Esterification of wood with unsaturated carboxylic acids. III. Dissolution of wood by the TFAA esterification method

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不飽和カルボン酸による木材のエステル化（第3報）

TFAA エステル化法による木材の可溶化

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Contents

Abstract

It was tried to dissolve wood directly in such organic solvents as acetone and chloroform by the TFAA esterification method. Only β-methylcrotonic acid among several aliphatic acids used gave its wood ester of the DS value (nearly 3) which would also enable the complete dissolution of cellulose carboxylic acid esters and, consequently, could dissolve wood up to approximately 30%, perhaps without degradation of its components under mild conditions. However, drastic esterifications accompanied by considerable degradation of wood components led to solubility of more than 60%. β-Methylcrotonylation of various wood species revealed some interrelation between lignin content and solubility, showing that the lignin component seemed to be an inhibitory factor in dissolving wood by the TFAA method.

要　　　旨

アセトンやクロロホルム などの有機溶剤に溶解させるため，反応条件を変え，TFAA 法で木材のエステル化を行なった。木材のエステル化度と溶解性は有機酸の種類によって異なるが，供試した脂肪酸の中では，β-メチルクロトン酸が最も優れ，この酸は木材をほぼ完全にエステル化すると共に，ほとんど木材構成成分の分解もなく，木材を30%程度まで溶解した。成分の分解を生ずるような激しい条件下では，溶解率はさらに大きくなり，最高で66%に達した。次に，各樹種のリグニン含有率と溶解率の間に，ほぼ逆比例関係が認められたことは，リグニン成分が，この方法での木材溶解を阻害することを示唆した。

1. Introduction

Cellulose, hemicellulose and lignin, that is, three principal components of wood are readily and completely soluble in some organic solvents, when they are individually esterified with carboxylic acids.[1)2)3)] It seems nevertheless difficult to dissolve wood itself by esterification.[4)] A few studies have been reported, in which wood meal has been acetylated with acetic anhydride and a catalyst such as sulfuric acid, pyridine or zinc chloride, and an acetylated wood has then been dissolved in acetone or chloroform. In addition to the acetylation, both methylation[5)] and nitration[6)] have also been applied to dissolution of wood.

The previous paper[7)] has described that birch wood specimens, β-methylcrotonylated by the trifluoroacetic anhydride (TFAA) method, had been decomposed to a great extent and had been soluble in acetone and chloroform partially. The present work deals with several reaction conditions for dissolution of wood by the TFAA esterification method.

2. Experimental

2.1. Materials

Wood meal (42–60 mesh), given in Table 5, was extracted with ethanol-benzene for 24 hr. All chemicals were of reagent grade and were used without further purification.

2.2. Esterification, dissolution and analyses

Oven-dried wood meal was esterified as described previously.[8)] Insoluble ester was then collected on a 1G2 glass filter, and washed with benzene and methanol, successively. Combined filtrate and washings were evaporated to dryness to recover ester dissolved in the reaction medium. All ester products were throughly washed with water in order to remove trifluoroacetyl groups.

Wood esters obtained were then extracted with acetone and chloroform, successively. Insoluble ester was dried and weighed (the insoluble fraction). Acetone- and chloroform-solution were evaporated to dryness and weighed (the soluble fractions).

Total weight increase percent was calculated for the ester (sum of three fractions), on the basis of oven-dried original wood. The term "solubility" expresses percentage in weight of all soluble fractions to total ester, that is, proportion of dissolved wood. Lignin content was determined for saponified wood by the Klason's method.[9)]

3. Results and discussion

3.1. Dissolution of wood with various aliphatic acids

It is generally necessary to esterify cellulose up to a desired degree of substitution (DS) in order to dissolve it in organic solvents such as acetone and chloroform. Hence, a primary factor in dissolving wood in such organic solvents is thought to be reactivity of a

carboxylic acid used for esterification. In Table 1, only β-methylcrotonic acid (β–MC) caused wood meal to be considerably soluble in acetone and chloroform, while the other

Table 1. Reactivity and solubility of BUNA wood meal esterified with various carboxylic acids

