Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Qin, Meifang , Mitchell, John D. and Vogl, Otto(1996) 'Oriental Lacquer. 10. The South East Asian Lacquer', Journal of Macromolecular Science, Part A, 33: 12, 1791 — 1803
To link to this Article: DOI: 10.1080/10601329608011005
URL: http://dx.doi.org/10.1080/10601329608011005

J.M.S.—PURE APPL. CHEM., A33(12), pp. 1791–1803 (1996)

ORIENTAL LACQUER. 10. THE SOUTH EAST ASIAN LACQUER

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Key Words: *Anacardiaceae*; Oriental lacquer; Laccol; Urushiol; Thitsiol; Contact dermatitis

ABSTRACT

The family *Anacardiaceae* consists of 76 genera and about 600 species. A comparison of the species of *Anacardiaceae* is discussed with special emphasis on the importance of the exudates, the so-called sap, for their importance as lacquer to produce lacquer ware. Many exudates are poisonous. The individual chemical compounds which constitute the active ingredients of the oleoresin part of the sap and their function are described based on space-filling molecular models. Emphasis is also given to the organic components of lacquer trees of the South East Asian region, which is compared to other species of the *Anacardiaceae* family.

THE *ANACARDIACEAES*

The *Anacardiaceae* is a moderately large family of 76 genera and about 600 species [1–4]. The plants produce a sap; the sap of some members of this family is poisonous [5, 6]. A few genera produce a sap that is suitable for use as the basis of exquisite coating materials for art objects [7, 8]. The curing of these coatings is similar to the behavior of drying oils. In fact, the chemistry involved in the curing of the drying oils and in the "oriental lacquers" is almost identical [9]. It consists primarily of oxidative radical polymerization of unsaturated compounds of long aliphatic chains that are part of the natural reservoir of these groups. Oriental lacquers are particularly attractive because the curing consists not only of the oxidative radical polymerization of di- and triolefins but also of the phenol oxidation of phenols and diphenols, particularly of catechols [8]. The final polymeric lacquer film provides a polymer network of unusual and very attractive properties [10–13].

The catechols present in many saps of *Anacardiaceae* can cause dermatitis in susceptible individuals [5]. The majority of poisonous *Anacardiaceae* grow in tropical environments and are not well known [1]. About 25% of the *Anacardiaceous* genera are documented as being poisonous, some of them highly poisonous, and belong to the genera *Anacardium, Comocladia, Gluta* (including *Melanorrhoea*), *Holigarna, Lithrea, Loxopterygium, Mauria, Melanochyla, Pseudosmodinglium, Semecarpus, Smodingium, Swintonia*, and *Toxicodendron*. *Mangifera, Campnosperma, Cotinus*, and several other genera are of secondary importance, but have been recorded as having induced contact dermatitis [1, 5]. Records show that dermatitis-causing components of only a few species have been reliably analyzed. They are *Anacardium, Campnosperma, Gluta* (including *Melanorrhoea*), *Holigarna, Lithrea, Mangifera, Metopium, Pentaspadon, Schinus, Semecarpus, Smodingium*, and *Toxicodendron*.

Most well-known among the dermatitis-causing species are poison ivy and the close relatives of poison ivy [4, 14]: poison wood [*Metopium toxiferum* (L.) Krug's Urban], the mango tree (*Mangifera indica* L.), poison sumac [*Toxicodendron vernix* (L.) Kuntze)], the poison oaks [*Toxicodendron pubescens* Miller and *Toxicodenron diversilobum* (Torrey & Greene)] and its close relative, the lacquer tree of China and Japan [*Toxicodendron vernicifluum* Stokes (Barkley)]. One of us (J.M.) has described in great detail the botanical, historical, dermatological, medical, and, to some extent, chemical aspects of the poisonous *Anacardiaceae* genera [1].

Dermatitis due to contact with poisonous *Anacardiaceae* is the source of misery for millions. The resin canals of the leaves do not open to the surface and a leaf must be injured in order to release the allergenic sap.

The poisonous species secrete a sap of oleoresins that causes contact dermatitis which can be contracted by handling and ingestion of the products. In addition to poison ivy, poison sumac, and poison oak, the most important *Anacardiaceae* species that cause dermatitis are the cashew-nut tree (*Anacardium occidentale* L.), the mango tree (*Mangifera indica*), the varnish or lacquer tree (*Toxicodendron vernicifluum*) and the Japanese wax tree (*Toxicodendron succedaneum* (L.) Kuntze] (also known as *Rhus succedanea*) [1]. The latter was studied by Gabriel Bertrand in the 1890s [15]. The offending oleoresins are present in virtually all plant parts with resin canals. These compounds are similar in chemical structure to the well-known dermatologically toxic components of the sap of poison ivy or poison sumac [5].

