and aromatic hydrocarbons. This finding, combined with the results of the model wood vinegar study, indicate that phenol, cresols, and syringol were primarily responsible for the formation of tar.

## Conclusions

Due to the increased utilization of wood and bamboo vinegars, a systematic investigation of tar formation associated with the production of these vinegars is required for the development of a rapid refining process. The phenolic components of all vinegars, including wood and bamboo crude vinegars, as well as the model wood vinegar, decreased as the aging period increased. The tars formed by these vinegars were analyzed using Py-GC-MS, which revealed that phenolic compounds were primarily responsible for the formation of tar in wood and bamboo crude vinegars. In addition to phenolic compounds, pyrroles, which may be derived from the primary pyrolysate of amino acids, nitrogen-containing extracts, or both, were also partially involved in the formation of tar during the aging period.

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