Carboxylic acid	Weight increase (%)	Solubility (%)	Carboxylic acid	Weight increase (%)	Solubility (%)
Acetic	35.38	3.27	Caproic	64.55	3.04
			Isocaproic	62.97	1.79
Propionic	42.03	3.87	β-Methylvaleric	73.48	3.14
Acrylic[a]	21.21	—	α-Methylvaleric	50.05	3.21
Propiolic	1.43	0.36	α-Ethylbutylic	51.09	3.25
			β, β-Dimethylbutylic	87.75	4.31
Butylic	52.32	2.87	α, β-Dimethylbutylic	—	—
Isobutylic	39.74	3.03	α, α-Dimethylbutylic	23.70	1.03
trans-Crotonic	51.85	4.56	Sorbic	112.06	0.40
Methacrylic[a]	14.18	0.74			
			Enanthic	70.19	2.97
Valeric	60.84	2.98			
Isovaleric	65.79	3.83	Caprylic	72.03	2.35
α-Methylbutylic	46.40	1.91	Triethylacetic	21.92	1.07
α, α-Dimethylpropionic	28.42	4.91			
β-Methylcrotonic	99.78	17.03	Trifluoroacetic	53.38[b]	1.81

esterified with wood 0.5 g, TFAA 2.1 ml, acid 15 mmole and benzene 30 ml, at 30°C for 24 hr
a) sulfuric acid 0.01 ml added
b) without water-soaking

aliphatic acids used could not dissolve wood. Assuming that BUNA wood of 25% lignin content (L) is esterified up to a DS of 2 without degradation of its components, weight increase percent (WI) becomes 38.9, 51.9, 64.8, 77.8, 90.7, 103.7, and 116.7% for saturated C_2- to C_8-aliphatic acids, respectively, calculated from the equation[7]; $WI = \frac{DS}{162}(100-L)(M_a-18)$ where M_a is molecular weight of a carboxylic acid. These values show that reactivity of β-methylcrotonic acid (a DS of more than 2) was also superior to that of the others (a DS of less than 2), except sorbic acid whose DS was above 2.5. It may be attributable to unsuitable extraction solvents that sorbic acid could not dissolve wood, in spite of its outstanding reactivity for esterification of wood. On esterification with the acid, cellulose (Whatman cellulose powder CF 11) was once dissolved in the reaction mixture. The resulting ester, weight increase of which was 184.0% and corresponded to a DS of about 3, became nevertheless insoluble in both acetone and chloroform, in the couse of the further precipitation, washing and drying. The fact suggests that every carboxylic acid, which will give a satisfactorily high DS value under the optimum condition, can dissolve wood to some extent, combined with the following extraction with the most adequate solvent.

In general, a β-methyl isomer is more reactive than the corresponding α-methyl isomer, as shown in Table 1. Thus pK_a seems also to be a dominant factor in the TFAA method.[8] A small amount of water as a contaminant, the inhibitory effect of which was diminished by addition of sufficient amounts of TFAA, reduced reactivities of acids and gave only decrease in solubility. Properties of wood treated with TFAA alone were not altered,

so long as those were determined by X-ray diffractometry and IR spectroscopy.

3.2. Dissolution of BUNA wood by β-methylcrotonylation

β-Methylcrotonylation of BUNA wood resulted readily in the maximum weight increase of 95–100%, as shown in Fig. 1. The value remained constant, regardless of reaction conditions studied such as temperature (Fig. 2), ratio of reactants (Fig. 3), additional catalysts (Table 3) and size or shape of wood sample. Furthermore, Table 4 shows that even repeated esterification of insoluble fractions could bring about no additional weight increase more than the maximum value for a control run (no repetition).

