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Oriental Lacquer. 11. Botany and Chemistry of the Active components of Poisonous Anacardiaceae

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ORIENTAL LACQUER. 11. BOTANY AND CHEMISTRY OF THE ACTIVE COMPONENTS OF POISONOUS ANACARDIACEAE

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ABSTRACT

Some aspects of the botany of the family Anacardiaceae are discussed with special emphasis on the poisonous genera and species. The focus is on the well-known members of the genus *Toxicodendrons*, i.e., the lacquer tree, poison ivy, poison sumac, and poison oak. These genera have as their toxic, dermatitis-causing ingredients catechols with C_{15} and C_{17} aliphatic side chains of various degrees of unsaturation and a variety of compositions of the individual components. Saps with a catechols mixture of a high triene content are used as lacquer for highly desired objects of art and daily use with great beauty and considerable value. Some other members of the Anacardiaceae family which grow in South East Asia have active catechol and phenol components with slightly different chemical side chain structure.

PREFACE

In this Symposium we are honoring *Bengt Rånby* as a scientist who has contributed substantially to the development of polymer science, to cellulose chemistry and technology, and to photochemistry and its technology. Bengt Rånby is, how-
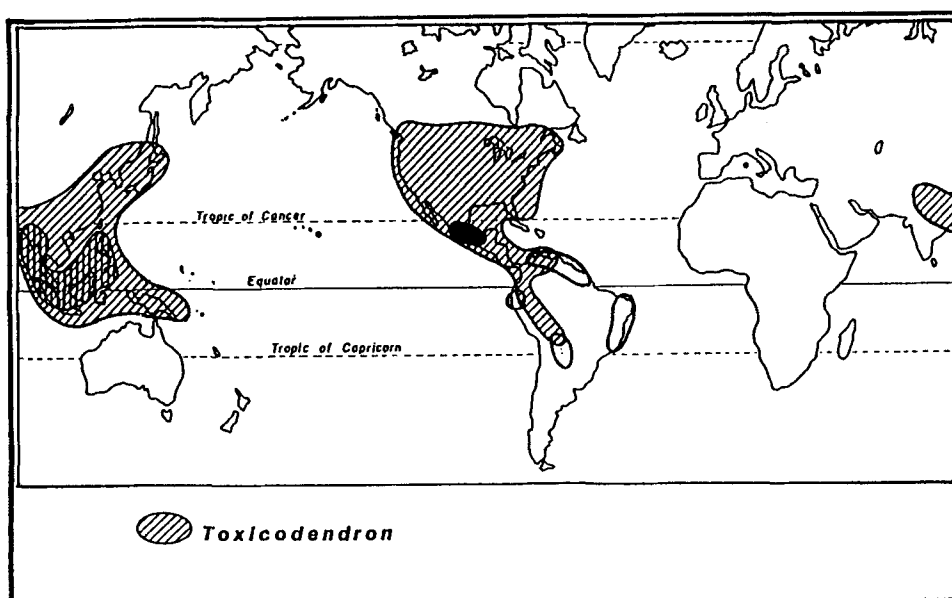
FIG. 1.   Distribution of *Toxicodendron*. (Modified from Ref. 1.)

ever, also an eminent botanist, which is no great surprise as he was and is closely related to the University of Uppsala where he received his Ph.D. degree and did his early teaching. It was in Uppsala where *Linnaeus* worked and where he gave botany much of its formal basis. I do not remember an occasion that Bengt Rånby ever failed to know the Latin name of any plant that we discussed.

My own interest (O.V.) in Japanese lacquer started many years ago in Japan; in displays, in Japanese temples, and in visits to stores which specialize in Japanese lacquerware. Our active work (O.V. and J.D.M.) began almost a decade ago [1–12] inspired by my friend and colleague Professor Jun Kumanotani, at that time *the* expert on urushi in Japan. Over the years in our work on Oriental lacquers we have contributed to the characterization of Japanese urushi, the oleoresins of the Oriental lacquer using modern analytical techniques.

BOTANY OF THE FAMILY ANACARDIACEAE

The Anacardiaceae is a family of over 70 genera and about 600 species [1, 13–16]; many grow in tropical environments (Fig. 1). The plants produce a sap; some of the sap can cause dermatitis; about 25% of the *Anacardiaceous* genera are poisonous and cause dermatitis. They belong to the tribes *Rhoeae*, *Semecarpeae*, and *Anacardieae*. The genus Toxicodendron belongs to the largest of these tribes, called *Rhoeae* [16].

Best known among the dermatitis causing species are *poison ivy* [*Toxicodendron radicans*] [17, 18, 18a]: poison wood [*Metopium toxiferum* (L.)], the mango

tree [*Mangifera indica* (L.)], poison sumac [*Toxicodendron vernix* (L.) Kuntze], the poison oaks [*Toxicodendron pubescens* Miller and *Toxicodendron diversilobum* (Torrey & Gray) Greene]. The dermatitis caused by *Toxicodendron* species is not restricted only to species that grow in North America. Some of the earliest descriptions of this type of dermatitis may be found in early Chinese medical books (Ping-yuan-hon-lon, 605–609 A.D. and Wanyo-rui-ju-sho, 923 A.D.) and were caused by members of the *Anacardiaceae* family found primarily in the Orient. The lacquer tree of China and Japan [*Toxicodendron vernicifluum* Stokes (F. A. Barkley)] (a schematic drawing of leaves, blossoms and fruits is shown in Fig. 2). *Toxicodendron vernicifluum* is the source of Japanese lacquer. The correct name of the "varnish tree" (Japanese lacquer tree) is *Toxicodendron vernicifluum* (Stokes) F. Barkley. The names *Rhus verniciflua* Stokes, and *Rhus vernicifera* D.C. are synonyms [1].

As mentioned earlier, about 25% of the species of the *Anacardiaceous* family is documented as being poisonous [19–23], some of them highly poisonous. The genera *Anacardium*, Comocladia, *P. Browne L., Gluta* (including *Melanorrhoea Wallich*), *Holigarna Buch.-Ham. ex Roxb., Lithrea Miers ex Hook & Arn., Loxopterygium Hook. f., Mauria Kunth, Melanochyla Hook. f., Pseudosmodingium Engl., Semecarpus L. f., Smodingium E. Meyer ex, Swintonia Sonder., Swintonia Griffith*, and *Toxicodendron Miller, Mangifera L., Campnosperma Twaites, Smodingium E. Meyer ex Sonder.*, and *Cotinus Miller* belong to this family. Several other genera of the family are of secondary importance but have been recorded as having induced contact dermatitis [21]. Dermatitis-causing components of only a few species have been reliably analyzed. A substantial number of this family of plants is "benign," that is, they are not poisonous.

