PART B

CHEMISTRY OF LAC RESIN

CHAPTER - I

INTRODUCTION

LAC RESIN

INTRODUCTION

Lac is a natural resin, secreted by a tiny insect, *Laccifer lacca*, which infests certain species of trees in India, Burma and Molluccas. The insect exudes a secretion that covers it and the twig on which it resides. The exudate hardens to a dark red, tough coating known as lac. The name lac is derived from 'Laksha', the Sanskrit word for one hundred thousand, and refers to the fact that a very large number of insects are involved in the production of appreciable amounts of the product.

The lac insect

The lac insect belongs to the family *Lacciferidae*[1](super family:Coccidae) of the order *Hemiptera*. The common Indian lac insect belongs to the species *Laccifer Lacca*. It proliferates rapidly and usually passes through two generations annually. It feeds on the sap of the tender shoots of the host-trees, most common of which are Palas(*Butea monosperma*, Lamk), Ber(*Zizyphus jujuba*, Lamk) and Kusum(*Schleichera oleosa*, Lour).

Refining of lac

Lac is collected by cutting down the lac bearing twigs and the encrustation is scraped off by a knife. This crude lac, known as stick lac, is purified by powdering and soaking in water. This permits removal of extraneous matter, including twigs and insect bodies, which float to the surface, and is skimmed off. The particles are then soaked in dilute aqueous sodium carbonate, which mostly removes water-soluble components and the major colouring matter, the red laccaic acid. The resulting granules are dried in shade and this product is named as seed lac. Further treatment by melting and filtration through cloth or by dissolving in ethanol, filtration and evaporation yields shellac. It contains 4-5% of wax, which is removed to yield dewaxed shellac of commercial importance.

Properties and uses

Lac resin dissolves in alcohol, dries rapidly and produces smooth, decorative and durable films. These films show excellent adhesion to various types of surfaces and possess high gloss, hardness, strength and resilience. It has low thermal conductivity and high dielectric strength. Based on these properties, shellac has been put to multiple uses. Some of the major uses are as under:

1. Surface coatings,
2. Paper industry and printing inks,
3. Rubber compounding and adhesives,
4. Electrical industry, and
5. Cosmetic and pharmaceutical preparations.

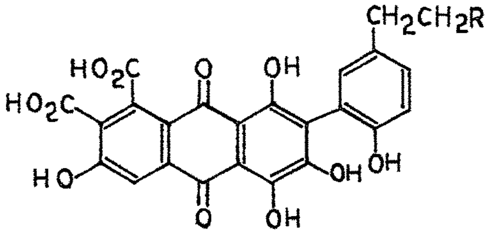
However, due to the growth of synthetic resins with specific properties, the market for shellac has been adversely affected.

Nature of lac

Geoffrey and Lamery considered[2] the lac as wax, but later on Gren[3] and Fourcroy[4] showed it to be a true resin, brittle in nature and having no sharp melting point. Stick lac, the composition of which is dependent, to some extent, on the nature of the host-tree, consists of wax(6-7%), colouring matter(4-8%),'resin'(70-80%), insect debries, moisture and other extraneous matters[1].

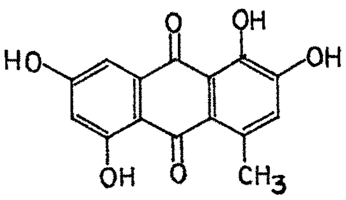
Wax. The wax makes the resin more thermoplastic and it is secreted along with the resin in the form of a white, thin filament. Shellac wax has been investigated by several workers[5-9]. Faurot-Bouchet and Michel[10] have studied the composition in detail by separating the hydrolyzed shellac wax into hydrocarbons (2%, composed of C_{27}-C_{31}), alcohols (77.2%, octacosanol is the major component) and acids (C_{28}-C_{34}), which were analyzed by GLC as methyl esters.

Colouring matter: From the aqueous washings of the powdered seed lac, Schmidt[11] isolated laccaic acid. Its structure was established by Venkataraman and co-workers[12], who were able to separate the earlier laccaic acid into two components, laccaic acid A and laccaic acid B, by chromatography using polycaprolactam powder and have assigned structures I and II, respectively, to these compounds.



The structure of laccaic acid A has been further confirmed by Schofield and co-workers[13].

Another colouring matter, named as erythrolaccin(III), has been isolated by Tschirch and Ludy[14]. Based on the spectral data, the structure for this compound has been simultaneously derived by two groups of workers[15,16]. Confirmation of the structure(III) has been obtained[17] by its unambiguous synthesis.



