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Formation of methyl iodide from methoxyl-free compounds by hydriodic acid treatment

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Introduction

Methoxyl groups (including methyl esters, methyl ethers, and methanol) react with hydriodic acid to produce methyl iodide. This reaction is applied for the determination of methoxyl groups in lignin.¹ Gran² suggested that glucose and other carbohydrates give rise to “apparent” methoxyl contents on use of the reaction although the formation of methyl iodide was not confirmed. In our recent study,³ however, methyl iodide was detected by gas chromatography (GC) in the reaction mixture of α -cellulose with hydriodic acid. As the reason for the formation of methyl iodide from α -cellulose, two possibilities were suspected. One possibility was that α -cellulose was contaminated with methoxyl-containing compounds. Another possibility was that methyl iodide was produced by an unknown mechanism from methoxyl-free compounds. In the present study, these possibilities were examined by the use of carbohydrates as methoxyl-free compounds and the effect of these compounds on the determination of methoxyl group content in lignin was evaluated.

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Materials and methods

Materials

Japanese cedar (*Cryptomeria japonica* D.Don) and Japanese birch (*Butula maximowiczii* Regel) wood meals, passing 80 mesh, were extracted with ethanol/benzene (1:2, v/v) for 6h, and used as wood meal samples. Parts of the wood meals were milled for 120h according to Björkman's method⁴ to prepare milled wood lignins (MWLs). Softwood and hardwood kraft lignins were obtained from Tokai Pulp and Paper. These kraft lignins were dissolved in dioxane/water (9:1, v/v) separately, and the solutions were dropped into diethyl ether. Then the precipitates were filtered to remove the soluble low molecular weight fraction, dried, and used as kraft lignin samples. α -Cellulose was prepared from fully bleached softwood kraft pulp (Kasugai Mill, Oji Paper) as follows. First, acetone extraction was carried out for 1 h at 60°C to eliminate extractives, followed by sulfuric acid treatment (pH 1.3, pulp content 5%) for 3 h at 90°C to eliminate uronic acids.⁵ The resulting pulp was treated with 17.5% aqueous sodium hydroxide according to TAPPI standard T 203.⁶

General scheme for determination of methoxyl groups

The procedure of the determination of lignin methoxyl content is basically the same as Baker's method.⁷ The sample (wood meals and lignin samples 10mg, carbohydrates 500mg) was mixed with 57% hydriodic acid in a vial with a pressure-resistant seal. In standard conditions, 10ml of 57% hydriodic acid was used, reaction time was 20min, and reaction temperature was 130°C. Immediately after the treatment, the vial was cooled in ice-water and 1ml of carbon tetrachloride containing ethyl iodide as an internal standard was added with a syringe through the sealed cap. Then the reaction product (methyl iodide) and the internal standard were extracted with 10ml of carbon tetrachloride, dried over anhydrous sodium sulfate, and subjected to GC analysis.

Deuteriodic acid treatment

In deuteriodic acid treatment, because 57% of deuteriodic acid was not available, the reaction medium was prepared on-site by dissolving 0.5 g of sodium iodide in 1 ml of 7.6 mol/l deuteriochloric acid (D_2O solution). The concentration of the iodide in the prepared reaction medium was still lower than 57% aqueous hydriodic acid. Thus, the reaction time was prolonged to 1 h instead of 20 min in order to compensate for the lower iodide concentration. The reaction products were extracted with carbon tetrachloride and subjected to gas chromatography-mass spectrometry (GC-MS) analysis.

Gas chromatography

In GC analysis, a Shimadzu GC-14B equipped with a flame ionization detector was used. The capillary column used in this analysis was a Varian CP-SIL 13CB for halocarbons (25 m \times 0.32 mm i.d., thickness: 1.2 μ m). Column linear velocity was 1.1 ml helium/min. Column temperature was held at 40 $^{\circ}C$ for 5 min, and then raised at 10 $^{\circ}C$ /min to 180 $^{\circ}C$. Injection port temperature and detector port temperature were 200 $^{\circ}C$ and 230 $^{\circ}C$, respectively.

In GC-MS analysis, a Shimadzu QP-5000 mass spectrometer equipped with a Shimadzu GC-17A was used. Chemical ionization (CI) was applied to detect parent ion peaks. Other analytical conditions were the same as those of the GC analysis.

Results and discussion

Wood meals (Japanese cedar as softwood, Japanese birch as hardwood), their MWLs, kraft lignins, and carbohydrate samples were treated with hydriodic acid under the standard conditions (57% hydriodic acid, 130 $^{\circ}C$, 20 min) and the resulting methyl iodide was determined with GC (Table 1). The carbohydrates generated methyl iodide, even though the yields were very low compared with those from MWLs and wood samples. The origin of methyl iodide detected here did not seem to be methoxyl groups in the carbohydrates, because the formation of methyl iodide from α -cellulose increased when the reaction time was increased to 2 h (Table 1). On the other hand, the level of methyl iodide from wood and lignin samples did not increase with increased reaction time after 20 min.