FIG. 2.   *Toxicodendron vernicifluum* Stokes (F. A. Barkley).

Contact dermatitis due to contact with poisonous *Anacardiaceae* is the source of misery for millions of people and is caused by chemical compounds that are in reservoirs of the resin canals [1, 24] in the plant leaves and other parts of the plants (Fig. 3). The canals are not open to the surface, and they must be injured in order to release the poisonous sap of the oleoresins.

The dermatological activity depends not only on the phenol component of the molecules but also on their unsaturation in the aliphatic side chain. It has been established that the activity of the catechols decreased from the catechol triene > > catechol diene > catechol monoene. The dermatitis-causing activity is substantially higher when the aliphatic group is in *meta*-position to a phenolic group as compared to a *para*- or *ortho*-position. It is believed that a compound is formed between the urushiol components and a skin protein which causes the immune reaction. Today no reliable antidote has been found to prevent *Toxicodendron*-caused dermatitis, only the effects can be treated.

In addition to poison ivy, poison sumac, and poison oak, the most important *Anacardiaceae* species that cause dermatitis are the cashew-nut tree [*Anacardium*
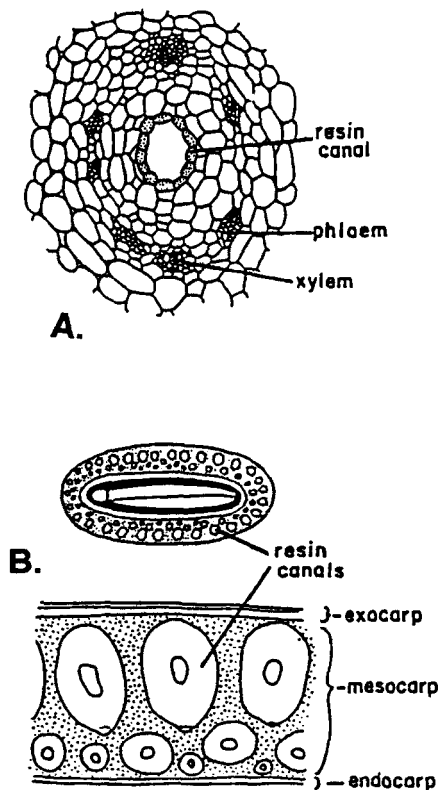

FIG. 3. Resin canals and their locations in Anacardiaceae tissues. A: Transverse section of mesocarp of *Toxicodendron vernicifluum* (Stokes) F. A. Barkley. B: Schematic diagram of *Toxicodendron vernicifluum* drupe and resin canals in the mesocarp (adapted from Fig. 27.IV, p. 234 in Mobius [24]). (Modified from Ref. 1.)

occidentale L.], the mango tree [*Manfigera indica*], the varnish or lacquer tree [*Toxicodendron vernicifluum*], the Japanese wax tree [*Toxicodendron succedaneum* L. Mold.] and the *Rengas* trees (species of *Semecarpus, Gluta, Melanochyla,* etc.) [25, 26].

The genus *Toxicodendron*, which primarily occurs in temperate climates, is perhaps the most notorious of the *Anacardiaceae* and has been the subject of considerable investigation by botanists, chemists, and the medical profession because of the components of its sap [21]. In Asia, *Toxicodendron vernicifluum* trees grow in China, primarily in the Sichuan region, and in Japan; similar species also grow in Vietnam, Thailand, and Taiwan. There has been a considerable amount of discussion and argument about the merits of the segregation of *Toxicodendron* from *Rhus*, but there is a large amount of data which supports this segregation.

Poison ivy (*Toxicodendron radicans*) [17] is indigenous to North America and East Asia but not to Europe and Africa, and it is perhaps the best known member of this family. It has been subdivided into a number of subspecies. The name *Toxicodendron* is the proper spelling for the genus which includes the lacquer tree and poison ivy. The occasional erroneous spelling, *Toxicodendrum*, refers to a genus in the *Euphorbiaceae* family which does not have catechol derivatives as their active chemical components.

Poison Ivy

Poison ivy can grow to a rather large size but the stem rarely exceeds one or two inches in diameter. Poison ivy has a tendency to climb. If there is no fence or tree to climb, bushes as high as 5-6 ft are quite common. Some poison ivy vines have been recorded as much larger (5-6" diameter). One tree-like poison ivy has been recorded as being 15 feet tall, similar to the size of the lacquer tree. Poison ivy might have as much as 1% of urushiol content in some parts of the plant. Smaller immature leaves growing on the top of a plant might have 5-10 times as much toxic substances as older leaves. This may account for the fact that the danger of being poisoned is greater in the spring and early summer than late in fall or winter. It seems that young leaves need more protection from *herbivores* by these toxic substances than older parts of the plants.

The total world distribution of the genus *Toxicodendron* includes Eastern Asia and North America south to Bolivia in South America. Poison ivy is found only in North America and Eastern Asia. Whether or not poison ivy originated in North America and spread to East Asia or vice versa is unknown. The genus *Toxicodendron* is more diverse in Asia and may have originated in Asia. With the formation of the Bering Strait, plants left in North America and Asia went their own way but similarities in the morphology of both forms of poison ivy suggests a common ancestry.

Poison ivy in its various variations is distributed from Nova Scotia to the Florida Keys, west to western Texas, and south in the highlands of Guatemala. Various subspecies exist in North America, some with leaf forms quite divergent from other poison-ivy populations. A close relative of the poison ivy of our East coast is found in Japan. Poison ivies seem to be plants of disturbed habitats in the

Orient as well as in North America. Poison ivy also occurs in mountainous regions in Taiwan and China.

Poison Oak

Poison oaks, in the strict sense, consist of the South East United States *Toxicodendron pubescens* (Eastern Poison Oak) and of the West coast *Toxicodendron diversilobum* poison oak. Poison oak usually refers to plants in the sumac family and not to any true oak (*quercus*). The term evolved because of the shape of the leaves and because the leaflets of some of the trifoliate Toxicodendrons are similar to several kinds of "oak." The names *Rhus* and *Toxicodendrum* have been applied in the past to both poison-ivy and poison-oak species.