Foregoing discussions have neglected esterification of the lignin component in the calculation of DS values from weight increases. Lignin is, however, known to react readily with acids.[10] If only lignin, whose apparent molecular weight is 850, reacts with β-methylcrotonic acid up to the maximum DS of 5, where reactive hydroxyl groups of lignin are throughly esterified, BUNA wood of 25% lignin content will increase in its weight by about 10%. Weight increase of 85–90%, reducing the 10% value from the maximum (95–100%) cited above, is consequently due to β-methylcrotonylated holocellulose of a DS of 2.24–2.37. In spite of a little lower DS relative to cellulose carboxylic acid tri-ester, it is thought that all of available hydroxyl groups of wood was practically esterified in this case, considering that apparent acetyl content of the original BUNA wood was roughly 8%. It may also be deduced that wood components were degraded to some extent, under the condition
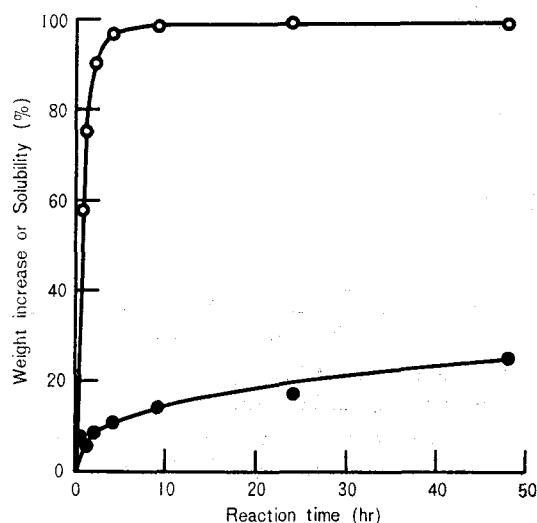

Fig. 1. Rate of β-methylcrotonylation (○) at 30°C and increase in solubility (●) of resulting ester.
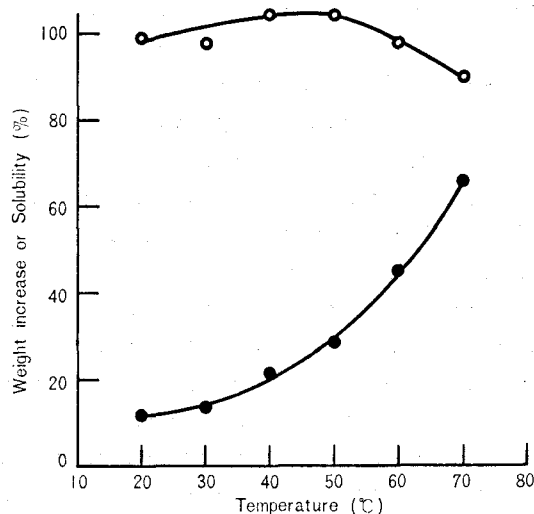BUNA wood 0.5 g, TFAA 2.1 ml, β-MC 1.6 g and benzene 30 ml.

Fig. 2. Dependence of weight increase (○) and solubility (●) on β-methylcrotonylation temperature.
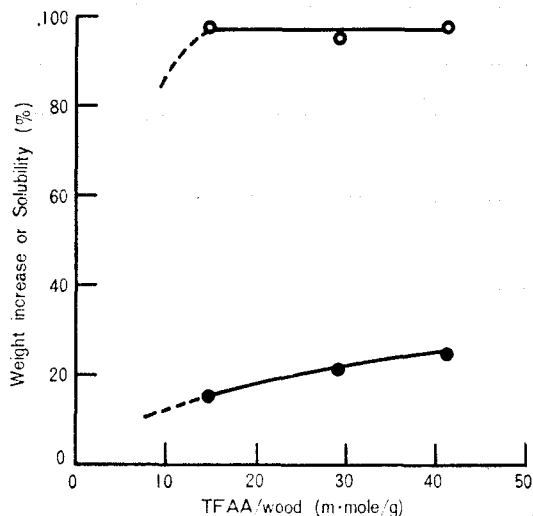BUNA wood 0.5 g, TFAA 2.1 ml, β-MC 1.6 g and benzene 30 ml, for 6 hr.

Fig. 3. Effect of ratio of TFAA (or β-MC) to wood on
reactivity (O) and solubility (●).
BUNA wood 0.5 g, benzene 30 ml, TFAA: β-
MC=1: 1 (mole/mole) at 30°C for 24 hr.

