

# SYNTHESIS OF URUSHI ANALOGUES. I.

## *N*-(3,4-DIHYDROXYBENZYL) UNSATURATED HIGHER FATTY ACID AMIDES<sup>1)</sup>

Akira TERADA

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### ABSTRACT

*N*-(3,4-Dihydroxybenzyl) oleamide (VIIa) and *N*-(3,4-dihydroxybenzyl) linoleamide (VIIb) were prepared to investigate the possibility to use as urushi-type lacquer. These products can be dried at room temperature and also baked at 150°C when they were blended with Shuai Urushi, a Japanese lacquer paint. The drying rate of the blended samples was fast as that of 100% shuai urushi. The hardness test of their baked films showed that harder film than that of 100% shuai urushi was obtained with higher concentration of the amides, VIIa and VIIb, in the blended sample, but good films were not obtained by the respective amides themselves under such baking conditions. The mechanism of the hardening process was also proposed.

### 1 INTRODUCTION

From the early ages, urushi paint such as Japanese and Chinese lacquers, Indochinese lac, Formosa lac and Tsuti-urushi lac have been used for general painting and making lacquer wares in the eastern and southeastern parts of Asia. It was an excellent and unique coating paint for articles, and its situation was similar to the oil paints and varnishes of the Western countries. The excellent chemical quality of urushi paint can be seen by inspection of the many art objects and artistic lacquer wares of old time made from urushi which still remain at present and by comparing with modern artificial resin paints which are not suitable for this kind of special painting work. The coated films are not only beautiful and elegant but also very hard and resistant to high temperatures and chemicals. Although we have many good paints of synthetic resin now, the qualities of urushi paints are still highly evaluated as air-drying lacquer at room temperature as well as baking varnish for hardware coatings at elevated temperatures. Urushi may therefore be considered as one of universal paints.

Japanese lacquer contains 53~66% urushiol oil, 3~5% nitrogenous matter (nitrogen-containing matter which contains laccase also; its chemistry is still unknown.) and 5.3~7.3% gum (a mixture of water-soluble polysaccharides), and is

a water-in-oil type emulsion.<sup>2)</sup> Systematic chemical studies of Japanese lacquer have been started after the end of the last century under the leadership of some Japanese investigators, and the lacquer components and their chemical behaviors have been elucidated somewhat in detail up to the present day.<sup>2)</sup> The chemistry and chemical structure of urushiol which is the main component of Japanese lacquer, and also synthesis of the urushiol components and related compounds have been investigated pertinaciously by several workers, particularly by Majima and his co-workers in Japan.<sup>3)</sup> According to their results,<sup>3,4)</sup> urushiol is probably a mixture of I, II, III, and IV in detailed in Fig. 1. The composition of the oil is assumed to be approximately the same as III and this is usually referred to by the name of urushiol which has been given by Miyama.<sup>5)</sup>

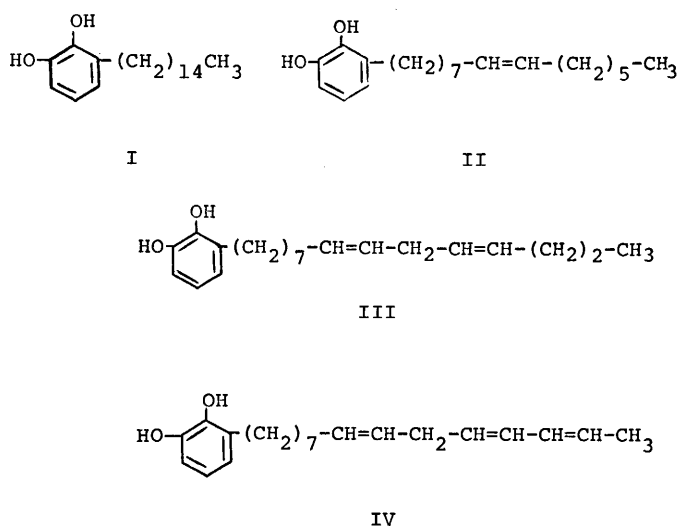


Fig. 1.

Majima and his co-workers also determined the structures of thitsiol (V, from Indochinese lac.) and laccol (VI, Formosa lac for an example).<sup>3)</sup>

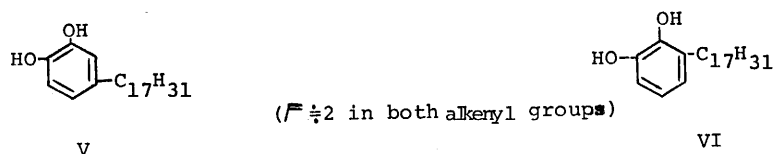


Fig. 2.