Poison Sumac

Poison sumac belongs to the same section Venenata to which the lacquer trees belong in Asia. Poison sumac (*Toxicodendron vernix*) is a more distant relative of poison ivy than of poison oak. It has bronze-colored cherry-red leaves in autumn and is one of our more attractive shrubs with smooth shining leaflets; it grows in swamps, fens, and other wet places in the eastern United States. It is one of the closest relatives of the lacquer tree (*Toxicodendron vernicifluum*) of Asia.
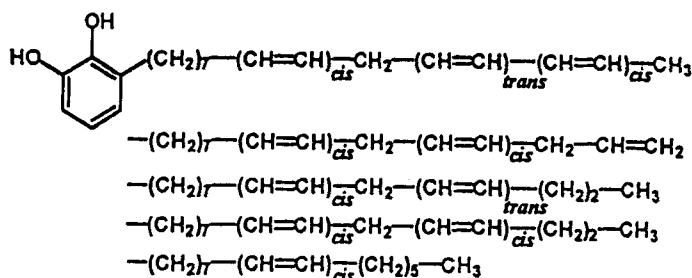
Japanese Lacquer Tree

A *Toxicodendron vernicifluum* tree can grow to a height of 30 feet; its leaves, blossoms, and seeds are shown in Fig. 2. After ten years of growth the stem of the lacquer tree is mature enough for tapping; it can be cut and a sap oozes out of the tree. The actual placement of the cut is slightly different from place to place and depends on the region where the lacquer tree is grown. The difference between the sap of the lacquer tree and the rubber tree is that the rubber trees have *cis*-polyisoprene as the material of interest while the urushi components are mixtures of substituted catechol derivatives.

THE OLEORESINS OF THE SAPS OF ANACARDIACEAE

The *Anacardiaceous* oleoresins that induce contact dermatitis are mixtures of phenolic compounds [1, 18a]. They discolor upon exposure to air, and the original colorless liquids or emulsions oxidize and polymerize in a few hours to a black gummy substance. The reactions are caused both on the phenolic portions of the molecules, and, in part, by the highly reactive and oxidatively sensitive unsaturated side chain.

The phenols have long aliphatic unbranched paraffin chains with a number of double bonds placed in various positions of the aliphatic chain. Phenolic hydroxyl-groups may also be placed in different positions of the benzene ring. They may be catechols, resorcinols, hydroquinones, salicylic acid derivatives, or simple phenols (Fig. 4).

The most common active ingredients of the *Anacardiaceae* saps are pentade-cyl-catechols and heptadecyl-catechols.

$$\text{HO} \quad \overset{\text{OH}}{\underset{}{\bigcirc}} \quad \text{(CH}_2)_7\text{—(CH=CH)}_{\overline{cis}}\text{CH}_2\text{—(CH=CH)—(CH=CH)}_{\overline{cis}}\text{CH}_3$$

$$\text{—(CH}_2)_7\text{—(CH=CH)}_{\overline{cis}}\text{CH}_2\text{—(CH=CH)}_{\overline{cis}}\text{CH}_2\text{—CH=CH}_2$$

$$\text{—(CH}_2)_7\text{—(CH=CH)}_{\overline{cis}}\text{CH}_2\text{—(CH=CH)}_{trans}\text{—(CH}_2)_2\text{—CH}_3$$

$$\text{—(CH}_2)_7\text{—(CH=CH)}_{\overline{cis}}\text{CH}_2\text{—(CH=CH)}_{\overline{cis}}\text{(CH}_2)_2\text{—CH}_3$$

$$\text{—(CH}_2)_7\text{—(CH=CH)}_{\overline{cis}}\text{(CH}_2)_5\text{—CH}_3$$

The components of the sap of the lacquer tree (*Toxicodendron vernicifluum*) are known as "urushi." They have been analyzed and individual components have been identified; their chemical structures and their compositions have been estab-lished. In other species of *Toxicodendron*, pentadecyl- and heptadecyl-resorcinols and pentadecyl-phenols, and even nonadecyl hydroquinones, have been identified [27–29].

A.

Urushiol   Laccol

B.

Anacardic acid

C.
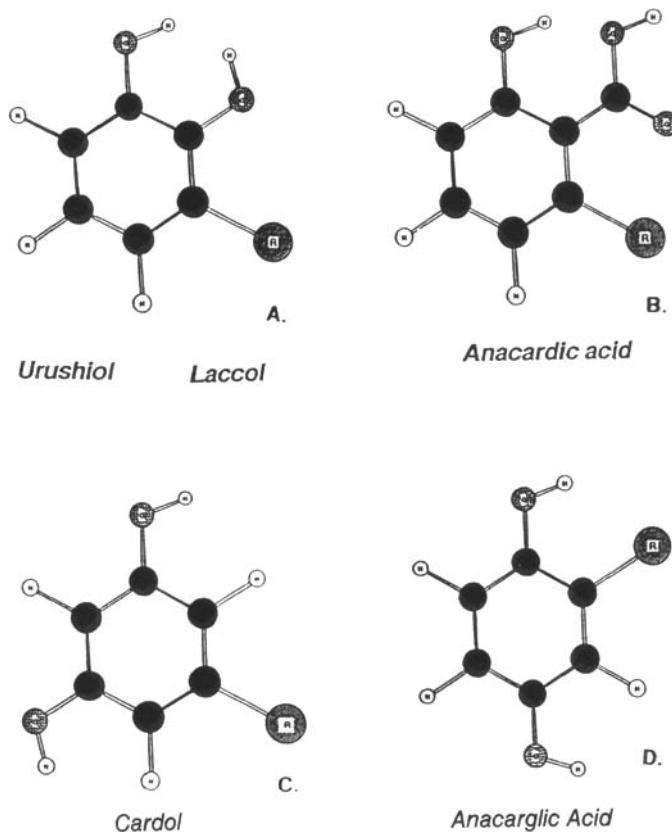
Cardol

D.

Anacarglic Acid

FIG. 4.

The sap of the Japanese lacquer tree is a water-in-oil emulsion; it is obtained by tapping lacquer trees in the same way that natural rubber is harvested from rubber trees. It consists of the "oily" or urushiol fraction (about 65%) and an aqueous fraction (35%). Urushi is a mixture of 3-substituted catechol derivatives with saturated and unsaturated side chains of 15 and a small amount of 17 carbon atoms. Nitrogen-containing substances, which are not water-soluble but dispersed or dissolved in urushiol, are stabilizers for the water droplets of the native sap and are glycoproteins. Some gummy substances and mono-, oligo-, and polysaccharides are also present in the aqueous portion of the sap. The sap also contains enzymes; most importantly, the oxidation enzyme laccase.

To prepare the lacquer from the natural sap, the sap is stirred in an open vessel at room temperature for about 1.5 hours and then at a temperature increasing from 20 to 45°C where it is kept for 2 to 4 hours until the water content is reduced to 2–4% (*sugurome* process). (The details of the process are closely guarded secrets and differ from manufacturer to manufacturer.)