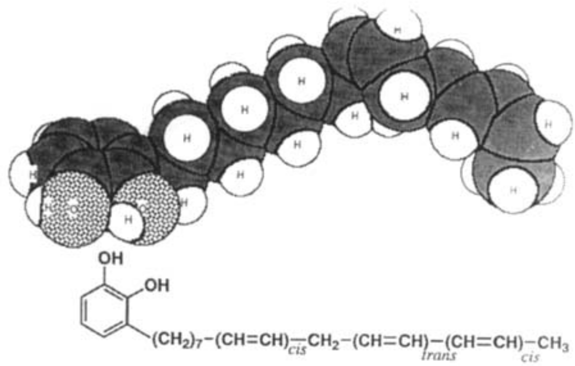


FIG. 1.

THE OLEO RESINS OF THE SAPS

Virtually all of the *Anacardiaceous* oleoresins that induce contact dermatitis are mixtures of phenolic compounds [5, 6]. Being composed of oxidatively unstable compounds, the original colorless liquid or emulsion oxidizes and polymerizes in a few hours to a black gummy substance. The reactions are caused both on the phenolic portions of the molecules as well as by the highly reactive and oxidatively sensitive unsaturated side chain. We have recently reinvestigated and further investigated the components of urushiol [11-13, 16]. We have even developed UV stabilizers for oriental lacquer compositions [17, 18].

The phenols have long aliphatic paraffin chains with a number of double bonds placed in various positions of the aliphatic chain [1, 7]. The phenolic hydroxyl groups may also be placed in different positions of the benzene ring. The active ingredients on the *Anacardiaceae* saps are pentadecyl-catechols and heptadecyl-catechols. The components of the sap of the lacquer tree (*Toxicodendron vernicifluum* or its synonym *Rhus verniciflua*), also known as "urushi," have been extensively analyzed and identified (Formulas 1a-1c, Figs. 1-4). In other species of *Toxicodendron*, pentadecyl- and heptadecylresorcinols and pentadecylphenols, and even nonadecyl hydroquinones have been identified (5, 19).

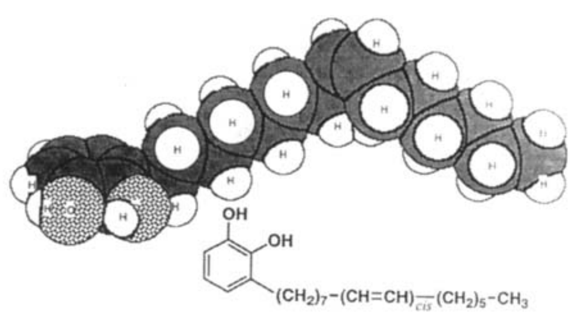
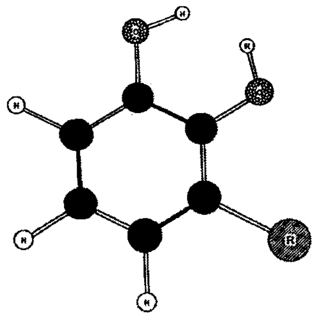
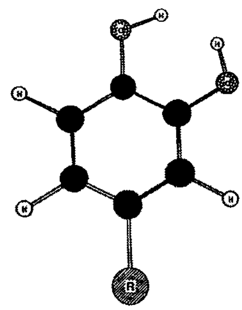


FIG. 2.



1a



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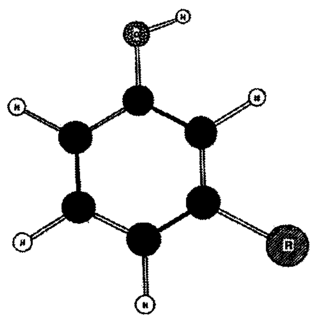