Table 2. Effect of reaction solvent on
reactivity and solubility

Solvent	Weight increase (%)	Solubility (%)
Solvent-less[a]	120.01	39.00
Acetone	12.14	1.34
Dioxane	6.73	1.01
Benzene	100.64	14.14
Chloroform	95.04	11.44

BUNA 0.5 g, β–MC 1.6 g, TFAA 2.1 ml,
and solvent 30 ml, at 30°C for 6 hr
a) BUNA 0.5 g, β–MC 4.0 g, and TFAA
6.6 ml

Table 3. Effect of additional inorganic
acid-catalyst on solubility

Additional inorganic acid	Weight increase (%)	Solubility (%)
None	99.78	17.03
control	6.51	0
Sulfuric acid	101.37	51.97
control	12.83	0.68
Phosphoric acid	95.88	24.04
control	6.28	0.62
Nitric acid	95.70	15.07
control	15.55	1.19

BUNA 0.5 g, TFAA 2.1 ml, β–MC 1.6 g,
benzene 30 ml and inorganic acid 0.044 N,
at 30°C for 24 hr
Control is without β–MC

where weight increase reached more than
100% (Talbles 2 and 3). Remarkable drop
in weight increase, in Fig. 2, is due to severe
degradation of products.

Fig. 1 shows that elongation of reaction
time led to a gradual increase in solubility
up to a definite value. Thus solubility did
not exceed 25%, even by esterifying at 30°C
for 48 hr. Such a limited solubility was
also obtained in the following cases. Solubility
slightly increased with increasing amounts of TFAA or β-methylcrotonic acid, as shown
in Fig. 3. For 1 g of BUNA wood, approximately 15 m moles is the calculated amount
of available hydroxyl groups, in which 1 and 14 m moles are those of lignin and holocel-
lulose components, respectively. Solubility of 25% was therefore obtained by esterifying
with three times excess of TFAA or the acid. Table 2 shows that the value in chloroform,
a good solvent for esters, was similar to that in benzene. A similar less reactivity in acetone
or dioxane has been reported.[11] In Table 3, no additional increment of solubility was
brought about by use of nitric and phosphoric acids which had been used for nitration
of cellulose and wood, perhaps because of their less degradative actions. The repeated
esterification study, in Table 4, shows that the maximum weight increase and some sol-
ubility were given by the first treatment, but dissolution alone occured without further
esterification by the following treatments. Nevertheless, total solubility of the three
times-repeated run differed little from that of the control (once-treated) run (see Table 4).
In a word, a mild reaction condition, where wood components were rarely degraded,

Table 4. Change of solubility by repeated esterification of insoluble fraction

Run		Time (hr)	Relative weight (%)			Solubility (%)
			Insoluble part	Soluble part	Total	
Repetition,[a]	1st	7	166.87	22.58	189.45	11.92
	2nd	7	157.16	9.41	166.57	5.65
	3rd	24	140.71	15.73	156.44	10.05
	total	38	140.71	47.72	189.45	25.19
No repetition[b]		38	161.30	46.99	208.29	22.56

a) BUNA wood 1 g, TFAA 4.2 ml, β-MC 3.2 g, benzene 60 ml, at 30°C
b) wood 1 g, TFAA 12.6 ml, β-MC 9.6 g, benzene 180 ml, at 30°C

seems to be unable to bring about solubility of more than 30%. In this case, a probable inhibitory factor in dissolving wood is thought to be the lignin component, because of the ready and complete dissolution of pure cellulose ester, as described below.

In other cases, much more solubility was obtained. Fig. 2 shows that wood was increasingly dissolved with a rise in reaction temperature, especially in the range of above 50°C, in which remarkable degradation of wood components might set in, as described above. Solubility reached 66%, at 70°C for 6 hr. Even TFAA, which has been reported hardly to break the glucosidic bond,[12] caused some degradation stated above and, consequently, more dissolution of wood, under the solvent-less condition where TFAA itself served as a kind of solvent (Table 2). Solubility of about 50% was given by a little addition of the sulfuric acid catalyst well known to cause acetolysis of cellulose (Table 3). Acceleration effect of sulfuric acid on esterification[7] was indefinite in the case of β-methylcrotonylation. Weight increase of each control run was ascribed to remaining trifluoroacetyl groups, from IR spectra. These fact suggest that dissolution of wood up to over 30% may be achieved only under drastic conditions where its components will be considerably degraded.

