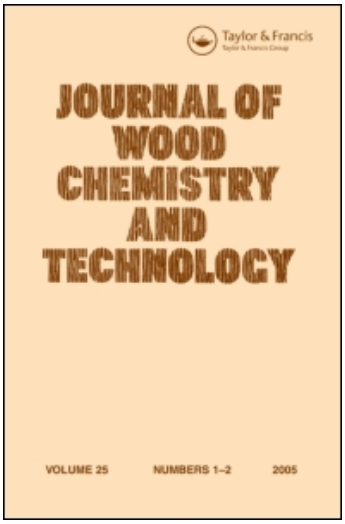

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Manufacture of Wood-Cement Boards. III. Cement-Hardening Inhibitory Components of Western Red Cedar Heartwood

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MANUFACTURE OF WOOD-CEMENT BOARDS III
CEMENT-HARDENING INHIBITORY COMPONENTS OF WESTERN RED CEDAR HEARTWOOD

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ABSTRACT

A systematic investigation of cement-hardening inhibitory components from the heartwood of western red cedar (Thuja plicata D. Don) led to the isolation of three lignans. Their inhibitory indices confirmed that plicatic acid has a strong inhibitory effect, and two phenolic lactones, plicatin and dihydroxythujaplicatin, a weak effect.

INTRODUCTION

Earlier research[1] on cement-hardening inhibition by the extractives of western red cedar heartwood has showed that main inhibitory substances were contained in the ethyl acetate-soluble fraction of the methanol extractives. This solubility suggests that the substances are different from carbohydrates such as arabinogalactan[2), 3)], only one wood component known as an

inhibitor in larch wood. In general, hardening inhibitors are water-soluble. Carbohydrates and some phenolic substances such as a tannin[2] are known to be inhibitors.

Western red cedar contains many hot-water soluble phenolic compounds[4], and has a pronounced tendency to change color under light. It has recently been demonstrated by Watanabe et al.[5] that several lignans containing the 3,4-dihydroxy-5-methoxyphenyl moiety are largely responsible for photo-induced discoloration of the wood.

The present paper describes the isolation and structure of cement-hardening inhibitory components of western red cedar heartwood.

EXPERIMENTAL

Extraction

One kg of wood meal from western red cedar (Thuja plicata D. Don) heartwood was extracted three times for 3 days each time with methanol at room temperature. After concentration under reduced pressure, the combined methanol extract was extracted with ethyl acetate (2 x 600 ml) to give 112 g (11.25 % on wood meal) of the ethyl acetate-soluble fraction.

Fractionation of the ethyl acetate-soluble fraction

The fraction (about 14 g) was progressively eluted from silica gel with 500 ml batches of mixtures of n-hexane and acetone (9:1, 7:3, 5:5 and 3:7 v/v), and then with acetone and methanol. The results are summarized in Table 1.

Isolation of plicatic acid, dihydroxythujaplicatin and plicatin

The A-70 fraction (3.122 g)(Table 1), in 25 ml of ethyl acetate was extracted with 5 % sodium bicarbonate. The bicarbonate solution after back extraction with ethyl acetate was carefully acidified with dilute hydrochloric acid (1N), saturated with sodium chloride and then extracted with ethyl acetate to

Table 1. Yields and inhibitory indices of the elutes separated by the column chromatography of the ethyl acetate soluble fraction

Fraction	Yield (g)	(% on wood)	Inhibitory index
A-10	0.21	0.16	0.5
A-30	1.87	1.45	0.7
A-50	2.83	2.20	9.0
A-70	6.82	5.31	>150
A-100	1.83	1.42	4.3
Me	0.90	0.70	1.9
Total	14.46	11.24	

Legend; A-10: The fraction eluted with n-hexane-acetone (90:10 v/v)
Me: The fraction eluted with methanol

give 1.782 g (3.37 % on wood meals) of an acidic compound (I), which showed no contamination on a thin layer chromatography plate of polyamide (solvent; acetone-methanol, 1:1 v/v) and was identified as plicatic acid (I) by comparing its infrared spectrum with that of an authentic sample.

