Dried Urushi Lacquer Film Comprizing Several New Types of Inorganic Linkage and Urushiol Matrix

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This paper concerns the hardening mechanism of urushi lacquer. The author wished to propose an entirely new mechanism for the room-temperature hardening of urushiol in this natural resin. An investigation of the unit reactions correlated to the mechanism indicated that the catechol moiety of urushiol and metalhydroxides play an important role in hardening.

According to the results, the structure of one component of urushiol as "acetone powder", obtained from raw urushi sap, was clearly determined. On this basis, it is disclosed that the polymerization of urushiol does not depend on the opening of the sesquiterpene double bond, but is mainly associated with a new type of inorganic ionomer bonding, such as silanolate and carbohydroperoxide–calcium hyroxide, –magnesium hydroxide or –other metal hydroxide combinations' hydrogen bonding bridges with the urushiol matrix.

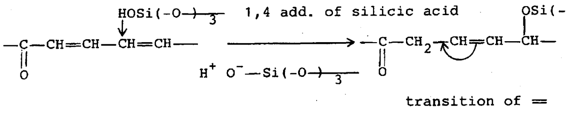
1. Historical Background of Urushi-Lacquer Chemical Research. The study of urushi in Japan (Japan Urushi, Rhus Vernicifera) was started (first in the world) by Edward Diverse and H. Yoshida.[1] Their paper on urushi chemistry attracted many European chemists, especially G. Bertrant,[2] who reported that the main component of urushi, which was called urushi acid at that time and later urushiol by R. Majima,[3] might be polymerized by the catalytic action of an emzyme. He named it "laccase", as Yoshida gave the name "diastease" to the gum portion. He attempted an experiment by himself. The study, however, had to be interrupted due to terrible skin problems caused by the urushi juice.

Following him, English chemists D. Keilin and A. Tissieres collaborated to clarify the properties of laccase.[4,5] There was little important progress, except for the discovery of "acetone powder" by Keilin. Acetone is a better solvent than the ethanol previously used to obtain a fine white powder (which is considered to be pure laccase) by pouring acetone into the original sap of Ki-urushi (customary called by worker) and mixing well in an open beaker.

According to Japanese research history, the structure of the organic components in urushiol[3,6] (UO-urushi juice-organic essence) was correctly determined by Majima 24 years after the work by Yoshida. Urushiol (essential organic component instead of Yoshida's Urushi-acid) was a catechol derivative with C-3 positioned, unsaturated sesquiterpene hydrocarbon, the accurate compositions of which were lately determined by Kumanotani.[7—9]

These days, the cultivation of the so-called laccase substance from several kinds of mushroom callus has been successful, and has contributed to the yields and improvements in urushi hardening.[10—12] In this paper, the author wishes to introduce his recent findings from research carried out concurrently with the assistance of many members of those groups.[13]

2. Recent Urushi Studies and Conclusive Developments by the Author. The author has concentrated on Rice Bran Oil (RBO) research as a health food for the past 18 years and has recognized the close relationship between Urushiol and Oryzanol[21] (OZ, key component of RBO) (Scheme 1). It is now very famous that RBO contains much oil-soluble silicic acid (SA) which acts as a scavenger of surplus cholesterol from serum. Here, the terminal group of the siloxane linkages changes to ≡SiOH, which can easily add to the conjugated trienoic bond (CTB)[15,18,22,23] to generate an Oleo-SA-complex according to the following Eq. 1:

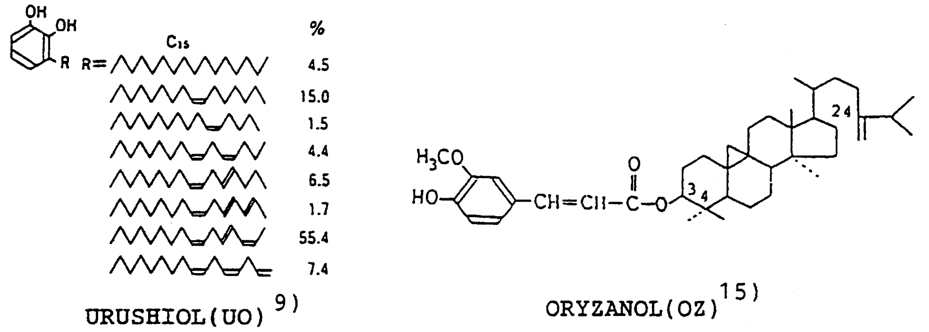


$$-\underset{\underset{O}{\|}}{C}-CH{=}CH-\overset{\overset{HOSi(-O\rightarrow)_3}{\downarrow}}{CH}{=}CH- \xrightarrow[H^+\ O^--Si(-O\rightarrow)_3]{1,4\ \text{add. of silicic acid}} -\underset{\underset{O}{\|}}{C}-CH_2-CH{=}CH-\overset{\overset{OSi(-O\rightarrow)_3}{|}}{CH}- \quad (1)$$

transition of ═

In the above Eq. 1, the author used the simple sign of silicic acid (SA) (differs from silica in having a silanol group besides siloxane bindings), such that $HOSi(-O\rightarrow)_3$, which has been explained for the RBO case.[15] Also in this experiment, white carbon was used as one representative synthetic SA. The structure was disclosed and presented at the US-Japan Clay-Organic Complexes Seminor by the present author.[16]

