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NOTE

Seiichi Yasuda · Kazushige Ima · Yasuyuki Matsushita

Manufacture of wood-cement boards VII: cement-hardening inhibitory compounds of hannoki (Japanese alder, *Alnus japonica* Steud.)

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Abstract To identify the cement-hardening inhibitory components of hannoki (Japanese alder, *Alnus japonica* Steud.), methanol extractives were fractionated by successive organic solvent extraction and column chromatography. Chromatographic analysis and inhibitory indices of the solvent-soluble fractions suggested that glucose and sucrose seem to be the main cement-hardening inhibitory components of Japanese alder. As these compounds are metabolized in vivo even after cutting, the particles after withering are desirable as raw material for wood-cement board.

Key words Wood-cement board · *Alnus japonica* · Cement-hardening inhibitory compound · Sucrose

Introduction

The nature and quantity of wood components affect cement hydration reactions and strength of composite boards. The typical cement-hardening inhibitory components known up to now are divided into two groups. One is comprised of carbohydrates of sucrose[1] in beech and arabinogalactan[2] in larch and the other of phenolic compounds with a catechol unit of plicatic acid[3] in western red cedar, teracacidin[4] in *Acacia mangium*, and sequirin C[5] in sugi (*Cryptomeria japonica* D. Don).

Hannoki (Japanese alder, *Alnus japonica* Steud.)[6] is native to Japan, northeast China, and Korea and is used for furniture, particleboard, interior wood and pulp in Japan. During the manufacture of wood-cement boards, refuse and waste woods are utilized as raw materials in addition to logs. The Japanese alder wood[7] is an unsuitable material and is known to be incompatible with cement. The present paper deals with the identification of that wood's cement-hardening inhibitory compounds.

S. Yasuda (✉) · K. Ima · Y. Matsushita
Division of Biological Material Sciences, Department of Biosphere Resources Science, Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan
Tel. +81-52-789-4159; Fax +81-52-789-4163
e-mail: syasuda@agr.nagoya-u.ac.jp

Material and methods

Material

A freshly felled 30-year-old hannoki (Japanese alder, *Alnus japonica* Steud.) tree was used.

Extraction and fractionation

About 3 kg of the wood meal was extracted three times with methanol at room temperature. The combined methanol solution was then evaporated under reduced pressure to give 91 g (2.8% on wood) of methanol extractives, which were successively extracted with *n*-hexane, benzene, ethyl acetate (AcOEt), methanol (MeOH), and 75% methanol (methanol/water 75:25 v/v) to give their soluble fractions. The methanol-soluble fraction was further separated by silica-gel column chromatography with solvents of ethyl acetate, ethyl acetate/ethanol (4:1 v/v), ethyl acetate/ethanol (1:1), ethanol (EtOH), and methanol, successively.

Thin-layer chromatography

Thin-layer chromatography (TLC) analysis of carbohydrates was performed on silica-gel plates with mixed solvents of benzene/ethyl acetate/methanol (1:1:1 v/v), ethyl acetate/pyridine/water/acetic acid/propionic acid (10:10:2:1), and 1-butanol/acetic acid/diethyl ether/water (9:6:3:1) as eluents. Spots were made visible by spraying with phenol/concentrated sulfuric acid/ethanol (3 g:5 ml:95 ml) and subsequent heating.

Hydration reaction

The heat of hydration[5] was measured as follows: 15 g (oven-dried basis) of hannoki wood meals or hot water-extracted

Table 1. Inhibitory index and compatibility factor of hannoki wood meals[a]

Accelerator	Time (h)[b]	Inhibitory index	Compatibility factor[c]
$CaCl_2$	>50	∞	50
$MgCl_2$	12	8	83
$AlCl_3$	>50	∞	64

[a] Hot water-extracted hinoki (*Chamaecyparis obtsusa* Endl.) was used as a control
[b] Time to reach maximum temperature (hinoki: 5.5 h)
[c] Area under hydration heating rate curve for 24 h

hinoki (*Chamaecyparis obtsusa* Endl.) wood meals (40–120 mesh) impregnated with the extractives, 60 g of portland cement, 25 g of pearlite, and 100 g of water with 1.2 g of a cement-hardening accelerator (2% weight on cement) were kneaded for 3 min. The temperature rise of the mixtures in a polyethylene cup placed in a Dewar flask were plotted against time.

Inhibitory index and compatibility factor

The inhibitory index[8] and compatibility factor[9] were calculated from the hydration temperature curve for wood-cement mixtures. The inhibitory index of hot water-extracted hinoki wood meals (control) was 1.5.

Spectrometry

The infrared (IR) spectrum was recorded on a Hitachi 260–10 infrared spectrophotometer.

Results and discussion

Cement-hardening inhibition of wood meal

Based on the inhibitory index and compatibility factor in Table 1, the wood meals were confirmed to contain cement-hardening inhibitory components. Furthermore, the addition of calcium chloride and aluminum chloride as accelerators did not have any effect on the inhibitory components, but they were considerably depressed by magnesium chloride, suggesting that the inhibitory components may be carbohydrates or aliphatic compounds such as inositol with several hydroxyl groups. This type of phenomenon has been encountered in the hydration reaction of sugi heartwood[5] and beech (*Fagus crenata* Blume)[1], in which the inhibitory components were sucrose and pinitol, and sucrose, respectively. Almost the same conditions were observed in the hydration reactions of this series.

