

# Shellac—Structure, Characteristics & Modification

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**Abstract.** The paper attempts to document upto date status of the structural studies of Shellac. Attempt has also been made to review the literature on modification of shellac molecules to make it more acceptable to meet the growing demand of the users.

## 1. Introduction

Shellac has occupied the most important position among the natural occurring resins. India and Thailand are the only countries where shellac (lac) is cultivated<sup>1</sup>. The principal lac hosts in India are *Palas* and *Ber* for the Rangini strains and the *Kusum* for *Kusmi* strains. The term shellac and lac are often used synonymously. Its industrial applications are many, yet its expansion is limited due to its inferior thermal stability and resistance to moisture<sup>2</sup>. The entire field of structure-property relationship of the polymeric material has undergone considerable growth in recent years. This is manifested by the number of papers appearing in the scientific literature and by the appearance of a book<sup>2</sup> devoted to the chemistry of shellac.

Inspite of considerable industrial, and academic research work done on shellac, there is still lack of general agreement about its structure. Although its constituent acids have been isolated and identified, yet it is not precisely known about their mode of combination in a shellac molecule<sup>3</sup>.

This paper is devoted to an examination of the experimental and theoretical evidences presently available concerning structure of shellac molecule and its modifications.

## 2. Chemistry of Shellac

The lac (shellac) resin is not a single compound but consists of intimate mixture of several polar and non-polar components in a molecule. The manner in which these

molecules are linked together to build up shellac complex has led to intensive chemical research during the last few decades. Shellac is always associated with an odoriferous compound, a wax and a mixture of dyes such as erythrolaccin and desoxyerythrolaccin which are hydroxyanthraquinone derivatives<sup>4</sup>. Due to the presence of the dyes, shellac gives a characteristic colour reaction with alkali. The shellac has been fractionated into three main components namely hard resin, soft resin and wax. Resinous character of shellac is believed to be due to the association of the components through hydrogen bonding. When dewaxed shellac is slowly heated, it softens at 65–70°C and melts between 75–80°C. Both the resinous constituents of shellac, soft resin and hard resin, contain hydroxy acids<sup>5,6,7</sup>, and their polar groups are present at the interface of the molecule. It is presumed<sup>8</sup> that the ability of shellac to adhere strongly to smooth surfaces is the result of orientation of these polar groups. Specific gravity of shellac varies between 1.14 to 1.21. It has an average molecular weight 1006, acid value 65–75 and saponification value 220–230. Shellac is insoluble in water, glycerol, hydrocarbon solvents and esters but dissolves readily in alcohol, aqueous solution of alkalis, organic acids and ketones. This finding has led to the conclusion that hydroxyl, carboxyl and carbonyl groups are present in shellac<sup>9</sup>.

Palit<sup>10,11</sup> found that a non-solvent of shellac like acetone can be converted into a solvent of shellac if 5 to 10 percent of water is added to acetone. The polar part of shellac molecule seems to absorb the polar solvent of the mixture (i.e. water). The molecule thus appearing like a big hydrocarbon molecule gradually goes into solution in fat solvent like acetone.

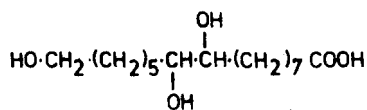
### 3. Chemical Structure

Shellac in its refined form is a polyester type of resin consisting of inter- and intra-esters of polyhydroxy carboxylic acids<sup>12</sup> formed from certain hydroxy acids and sesquiterpene acids. It is believed to have five hydroxyl<sup>13,14</sup> groups including vicinal hydroxyl group<sup>4</sup>, one carboxyl group, in free state, three ester groups, one double bond and one partly masked aldehyde group<sup>15</sup>, and the probable linkages ester, acylal, acetal and ether in an average molecule. Shellac easily undergoes periodic acid oxidation which is specific for vicinal hydroxyl groups and also to Tollen's reagent due to the presence of aldehyde group<sup>4</sup>. The hydroxyl groups have been reported to react with various monohydric alcohols viz, ethyl alcohol, butyl alcohol, allyl alcohol and dihydric alcohols<sup>16–23</sup> to form ethers. This also seems to be the reason for the action of water on shellac molecules, although no chemical reaction takes place on its short contact.