The presence of the silica component in the usual gum portion of urushi sap was already shown by its presence in the ash by Yoshida.[1] The hydroxy group on the catechol ring reacts with silicic acid gel[17] in the soil to form silicic acid ester derivatives of urushiol, which can be water-soluble Aqua-SA-Sol. From an analogy obtained concerning the linoleic acid group oxidation mode in RBO, the unsaturated sesquiterpene hydrocarbon ($C_{15}H_{31-2n}$) located at the C-3 position of the catechol ring can be oxidized in air, for instance, as shown in Scheme 1. As the most abundant com-



Scheme 1. Molecular structures of Urushiol and Oryzanol.

ponent (55%), the methylene group at C-10 inserted between the two double bonds, and the terminal methyl group adjacent to the cis-double bond are easily oxidized by O_2 from air through the acetone phase. The hydroperoxide groups (acidic) generated in this fashion react mainly with $Ca(OH)_2$, $CaCO_3$ (divalent acts as bridging) or KOH (monovalent acts as stopper) due to their strong alkali nature, and form a diperoxy-calcium bond or a peroxy-potassium bond, both of which become very stable compared to free types by the Kurome process.

There were two concepts with respect to laccase action theory for the hardening of urushi film. One was affirmative and one was negative. The author assumes for the moment that it is active for urushi hardening. However, it seems most fruitful to re-examine the results of Yoshida1) (with Divers) and to measure the material balances of all metal oxides contained in raw urushi sap using superior modern analytical instruments for a comparison with Yoshida's results based on those using inferior classical ones.

Experimental

Materials. Raw Urushi sap (RU), the sap from the Japanese Rhus Vernicifera, was purchased from the Nishizawa Urushi-shop located in Osaka City, and is one of the members of the J. I. C. (Japan Industrial Art Material Communication—the special organization of U-scientists, U-artist workers, and U-sap sellers). The composition was; water 19.5%, Urushiol 67.8%, "acetone powder" 12.7%, and an ash 1.84% which was within the scope of the literature.9)

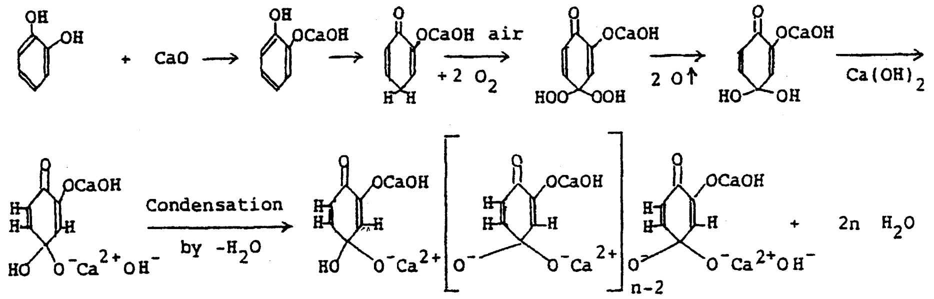
Kurome-urushi sap (KU), another kind of commercial sample, is formed by a blackening pretreatment of raw sap by dehydration and oxidation in air at about 40—45 °C with a special thickner. With this method, most of the water contained in the sample was expelled. This sample was purchased from the same shop mentioned above. Both samples were charged in an aluminum-plated tube.

Calcium oxide was purchased from Kantokagaku, and had a purity of 98%. Potassium hydroxide consisted of small tablets of 0.1 g each. Catechol (crystal powder *o*-C_6H_4–$(OH)_2$, mp 104—105 °C) was purchased from Wako Junyaku and had a distinct white lustre.

Spectroscopy and Elemental Analysis of the Products. The FTIR spectra were measured on KRS5, or with a KBr disk, and the UV spectra in a chloroform solution. The metal content was determined by ICP or EPMA analysis after the samples had been ashed by calcining with a few drops of H_2SO_4 (to prevent the loss of fly ash in a flame). Elemental analyses were carried out as needed.

Essential Unit Reaction Testing and Product Analysis. 1. Preparation of the Calcium Oxide Complex (CCC). Catechol fine crystals (1.1 g, 10 mmol) were fused by heating to 110 °C in a 20 ml beaker. To the melted mass was slowly added 0.6 g of CaO powder; a reaction began, as recognized by the deep-green color and steam evolution. This color gradually changed to black as the sample was continuously mixed and heated until stream evolution ceased. Water (0.2 g) was evaporated leaving 1.5 g of the product. This product was washed with acetone, and the unreacted catechol was removed as a filtrate to leave a black residue. Another complex was prepared by substituting half of the CaO with KOH. Although the same black solid was obtained in both the Ca and Ca/K samples, in the Ca/K case the filtrate was a slightly brown transparent liquid which consisting of acetone-soluble potassium catecholate. The structure of the polymeric black powder in the former case was formed as illustrated in Scheme 2 according to its IR spectrum (Fig. 1A) and CHN values of the recurring unit.