The temperature cycle must be carefully controlled to retain the activity of the enzymes. The sap is now clear, has become darker, and has increased in viscosity. Sometimes small amounts of iron salts or other chemicals are added as catalysts for the production of the Oriental lacquer.

This liquid, known as "raw lacquer," consists of urushiol and oligo-urushiol, small amounts of water, and other components, and is ready for application. Urushiol is cured by air oxidation; the effectiveness of curing depends very much on the triene components, other ingredients, and the amount and activity of the oxidation enzyme laccase. Laccase is a copper-glycoprotein and functions as the polymerization (primarily dimerization) catalyst of urushiol by assisting the oxidative dimerization of the phenolic portion of the catechol derivatives of urushiol.

The urushiols harvested from varnish trees other than those grown in China or Japan may have different amounts and compositions of the ingredients. Analyses from Vietnamese, Taiwanese, and Thai lacquer trees have shown higher amounts of monoene components in addition to the trienes. Although the aliphatic side chain is still basically a C_{15} side chain, the group might be attached in the 4-position of the catechol group or just substituted in the 3- or 4-position of a phenol.

As has been indicated earlier, the curing of the lacquer is a mixture of enzymatic oxidation and radical curing of the highly unsaturated systems initiated by the hydroperoxides that are formed on the methylene groups between the double bonds. The curing of the lacquer does not work well in a dry atmosphere, but the exact nature of the curing mechanism is not known. However, it is known that even after several weeks the curing is not complete and some postcuring still continues; the lacquered sample is still slightly soft even after one month!

On the other hand, the activity of the curing capability of the catechols increases drastically from the monoene to the dienes and especially to the trienes. To have a good and fast-curing lacquer composition it is necessary to have more than 50% trienes in the organic part of the sap. Consequently, the urushiols are known to be good and fast drying lacquers while the Vietnamese lacquers are normally considered slow curing.

The *Vietnamese* and *Taiwan lacquer trees* have as their active ingredient *laccol* [11, 30–35]. Laccol is also a mixture of phenols with long linear aliphatic side chains. Generally speaking, *laccol* consists of almost 90% of catechol derivatives

and the rest of meta-substituted resorcinol and monophenol derivatives. The catechols consist of about 99% of 3-alkyl-substituted catechols with a small amount of 4-substituted catechols.

CHEMICAL STRUCTURES OF THE URUSHI COMPONENTS

The oil-soluble fraction of the sap of the lacquer tree (urushiol) is a mixture of catechol derivatives substituted in the 3-position with unsaturated (trienes, dienes, monoenes) and some saturated hydrocarbon chains of C_{15} and C_{17} chain lengths. The quality of urushiol as the Japanese lacquer depends to a great extent on the quantity of the triene component. The composition of the urushiol varies depending on the location, on the growing conditions of the *Toxicodendron vernicifluum* tree, and on the season of harvesting.

A number of techniques have been used to analyze and characterize the components of urushiol of *Toxicodendron vernicifluum* and other *Toxicodendron* species [2, 5-7, 36-46]. They include regular and capillary gas chromatography (of urushiols that had their phenol groups protected, but ultimately as the native sap, as it is harvested), supercritical fluid chromatography, high pressure liquid chromatography, and various techniques of high resolution NMR spectroscopy and two techniques of mass spectrometry, especially potassium ionization of desorbed species (K^+IDS) mass spectrometry [2, 5].

Compositions of the most important nine components of poison ivy, poison sumac, poison oak, and the lacquer tree are shown in Table 1. Figure 5 displays the maximum and minimum amounts of the individual components that have been

TABLE 1.   Chemical Structures of the Allergenic Principles of *Toxicodendron* Species[a] (after Ref. 25)

Catechol derivatives	Poison ivy, %	Poison oak, %	Poison sumac, %	Japanese lacquer tree, %	Taiwanese and Vietnamese lacquer tree, %
1. 3-Pentadecylcatechol	0-8	3-22	15	2-4	1
2. 3n-Pentadecenylcatechol	3-42	2-8	42	13-28	1
3. 3-*n*-Pentadecadienylcatechol	18-83	1-3	33	7-16	0-1
4. 3-*n*-Pentadecatrienylcatechol	3-63	0-1	11	55-68	0-1
5. 3-*n*-Heptadecylcatechol	0-1	0-2	0	0-1	3
6. 3-*n*-Heptadecenylcatechol	0-2	6-11	0	1	45
7. 3-*n*-Heptadecadienylcatechol	0-22	19-25	0	1-2	4
8. 3-*n*-Heptadecatrienylcatechol	0-5	35-63	0	1-2	34
9. 3-*n*-Heptadecatetraenylcatechol	0	0-2	0	0	0

[a]Poison ivy: *Toxicodendron radicans*. Poison oak: *Toxicodendron diversilobum*. Poison sumac: *Toxicodendron vernix*. Japanese lacquer tree: *Toxicodendron vernicifluum*. Taiwanese and Vietnamese lacquer tree: *Toxicodendron succedanea*.
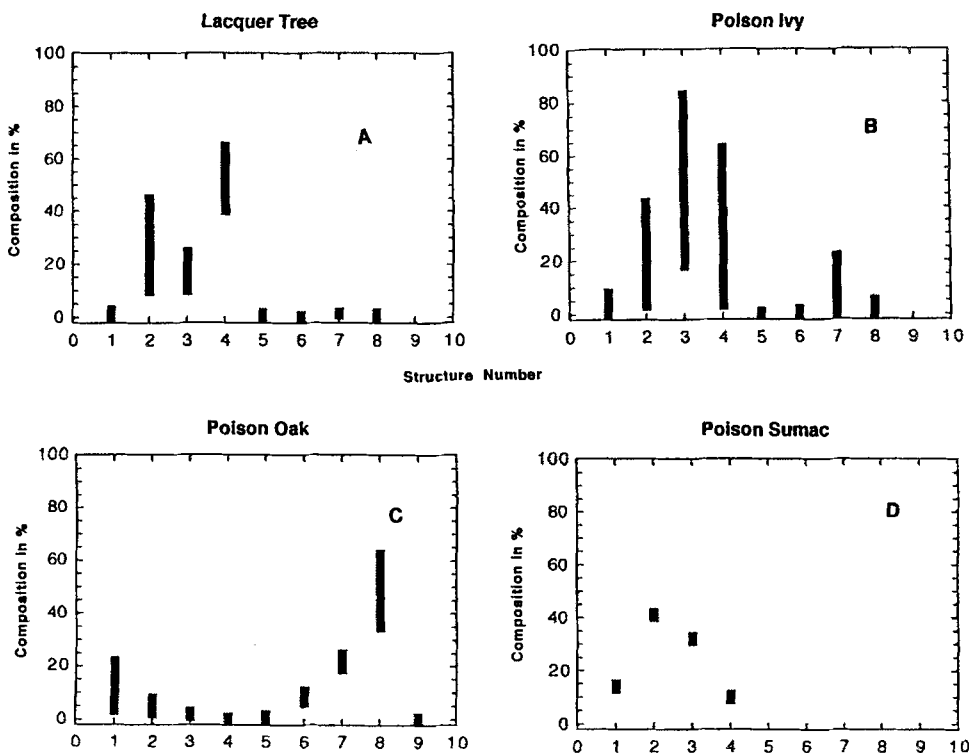
FIG. 5.