The ethyl acetate layer after extraction with sodium bicarbonate was washed with water and evaporated to afford 1.133 g (1.93 %) of the neutral fraction. This fraction (0.741 g) was chromatographed on silica gel using benzene-ethyl acetate-ethanol (17:2:1 v/v/v) as eluent to isolate 0.318 g (0.83 % on wood meal) of dihydroxythujaplicatin (II) and 0.182 g (0.48 %) of plicatin (III). II; IR ν_{max}: 1750, 1600; ^{1}H NMR δ: 2.53 (1H, d, J=14 Hz, H-α), 2.75 (1H, d, J=14 Hz, H-α), 3.05 (2H, s, H-α'), 3.80 (3H, s, OCH_3), 3.80 (1H, d, J=10 Hz, H-γ), 3.82 (3H, s, OCH_3), 4.34 (1H, d, J=10 Hz, H-γ), 6.50-6.82 (5H, m, arom.); ^{13}C NMR δ: 37.3 (C-α or -α'), 37.9 (C-α' or -α), 56.1 (OCH_3), 56.4

($O\underline{C}H_3$), 75.4 (C-β or -β'), 78.1 (C-β' or -β), 79.9 (C-γ), 107.7, 112.9, 114.7, 115.4, 123.3, 126.7, 128.0, 133.3, 145.2, 145.7, 147.8, 148.2, 178.6(C-γ'). III; IR ν_{max}: 1775, 1610; ^{1}H NMR δ : 2.86 (1H, d, J= 16 Hz,H-α), 3.40 (1H, d, J=14 Hz, H-α), 3.82 (6H, s, $O\underline{C}H_3$), 4.24 (1H, d, J=8 Hz, H-γ), 4.33 (1H, s, H-α'), 4.55 (1H, d, J=8 Hz, H-γ), 6.20-6.90 (4H, m, arom.); ^{13}C NMR δ: 33.6 (C-α), 46.5 (C-α'), 56.1($O\underline{C}H_3$), 74.4 (C-β or -β'), 76.4 (C-β' or -β), 79.1 (C-γ), 113.0, 115.5, 117.4, 123.5, 125.3, 130.2, 131.3, 145.0, 145.8, 146.8, 148.1, 175.8 (C-γ').

Determination of the heat of hydration and calculation of the inhibitory index

Fifteen g of Japanese hinoki (Chamaecyparis obtusa Endl.) meal (30-80 mesh) were added to the solution of the wood extractives in 10 ml of methanol and then mixed thoroughly. The wood samples for the determination of the heat of hydration were prepared after air drying. The heat of hydration generated from a wood-cement-water system without any hardening accelerators, in accordance with the details reported in the primary paper[1], was measured, and Moslemi's inhibitory index[6] was calculated from the results.

Spectrometry

The ^{1}H and ^{13}C NMR spectra were determined in hexadeutero-acetone-deuterium oxide (9:1 v/v) as a solvent with TMS as an internal reference on a JEOL JNM-MH-100 NMR spectrometer. The IR spectrum (KBr disk) was recorded on a Hitachi 260-10 infrared spectrophotometer.

RESULTS AND DISCUSSION

Our previous results[1] from successive extraction of the methanol extractives of western redcedar heartwood with n-hexane, ethyl ether, ethyl acetate, n-butanol, methanol and water showed that main cement-hardening inhibitory components are contained in the ethyl acetate-soluble fraction. Therfore, in order to

isolate the inhibitory components, western red cedar heartwood meal was subjected to extraction procedure on a larger scale. In this experiment, the methanol extractives were directly extracted with ethyl acetate, without any preextraction with n-hexane and ethyl ether, to give the ethyl acetate-soluble fraction in a 11.25 % yield. This value is almost equal to the sum total of the previous combined yields of the n-hexane-, diethyl ether-, ethyl acetate- and n-butanol-soluble fractions. This may be explained in two ways: 1) Remains of polar methanol, which was used for the first extraction, in methanol extractives; and 2) Action of the solution, composed of ethyl acetate and the ethyl acetate-soluble extractives, as an extraction solvent, because of a high ratio of the extractives to ethyl acetate. Since the n-butanol-soluble fraction[1)] also has high inhibitory index, the excess extraction did not cause any trouble.

Relationship between hardening inhibition index and the amount of the ethyl acetate-soluble fraction is shown in Fig. 1. Here, the fraction was impregnated into Japanese hinoki meal, which has no inhibitory effect on cement hydration. Then, the inhibitory index of the fraction was calculated from the hydration heat data for the treated wood meal-cement-water system. From Fig. 1 it can be seen that the inhibitory index as a function of the concentration of the additives follows as S-shaped curve levelling off at 5% concentration. Therefore, this figure is significantly important to evaluate inhibitory effect of fractionated extractives described below, and suggests that inhibitory effect depends on the quantity of inhibitors.