With regard to synthesis, all works on the two urushiol components, they are hydrourushiol (I)<sup>6-11)</sup> and urushenol (II),<sup>12)</sup> have been carried out on laboratory scale until to-day. However, it is generally considered that production on a commercial scale will be very difficult even at present though we have many good

techniques in organic synthesis. Consequently, various urushiol analogous compounds were synthesized by many chemists, and several of them were successful industrially to some extent.<sup>13-17,19,20)</sup> The basic idea of these syntheses consists of alkylation of catechol with an alkylating agent having long carbon chain of C<sub>16</sub> or C<sub>18</sub> and unsaturation degree of two or three, for examples, unsaturated fatty oils or unsaturated higher fatty alcohols. Since drying oils and their products were chiefly used for these alkenyl group introduction and the following polymerization took place during the reaction, the urushiol analogues obtained were often very viscous while they usually gave excellent hard, tough and beautiful films upon baking.

In the present paper, the author takes up a synthetic principle reported by Haworth and Lamberton<sup>18)</sup> in order to overcome the above mentioned defect of high viscosity and also as it was expected that the following type of catechol nucleus would accept a laccase oxidative action to form a good coating film. They have reported the preparations of *N*-(3,4-dihydroxybenzyl) sorbic acid amide and *N*-(3,4-dihydroxybenzyl) undeca-10-enic acid amide by condensation of catechol with *N*-monomethylol of corresponding unsaturated acid amides. This condensation is a room-temperature reaction of *N*-methylol fatty acid amide with catechol in the presence of concentrated hydrochloric acid, and appeared to be suitable for our purpose because of its relatively moderate reaction conditions. Thus polymerizations during the side-chain introduction can be avoided. It is well known that oxidative solidification of urushiol in urushi paints is initiated by oxidation of the two hydroxyl groups of the catechol nucleus to form orthoquinone in the presence of laccase in an oxygen atmosphere. The polymerization and net-working by addition reaction of the quinone nuclei and alkenyl side-chains take place continuously and finally give a hard and infusible film. The nitrogenous matter and gum described at the beginning of this text also participate in the polymerization. Miyagawa has reported that urushiol analogous compound having a long alkenyl side-chain more than 15 carbon atoms which he prepared indicated good results in his film test.<sup>15)</sup> From these points of view, *N*-methylololeamide and *N*-methylolinoleamide were chosen here as the side-chain groups because they are readily available for practical purposes.

The present report thus deals with the synthesis of *N*-(3,4-dihydroxybenzyl)oleamide (VIIa) and *N*-(3,4-dihydroxybenzyl)-linoleamide (VIIb), and the subsequent test of films obtained when these two catechol derivatives, VIIa and VIIb, are used as the extending agents for a Japanese lacquer, Shuai urushi.

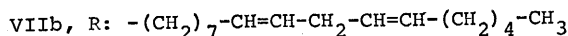
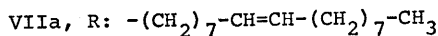
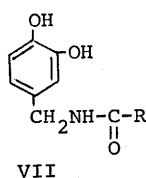
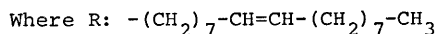
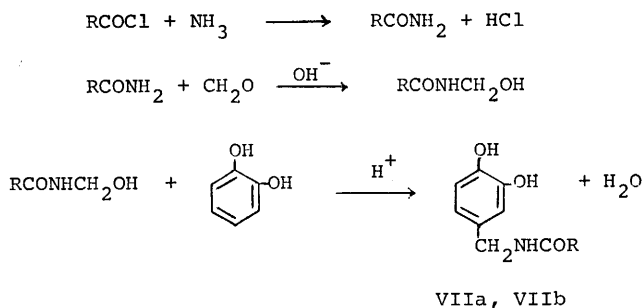


Fig. 3.

## 2 RESULTS AND DISCUSSION

### 2-1 Synthesis

The linoleamide was obtained as a crude product since it was prepared by using an unsaturated acid chloride mixture which consisted mainly of linoleoyl chloride. The *N*-methylol was therefore obtained as an impure semi-crystalline paste, while the oleamide clearly gave its *N*-methylol as white crystals melting at 64.5-65°C. These *N*-methylolamides were allowed to react with catechol in a hydrochloric acid medium to obtain attempted products, VIIa and VIIb, as non-crystalline, dark-red oils. The synthetic reactions are assumed to proceed as follows:



and

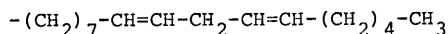


Fig. 4.