Extraction of wood meal with methanol and subsequent fractionation of the methanol extractives

To separate the inhibitory components, the wood meals were extracted with methanol. The methanol extractives

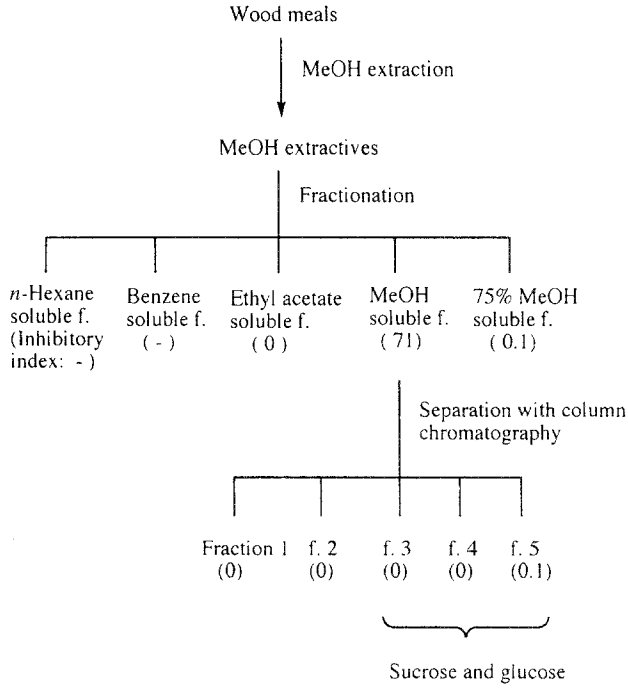

Fig. 1. Separation of inhibitory components

Table 2. Yield, inhibitory index, and compatibility factor of the organic solvent-soluble fractions

Solvent	Yield (% on wood)	Time (h)	Inhibitory index	Compatibility factor
n-Hexane	0.30×10^{-2}	–	–	–
Benzene	0.20×10^{-1}	–	–	–
AcOEt	0.25	5.0	0	100
MeOH	2.00	20.5	71	72
75% MeOH	0.40	5.6	0.1	100

were then successively fractionated in the usual way with *n*-hexane, benzene, ethyl acetate, methanol, and 75% methanol to obtain their soluble fractions, as shown in Fig. 1. As the polarity of these solvents differs greatly, the components dissolved in the solvents also differ to a great extent. The inhibitory index of the soluble fractions could be calculated from the hydration temperature curves of the hot water-extracted hinoki (*Chamaecyparis obtsusa* Endl.) wood meal, which was impregnated with the soluble fractions. The yield, inhibitory index, and compatibility factor of the fractions are summarized in Table 2. Because the inhibitory effects of compounds could be largely ascribed to the amount of inhibitory compounds in the wood, low-yield *n*-hexane- and benzene-soluble fractions were excluded from the hydration reaction tests. As can be seen from Table 2, the methanol-soluble fraction contains large amounts of inhibitory components. Dissolution into the polar solvent of methanol indicates the high polarity of the inhibitory components.

To separate the inhibitory components, the methanol-soluble fraction was further fractionated by silica gel

Table 3. Yield, inhibitory index, and compatibility factor of fractions obtained by column chromatography of the methanol-soluble fraction

Fraction	Solvent	Yield (% on wood)	Inhibitory index	Compatibility factor
1	AcOEt	0.28	0	103
2	AcOEt-EtOH (4:1)	0.53	0	102
3	AcOEt-EtOH (1:1)	0.26	0	94
4	EtOH	0.25	0	100
5	MeOH	0.53	0.1	86

column chromatography to yield five fractions (Fig. 1), as shown in Table 3. Even compounds with a large inhibitory index exert only a small effect when the content in wood[3] is less than 1%. Depending on the content of inhibitory compounds, all five low-yield fractions had a small inhibitory index and large compatibility factor. The above findings can be explained by dispersion of the inhibitory components to the five fractions, as their combined fraction is equal to the methanol-soluble fraction, which yielded a considerable inhibitory effect.

The IR spectra of fractions 3–5 were measured and found to be similar to that of commercial crude xylan. Because the five fractions passed through the silica-gel column eluted with methanol as a final eluent, carbohydrates with a molecular weight higher than those of oligosaccharides were removed. Therefore, the fractions are assumed to be composed of monosaccharides or lower oligosaccharides as major components. The sum of these fractions amounts to 1% content of the wood, suggesting that the major components of fractions 3–5 are cement-inhibitory components of the wood.

Identification of components

The TLC analysis of fractions 3–5 with suitable solvents for carbohydrates confirmed the presence of glucose and sucrose judging from the R_f value and color tones by visualization with a phenol-sulfuric acid method.

Countermeasures

It is known that glucose and sucrose are widely distributed in plants[10] and sapwood[11] and that they disappear soon after the withering process[12] of woods.

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