2. Preparation of the Catechol and Calcium Hydroxide Complex. As described above, this complex was obtained by using calcium hydroxide instead of calcium oxide. $Ca(OH)_2$ powder (0.8 g) was added to 1.1 g of melted catechol. Almost no weight change was observed upon the evaporation of water. This was in contrast



Scheme 2. Formation process of catechol–CaO-Complex.

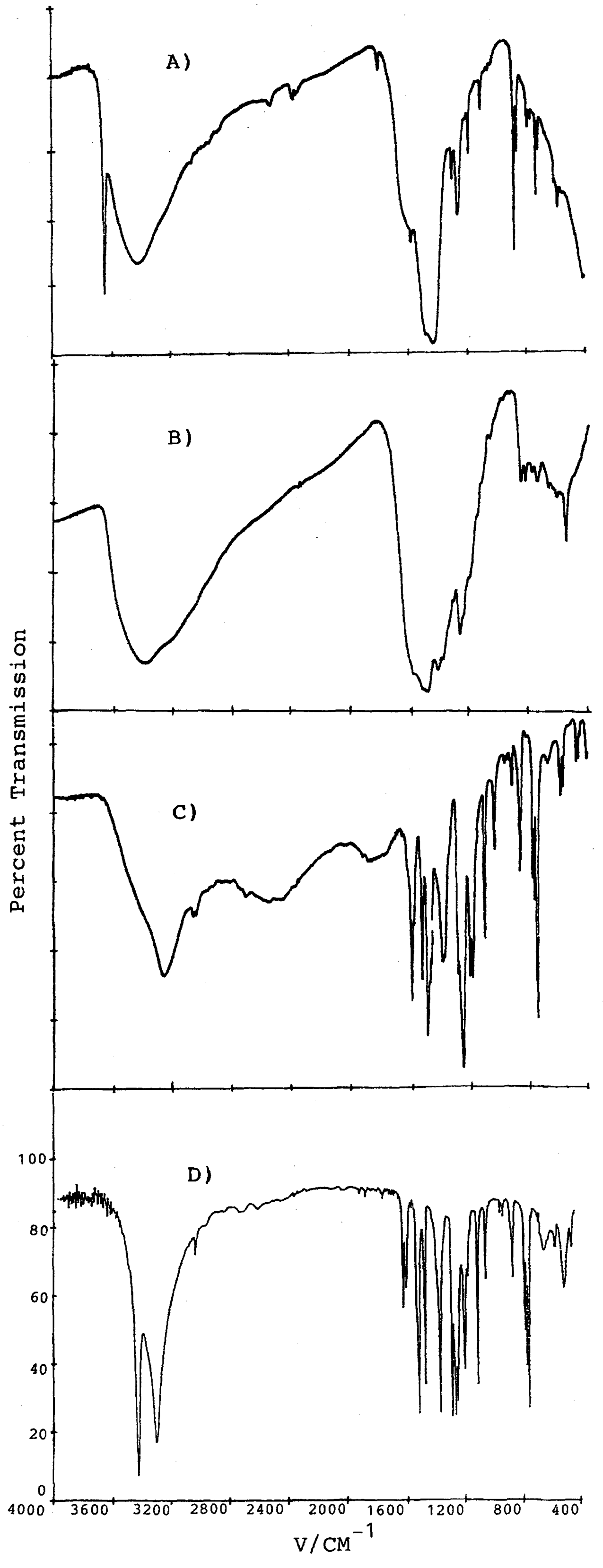


Fig. 1. A. IR spectrum of catechol–CaO-complex. B. IR spectrum of catechol–$Ca(OH)_2$-complex. C. IR spectrum of catechol potash complex. The sample was left at r.t. for 4 months. D. IR spectrum of catechol.

to the case with CaO. A greenish solution was obtained in which a black precipitate was gradually formed due to air oxidation. The elemental analysis data showed good agreement with the empirical formula $C_{24}H_{22}O_{16}Ca_2$, and the IR spectra shown in Fig. 1B agrees very well with the structure in Scheme 2.

3. Preparation of the Catechol Potash Complex (CKC). Similar to the above two items, a mixture of catechol (1.1 g) and KOH (0.3 g, 5 mmol) was heated above its melting point (ca. 110 °C). The KOH tablets reacted with the catechol melt to afford a uniform liquid, which gradually changed to gray due to air oxidation. After the evolution of vapors (probably water), the weight loss was found to be 0.3 g (calculated value of 0.18 g). A transparent brown filtrate was obtained by dissolving the reaction mixture in acetone, which contained almost no insoluble precipitate. A black precipitate again gradually appeared in the filtrate. The IR spectra of this product is shown in Fig. 1C. When chloroform was used as a solvent instead of acetone, the same product was obtained as determined from the IR spectrum and the result of its CHN analysis.