The infrared spectra of these intermediates and final products of this synthesis, and also those of urushiol and thitsiol are shown in Figs. 5 through 7 for their structural identifications. These spectroscopic studies strongly suggest both the final products have principally the 4-substituted-catechol structures, VIIa and VIIb. However, both spectra of them in Fig. 6 also show absorption peaks at  $740\text{ cm}^{-1}$  which are assignable to 1, 2, 3-tri-substituted benzene, similar to those of urushiol and thitsiol in Fig. 7. These facts suggest the presence of another structural isomer, the 3-substituted type, in each product. Vacuum distillations

for further purification of the *N*-methylolamides and of VIIa and VIIb were not successful since they immediately resinified on heating.

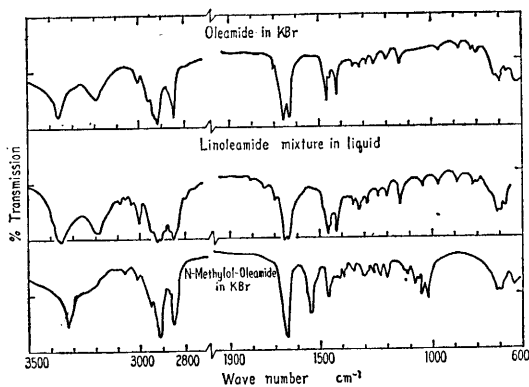


Fig. 5.

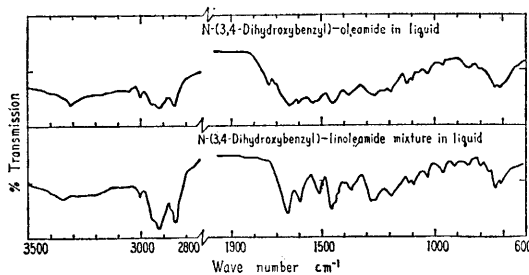


Fig. 6.

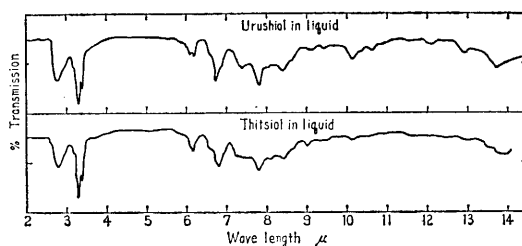


Fig. 7.

## 2-2 Film Tests

Drying test of the above products, VIIa and VIIb, was carried out in mix with shuai urushi in given ratios, and the mixture was coated on aluminum plate to form a film of 6×11cm width and 0.2 mm thickness. The aluminum plate was kept in an electric incubator at 25°C and 80% relative humidity for 12 hr. Samples No. 3 and No. 4 in Table 1, which respectively contained 50% and 75% of VIIa, did not solidify under such conditions, while No. 7 and No. 10, containing 50% of VIIb dried within 12 hr. Commercial urushi paints, such as the shuai urushi used here, usually contain some extending agent up to about 20%. The extending agents are usually drying oils such as linseed oil and tung oil, for example. The quality of natural raw urushi sold on the market is also the same. Consequently, the exact contents of urushiol in commercial urushi are unknown, so that the ratio of VIIa or of VIIb to pure urushiol in our film samples remained uncertain. However, it is possible to conclude from these results and discussion that these *N*-(3,4-dihydroxybenzyl) unsaturated higher fatty acid amides do not inhibit laccase action.

Table 1 also shows results of the film hardness test. Measurement was

carried out with a Clemen's hardness tester three days after the film was prepared. The film hardness decreased with increase of amide concentration in the blended sample. The films made from VIIb were somewhat harder than those from VIIa. This fact may be attributed to the degree of unsaturation of their alkeny side-chains.