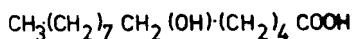
From a study of the composition of total shellac acids, Khurana *et al*<sup>24</sup>, concluded that the chief building blocks of shellac are aleuritic acid and Jalaric acid-A (a tricyclic sesquiterpene). The structure of jalaric acid-A as an aldehydic acid has been established by Wadia *et al*<sup>25</sup>. According to them shellolic acid and epi-shellolic acid are not the primary products of shellac, and these acids together with laksholic acid

and epilaksholic acid, arise from a cannizaro reaction of jalaric acid-A. Sahu and Misra<sup>26</sup> have reported that there is no doubt that the most important components of shellac are aleuritic acid (9, 10, 16 tri-hydroxy palmitic acid) and jalaric acid-A (a tricyclic sesquiterpene). These are connected by lactide and ester linkages.

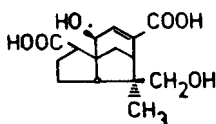
On hydrolysis<sup>4</sup>, the constituent acids of shellac are liberated and consist mainly of hydroxy aliphatic and terpenic acids. The aliphatic acids are almost insoluble in water, whilst the terpenic acids are readily soluble and these are present almost in the proportion of 50 : 50. Among aliphatic acids, the main constituent acid is aleuritic (~ 35%) and amongst terpenic acids the main constituent acid is jalaric (~ 25%). Other acids isolated are butolic (~ 8%), shellolic/epishellolic and laccijalaric (~ 8%) acids (Fig. 1). Water soluble jalaric acid and laccijalaric acids have aldehyde functions in the molecule.



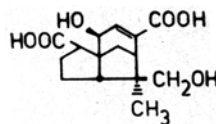
Aleuritic Acid



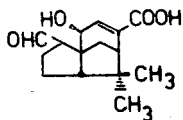
Butolic Acid



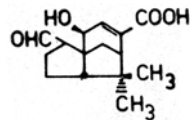
Shellolic Acid



Epishellolic Acid



Laccijalaric Acid



Jalaric Acid

Fig. 1

The structures of aleuritic acid and shellolic acid had been established by 1962, when Sukh Dev<sup>27</sup> undertook work on shellac for (i) elucidation of structures of remaining lac acids, isolation and characterisation of many new ones, (ii) determination of the nature of hard and soft resins as derived from shellac. He isolated laksholic acid<sup>25,28</sup>, epilaksholic acid<sup>25,28</sup>, laccishellolic acid, epilaccishellolic and laccijalaric acid

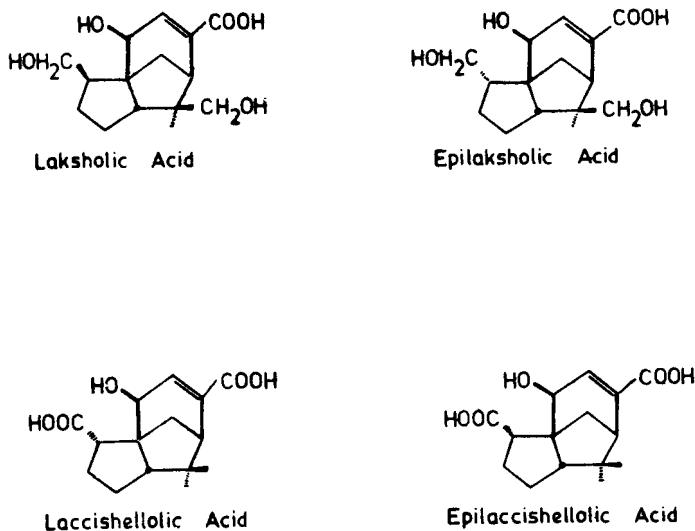


Fig. 2.

(Fig. 2) from shellac hydrolysate<sup>29</sup>. It was considered that jalaric and laccijalaric acids are the primary terpenic lac acids and the other acids arise from these during alkali hydrolysis by equilibration (via epimerisation) at C7 and Cannizaro reaction. In support of this hypothesis, it has been demonstrated that these aldehydic acids can be isolated only after a brief hydrolysis of shellac by alkali. Pure jalaric acid on prolonged reaction with aqueous alkali gives shellolic acid, epishellolic acid, laksholic and epilaksholic acid. Cedrene skeleton for shellolic acid and related compounds is well secured by degradation<sup>30,32</sup>, and X-ray studies<sup>33</sup>. Structure of laccijalaric acid, laccishellolic acid and epilaccishellolic acid has been established by a direct chemical correlation<sup>34</sup> with (–) –  $\alpha$ -cedrene.