To confirm the origin of the unexpected methyl iodide, deuteriodic acid treatment was conducted. If methyl iodide is produced unexpectedly from methoxyl-free compounds, it should contain deuterium, because all carbon atoms except methyl carbons carry at the most only two hydrogens. If this is the case, methyl iodide originating from methoxyl groups could be distinguished from that produced from methoxyl-free compounds, when the reaction is carried out with deuteriodic acid in heavy water. Namely, methyl iodide produced from methoxyl-free compounds

Table 1. Recoveries of methyl iodide from carbohydrates and lignin samples treated with hydriodic acid

Samples	Methyl iodide (μ mol/g)	
	20 min	120 min
Glucose	7.8	nd
Galactose	8.6	nd
Arabinose	8.6	nd
Xylose	9.5	nd
Mannose	6.0	nd
α -Cellulose	5.5	10.8
Japanese cedar		
Wood meal	1.4×10^3	1.3×10^3
MWL	3.6×10^3	3.3×10^3
Japanese birch		
Wood meal	1.8×10^3	1.7×10^3
MWL	4.9×10^3	4.3×10^3
Softwood kraft lignin	3.1×10^3	3.0×10^3
Hardwood kraft lignin	4.6×10^3	4.4×10^3

MWL, milled wood meal; nd, not determined

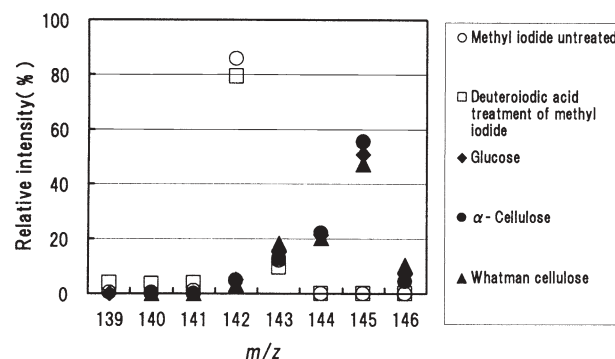


Fig. 1. m/z Distribution of methyl iodide produced by hydriodic acid treatment of methyl iodide and carbohydrates

will contain deuterium and, thus, the m/z of its parent ion peak will be bigger than that of ordinary methyl iodide, m/z 142. First, it was confirmed that the m/z of the parent ion peak of methyl iodide did not change from the m/z 142 after 1 h of deuteriodic acid treatment (Fig. 1). This result indicated that deuterium-proton exchange in methyl iodide had not occurred during the treatments. Compounds such as lignin samples and lignin model compounds, which carry methoxyl groups, also produced methyl iodide with m/z 142 as a predominant peak (Figs. 2, 3). Thus, it was confirmed that methyl iodide originating from methoxyl groups should have a parent ion peak at m/z 142. However, when methoxyl-free compounds were subjected to the reaction, the methyl iodides produced showed m/z distributions that were different from normal methyl iodide (Fig. 1). The m/z values of these parent ion peaks were higher than 142. This result proved that methyl iodide could be produced from nonmethyl carbons. From this fact, the methyl iodide formed from carbohydrates (Table 1) did not seem to be derived from methoxyl-containing contaminants but from methoxyl-free compounds, i.e., the carbohydrates themselves. The m/z value of the most intensive peak observed was 145, which indicated that methyl iodide was produced

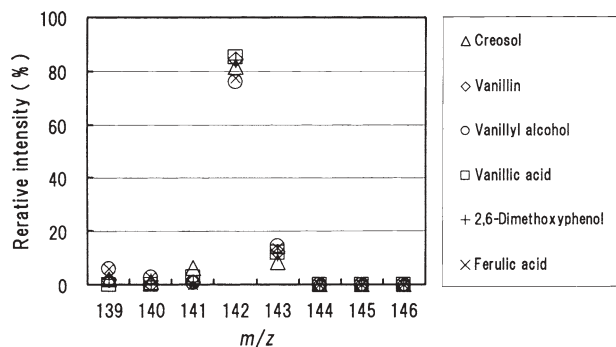


Fig. 2. m/z Distribution of methyl iodide produced by hydriodic acid treatment of selected samples of lignin model compounds

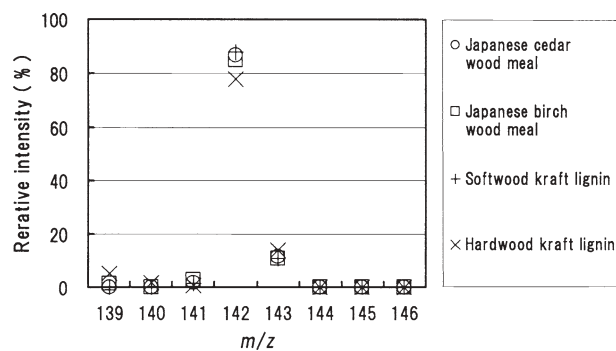


Fig. 3. m/z Distribution of methyl iodide produced by hydriodic acid treatment of wood meals and lignin samples

as CD_3I . Although the formation mechanism of CD_3I is unknown, it is obvious that the CD_3I formation requires not only the incorporation of a deuteron from the solvent but also some deuteron-proton exchange steps.

Table 1 shows the formation of methyl iodide from carbohydrates was about 5–10 $\mu\text{mol/g}$, while that from MWLs were 3.6 and 4.9 mmol/g . Although the amounts formed from carbohydrates were very low, an erroneous result will be given when samples with low lignin content are subjected to methoxyl group determination. When a softwood pulp and hardwood pulp of kappa number 7 are subjected to methoxyl determination, the estimated error range due to this formation of methyl iodide was about 20% and 16%, respectively.

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