Thermosetting test with various concentrations of VIIa and VIIb in shuai urushi were carried out (Table 2). The setting rates of the blended samples were just as fast as that of the original shuai urushi itself. The hardness test of the films prepared at 150°C showed that higher ratio of amides in the blended samples resulted in the formation of harder films than film of shuai urushi only, but good films could not be formed with 100% VIIa or VIIb under these conditions. The film prepared from 100% VIIa by baking on aluminum plate had many cracks and spontaneously peeled off from the plate. The following mechanisms may be considered for the film-hardness increasing with the increase of the amide concentration but this has not been proved in detail as yet. The amides, VIIa and VIIb, in urushi paint are converted into the corresponding *o*-quinones by air oxidation and subsequently fixed by polymerization among their alkenyl side-chains, and form hard infusible films as (VIIa and VIIb→VIII in Fig. 8), in a similar manner as setting of urushiol by baking. Also, condensation between VIII and urushiol, and VIII and VII take place by the same mechanism as the most of Mannich reaction products react with liberation of acid amide (VIII→IX). While the coating films made from Japanese lacquer are not only hard and tough but also resistant to high temperatures, the film hardness of 100% VIIb or of 100% VIIb markedly decreased, and, in case of VIIa, film cracking resulted. These facts may support the mechanisms (VIII→IX). Matsui also studied preparation of urushiol-formaldehyde resin and resin properties.<sup>19)</sup>

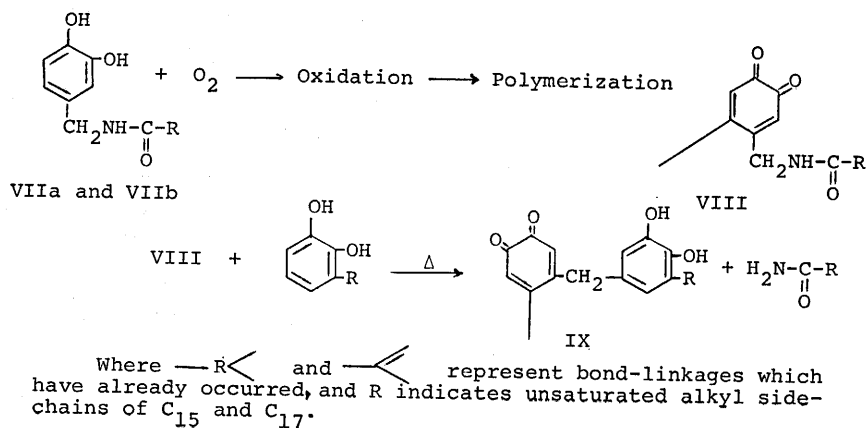


Fig. 8.

### 3 EXPERIMENTAL

**3-1 Materials.** A commercial grade oleamide (mp 73-75°C, lit.,<sup>21)</sup> 74-76°C) was provided by Nippon Seika Co., Ltd. The linoleamide was prepared by ammonolysis of the fatty acid chloride obtained from a fatty acid mixture having iodine value of 120 which consisted mainly of linolic acid. This linoleoyl chloride mixture was also provided by the same company. The shuai urushi was purchased from the market.

**3-2 *N*-Methylololeamide.** A solution of 39.3 g of oleamide in 38.8 ml of ethanol was prepared. To this solution, 11.8 ml of 37% formalin, 0.78 g of anhydrous potassium carbonate and finally 38.8 ml of water were added. After 8 hr-reaction with stirring at room temperature, the precipitate was collected on a filter, washed with water and dried under vacuum. Recrystallization from benzene gave colorless crystals (42.5 g) of mp 64.5-65°C. This product depressed the melting point of oleamide on admixture.

Found: N, 4.68%. Calcd for  $C_{19}H_{38}NO_2$ : N, 4.48%.

$\nu_{\max}^{KBr}$ : 3326, 3250 (NH, OH); 3006 (H-C=); 2953, 2870 ( $CH_3$ ); 2917, 2848 ( $CH_2$ ); 1655 (C=O, amide I); 1540 (NH, amide II); 1630 (C=C); 1020  $cm^{-1}$  (C-O, alcohol) (Fig. 5).

**3-3 *N*-(3,4-Dihydroxybenzyl) oleamide (VIIa).** To a solution of 20.7 g of *N*-methylololeamide in 26 ml of ethanol, 7.3 g of catechol and 26 ml of 30% hydrochloric acid were added and stirred for 54 hr. The reaction mixture was extracted with ether, and the ether solution was sufficiently and repeatedly washed with saturated brine to remove unchanged catechol completely. The ether layer was extracted with *N* sodium hydroxide and the combined alkaline solution was acidified with hydrochloric acid and extracted with benzene. The benzene solution was washed with water to remove further residual catechol and dried over anhydrous sodium sulfate. Upon removal of the benzene, 5.60 g of a dark-red oil remained. This product was used for the following tests without further purification.

Found: N, 3.23%. Calcd for  $C_{25}H_{41}NO_3$ : N, 3.47%.