Although it is generally accepted that shellac is a polyester<sup>35</sup> formed from terpenes possessing the cedrene skeleton<sup>31,32,36</sup> and threo-aleuritic acid (9, 10, 16-trihydroxyhexadecanoic acid), Subramaniam *et al.* have stated in their earlier communication<sup>37,41</sup> that (i) alkaline hydrolysis of shellac or of pretreated hard resin does not release either the terpene acids or aleuritic acid completely, (ii) the 9- and 10-hydroxy-groups of aleuritic acid are involved in alkali-stable linkages, and (iii) a large part of the aleuritic acid remains in the combined form in the primary gum obtained after treatment with aqueous 20% sodium hydroxide. One of the main terpenes of shellac is jalaric acid, the likelihood of the vicinal glycol system in aleuritic acid being involved in dioxolan ring formation with the aldehydic function of terpene has been investigated by Subramaniam *et al.*<sup>42</sup>. In view of the known stability of dioxolans and 1, 3-dioxans, the 9- and 10-hydroxy-groups are expected to be preferred sites for acetalisation than 16-hydroxy group of aleuritic acid<sup>43</sup>. They have shown that the

alkali-stable linkage in shellac is acetalic in nature, in the light of the formation of dioxolans from threo—9, 10, 16—trihydroxy hexadecanoic (aleuritic) acid and the terpene aldehydes of shellac. The minor terpene constituents of shellac have now been identified as of the oxo-ether type.

According to Sukh Dev *et al.*<sup>28</sup>, the aldehydic acids are the primary acids of lac resin, the corresponding alcoholic and acid components arise from cannizaro-type reactions during hydrolysis by strong alkali. Subramanian *et al.*<sup>42</sup>, hydrolysed shellac under the conditions used by Sukh Dev *et al.*<sup>28</sup>, followed by esterification—acetalisation with methanolic hydrogen chloride and separation by chromatography on silica gel yield a number of compounds. Dimethyl shellolate, dimethyl 2-epi shellolate, methyl laksholate and methyl 2-epilaksholate have been isolated pure, the 2-epishellolate being the major product. The two oxo-ethers earlier obtained by Cookson *et al.*<sup>36</sup>, Yates *et al.*<sup>31,32</sup>, by oxidation of dimethyl shellolate and dimethyl 2-epi-shellolate with manganese dioxide have also been obtained. The major aldehydic acid which Sukh Dev *et al.*<sup>28</sup> designated jalaric acid is configurationally related to 2-epishellolic acid and not to shellolic acid. Shellolic acid can readily form a  $\gamma$ -lactone, while the 2-epishellolic acid can not. Neither shellolic acid nor 2-epishellolic acid has a tendency to epimerise to any appreciable extent, even in strongly alkaline aqueous solution.

Shellac contains nearly 40% each of aleuritic acid and terpene acid, the amounts actually isolated by alkaline hydrolysis range at 20% and 5-10%, respectively. Apparently the remainder is present as acetals. The terpene acids, both aldehydic and non-aldehydic have been usually isolated from the aqueous mother liquors after hydrolysis. Under mild hydrolytic conditions, in the absence of cannizaro reactions, the products are obtained without epimerisations. On strong alkaline hydrolysis that part of the 2-epijalaric acid with a free aldehyde function disproportionates, with epimerisation to yield shellolic acid as a primary product. 2-epishellolic acid has an independent existence alongwith 2-epijalaric acid in shellac.

#### 4. Hard Resin or Pure Resin

The earliest resolution of lac resin was effected by Tschirch and Farner<sup>44</sup> by using ether which separates it into two fractions, (i) Portion insoluble in ether called Pure or Hard Resin (ii) Portion soluble in ether called Soft Resin. Hard resin seems to be mainly responsible for most of the characteristic resinous properties of shellac. Hard resin and soft resin are themselves not single compounds but mixtures. Khurana *et al.*<sup>29</sup> adopted a modified procedure for the preparation of hard and soft resins. Hard resin constitutes ~ 70% of the total shellac and is a mixture of several components.

Upadhye *et al.*<sup>45</sup> have worked on constituent acids of hard resin. Saponification of hard resin by 12% aqueous alkali yields a hydrolysate containing aleuritic acid, jalaric acid, laccijalaric acid, shellolic and epishellolic acid which were identified by paper chromatography. This finding has been supported by hydrolysis of hard resin

( $\sim 30^\circ$  for 10 days) and identifying the products by paper chromatography and after esterification by thin layer chromatography. It is obvious that hard resin is derived from aleuritic acid, jalaric acid (shellolic acid, epishellolic acid) and laccijalaric acid.