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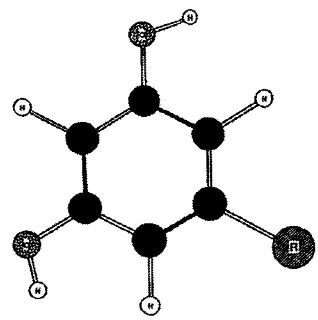
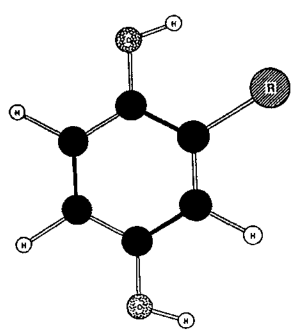
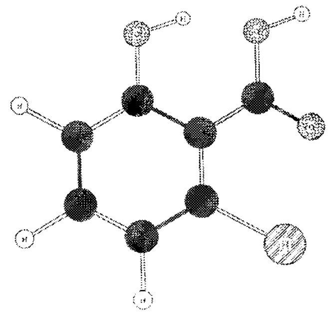


1d

FORMULA 1. Thitsiol constituents of the Thai lacquer tree (*Melanorrhoea usitata*). (a) 3-Alkyl-substituted catechols; (b) 4-alkyl-substituted catechols; (c) 3-alkylphenol; (d) 5-substituted resorcinols.



FORMULA 2.

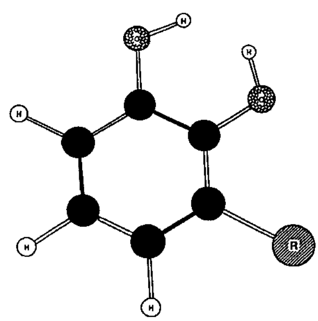


FORMULA 3. Anacardic acid.

In our discussion in this article we are primarily interested in the botany and the chemistry of the oleoresins of South East Asia and their relationship with the Japanese lacquer tree and the *Anacardiaceae* species of the Americas.

TOXICODENDRON SUCCEDANEUM

The Vietnamese and Taiwan lacquer trees, *Rhus* or *Toxicodendron succedaneum* (Rhus tree or wax tree), but also *Toxicodendron radicans* subspecies orientale (Greene) Gillis, *Semecarpus longifolius* Bl., *Semecarpus travancorica* Bedd. and *Holigarna arnottiana* Hookf. have as their active ingredient *laccol* (Formula 4, Figs. 3–7, 14). Laccol is a mixture of phenols with long linear aliphatic side chains. Roughly speaking, laccol consists of almost 90% catechol derivatives and the rest of *meta*-substituted resorcinol and monophenol derivatives [20–25]. The catechols (taken as 100%) consist of about 99% of 3-alkyl-substituted catechols and 1% of 4-substituted catechols [7].



FORMULA 4. Laccol, urushiol, renghol, glutarenghol.

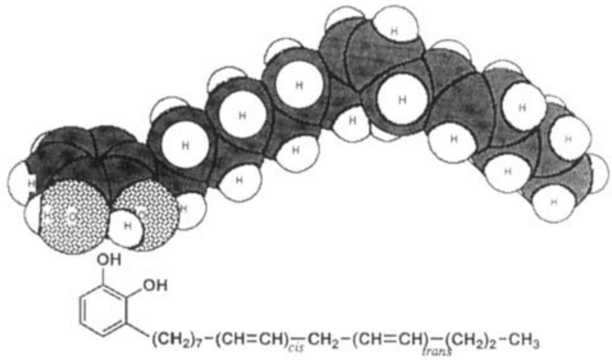


FIG. 3.

The 3-substituted catechols consist of over 95% of catechols with a C17 side chain and a very small amount of catechols with a C15 side chain. Individual components have also been identified. Of the 95% of the catechols with a C17 side chain, about 34% is the triene 3(10-*cis*-13-*trans*-15-*trans*-heptadecatrienyl)catechol, 42% is 3(8-*cis*-heptadecenyl)catechol, over 3% is 3(10-*cis*-heptadecenyl)catechol, about 3.5% is 3(8-*cis*-heptadecadienyl)catechol, and 3% is 3-heptadecanylcatechol with a saturated side chain.

Small amounts of C_{15} catechol, 0.2% 3(10-*cis*-pentade-cenyl)catechol, and about 1% of 3-pentadecanylcatechol have also been identified.

As mentioned before, a small amount (perhaps 1%) of 4-substituted catechols have been isolated from laccol; these compounds have C_{15}, 4-pentadecanylcatechol, and C_{17} side chains (Formula 1b).

As much as 3% or even more of 3-substituted phenols have been identified in laccol. Most of it is the monoene 3(8-*cis*-heptadecenyl)phenol and a small amount (about 1%) of 3(10-*cis*-13-*trans*-15-*trans*-heptadecatrienyl)phenol.