reported in the past. Figure 6 shows compositions of one typical sample each of the "urushiol" mixtures of one typical example of the lacquer tree, poison ivy, poison oak, and poison sumac.

It is interesting to view selected compounds of the urushi portion of the Japanese lacquer not only from the point of view of the commonly used chemical formulas but also from the point of space-filing models. The availability for chemical reactions of reactive groups (olefin double bonds and the phenyl groups) becomes much clearer. The C_{15} compounds, 3-substituted alkyl catechols, are displayed in Figs. 7(A–D). Figure 7(A) shows the model of 3-pentadecylcatechol with its saturated side chain, and Fig. 7(B) the 8-*cis*-monoene. Only one geometric isomer, the *cis*-compound, has been isolated. Figure 7(C) shows the 8-*cis*-11-*cis*-pentadecadienylcatechol, and Fig. 7(D) the 8-*cis*-11-*trans*-13-*cis*-pentadecatrienylcatechol. Several geometric isomers of trienes are present in urushiol, but the main component is 8-*cis*-11-*trans*-13-*cis*-pentadecatrienylcatechol. To have a well-curing oriental lacquer, the pentadecatriene fraction should be about 60% of the 3-substituted catechols (Fig. 7D).

Figure 8 shows the space-filling model of the reaction product of the main component pentadecatriene (Fig. 8A) which is sometimes transformed during the "sugurome" process into a stereospecific and regiospecific water addition product (Fig. 8B) [6]. This addition is undoubtedly catalyzed, especially when ferric chloride is used for the lacquer preparation. This undesirable side product eliminates the
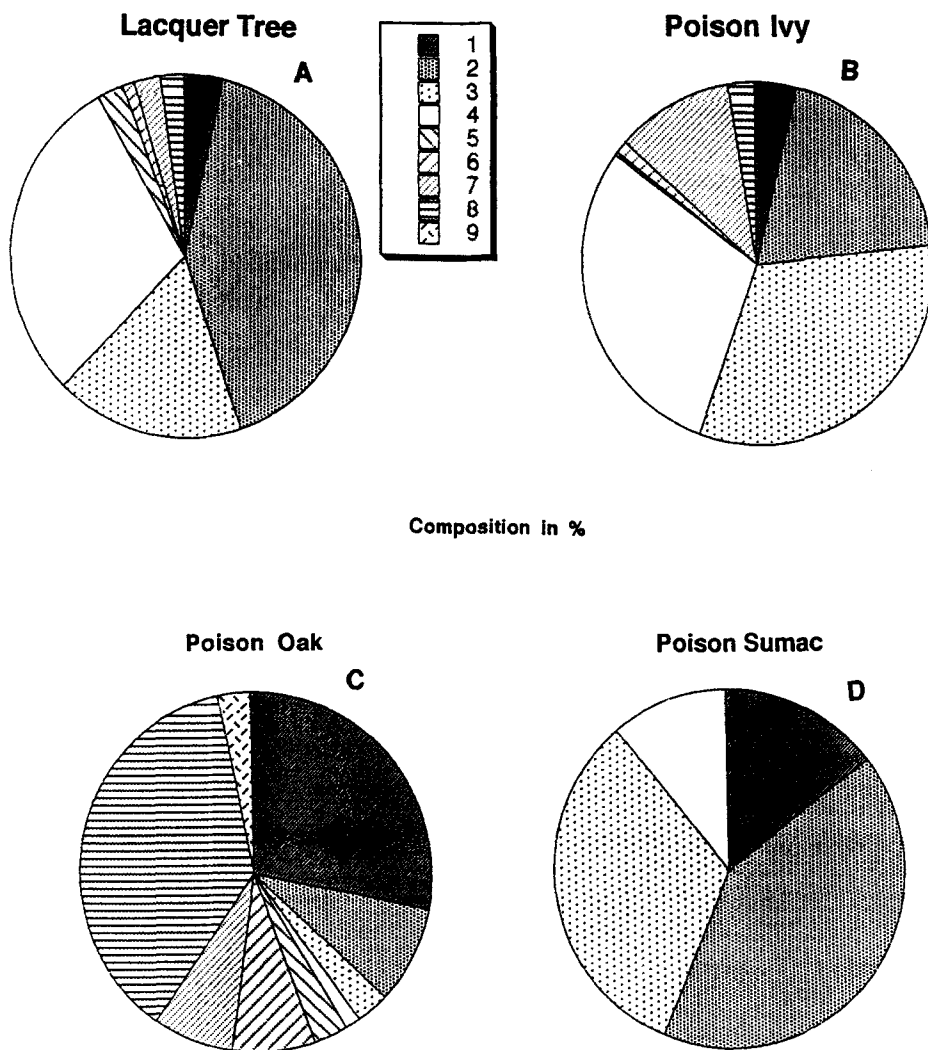
FIG. 6.

desired pentadecatriene from the lacquer composition and makes the composition less susceptible to the rate of "drying."

The desirable 8-*cis*-11-*trans*-13-*cis*-pentadecadienylcatechol is present in the saps of various Japanese lacquer samples in amounts of 55–65%, the monoene 8-*cis*-pentadecenylcatechol in between 15 and 25%, the dienes (both the 8-*cis*-11-*cis*-pentadecadienylcatechol and the 8-*cis*-11-*trans*-pentadecadienylcatechol) are present in less than 10%, while the pentadecanylcatechol amounts to about 2–4%. All other components are present at 3% or less, usually only trace amounts; they are 5-alkyl-substituted resorcinols, so-called *cardol* (Fig. 4C), and 3-alkyl substituted phenols.