Estimation of constituent acids of hard resin has been accomplished by the following methods<sup>45,46</sup>.

- (i) Chromic acid (Jones reagent) oxidation-esterification—gas liquid chromatography (GLC) has been applied to the lac acid mixture obtained after 48 hrs alkaline hydrolysis of hard resin. It has been found that for every one mole of laccijalaric acid, approximately three moles of aleuritic acid and five moles of jalaric/epishellolic acid are produced on hydrolysis of hard resin.
- (ii) Alkaline silveroxide hydrolysis/oxidation—esterification on—formylation—gas liquid chromatography (GLC) when applied to hard resin generates for every one mole of laccijalaric acid approximately three moles of jalaric acid and 4 moles of aleuritic acid.

It has been concluded<sup>27</sup> that of the two methods described above, the second is more straight forward and has been tested on a number of synthetic mixtures. It has also been concluded that in hard resin aleuritic acid and terpenic acid (jalaric/laccijalaric acid and the derived dicarboxylic acids) are in a ratio of 1 : 1. This conclusion, however, conflicts with the previous finding that hard resin on hydrolysis yield  $36 \pm 1\%$  aleuritic acid by periodic acid estimation. This point is reconciled by the fact that during hydrolysis of shellac other side reactions take place. The 1 : 1 molar ratio is fully borne out by NMR analysis of formylated hard resin.

It may, therefore, be concluded that each molecule of hard resin is derived from four terpenic (three jalaric/epishellolic acid and one laccijalaric/epilaccishellolic acid) and four aleuritic acid units. Such a molecule will have molecular weight 2194 (while considering aldehyde function at C7) which is in agreement with the value of  $2095 \pm 110$  reported by Upadhye *et al*<sup>45</sup>.

## 5. Soft Resin

The soft resin is a soft sticky balsam like material having bright orange to reddish brown colour due to the presence of erythrolaccin. Tschirch *et al*<sup>46</sup> have observed that soft resin is a mixture of esters (or lactides) of various hydroxy palmitic acids. Analysis of acetyl derivative of the hydrolysed soft resin revealed<sup>47</sup> that it has two OH groups thus supporting the presence of one lactide, lactone or ester group in addition to a OH. In view of these factors it appears that soft resin is made up of several fatty acids, partly in combination as inter-esters and partly free, among which mono-hydroxy palmitic acid, palmitic acid, aleuritic acid and its isomer, butolic acid and an aldehdydic acid have been isolated. Singh *et al*<sup>48</sup> succeeded in isolating the following four pure acid esters, which together constitute the bulk of the soft resin. These compounds are laccijalaric ester-I, jalaric ester-I, laccijalaric ester-II and jalaric ester-II respectively (Fig. 3).

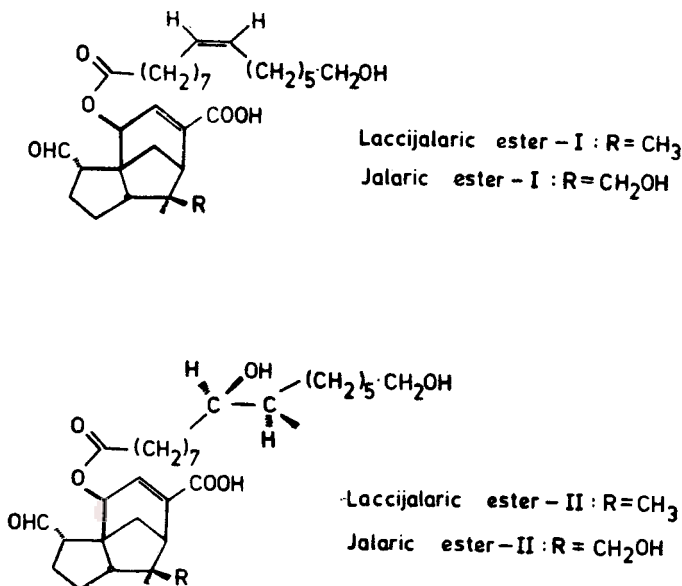


Fig. 3.