In addition to laccol, consisting primarily of C_{17} 3-alkyl substituted catechols, there is the famous urushiol, present in *Toxicodenron vernicifluum, Toxicodenron pubescens, Toxicodendron radicans*, and *Toxicodendron vernix*, which consists of

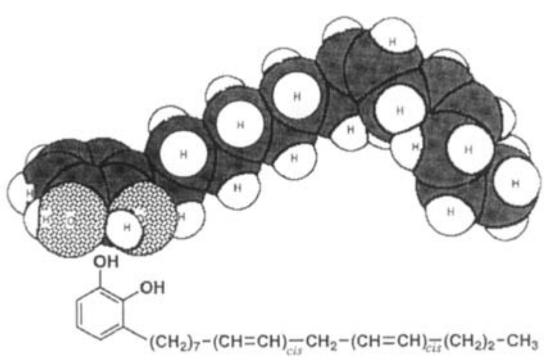


FIG. 4.

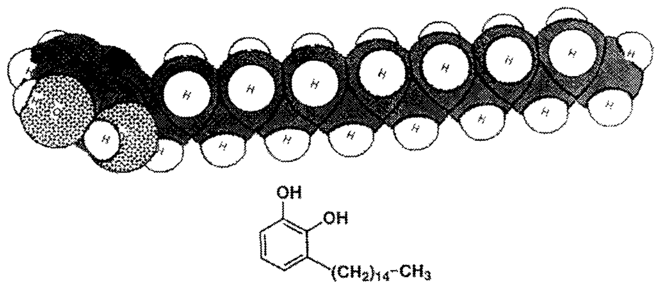


FIG. 5.

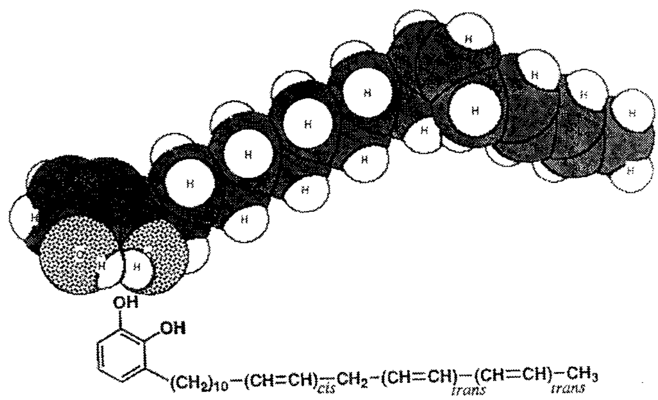


FIG. 6.

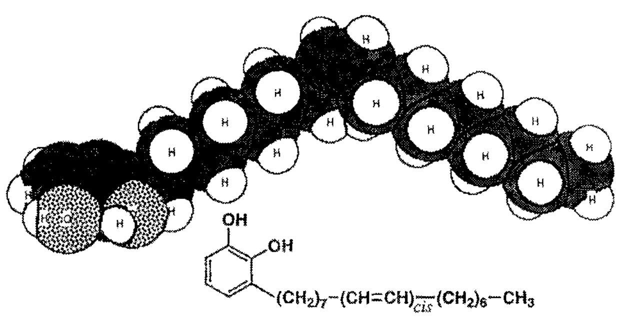


FIG. 7.

about 60% of C_{15} 3-alkyl-substituted catechol trienes. A mixture similar in the type of composition of the various components of urushiol [7, 16] but slightly different in the amounts is bhiliwanol [26].

MELANORRHOEAE

The Thai lacquer tree, more properly called *Melanorrhoea usitata* Wall. [7], is known as *Gluta usitata* (Wall.) Ding Hou. Ding Hou (1978) lumped the genus *Melanorrhoea* with *Gluta*, which is a source of lacquer in Burma [27]. *Melanorrhoea laccifera* Pierre also has a sap which has as its primary and dermatitis-causing components phenols with aliphatic side chains which are called "thitsiol." About 80% are catechol derivatives, which consist of about 70% of 3-alkyl-substituted catechols and about 25% 4-alkyl-substituted catechols. About 3% of 5-substituted resorcinols and 2% of 3-alkylphenol have also been identified [28]. *Melanorrhoea wallichii* [*Gluta walichii* (Hook.f.) Ding Hou] has as the irritant moreakol, which is similar and perhaps identical with thitsiol (Formulas 1a–1d, Figs. 8–14).