4. Separation of Acetone-Powder (AP) and Monomeric Urushiol. To 10 g of raw urushi sap in a 25 ml beaker was added 15 ml of acetone. The mixture was then divided into 3 equal parts in 25 ml beakers. To each beaker an additional 10 ml of acetone was added and mixed well. During this process, a white solid gradually appeared. These precipitates were then filtered and washed with an additional 10 ml of acetone. This precipitation and filtration method is important for obtaining a fine white powder. By drying in air, 12.7 wt% of the product was obtained (based on the original weight of sap). The IR of this product is shown in Fig. 3A. Monomeric urushiol (UO) was obtained in 65% yield by vacuum distillation of the solvent and water filtrate. The resulting UO, which was a black viscous liquid due to some air oxidation, was subjected to a molecular-weight determination using a cryoscopic method. The value of the elemental analysis, however, were close to those from an empirical formula of $C_{21}H_{32}O_2$ (UO). Calcd for $C_{21}H_{32}O_2$: C, 79.7; H, 10.2%. MW = 316. Found: C, 78.8; H, 9.7; N, 0.3%. MW = 323 (somewhat oxidized but no metal component remained).

The result on the analysis of (AP)'s $M(OH)_n$ were: silica 2.68%, lime 44.92%, magnesia 5.30%, potassium and sodium oxides 27.40 and 3.30%, phosphoric oxide 2.11%, and the sum of Fe, Ni, Cu oxides were 4.29%. Some of these values agree very well with those of Yoshida, except that aluminum oxide was not detected (7.85% by Yoshida.[1]) This material gave C, 40.5; H, 6.6; N, 1.9% (Scheme 5A, and Yoshida's close value C, 42.11; H, 6.43%).

5. Tentative Material Balance of Raw Urushi Sap. Since the yield of monomeric urushiol (UO) with MW 323 (calculated from the C,H values) was 65% based on RU, 100 g RU contains 0.201 mol of UO. These UO molecules found outside of AP contain no metal oxides which are concentrated only in AP. Since AP, obtained from 100 g of RU, was 12.7 g and its MW calculated by the empirical formula was 633.8, a mole of this complex 12.7/633.8 = 0.0200, was just the same as 1/10 mol of UO (in other words, 10 times the number of moles of UO than the AP recurring unit).

6. Preparation of a Dried Film from Kurome Urushi. A film of KU on a glass plate was dried overnight under 70% humidity at room temperature. The resulting film was transparent having a light-brown color (in Japanese "Ameiro"). This dried film, prepared by the orthodox method, was pulverized and subjected to IR analysis using a KBr disk (Fig. 2A) and X-ray diffraction analysis (Fig. 4B, lower line). Amorphous silicic acid could not be detected (as in the dried urushi sample, which will be mentioned in item 7). However, when this film was prepared under dry conditions, the film on the

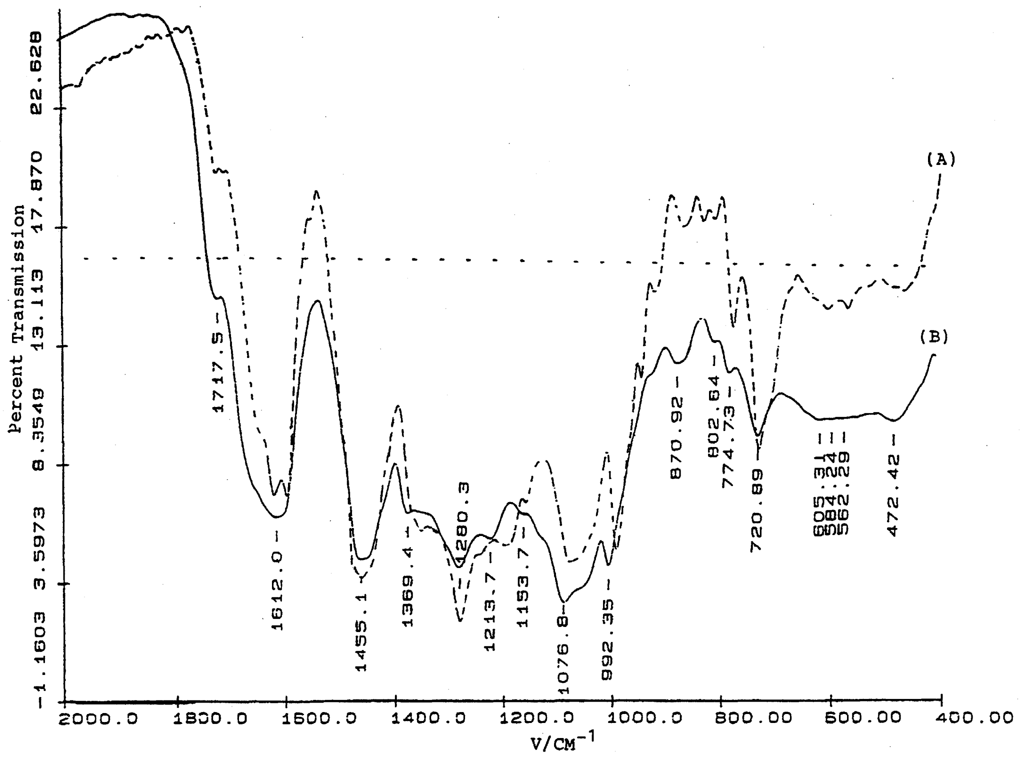


Fig. 2. A. IR spectrum of Ameiaro dry film prepared from Kurome Urushi by the rutine procedure (Upper line). B. IR spectrum of black dry mass sample obtained from raw urushi sap without Kurome procedure (Lower line). Those two spectrum were taken in the region of 2000—200 cm^{-1}.

