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CHEMISTRY OF LAC RESIN—I

LAC ACIDS (Part 1): BUTOLIC, JALARIC AND LAKSHOLIC ACIDS*†

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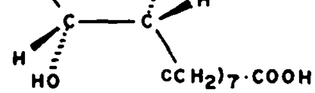
Abstract—Work leading to the structure elucidation of butolic and jalaric acids has been described. A new "lac acid" laksholic acid has been isolated and its structure established. It is suggested that the primary lac acid is jalaric acid and that shellolic and laksholic acids (and their epimers) arise from jalaric acid by a Cannizzaro reaction under conditions of alkaline hydrolysis.

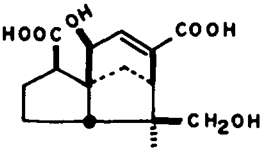
INTRODUCTION

LAC, a versatile resin, secreted by a tiny insect, *Laccifer lacca* Kerr (Family: *Lacciferidae* Cockerell) is the only commercial resin of animal origin and has considerable socio-economic significance for India.[1] The chemistry[2] of this material has been under investigation, for over a century and a half. Stick-lac,‡ the composition of which is dependent to some extent, on the nature of the host tree on which the insect feeds, consists of wax (6–7%), colouring matter (4–8%), "resin" (70–80%), insect debris, moisture and other extraneous matter.[2] Though the chemistry of wax[3] and colouring matter (erythrolaccin,[4] laccaic acids[5]) is quite well understood, considerable area in the chemistry of lac "resin" remained uncharted at the time present investigations were undertaken (1962).

It is well established[2] that lac resin consists of polyesters derived from certain hydroxy acids. A number of acids (lac acids) have been obtained by alkaline hydrolysis of lac. At the time the present investigations were undertaken, structures of only two of these, *viz.* aleuritic acid[6] (I) and shellolic acid[7] (II), had been established and practically nothing was known about the structures of other lac acids and of lac-resin. In this and the succeeding communications, we now report on the structures of



I



II

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[*] Communication No. 1333, National Chemical Laboratory, Poona.

[†] Abstracted from the Ph.D. theses of R. G. Khurana (Poona University, 1965) and M. S. Wadia (Poona University, 1967).

[‡] Raw lac, just collected by scraping from twigs is called *stick-lac*. This material after partial purification by crushing, sieving, water washing and sedimentation in water is known as *seedlac*. Further purification gives the *shellac* of commerce.[1]

remaining lac acids (butolic acid, jalaric acid), isolation and structure elucidation of new lac acids (laksholic acid, laccijalaric acid), purification of lac resin, identification and quantitative determination of acids constituting the "pure" lac resin and, determination of points of linkage of the constituent acids. As a result of this work, it has become almost clear that the lac resin constituting the backbone of lac is essentially derived from aleuritic acid, jalaric acid and lacci-jalaric acid. Esters based on other fatty acids (e.g. butolic acid) possibly serve only as plasticizers.

*Butolic acid.** Sen Gupta and Bose[8] isolated from shellac hydrolysate a fatty acid which was named butolic acid after the lac host *Butea monosperma*. This acid which was obtained by an elaborate procedure in ~2% yield was tentatively assigned the structure of 6-hydroxypentadecanoic acid.

In order to finalize the structure of this acid and also to obtain more material, we have isolated the same acid (Table 1) from shellac by a simple procedure. We now find that butolic acid is correctly represented as 6-hydroxytetradecanoic acid, a conclusion also independently reached by Christie *et al.*[9] by different methods.

TABLE 1. PROPERTIES OF BUTOLIC ACID

	Acid		Me ester		Derived keto acid (CrO_3)
	m.p.	$[\alpha]_D$	m.p.	$[\alpha]_D$	m.p.
Present work	58–59°	−1·5°	26–27°	−2·2°	70–71°
Sen Gupta and Bose[8]	54–55°	—	27–28°	—	69·5–70·5°

Butolic acid is clearly a monohydroxy (secondary) aliphatic carboxylic acid (IR: OH 3230 cm^{-1}; COOH 2680, 1708 cm^{-1}. PMR of Me ester: $C\underline{H}_3$—CH_2, 3H, deformed triplet, 54 c/s, $J = 5$ c/s; —$CH_2 \cdot C\underline{H}OH \cdot CH_2$—, 1H, essentially a doublet of superimposed triplets centred at 134 c/s, $J = \sim 7$ c/s). On oxidation with Jones reagent,[10] it yielded a keto acid, the methyl ester of which (IR: C=O 1745, 1720 cm^{-1}) on treatment with perbenzoic acid in the presence of *p*-toluenesulphonic acid[11] yielded a diester (chiefly one component by GLC; IR: C=O 1754 cm^{-1}). This on base hydrolysis furnished n-octanol and adipic acid. This degradation of butolic acid leads unequivocally to its formulation as 6-hydroxytetradecanoic acid.

It would appear from published data[12] on hydroxy long-chain fatty acids that all (−)-rotatory acids have R-configuration irrespective of the length of the chain and position of the OH group. On this basis, levorotatory butolic acid is tentatively assigned the R-chirality for its asymmetric centre. (±)-Butolic acid has been synthesized.[9]

Jalaric acid.† Kamath and Potnis[13] describe the isolation, in 50% yield, of an aldehydic acid (m.p. 85–87°; 2,4-dinitrophenylhydrazone, m.p. 231–232°) by the alkali hydrolysis of *jalari* seedlac (host tree: *Shorea talura*, Roxb.) in presence of

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* An advance communication appeared in *Tetrahedron Letters* 1537 (1964).