Of the 70% 3-alkylcatechols, 20% is 3(8-*cis*-11-*cis*-heptadecadienyl)catechol and 4% is 3-pentadecanylcatechol. Two compounds with most peculiar structures were also found in the catechol mixture. One is present in about 8% and has a $(CH_2)_{10}C_6H_5$ side chain, 3(10-phenyldecanyl)catechol, and the other, present to about 36%, has a $(CH_2)_{12}C_6H_5$ side chain, 3(12-phenyldodecanyl)catechol.

Of the 25% 4-alkylcatechols, half of them or about 20% of the total amount of phenols are C_{17}-substituted catechols, 4(8-*cis*-11-*cis*-heptadecadienyl)catechol. Of the previously mentioned ω-phenylalkylcatechols, one is present in about 1% and has a $(CH_2)_{10}C_6H_5$ side chain, 4(10-phenyldecanyl)catechol, and the other, present to about 4%, has a $(CH_2)_{12}C_6H_5$ side chain, 4(12-phenyldodecanyl)catechol. The former is obviously equivalent to the regular C_{15} and the latter to the C_{17} side chain of the other poisonous components of *Anacardiaceae*. Other minor ingredients of thitsiol, derivatives of resorcinol, have $(CH_2)_{10}C_6H_5$ (1%) 4(10-phenyldecanyl)resorcinol and $(CH_2)_{12}C_6H_5$ (2%) 4(12-phenyldodecanyl)resorcinol aliphatic side chains. The 3-alkyphenol derivatives have a $(CH_2)_{10}C_6H_5$ (2%) and a CH_2-$CO(CH_2)_{10}C_6H_5$ (1%) side chain. The rest are 3-substituted catechols with C_{17} and C_{15} long aliphatic saturated side chains.

In addition to the Vietnamese, the Taiwanese, and the Thai lacquer trees, several other species of the *Anacardiaceae* family have been found to have saps that cause contact dermatitis. In *Anacardium occidentale* (the cashew nut tree) the active component is cardol [5(pentadecadienyl)resorcinol] (Formula 1d) [29] and anacardic acid [6(pentadecadienyl)salicylic acid] (Formula 3).

OTHER *ANACARDIACEAE*

Semecarpus anacardium L.f.Mason has as its active component bhiliwanol, which is 3(8-*cis*-pentadecenyl)catechol. *Semecarpus heterophylla* Bl. has as its active component renghol [30], with the same catechol monoene as the major ingredient.

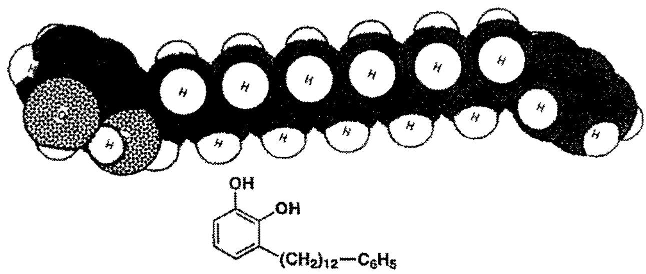


FIG. 8.

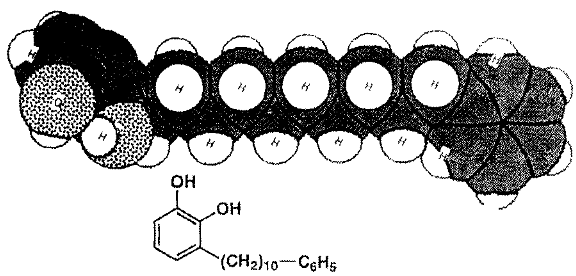


FIG. 9.

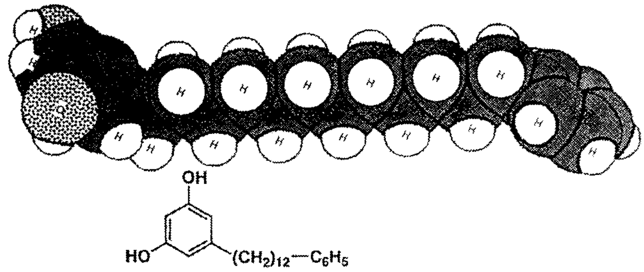


FIG. 10.

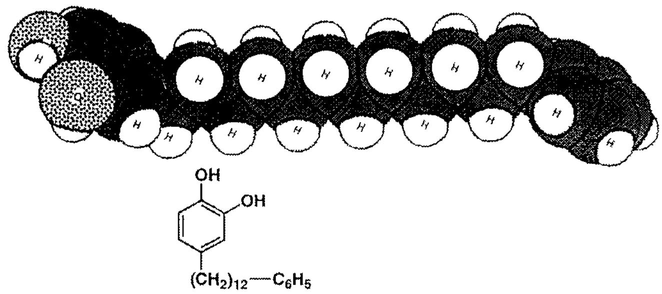


FIG. 11.