From the chemical point of view, important for the curing process of the Japanese lacquer is the methylene group in the 10-position. A methylene group in
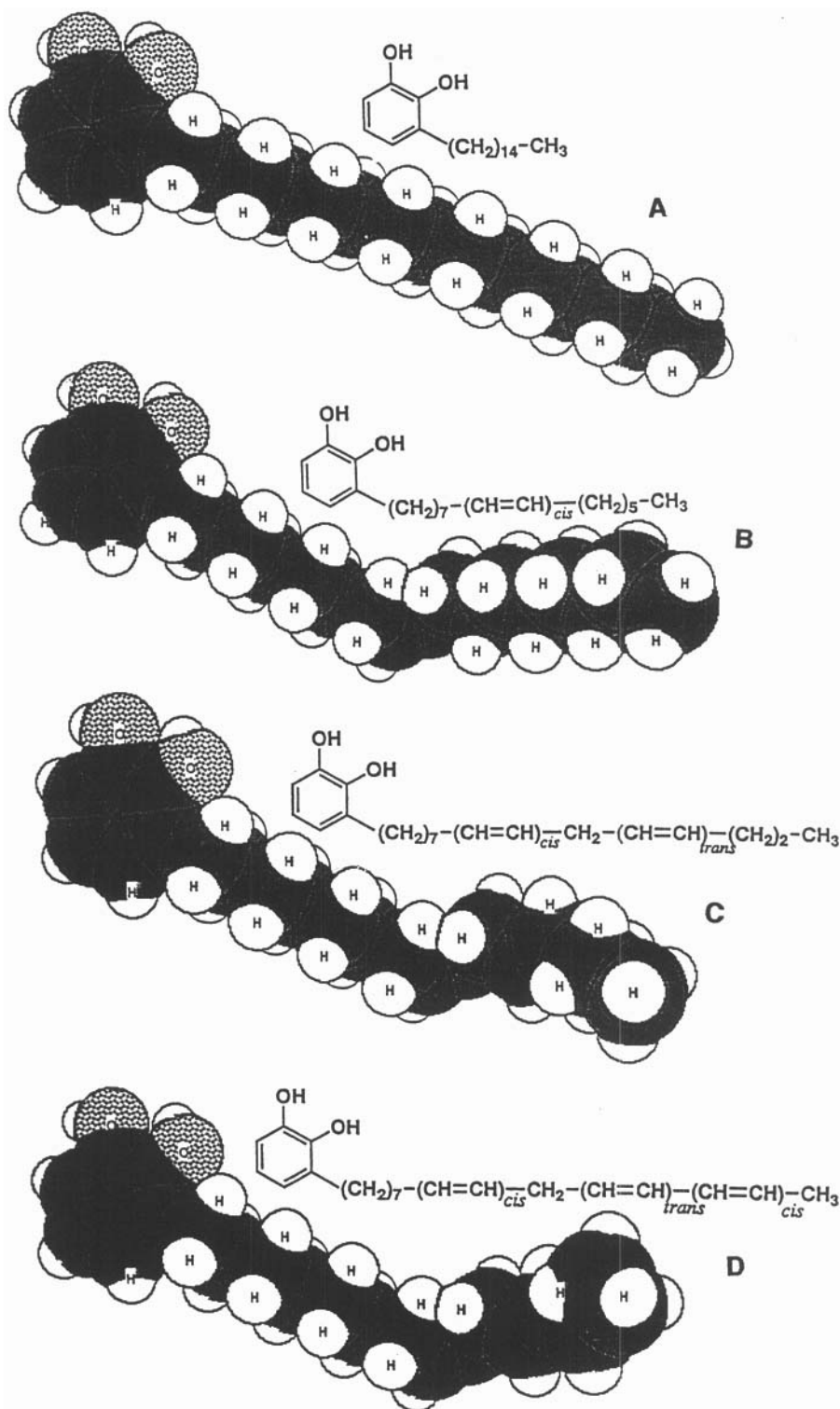
A

$(CH_2)_{14}-CH_3$

B

$(CH_2)_7-(CH=CH)_{\overline{cis}}(CH_2)_5-CH_3$

C

$(CH_2)_7-(CH=CH)_{\overline{cis}}CH_2-(CH=CH)-(CH_2)_2-CH_3$
$_{trans}$

D

$(CH_2)_7-(CH=CH)_{\overline{cis}}CH_2-(CH=CH)-(CH=CH)-CH_3$
$_{trans}$ $_{cis}$

FIG. 7.

OH
OH
(CH₂)₇– CH=CH $\overline{cis}$ CH₂– CH=CH – CH=CH –CH₃
                                      $trans$ cis

A

OH
OH
(CH₂)₇–CH–CH₂–CH₂–CH=CH–CH=CH–CH₃
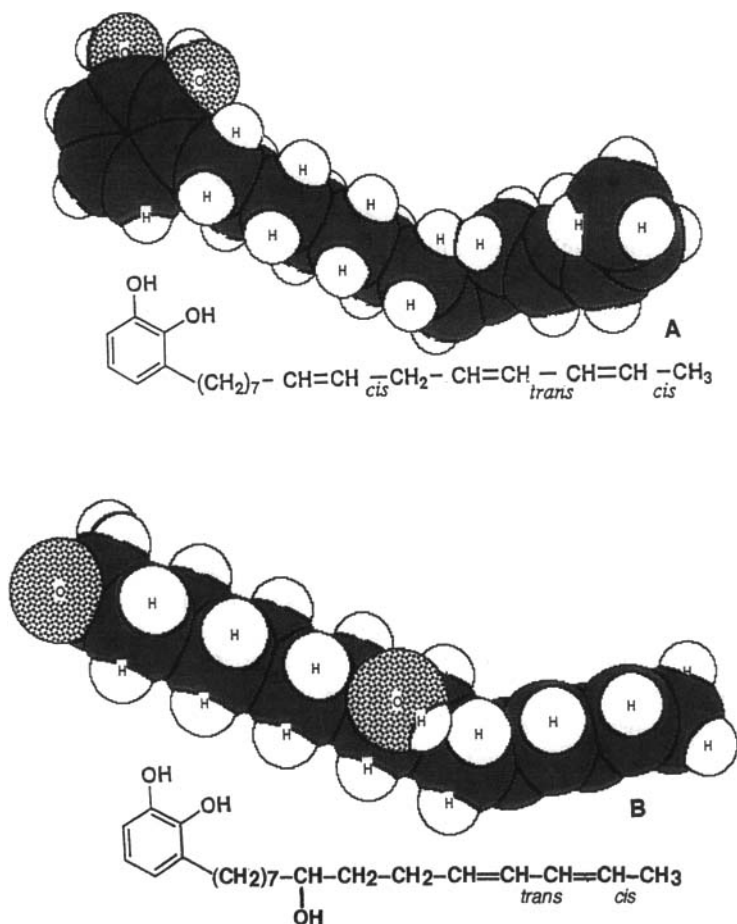 | $trans$ cis
          OH