As the ethyl acetate-soluble fraction contained a large number of compounds, the components were separated by column chromatography on silica gel. The yields and inhibitory indices of the fractionated elutes are summarized in Table 1. A-10 and A-30 are the fractions eluted with solvents containing 10 and 30 % of acetone, respectively, and should therefore be composed of

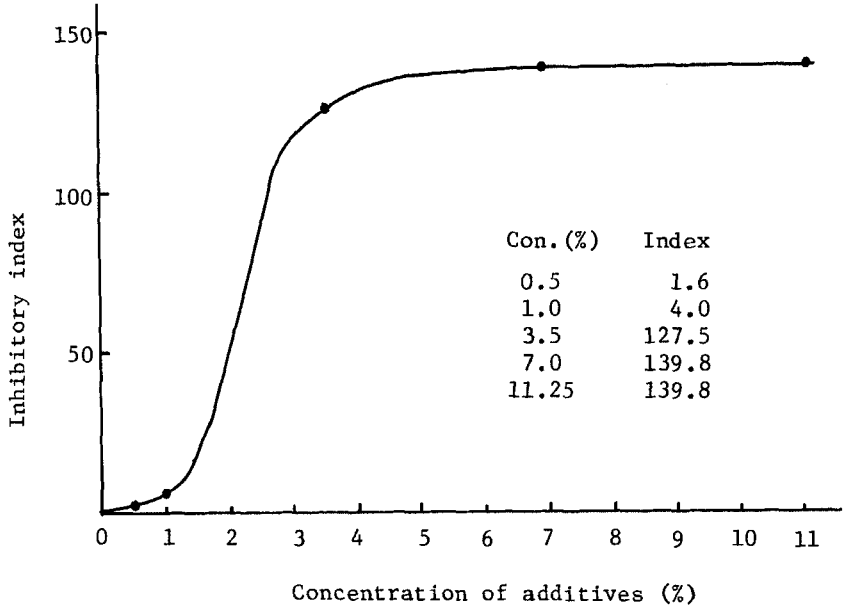


Fig. 1. Relationship between inhibitory index and the amount of the ethyl acetate soluble fraction

non-polar substances. The fact that these fractions have lower indices than than 1.0 of Japanese hinoki used as an absorber indicates an accelerating effect of their components on cement -hardening. This may be in accord with an earlier finding[7] that pretreatment of larch wood flakes with hydrophobic materials accelerates cement-hardening and improves bending strength of the cement board, by sealing inhibitory components in the tissue. The high inhibitory index and the high yield of the A-70 fraction indicate that the main inhibitory components of western redcedar are polar compounds.

In the IR spectrum of the A-70 fraction, the strong absorptions at 1715 and 1770 cm^{-1} indicated the presence of a

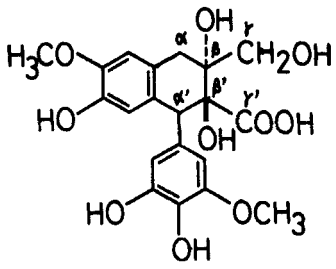
Table 2. Yields and inhibitory indices of the acidic and neutral fractions from A-70

Fraction	Yield (% on wood)	Inhibitory index*
Acidic	3.37	57.9
Neutral	1.93	29.7

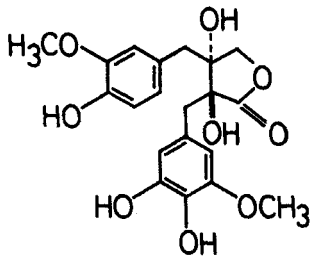
* Inhibitory index from the system of 15 g of Japanese hinoki, 300 mg(2% on wood) of extractives and 200 g of cement

carboxyl group and lactone ring, respectively. Therefore, in order to separate an acidic compound, the A-70 fraction in ethyl acetate was extracted with 5 % sodium bicarbonate. After careful acidification with dilute hydrochloric acid, the carbonate solution was extracted with ethyl acetate. The separated acidic substance showed no contamination with other phenols in polyamide thin layer chromatography, and was identified as plicatic acid (I)[4), 5), 8)] by comparing its IR spectrum with that of an authentic sample. The yield and high inhibitory index of the acidic substance, as shown in Table 2, revealed that plicatic acid is a major cement-hardening inhibitory component of western redcedar heartwood.