The resin. Tschirch and Farner[18] attempted, for the first time, to fractionate the resin. Using ether, they resolved the resin into two fractions, an ether-soluble portion called 'SOFT-RESIN' and an ether-insoluble portion called "HARD RESIN". Several ether solvents have been used for the fractionation of lac resin[19-22], the separations, however, were laborious and incomplete. Tschirch and Ludy[14] used absolute ethanol to dissolve only resin, but wax also is soluble to some extent. They caused the precipitation of the resin by addition of water, removal of which was not possible at lower temperatures(resin is thermolabile). Sukh Dev and co-workers[23] achieved a better separation by dissolving the resin in 78% aqueous ethanol (in which the wax is insoluble) and precipitating the "HARD RESIN" by adding ether. Removal of solvent from the mother liquor afforded "SOFT RESIN".

Several methods[19,21,22] have been described for the isolation of 'pure fraction' or 'homogeneous fraction'. However, these gave several fractions, obviously mixtures, containing resin components in different proportions.

Sukh Dev and co-workers[24] further purified the 'HARD RESIN' to a homogeneous 'PURE FRACTION'. This method involves dissolution of 'HARD RESIN' in dioxan and fractional precipitation by graded addition of benzene. By studying the TLC of the different fractions and grouping them into pools according to their purity and by carrying out further fractional precipitation of the most homogeneous pool, they could isolate a pure homogeneous fraction(~12%), which they termed as "PURE LAC RESIN". Homogeneity of this fraction was shown by its TLC in different solvent systems. Pure lac resin is a pale yellow, fine powder, m.p. 102-104°, $[\alpha]_D^{31.5}$ + 63.4(alcohol). Its UV spectrum shows λmax 225 nm ($E_{1\,cm}^{1\%}$ = 134) and absorptions at 3446, 1724 and 1631 cm^{-1} are seen in its IR spectrum,characteristic of hydroxyl, carbonyl and olefinic function respectively. It was shown (VPO method) to have a molecular weight of 2095±110.

LAC ACIDS

On alkali hydrolysis, the lac resin gives a number of hydroxy acids. These have been the matter of investigation for several years. Some of these acids are fatty acids and the others being sesquiterpenic.

Fatty acids: A brief survey of the chemistry of these acids is presented below:

1. Aleurttic acid(IVA). This was the first acid to be isolated from hydrolyzed lac. Endemann and Nagel[25-27] have reported some of their attempts to arrive at the structure of this acid. By degradative experiments,

Nagel[28] formulated aleuritic acid as 9,10,16-trihydroxypalmitic acid(IVA). This structure was further confirmed by its unambiguous synthesis by Baudert[30](natural <u>erythro</u> isomer, m.p. 100-101°). Mitter, Bose and Sen Gupta[31] synthesized another isomer of m.p. 125°, which was supposed to be the <u>threo</u>-isomer(IVB). This was confirmed by the interconversion of these isomers by Hunsdiecker[32].

2. <u>Butolic acid(V)</u>. Sen Gupta and Bose[33] reported the isolation of a new acid, m.p. 54-55°, from the total lac hydrolysate and named it butolic acid. The same acid was later isolated by Gunstone and co-workers[34] from the same source. Its structure was proved to be 6-hydroxytetradecanoic acid on the basis of its chemical degradation to n-octanol and adipic acid[34,35]. A synthesis of the <u>dl</u>-isomer confirmed its structure[34].

Butolic acid(V) was shown to have R-configuration by comparing the rotations of hydroxy acids of known configuration[35].

3. <u>Other minor fatty acids</u>. Christie <u>et al</u>[36] have reported the following aliphatic acids to constitute ~7% of total lac-hydrolysate: Normal long chain fatty acids, in which myristic and palmitic acids predominate; unsaturated fatty acids, having the same chain length; hydroxy acids of C_{14} and C_{16} chain length, and C_{14},C_{16} fatty acids with vicinal glycols at C_9 and C_{10}.

Sesquiterpenic acids:

1. Shellolic acid (VI). Harris and Nagel[26] were the first to isolate this acid from lac-hydrolysate as a colourless crystalline solid, m.p.200°. They showed it to be an unsaturated dihydroxy, dicarboxylic acid of molecular formula $C_{15}H_{20}O_6$. Isolation of this acid was later reported by several workers. But, its structure was proved much later by Yates and Field[37], by sound chemical degradation and spectral study.