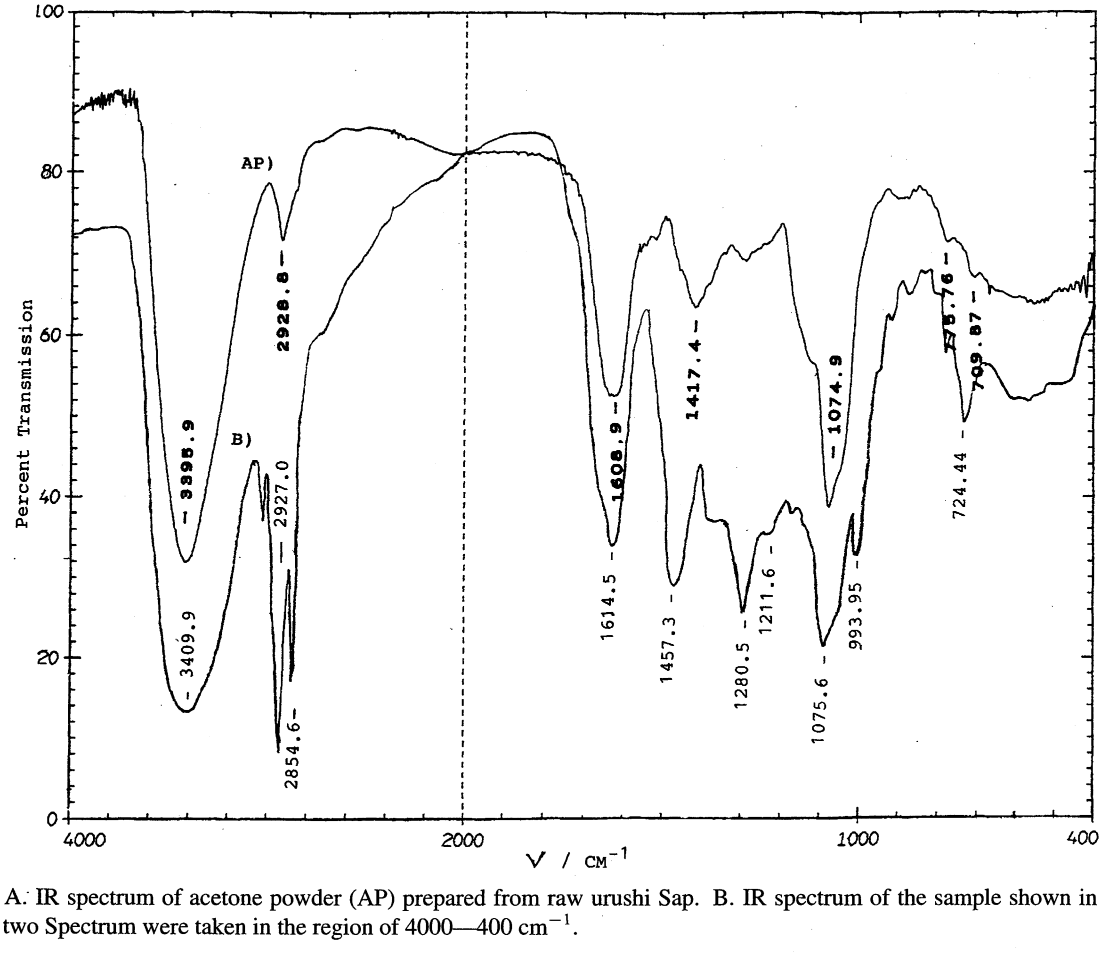


Fig. 3. A. IR spectrum of acetone powder (AP) prepared from raw urushi Sap. B. IR spectrum of the sample shown in Fig. 2B. Those two Spectrum were taken in the region of 4000—400 cm^{-1}.