B

FIG. 8.

the α-position to one or more double bonds is also present in the carboxylic acid portion of the glycerides that are used as drying oils. A curing mechanism of the Oriental lacquer, similar to the curing mechanism of drying oils, seems to be functioning [9]. In the triene portion of the urushiol mixture in Japanese lacquers this methylene group is flanked by two (preferably three) double bonds, and this structure guarantees the efficient oxidative cure of the lacquer at the desired rate. The other reactive part of the urushi molecules, namely the catechol part of the structures, is capable of undergoing the laccase-catalyzed oxidation reaction of the phenol groups of the catechols [10].

The 3-substituted catechols of urushi consist of catechols with a C_{15} and with a C_{17} side chain (Table 1). The composition depends on the source, the individual botanic species from which the urushiol has been obtained, and the growing season.

K^{+}IDS mass spectrometry was used as one of the major techniques to analyze and characterize several samples of urushi. It showed the typical peaks that were expected for the trienes at $[M]K^{+} = 353$ daltons, the dienes at $[M]K^{+} = 355$ daltons, and the monoenes at $[M]K^{+} = 357$ daltons. There was also a peak noticed at $[M]K^{+} = 371$ daltons that could initially not be identified and seemed to be

associated with the $[M]K^+ = 353$ dalton peak. The peak showed up at different intensities in the various samples and seemed to be the triene peak $[M]K^+ = 353$ daltons with an additional mole of water [5, 6].

In addition, especially in the processed urushi samples, peaks with masses $[M]K^+ = 665$ daltons and $[M]K^+ = 667$ daltons, which are the expected products of the dimerization reaction obtained by oxidation of the phenol part of the catechol derivatives of urushiol, were present. Supercritical fluid chromatography in combination with electron bombardment mass spectrometry was then used for the identification of some of the major components of the urushiol samples; most prominently found were the trienes with $[M] = 314$ daltons, and $[M] = 317$ daltons and the monoenes. Again the compound with the mass of $[M] = 332$ daltons was noticed which was the water adduct of the triene $[M] = 314$ daltons.

For the analysis of the urushi samples, they were also subjected to capillary gas chromatography. A considerable number of components were found in the samples, but many compounds were present in amounts less than 1–2%. Only two large peaks were found in all samples, one with a retention time of 11.2 minutes and the other with a retention time of 12.2 minutes. The two main components were present in a 6:2 ratio. This result, together with the mass spectrometry result and later the NMR result, indicated that the peak with the retention time of 11.2 minutes was the triene and the peak with the retention time of 12.2 minutes was the monoene.

A more careful study was now carried out by ^{1}H 500 MHz and ^{13}C-NMR spectroscopy, and also by ^{1}H COSY NMR spectroscopy [6]. Individual compounds were isolated by preparative HPLC of urushiol mixtures, and all the components and isomers were identified and characterized [6]. Particular care was taken to identify the compound that had shown up at $[M]K^+ = 371$ daltons. It was found that water had indeed been added to the cis-8,9 double bond of the triene to form a C_{10} hydroxylated diene [5]. This water addition was catalyzed by some additives that were used in the sugurome process, such as ferric chloride. Freshly collected samples of urushiol did not have $[M]K^+ = 371$.

As mentioned before, small amounts (perhaps 3%) of 4-substituted catechols and 3-substituted phenols have been isolated from urushiol and laccol; these compounds may have C_{15} and C_{17} side chains.

The Thai lacquer tree, more properly called Melanorrhoea usitata Wall. [Gluta usitata (Wall) Ding Hou] and Melanorrhoea laccifera Pierre, also produces a sap called thitsiol, which has dermatitis-causing phenols with aliphatic side chains of which over 90% are catechol derivatives; they consist of about 50% 3-alkyl-substituted catechols and of about 25% 4-alkyl-substituted catechols. About 3% of 5-substituted resorcinols and 2% of 3-alkyl phenol have also been identified. The chemical compounds found in these and other Toxicodendron species of South East Asia have been studied and described [11, 47–52].

Most of the 4-alkyl catechols with a small amount of phenols are C_{17}-substituted catechols, with a small amount of the C_{15} compounds present. Two compounds with most peculiar structures were also found to be present in this catechol mixture. One is present to about 8% and has a $-(CH_2)_{10}C_6H_5$ side chain, and the other, present to about 36%, has a $-(CH_2)_{12}C_6H_5$ side chain. The former is obviously equivalent to the regular C_{15} and the latter to the C_{17} side chain of the thitsiol components [27].

In addition to the Vietnamese, Taiwanese, and Thai lacquer trees, several other species of the Anacardiaceae family have been found to have saps that cause

contact dermatitis. In *Anacardium occidentale L.* (the Cashew nut tree) the active component is *cardol*, a resorcinol substituted in the 5-position of the benzene ring with the aliphatic side chain, and *Anacardic acid*, a salicylic acid derivative with the same C_{15} side chain in the 6-position [21].

A number of additional *Anacardiaceae* species have been analyzed for their active phenolic components. They will be discussed in a subsequent paper.

It seems obvious that the aliphatic side chains of the poisonous components of *Anacardiaceae* are related to the fatty acids of natural fats. Natural fats are triglyceride esters of palmitic and stearic acids, some of their lower homologues, and their unsaturated cousins. To the "stearic acid family" belong not only stearic acid (octadecanoic acid) but also oleic acid (*cis*-9-octadecenoic acid), linoleic acid (*cis*-9-*cis*-12-octadecenedioic acid), and linolenic acid (*cis*-9-*cis*-12-*cis*-15-octadecatrienoic acid), present in linseed oil, but also the primary component of tung oil, eleostearic acid (*cis*-9-*trans*-11-*trans*-13-octadecatrienoic acid), which is used as one of the drying oils [53].
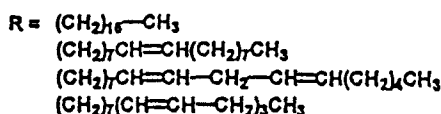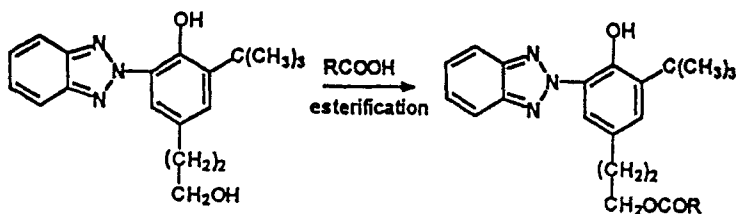
It appears that the active components of the *Anacardiaceae* could have been formed by decarboxylation and alkylation of the respective phenols, resorcinols, and catechols. The aromatic rings could also have been built by starting with the carboxyl group of C_{16} or C_{18} carboxylic acids and addition of terminal methylene radical formed in a backbiting mechanism followed by dehydrogenation.