Taking the above structure into consideration, Gunstone and co-workers[38] explained the reactions of shellolic acid. Experimental support for the relative stereochemistry of shellolic acid[37] came from the work of Cookson, Lewin and Morrison[39]. The structure was further confirmed[40] by the PMR study of dimethyl shellolate and some of its transformation products. Its absolute configuration was also proved to be in accord with its formulation by optical rotatory dispersion of certain derived ketones[39]. Final proof of the above conclusions was obtained from X-ray analysis[41] of the bromolactone derived from shellolic acid.

Cookson *et al*[39] have isolated an isomer of shellolic acid from lac hydrolysate and have named it as *epi-shellolic acid*. They have assigned structure VII to it (i.e. C_7 epimer of shellolic acid). Formation of dimethyl epishellolate[37] from dimethyl shellolate in MeOH-MeONa leads to the conclusion that they differ only in their configurations at C_7.

2. Jalaric acid(VIII). Kamath and Potnis[42] reported isolation of an aldehydic acid from Jalari seedlac, which they named as jalaric acid. Sukh Dev et al[35], for the first time, isolated this acid in a pure crystalline form (m.p. 178-180°) by partition chromatography. Silver oxide oxidation of this acid gave epishellolic acid. This along with the spectral characteristics defined jalaric acid as VIII, which also represents its absolute stereochemistry.

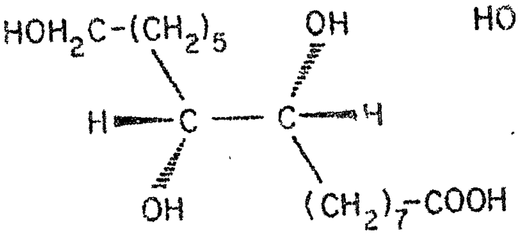
3. Laksholic (IX) and epilaksholic(X) acids. Sukh Dev et al[35] established the presence of two more acids in the lac hydrolysate. These were named as laksholic acid (IX) and epilaksholic acid(X). Structures to these compounds were assigned on the basis of their spectral characteristics and chemical correlation with shellolic and jalaric acids. Shellolic, epishellolic, laksholic and epilaksholic acids have also been shown to be the Cannizzaro reaction products of jalaric acid[35].

4. Laccishellolic(XI) and epilaccishellolic(XII) acids.

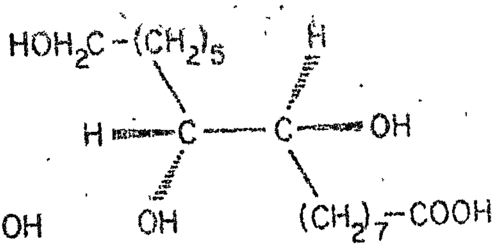
While working on the mode of linkage of constituent lac acids, Sukh Dev and co-workers[43] noticed the presence of two more new sesquiterpenic acids. They isolated these acids(as methyl esters) by the hydrolysis of seedlac and systematic column chromatography of the methyl esters. These acids have been termed as laccishellolic(XI) and epilaccishellolic (XII) acids.

Structures to these acids were assigned[43] on the basis of their close spectral behaviour with those of other terpenic acids of known structure and configuration. It was also shown[43] that these two acids are epimeric at C_7. Acids of this series are present to the extent of ~ 8% in the seedlac samples of different origin.

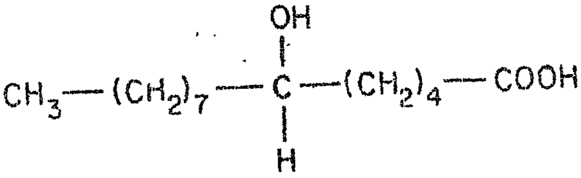
5. Laccijalaric acid(XIII). Sukh Dev and co-workers[43] isolated another new acid, named laccijalaric acid, from lac hydrolysate and based on its spectral data, they assigned structure XIII to this acid.