$\nu_{\max}^{Liquid}$ : 3309-3050 (NH, OH, broad); 3002 (H-C=); 2915, 2849 ( $CH_2$ ); 1640 (C=O, amide I); 1600, 1520 (phenyl); 1260 (C-O, catechol); 852 (one isolated hydrogen atom of aromatic); 810 (two adjacent hydrogen atoms of aromatic); 740  $cm^{-1}$  (three adjacent hydrogen atoms of aromatic) (Fig. 6).

**3-4 Linoleamide Mixture.** Forty five grams of linoleoyl chloride was added drop by drop into 205 g of 28% ammonia with vigorous stirring (90 min.). After addition, 70 ml of ethanol was added and the solution was kept at 50°C with stirring for another 5 hr. The reaction mixture was poured into a large amount of water and the precipitate obtained was taken up in benzene and dried over anhydrous

sodium sulfate. Removal of the benzene under vacuum gave 41.0 g of a semi-crystalline mush.

$\nu_{\max}^{\text{KBr}}$ : 3360, 3190 (NH); 3060 (H-C=); 2955, 2870 (CH<sub>3</sub>); 2920, 2850 (CH<sub>2</sub>); 1660, 1630 (C=O, amide I); 1615 (C=C); 967 cm<sup>-1</sup> (*trans* RCH=CHR') (Fig. 5).

**3-5 *N*-Methylollinoleamide Mixture.** To a solution of 41.0 g of the amide obtained above in 34.9 ml of ethanol, 10.5 ml of 37% formalin, 35 ml of water and 0.71 g of anhydrous potassium carbonate were added and stirred at room temperature for 5.5 hr. Extraction with a large amount of benzene and usual work-up gave 33.3 g of a semi-crystalline paste.

**3-6 *N*-(3,4-Dihydroxybenzyl) linoleamide Mixture (VIIb).** The *N*-methylol amide obtained above (33.3 g) was dissolved in 42 ml of ethanol. To this solution 42 ml of 30% hydrochloric acid and 33.3 g of catechol were added. After stirring for 61 hr at room temperature, the reaction mixture was repeatedly extracted with a large amount of ether. The combined ether layer was repeatedly washed with water and extracted several times with *N* sodium hydroxide. The alkaline solution was made acidic with hydrochloric acid and the oil which separated was taken up in benzene. The benzene solution was repeatedly washed with a large amount of hot water to remove unchanged catechol. Work-up as usual gave 7.2 g of a dark-red oil.

Found: N, 3.34%, Calcd for C<sub>25</sub>H<sub>39</sub>NO<sub>3</sub>: N, 3.49%.

$\nu_{\max}^{\text{Liquid}}$ : 3450-3180 (NH, OH, broad); 3060 (H-C=); 2952, 2870 (CH<sub>3</sub>); 2922, 2850 (CH<sub>2</sub>); 1655 (C=O, amide I); 1600, 1509 (phenyl); 1275, 1260, 1192 (C-O, catechol);

Table 1. Hardness tests of films dried at 25°C and 80% relative humidity for 12 hr.

Sample No.	Ratio in blended sample (in Part)		Film hardness by Clemen's Hardness Tester at 20°C and 50% relative humidity†	
	VIIa	Shuai Urushi	g.	%
1	0	4	70	100
2	1	3	44	62
3	2	2	No Drying	—
4	3	1	"	—
	VIIb	Shuai Urushi	g.	%
5	0	4	68	100
6	1	3	50	73
7	2	2	38	56
8	3	1	No Drying	—
9*	1	3	50	73
10*	2	2	42	62
11*	3	1	No Drying	—

† Measured three days after preparation.

\* Another prepared samples.



Table 2. Hardness tests of the films baked at 150°C in air

Sample No.	Ratio in blended sample (in Part)		Baking time min.	Film hardness by Clemen's Hardness Tester at 20°C and 50% relative humidity	
	VIIa	Shuai Urushi		g.	%
12	0	4	60	74	100
13	1	3	60	72	97
14	2	2	105	70	94
15	3	1	150	63	85
16	4	0	225	22	29
	VIIb	Shuai Urushi	min.	g.	%
17	0	4	60	78	100
18	1	3	60	118	151
19	2	2	60	126	161
20	3	1	60	137	175
21	4	0	180	23	29

851 (one isolated hydrogen atom of aromatic); 805 (two adjacent hydrogen atoms of aromatic); 740  $\text{cm}^{-1}$  (three adjacent hydrogen atoms of aromatic) (Fig. 6).

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