They undertook investigation to find out whether the soft resin contain inter-esters of substantially lower molecular weight than those found in hard resin. Thin layer chromatographic (TLC) study of the soft resin indicates that four components namely laccijalaric ester-I, jalaric ester-I, laccijalaric ester-II and jalaric ester-II having R<sub>f</sub> value 0.90, 0.65, 0.40 and 0.15 in the solvent system (benzene-ethyl acetate-acetic acid) on silica gel adsorbent are found predominating. The laccijalaric ester-II and jalaric ester-II are major. Ultraviolet absorption study of these compounds indicate that all these four compounds contain a terpene lac acid moiety and further from a comparison of the  $E_{1\text{cm}}^{1\%}$  values of these compounds with the range  $E_{1\text{cm}}^{1\%}$  value (202) of terpene lac acids it appears that the terpenic acid moiety constitutes approximately half of the molecule. These structures are fully supported by their PMR spectra.

## 6. Modification of Lac

Due to the well known limitations of lac, namely low heat resistance, poor resistance to water, solvents and chemicals, brittleness, modification of lac has been attempted from time to time to upgrade its performance in specific directions.

Modification of lac to increase its versatility has been broadly classified into four categories: namely reactions with (a) chemicals, (b) monomers, (c) synthetic resins, and (d) natural products. Khanna and Tripathi<sup>2</sup> have surveyed the subject in some

details. By judicious choice of some organic acids and conditions of reaction, it is possible to esterify one or all the five hydroxyls present in lac molecule<sup>14</sup>. Similarly the carboxyl group can also be esterified by reaction with mono or polyhydric alcohols. The solubility of the esters in hydrocarbons was found to increase with progressive reduction of hydroxyl group.

Copolymers of lac with various monomers having outstanding film properties, improved heat, water, impact and chemical resistance have been reported<sup>49</sup>. The copolymerization of lac with vinyl monomers (acrylates, styrene and acrylamide) in aqueous media has been the subject of study of several workers<sup>50,51,52</sup>. These workers have found that the mechanism of reaction is similar to that postulated by Lott and Symons<sup>53</sup>. The tertiary hydrogen of shellac molecule is affected producing shellac free radical, which initiates the graft polymerization of vinyl monomers.

Lac has been combined with several synthetic resins such as phenolic, melamine, to produce material for baking varnishes. Kumar *et al*<sup>54,55</sup> have observed likelihood of cross linking taking place under the influence of heat between resin and shellac molecules.

Shellac has been modified with various oils<sup>56-59</sup> (both drying and non-drying oils) for surface coating compositions. The resulting films cure at ordinary temperature and are resistant to water, chemicals and solvents. The combination of shellac and cashewnut shell liquid (CNSL) produces many products<sup>60-63</sup> namely weather resistant varnish, anticorrosive varnish, water and solvent resistant coating, insulating varnishes and laminated insulators. Shellac and CNSL bonded paper laminated insulating tubes have been used on cores of transformers in electrical industry<sup>64</sup>. Not much attention has been paid to the investigation of the chemical reactions involved during the combination of shellac with CNSL. According to Gidvani<sup>18</sup> the following reactions probably occur.

- (i) Two carboxyl groups reacting with each other forming anhydrides.
- (ii) A carboxyl of one molecule reacting with a hydroxyl of another forming ester or lactides.
- (iii) Two hydroxyls reacting with each other to form ethers.
- (iv) A hydrogen and a hydroxyl of two adjacent carbon atoms reacting to form an unsaturated linkage thus generating some active centres of polymerisation. The part played by the carbonyl group is however yet to be determined.

Subramanian *et al*<sup>37</sup>, have prepared trimethylsilyl derivatives of methyl laksholate, 2-epi-laksholate and 2-epi-laccilaksholate, which however were not separable on a number of G. L. C. columns. However the separation of trimethylsilyl derivatives of dimethyl shellolate and 2-epi-shellolate on SE-30 G. L. C. columns was achieved by them<sup>37</sup>.

Recently some attempts have been made by us to introduce silicon into the shellac molecule by the process of silylation. Trimethylsilylation or silylation is the technique<sup>65-67</sup> by which an organosilyl radical namely trimethylsilyl group is substituted for an active hydrogen in a molecule. Lentz<sup>68</sup>, Gotz and Masson<sup>69-70</sup>, have



done pioneer work in the field of trimethylsilylation studies. We have used their methods and also modified to meet the conditions of trimethylsilylation of shellac molecules which are affected by acid. Due to susceptibility of polymerization of shellac under acidic conditions attempt to modify the technique was carried out so that the effect of acid may be minimised if not eliminated before the process of trimethylsilylation commences.

Various silylating agents e.g. trimethylchlorosilane, hexamethyldisilazane, bis (trimethylsilyl) acetamide have been employed in the technique by us.

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