IV -A

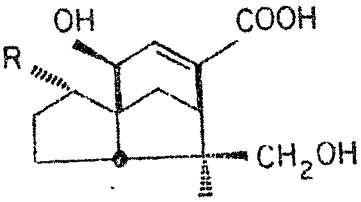


IV—B

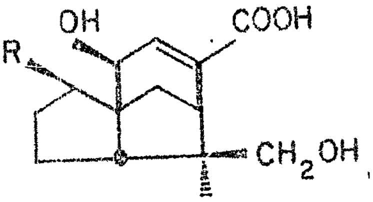


$$CH_3-(CH_2)_7-\underset{\displaystyle H}{\overset{\displaystyle OH}{C}}-(CH_2)_4-COOH$$

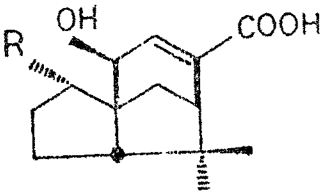
V



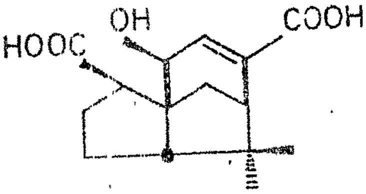
VII : R = COOH
VIII : R = CHO
X : R = CH_2OH



VI : R = COOH
IX : R = CH_2OH



XII : R=CO_2H
XIII: R=CHO



XI

FIG.1: KNOWN LAC ACIDS

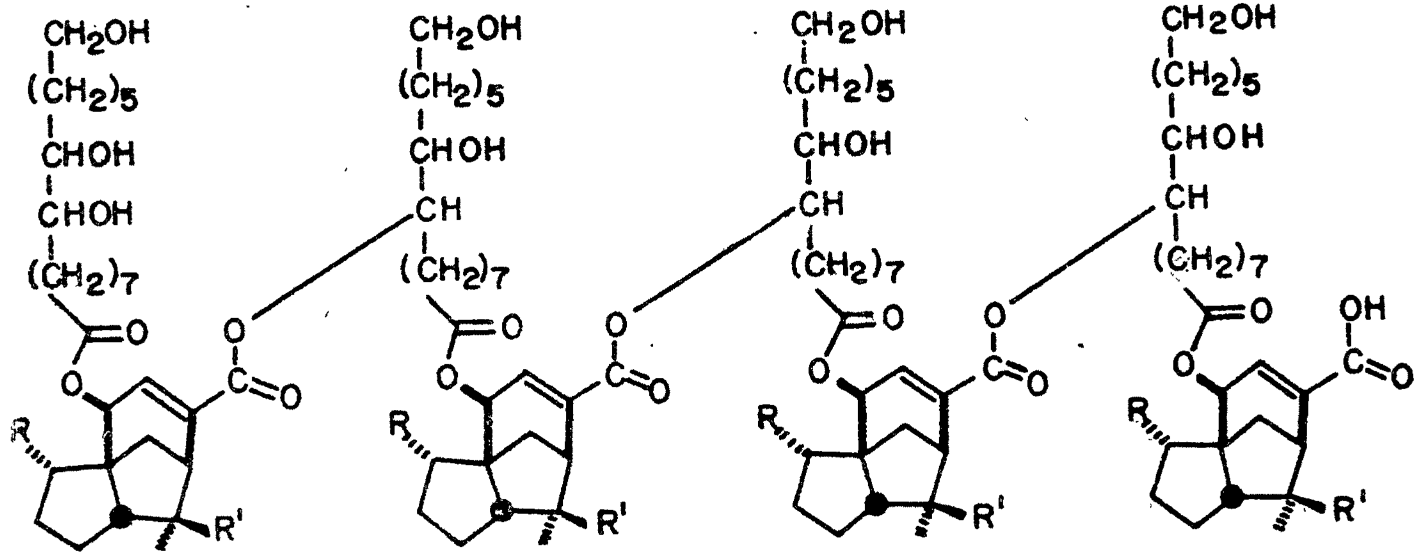
STRUCTURE OF LAC RESIN

From time to time, several tentative structures for "hard" and "soft" resins have been proposed[44-51]. As nothing was known about the structures of the constituent lac acids, except that of aleuritic acid, and the fractions used for determining the experimental data were non-homogeneous, the structures proposed are of no significance.

In order to establish the structure of lac resin, Sukh Dev and co-workers[52] used "pure lac resin". These workers[24] estimated aleuritic acid and the aldehydic acids in the "pure lac resin" to be 34.4% and 30.3%, respectively. However, total terpenic acids were estimated to be 67%. At this stage, it was clear that pure lac resin is a polyester of aleuritic and terpenic acids. These acids possess three and two hydroxyl groups, respectively, and hence, a knowledge of free and linked hydroxyls in the resin molecule was of prime importance in its structure determination.