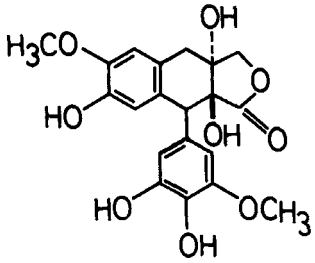
The neutral fraction which remained in the ethyl acetate solution was separated by column chromatography on silica gel to isolate two compounds. The first compound (II) in the IR spectrum showed strong absorption at 1760 cm^{-1} due to a lactone ring. In the ^{13}C NMR spectrum of II, a comparison was made with the corresponding spectrum of plicatic acid (I), in which characteristic signals at 35.7, 49.9, 66.5, 75.1 and 78.7 ppm were definitely assigned to α-, α'-, γ-, β(or β')- and



Plicatic acid (I)



Dihydroxythujaplicatin (II)



Plicatin (III)

Fig. 2. Structures of the isolated compounds

β'(or β)-carbons, respectively. By comparison with the signals of plicatic acid(I), the upfield shift of the α'-carbon signal at 49.9 ppm in I to 37 ppm suggests that compound (II) has no linkage between an aromatic ring and benzylic α'-carbon. Such a suggestion was supported by a singletdue to methylene protons at 3.05 ppm in the ^{1}H NMR spectrum of II. Furthermore, the downfield shift of the γ-carbon signal at 66.5 ppm in I to 79.9 ppm in the ^{13}C NMR spectrum indicates that II has a lactone ring (1750 cm^{-1} in IR spectrum). The presence of a pyrocatechol group in II was confirmed by a positive ammonium molybdate color reaction. These data suggest that compound (II) is dihydroxy thujaplicatin as shown in Fig. 2. Further spectral support for

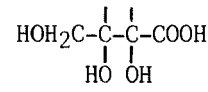
the structure was obtained on the very close similarity of the ^{1}H NMR spectrum of II with that[9] of dihydroxythujaplicatin methyl ether.

The ^{13}C NMR spectrum of compound (III) except for the downfield shift of the α'-carbon signal to 46.5 ppm was very similar to that of II. In plicatic acid, the methine α'-carbon resonated at 49.9 ppm. Hence, the signal at 46.5 ppm must indicate the presence of a carbon-carbon bond between the aromatic ring and benzylic α'-carbon, suggesting that the compound (III) is plicatin[10]. A positive ammonium molybdate reaction and the ^{1}H NMR spectrum of III support the structure. The direction of biochemical pathway[11], that is, dihydroxy-thujaplicatin → plicatin → plicatic acid → (plicatinaphthol), has been shown by investigaton of extractive variation in the radial direction of the wood.

Thus, the neutral fraction is composed of phenols having dihydroxythujaplicatin and plicatin as main components, and has a ow inhibitory index, as shown in Table 2, indicating that these compounds have only minor inhibitory effect.

Both guaiacol with one phenolic hydroxyl group and glycerol with three aliphatic hydroxyl groups, as partial structural models of II and III, were found to have low inhibitory index in a separate experiment[12]. This means that cement-hardening inhibitory nature of the neutral fraction may be ascribable to that of a pyrocatechol group. In fact, catechol[12] itself showed a high inhibitory index (149.5, under experimental conditions in Table 2). The low index of the neutral fraction may be interpreted as due to the low proportion of the pyrocatechol group in the total molecular weight of components, in other words, low concentration of the pyrocatechol group. In general, it is well-known[13), 14), 15] that compounds containing a HO-C=O group retard cement-hardening to a great extent. However the

lactone structure with hydroxyl groups as in II and III seems to show no particular ability to retard the reaction of cement with water.

The strong inhibitory action of plicatic acid may be associated with the active partial structure of  together with the pyrocatechol group in comparison with the structure II and III.

The large difference between the inhibitory indices of plicatic acid and the neutral fraction suggests that lactonization of the partial structure in the former may reduce the inhibitory action of western redcedar heartwood. At any rate, further experimental studies on relationships between the structure of cement-hardening inhibitors and inhibitory action are required.

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