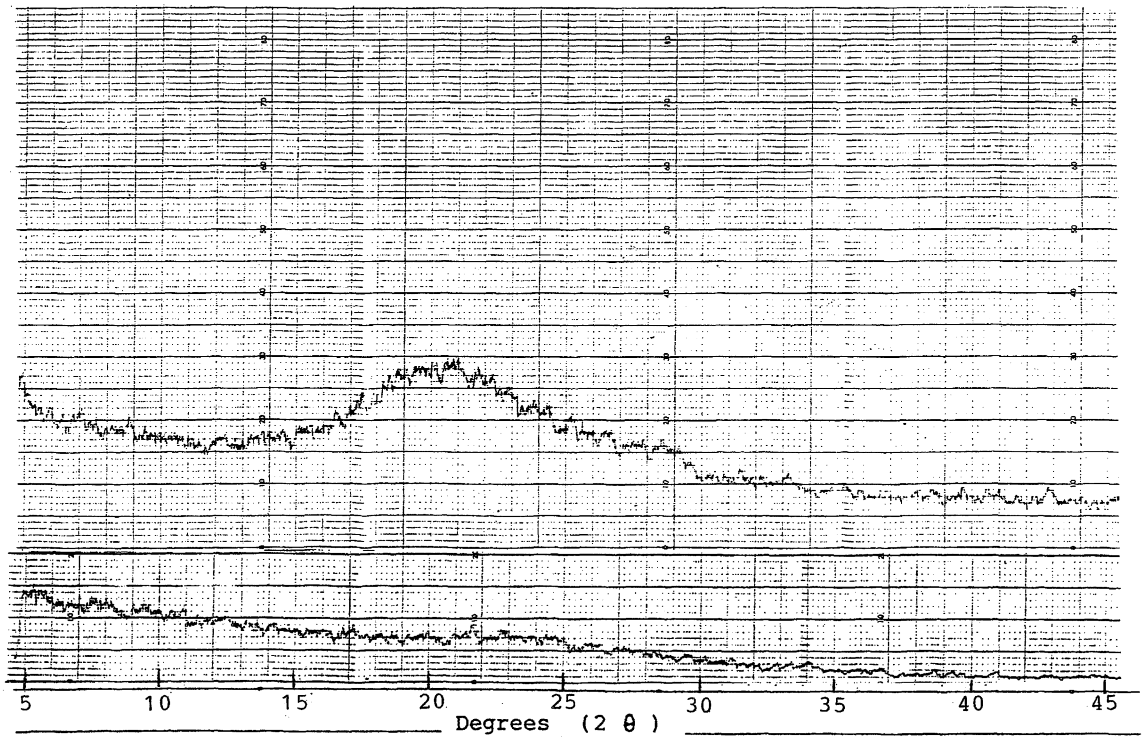


Fig. 4. A. X-Ray diffraction pattern of amorphous silica obtained from Kiurushi Sap by directly solidifying in air (Upper curve). B. Dry film prepared from Kurome Urushi by the rutine procedure (Lower line).

surface of the glass was entirely black and formed many creases overnight. Moreover, the drying speed became very slow compared to that of a similar film under higher humidity. The IR spectra (Figs. 2A and 2B) showed different results for the two cases.

7. Preparation of a Dried Mass Directly from Raw Urushi Sap. A very interesting dried urushi mass (entirely black color) was incidentally observed at a break in the aluminum-plated tube containing the RU in the summer time, probably caused by high temperature and CO_2 gas evolution from the tube. By the time the author recognized this happening, the RU mass had already hardened. The sample was then subjected to a X-ray diffraction analysis to show that it contained a considerable quantity of amorphous silicic acid (SA), as shown by the $2\theta = 22°$ broard peak in the diffraction pattern[14a)] (Fig. 4A, upper line).

Results and Discussion

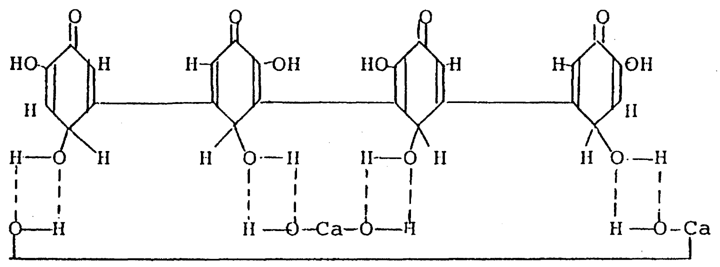
The reaction between catechol and silicic acid in aqueous ammonia[17)] was investigated in order to simplify the basic reaction of urushiol. However, the results were still much too complicated. The author studied the reaction of catechol (corresponding to the elimination of the C-3 positioned $-C_{15}H_{31-2n}$ from urushiol) and calcium oxide, and recognized the appearance of the black color CCC, which is related to the characteristic IR absorptions (Fig. 1A) at 3400, 1600, 1500, 1260, 860, and 740 cm^{-1}. The absorption at 3641 cm^{-1} shows the presence of –CaOH. In this case, where there was low humidity, it was easy to volatilize one equivalent of nascent active oxygen from the HCOOH to form a quinone from the C-1 position of HOPh.

The result of the CHN analysis corresponds to the recurring unit (dehydroquinone acetal type) of the polymer, which has the following empirical formula: $C_6H_3O_5Ca_2$ (H′); here, H′ is uncalcinated –CaOH. (Calcd for $C_6H_3O_5Ca_2$: C, 30.5; H, 1.27%. Found: C, 30.4; H, 1.11%). The process for the formation of the catechol–calcium oxide complex is summarized in Scheme 2.

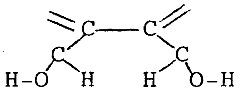
The reaction of catechol and calcium hydroxide was also evaluated for a comparison with the anhydrous case presented above. In this case, a different product was observed. The following chemical structure was identified after several trial-and-error calculations based on CH and IR analyses, which are explained in Scheme 3. However, the precise mechanism for the formation of this complex is not yet clear.

The catechol–potash product (Scheme 4) was easily soluble in acetone with a deep-gray color, showing a non-polymeric substance, unlike that formed with calcium hydroxide. It was known that the monovalent potassium cation cannot form a polymer with catechol. However, after standing for several days, a black precipitate gradually appeared. The IR spectrum was almost the same as the sample immediately after preparation, as shown in (Fig. 1C). In both complexes (new and old), the OH group in the derived cyclohexadiene has a somewhat sharp absorption at 3260 cm^{-1}, which means no formation of hydrogen bonding as in the case of $Ca(OH)_2$. For a comparison of the effect of KOH on catechol, the IR spectrum of catechol, itself, in a KBr tablet is shown (Fig. 1D).