Considering the formation of products of oxidation (CrO_3/acetone), hydrolysis and esterification of pure lac resin and their molar ratio, Sukh Dev and co-workers[52] could estimate the free and linked groups of different constituent lac acids as present in the lac molecule and assigned a tentative structure, wherein the ratio of terpenic acids to aleuritic acid is 2:1.

Later, oxidative degradation followed by GLC determination of the products showed[53] the resin to be based on equimolar proportions of jalaric acid(together with a small percentage of laccijalaric acid) and aleuritic acid and the structure XIV to pure lac resin was considered as the most plausible one. The presence of one laccijalaric unit, on average, out of every two molecules of lac resin has been suggested. Depending upon the age of the lac sample and the care taken during its collection, significant oxidation of the aldehyde function occurs. Thus, it is considered insignificant to establish the aldehyde content, though, in view of the PMR data one could state that out of four terpene acid units, two have aldehyde function.

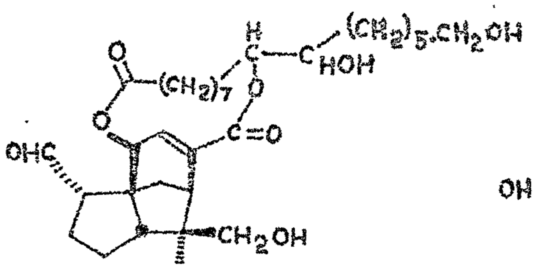


XIV : R = CHO/COOH; R' = CH_2OH/Me

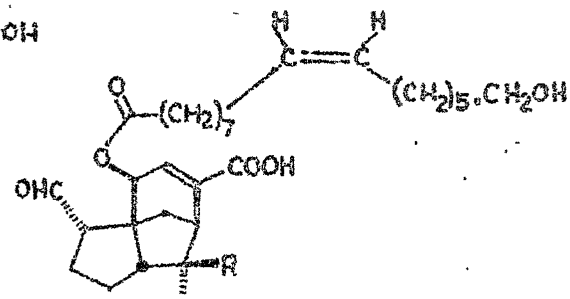
FIG.2: STRUCTURE OF PURE LAC RESIN

While working on the gross separation of 'Palas' seed lac into 'hard' and 'soft' resins, Sukh Dev and co-workers[23] isolated a neutral material to which they suggested[54] the structure XV. They also isolated[54] laccijalaric ester-I(XVI), jalaric ester-I(XVII), laccijalaric ester-II(XVIII), and jalaric ester-II(XIX) from 'soft' resin, which together are reported to constitute bulk of this resin. Jalaric ester-I(XVII) is stated[55] to be playing a key role in the elaboration of compounds XVI-XVIII, XIV and XV. Conceptually, jalaric ester-I(XVII), on epoxidation, should furnish XX, which, on hydrolysis, would give jalaric ester-II (XIX), or it can undergo intramolecular epoxide opening by the carboxyl function to generate XV, or it can lead to polyesters of type XIV, resulting from intermolecular oxirane ring cleavage.

The work carried out to test the above propositions forms, in part, the subject of the present investigation and is described in the following Chapter(s).

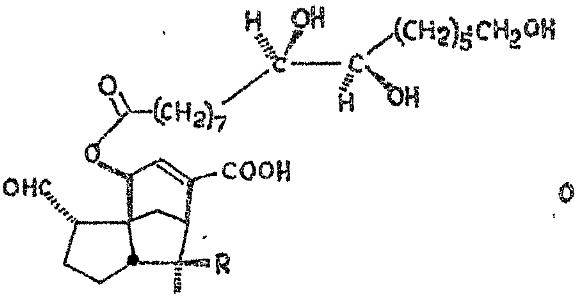


XV



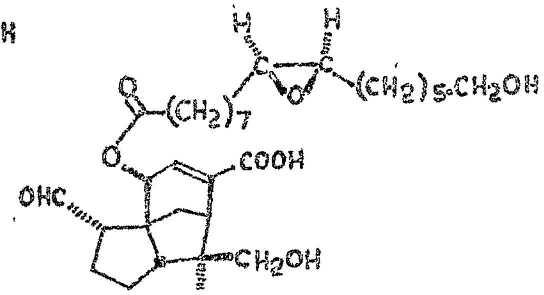
XVI : R = Me

XVII: R = CH_2OH



XVIII : R = Me

XIX : R = CH_2OH



XX

FIG. 3: POSSIBLE INTERMEDIATES TO NEUTRAL PART

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