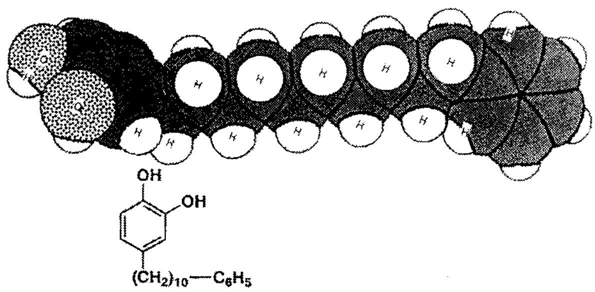


FIG. 12.

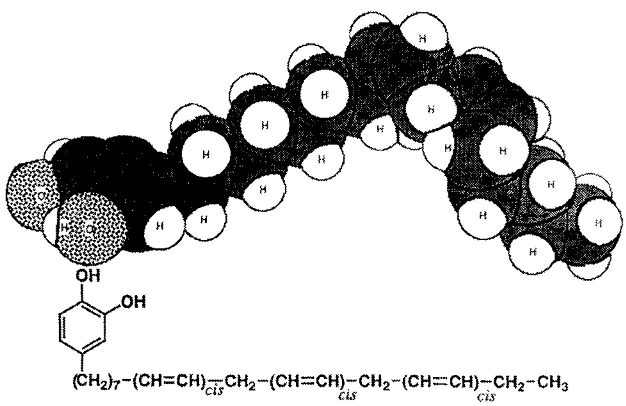


FIG. 13.

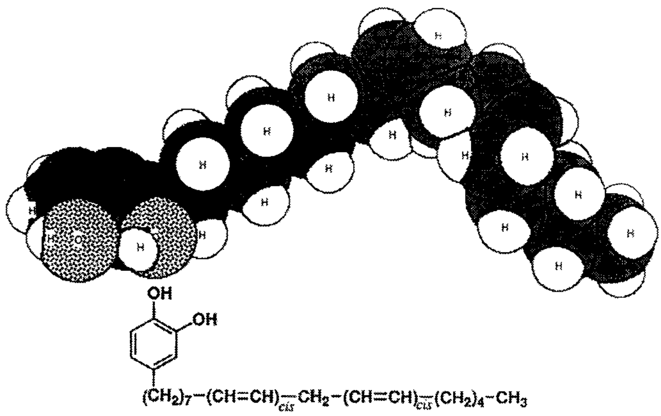


FIG. 14.

Gluta renghas L. has gluta renghol [31], a C_{17} 3-alkyl-substituted phenol 3(heptadecenyl)catechol.

GINKOACEAE

It is remarkable that *Ginkoaceae* with its living fossil *Ginko biloba*, a gymnosperm, contains chemical compounds closely related to the *Anacardiaceae.*

Ginkgo biloba L. has ginkgolic acid [6(pentadecadienyl)salicylic acid] [20] and *bilobol* [5(8-*cis*-pentadecennyl)resorcinol]. *Pentaspadon motley* Hook.f. has pelanjauic acid [6(pentadecanyl)salicylic acid] as its active phenol [32].

The tropical genus *Campnosperna* has about 10 species worldwide that has phenol derivatives in its sap. One of the species, *Campnosperna auriculatum* (Bl.) Hook.f., an evergreen tree, has a wood sap which has phenolic compounds as their ingredients that are quite different from those that were discussed before [5, 19]. They are hydroquinone derivatives with long chain alkylhydroquinones. Of particular importance is the major component of the sap, nonadecylhydroquinone (Formula 2; R = $C_{19}H_{39}$).

The dermatological activity depends on the phenol component of the molecules and also on their unsaturation of the aliphatic side chain. It has been established that the activity [2, p. 114] of the catechols decreased from the catechol trienes > > catechol dienes > catechol monoenes.

On the other hand, the activity of the curing capability of the catechols increased dramatically 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% of trienes in the urushi component of the sap. Consequently, the urushiols of the Japanese lacquer tree are good and fast drying lacquers while the Vietnamese lacquers are normally slow curing.

ACKNOWLEDGMENT

This work was supported by the Mark Chair of the Polytechnic University.

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