UV STABILIZATION OF JAPANESE LACQUER

Oriental lacquers have two weak points. First, the coating is not very stable to light, especially to UV light. On exposure to light, further oxidative photocrosslinking occurs which causes cracking and sometimes chalking. As a consequence, Oriental lacquer is mostly utilized for indoor uses, and lacquered boxes of museum quality are kept under dim lights.

Second, processed Oriental lacquers cannot be produced in colorless form. Artists who use Oriental lacquer would like to have colorless Oriental lacquers.

We have made it our objective to develop UV stabilizers that could be added to urushi and "co-cured" to obtain a photostabilized Oriental lacquer. We have synthesized several 2(2-hydroxyphenyl)2*H*-benzotriazole UV stabilizers: stearic, oleic, linoleic, and linolenic acid esters of 2[2-hydroxy-3-*tert*-butyl-5(3'-hydroxy-propyl)phenyl]2*H*-benzotriazole [3, 10, 12]. We have not yet moved in preparing colorless Oriental lacquer that cures easily.

$$R = (CH_2)_{16}-CH_3$$
$$(CH_2)_7CH=CH(CH_2)_7CH_3$$
$$(CH_2)_7CH=CH-CH_2-CH=CH(CH_2)_4CH_3$$
$$(CH_2)_7(CH=CH-CH_2)_3CH_3$$

The UV stabilizing compounds, pale yellow oils, were characterized by their UV and K$^+$IDS mass spectra. All four compounds showed nearly identical UV spectra with two maxima at 305 and 340 nm. The UV stabilizers have aliphatic side chains that are three carbon atoms longer than the carbon side chains of the catechol derivatives of the urushi components. The unsaturated esters, especially the linolenic ester, could readily be incorporated into urushiol, and the unsaturated esters can be "co-cured" into UV-stabilized Oriental lacquer films. They could also be added to linseed oil and cured into UV-stabilized films of drying oils.

Specifically, the linolates and the linolenates of 2[2-hydroxy-3-*tert*-butyl-5(3′-hydroxypropyl)phenyl]2*H*-benzotriazole were blended into several samples of urushi lacquers in about 3% per weight quantities, and this composition was used to paint cedar wood and polyethylene surfaces. After curing the Oriental lacquer composition appropriately, the coatings were exposed to ultraviolet light in an attempt to mimic accelerated weathering. The coatings showed increased UV stability by an estimated factor of 3 as compared to coatings made with urushi samples without UV stabilizer added.

THE BEAUTY OF ORIENTAL LACQUER WARE

The use of Oriental lacquer as coating material produces exquisite pieces of lacquerware [54–56]. For the preparation of lacquerware, the Oriental lacquer is usually applied on cedar wood, particularly from the Japanese cedar tree because it is the most warp-resistant wood. One coat or two coats of primer, unprocessed urushi sap, is applied followed by subsequent very thin layers (from 20 to 40 layers) of processed "raw urushi" lacquer, one layer at a time every 1 or 2 days per application and curing. High relative humidity at the time of application and during curing is very critical; it must be in the range from 65 to about 80%.

The number of layers depends on the intended quality of the final product. Each layer is cured and sanded to guarantee the smoothness of the layers. Specially prepared urushi samples are used for the preparation of high quality Japanese lacquerware.

The Japanese lacquer used for individual applications contains several ingredients in addition to the urushiol base, depending on what special effects and what coloring is desired. A clear raw lacquer coat is applied as the final layer. The final product of the Oriental lacquer is a crosslinked polymer; it is resistant to water, alcohol, and oils.

Japanese Oriental lacquer has been used for several thousands of years as a coating material for boxes and other articles. The first lacquered box of good quality dates from about 200 B.C., the Qin period in China. A number of Chinese lacquer boxes from the 14th century are well preserved. These types of boxes are known for their thick layers of lacquers which are then carved.

Two types of colors have been used to pigment Oriental lacquer boxes, even in early periods. One is the vermilion color caused by a ferric oxide pigment, and the other is a black color which is caused by either magnetite, elemental iron, or a special carbon black. Heavy pigmentation is needed because processed raw urushi used for painting has a deep bluish/black to black color.

Japanese lacquer trays from the Momoyama period of Japan, show the influence of the Zen culture, the simplicity of the *neguro* technique of applying the lacquer. Numerous items of this period, which include trays, all sorts of containers and boxes, even tea pots, sake containers, musical instruments like drums, and stirrups, were coated with Japanese lacquer.

A famous and well-preserved painting in Japanese lacquer is the interior of the Matayama mortuary in the temple Kodaiji in Kyoto which was built in 1606 upon the request of Hideyoshi Toyotomo, who was then the Generalissimo (Shogun) in Japan. The lacquering technique used for this temple is called *makie* and was done by artists of the Kaomi school.

In the late 18th century and early 19th century further advances were made in Japanese lacquerware, and sophisticated decorations for boxes, trays, and even tables of lacquerware, were made. Many were highly sophisticated structures with gold and silver flakes which were incorporated when the last few layers of lacquers, but before the final topcoat, was applied. As indicated earlier, fine lacquerware may have as many as 30–40 layers of thin coatings of Oriental lacquer.

Lacquerware originating from Okinawa and Korea, but also some Chinese lacquerware, uses a considerable amount of mother of pearl or of shells as an inlay for their decoration. The regional styles may differ considerably and are quite easily distinguishable from each other.

In the Meiji period, the end of the 19th century, Japanese lacquer products became very fashionable worldwide, and the European market demanded considerable amounts of Japanese lacquerware. A new art form and modifications of the traditional way of preparing Japanese lacquerware was developed to satisfy the European market.

Japanese lacquerware is also currently very popular. It is possible to purchase very nice lacquered boxes or trays in department stores in Japan. Very valuable items of high artistic value can be obtained in special art stores where artists sell very high quality lacquerware of traditional as well as of novel and modern styles.

ACKNOWLEDGMENTS

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