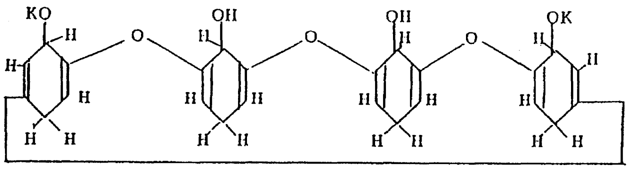
These experiments between catechol and alkaline substances showed that black-colored complexes were always formed. In contrast with the catechol case, if a kurome urushi (KU) film coating was exposed to a humid atmosphere, an Ameiro (light brown) colored film was always formed. This can be easily understood by the fact that with the kurome



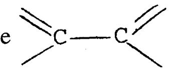
Scheme 3. Molecular structure of catechol–$Ca(OH)_2$-Complex.

Cyclic tetramer with hydrogen bond of $Ca(OH)_2$ and 

Empirical formula: $C_{24}H_{22}O_{16}Ca_2$, MW = 646.59 (Calcd for $C_{24}H_{22}O_{16}Ca_2$: C, 44.5; H, 3.4%. Found: C, 44.3; H, 3.1%). IR spectrum (Fig. 1B). The maijor difference from (CCC) is the absorption at 3641 cm^{-1} which indicated the presence of a low level of –CaOH, but after 30 min., this absorption, entirely disappeared owing to the dehydration reaction. The peak due to quinone 1630 cm^{-1} became big, and hydrogen bonding absorption at 3400 cm^{-1} becomes broad.



Scheme 4. Molecular structure of catechol–potash-Complex.

Cyclic tetramer with three –O– and one  bridges.

Empirical formula: $C_{24}H_{22}O_7K_2$, MW = 500.6. (Calcd for $C_{24}H_{22}O_7K_2$: C, 57.6; H, 4.4%. Found: C, 57.7; H. 4.6%). IR spectrum (Fig. 1C). A sharp absorption at 3300 cm^{-1} was observed for the two OH groups with no evidence of hydrogen bonding. Eight $>C{=}CH-$ appear at 3000 and 1700 cm^{-1}, and $>C{-}O{-}C<$,1200—1300 cm^{-1}, strong.

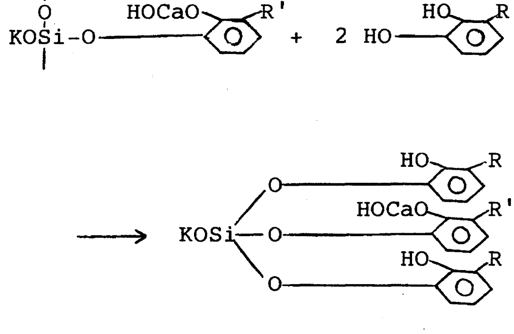
procedure all of the C-1 positioned OH's of the molecules are silanolated and form no cyclohexadiene.

As presented in a report by Toyoshima,[19] the increase in the weight of the KU film coating in the dark is 6.6% and remains stable for 6 months thereafter. This corresponds to the bonding of O_2 with one equivalent of UO monomer. In Scheme 1, the sum of unsaturated sesquiterpene in RU, which have a $-CH_2-$ group inserted between two double bonds (both *cis* compounds were omitted), reaches 63.6% (6.5 + 1.7 + 55.4) and a molecular weight of 323 (somewhat oxidized). The calculated value, 63.6/323 = 0.197 mol, and the inserted O_2 32×0.197 = 6.3% is fairly close to the observed 6.6%.

In the present experiment, the chemical composition and structure of the so-called AP was predicted, as shown in Scheme 5.

The IR spectrum of this complex is shown in Fig. 3A. The hydrogen bonding between the OH of $Ca(OH)_2$ is shown by the broad absorption at 3410 cm^{-1}. Although other absorptions are observed at 2927 cm^{-1} (the catechol ring's CH), at 1610 cm^{-1} ($-(H)\overset{|}{C}NH_2$, primary amine, but its position has not yet been determined), 1419 cm^{-1} (H_2CO_3) and 1074 cm^{-1} (the siloxane linkage). The absorption at 880 cm^{-1} (COOCa–) is very weak owing to the luck of dehydration of the hydrogen bond bridging due to the humidity. From this spectrum and CHN values, the chemical components and structure of this complex was identified. This is a cyclic trimer of siloxane, comprising a potassium silanolate bond at the top, with urushiol molecules pendant to each of the Si atoms. Then, by inserting of an O_2 molecule from air into the one C–H bond activated by the surrounding two double bonds, one hydroperoxide group is formed. Thus, one hydrogen bond with 0.5 $Ca(OH)_2$ is formed. On the other hand, the terminal $-CH_3$ is changed to $H_2\overset{|}{C}OOH$ by the insertion of O_2 into the C–H bond which is activated by one adjacent double bond, and forms a hydroperoxide complex with 1 mol of the KOH counterpart. With this proposed structure of AP, the measured values of elemental analysis agreed with those calculated from the empirical formula (see Schemes 5A and 5B). The observation that AP is sloluble in water at r.t. is consistent with the structure.