3.3. Dissolution of various wood species

Weight increase of softwoods (102–127; 109% on the average) on β-methylcrotonylation was generally larger by approximately 10% than that of hardwoods (84–108; 96%), as shown in Table 5. On the other hand, the formers (lignin content 25–37; 29.7% on the average) contained more lignin by about 6% than the laters (19–29; 23.6%). Thus a larger increment of weight appears to be obtained by wood species of a higher lignin content. Regardless of wood species, practically the same maximum weight increase is, however, expected, calculated by considering both lignin content and apparent acetyl content of 3–7 (4.8, on the average)% for softwoods and 7–10 (8.3)% for hardwoods. The fact may suggest that softwoods (or lignin-rich species) are more reactive than hardwoods (or lignin-poor species).

Table 5 further shows that solubility was in the range of about 9–22% and softwoods, compared with hardwoods, gave rather small solubility, under the mild reaction condition. In other words, increasing lignin content tends to reduce solubility, that is, the lignin component seems to prevent the dissolution of wood. The reason for this inhibitory

Table 5. Reactivity and solubility of various wood species, on β-methylcrotonylating by the TFAA method

Species	Weight increase (%)	Solubility (%)	Lignin content (%)
Inumaki (*Podocarpus macrophyllus* D. Don)	102.37	10.81	37.40
Todomatsu (*Abies sachalinensis* Fr. Schm.)	109.83	14.12	27.58
Beimatsu (*Pseudotsuga taxifolia* Britt.)	108.53	17.84	27.72
Beitsuga (*Tsuga heterophylla* Sarg.)	108.43	12.43	29.45
Karamatsu (*Larix leptolepis* Gord.)	107.33	14.91	25.53
Dahurika-karamatsu (*L. dahurica* Turcz.)	107.68	13.63	27.80
Akamatsu (*Pinus densiflora* S. et Z.)	109.05	15.56	26.29
Chosengoyo (*P. koraiensis* S. et Z.)	126.95	21.88	27.29
Sugi (*Cryptomeria japonica* D. Don)	102.11	13.06	34.20
Hinoki (*Chamaecyparis obtusa* Endl.)	108.93	13.91	31.02
Asunaro (*Thujopsis dolabrata* S. et Z.)	107.44	12.25	32.84
Makanba (*Betula maximowicziana* Regel)	96.40	14.35	22.45
Buna (*Fagus crenata* Blume)	97.78	16.86	24.08
Mizunara (*Quercus crispula* Blume)	107.82	13.15	25.77
Akagashi (*Q. acuta* Thunb.)	94.64	20.00	20.09
Kuri (*Castanea crenata* S. et Z.)	84.12	19.48	23.32
Akinire (*Ulmus parvifolia* Jacq.)	105.43	13.21	28.67
Keyaki (*Zelkova serrata* Makino)	85.76	15.41	27.22
Someiyoshino (*Prunus yedoensis* Matsum.)	93.95	13.37	22.69
Yamazakura (*P. jamasakura* Sieb.)	98.04	17.88	20.62
Sendan (*Malia azedarach* L.)	97.06	13.66	25.65
Kenponashi (*Hovenia dulcis* Thunb.)	90.84	15.96	23.48
Chanchinmodoki (*Chaerospondias axillaris* (Roxb.) Burtt et Hill)	100.25	21.15	19.16
Kapur (*Dryobalanops sp.*)	95.46	9.52	35.51
White lauan (*Parashorea sp.*)	105.66	10.54	25.74
Iroko (*Chlorophora excelsa* Benth. et Hook.)	116.75	11.97	30.04

esterified with wood meal 0.5 g, β-methylcrotonic acid 1.6 g, TFAA 2.1 ml and benzene 30 ml, at 30°C for 24 hr

effect of lignin is not yet fully understood, although distribution of lignin in wood, its chemical or three-dimensional structure, a covalent bond between lignin and carbohydrates such as LCC, etc. are assumed to take part in.[13] In addition to satisfactory esterification of wood, a behaviour of lignin is demonstrated to be another important factor in dissolving wood.

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