Further, the chemical reaction involved in the kurome process is considered. In this case, the siloxane linkage at the top of AP (see Scheme 5A) is cleaved by the HOPh positioned at C-1 in the catechol ring of the two free UO molecules[21] at ca. 40 °C, like that shown in the following equation:



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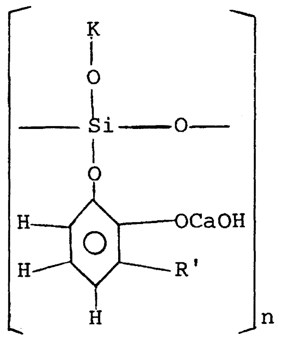


R' is explained by Scheme 5B.

Empirical Formula for total composition,

$C_{21}H_{39}{}^{**}O_8Ca_{1.5}\,K_1 + K_1SiO_3$

MW = 518.73 + 115.09 = 633

Calcd. C, 39.8 , H, 6.2 %

C + N, 41.7 %, $-(H)C-NH_2$

Found. C, 40.5 , H, 6.6 , N, 1.9 %

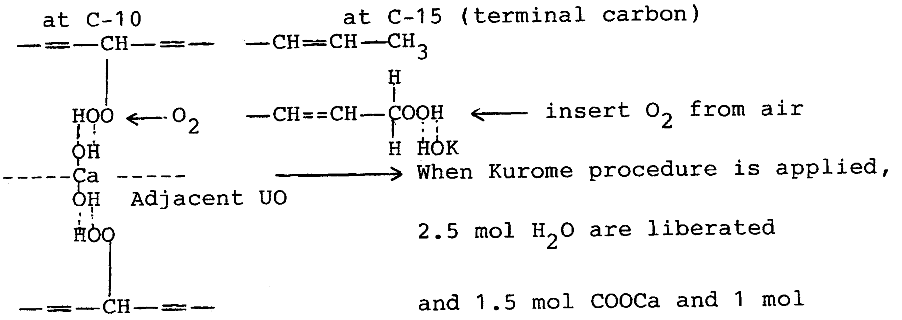
$N/MW = 14/633 \fallingdotseq 1.9\% \fallingdotseq H_2 + H_6 + H_{31}{}^{*} \longrightarrow H_{39}{}^{**}$

n=3 (cyclic trimer) from the calculation of 10 times of UO (3 x 3.3).

A. Molecular structure of acetone-powder from Kiurushi Sap.

Shown under; R′ content, Oxidations and hydrogen bond bridgings

in $-C_{15}H_{31}{}^{*} + O_4 + 0.5\ Ca(OH)_2 + KOH$



When Kurome procedure is applied, 2.5 mol H_2O are liberated and 1.5 mol COOCa and 1 mol COOK bonds are formed.

B. Oxidation and hydrogen bond bridging formations of sesquiterpene radical (R′) in acetone powder.

Scheme 5.

Here, R′ contains all of the $M(OH)_n$ by using acetone solvent, which easily carries O_2 from the air to the activated methylene at C-10 and forms carbon hydroperoxide; $-(H)\overset{|}{C}OOH$ and $M(OH)_n$ are separated by forming stable hydrogen-bond bridging at r.t. owing to the low solubility in the acetone solvent. Another R of the two UO side chains, which condensed later, have no $M(OH)_n$ and $-NH_2$ at all.

Then, the top KOSi $(OU\theta)_3$ (θ means minus HO from UO molecule) are subjected to hydrolysis with water vapour (70% humidity) and hydrated to $HOSi(OU\theta)_3 +$ KOH, which causes the final condensation with UO producing $Si(OU\theta)_4$. Potassium hydroxide with water can migrate to R, and act as a catalyst for producing hydrogen-bond bridging between carbon hydroperoxide and HOCa–.

Finally, it was disclosed by the present author that the dried urushi mass was obtained directly by air exposure without subjecting it to the Kurome procedure shown in the vivid X-ray diffraction pattern of amorphous silica (see Fig. 4A). These silica siloxane linkages are cleaved by free catechol HO–PH during the Kurome process, and show no diffraction pattern soon after preparing an Ameiro dried film.

In Fig. 4B, the IR spectrum of urushi dry film, obtained by the Kurome procedure, is shown compared with the Fig. 4A mentioned in Experimental Subsection 7. This special sample was hardened in a dry atmosphere. In both spectra, two small absorptions at 870 and 802 cm^{-1} are seen to correspond to the –COOCa and –COOSi bond.[19] These are formed by a reaction between hydroperoxide and $M(OH)_n$ at 40 °C in the kurome cure along with a loss of water. In Fig. 2B, the IR spectrim of a black dry-mass sample obtained from raw sap without the Kurome procedure has a low transmission due to its black color. The absorption at 1280 cm^{-1} shows the ethyl end group of the (UO) side chain.

In general, the metal oxides are concentrated in acetone powder; even though their concentrations are very low, they act as bridging groups of an inorganic polymer composed mainly from silanolate and hydroperoxide–$Ca(OH)_2$ hydrogen bond bridges with urushiol's matrix by the Kurome process.

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