† Preliminary communication: *Tetrahedron Letters* 513 (1963).

sodium sulphite. The same product was obtained later[14] from *kusmi* seedlac [host tree: *Schleichera oleosa* (Lour.) Oken], though in much lower yields.

The earlier workers[13] assigned the molecular formula $C_{15}H_{22}O_5$ to this acid and adduced some evidence to show that it is a monobasic dihydroxy acid having an aldehyde function.

In order to investigate the structure of this acid further, we attempted its isolation from commercial shellac* by following the procedures, reported earlier for seedlacs,[13, 14] but with little success. Later, by following a modified procedure,[15] we succeeded in isolating from shellac hydrolysate a product which furnished a 2,4-DNP (m.p. 234–235°), though in low yield. Paper chromatography† of this material showed it to consist of at least four components (R_f, 0·43, 0·54, 0·71 and 0·82). Of these, the constituent with R_f 0·71 could be attributed to an acid with an aldehyde or keto function as it could be detected by spraying the paper with 2,4-dinitrophenylhydrazine reagent; the component with R_f 0·82 corresponded to aleuritic acid. At this stage, a sample of jalaric acid prepared from *jalari* seedlac according to the procedure of Kamath and Potnis[13] could be procured.‡ Paper chromatography of this material, also revealed three spots (R_f 0·43, 0·54 and 0·71). After several unsuccessful attempts at the purification of these products, we succeeded in evolving an isolation procedure, which gave a product from which the component with R_f 0·71 could be obtained crystalline (m.p. 178–180°; 2,4-DNP, m.p. 241–242°); the most crucial feature[18] of this method (*vide* Experimental) is the saponification period,§ which was found to be 5 hr (20–22°). The name *jalaric acid*‖ has been retained for this compound. It is obvious from the foregoing that the earlier workers had only grossly impure samples of this acid on hand.

Structure. Jalaric acid analyses for $C_{15}H_{20}O_5$ and from its neutralization equivalent and mol. wt. is clearly monobasic. It shows the following structural features: (IR :OH 3443, 3433, 1134, 1106, 1068 and 1031 cm^{-1}), CHO (2740, 1704 cm^{-1}) and αβ-unsaturated carboxyl (UV: λ_{max} 220 mμ, ε 6200; IR: COOH 1684 cm^{-1}; C=C 1631 and 795 cm^{-1}, possibly trisubstituted).

In accordance with its formulation as an aldehydic acid, jalaric acid underwent smooth oxidation at room temp with alkaline Ag_2O to yield a mixture of two dicarboxylic acids, which could be separated as Me esters by chromatography. One of these acids (~25%; m.p. 205–207°; dimethyl ester, m.p. 150–152°) was soon identified as shellolic acid (by comparison with an authentic sample prepared by a known

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* Blond, dewaxed shellac: Angelo Bros., Calcutta, India.

† A number of solvent systems for the paper chromatography of lac acids have been described.[16] Based on the work of Hartley and Lawson[17] on the paper chromatography of organic acids, we developed the system ammonium carbonate buffer, n-BuOH and EtOH (30:35:35), which was found to be most effective for our purpose (also see: Part III of present series).

‡ We are indebted to Prof. S. V. Puntambekar for this sample.

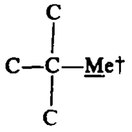
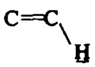
§ From an inspection of plot of sap. value against time, it was found that saponification of shellac with 1N KOH (aq.) is essentially complete after 5 hr (25 ± 1°).

‖ In the preliminary communication, the name jalaric acid-A has been used. This name was adopted because spraying of a paper-chromatogram of total lac acids with 2,4-dinitrophenylhydrazine reagent invariably showed the presence of at least two aldehydic (or ketonic) acids (R_f 0·71, 0·81). It was considered that these compounds may be epimeric at C_7 (cf. shellolic and *epi*shellolic acid, see text) and hence the suffix A for one of them. From the material containing mostly compound(s) of R_f 0·81, we have so far been able to isolate only one pure component which we find is not epimeric with jalaric acid (see: laccijalaric acid, Part II of the present series).

procedure[8]), which has been formulated[7] as II. Since in jalaric acid, the only carboxyl function is αβ-unsaturated, the aldehyde group must be located at C_7, which carries the saturated COOH group in shellolic acid.

The major product (~75%; m.p. 245–248°; dimethyl ester, m.p. 151–153°), like shellolic acid, analyses for $C_{15}H_{20}O_6$ and shows spectral characteristics for (IR :OH 3448, 3367, 1135, 1111, 1075 and 1028 cm^{-1}), COOH (2667, 1689 and 938 cm^{-1}) and αβ-unsaturated carboxyl (UV: λ_{max} 218 mμ, ε 9500; IR: C=O 1678 cm^{-1}; C=C 1610 cm^{-1}) and hence, was considered to be closely related to shellolic acid.* A comparison (Table 2) of PMR spectra of dimethyl shellolate and of the ester from the new acid (*epi*shellolate), fully confirms the above contention, and further suggests that the two acids may differ at the sterochemistry at C_7, so as to account for the difference in the chemical shifts of C$\underline{H}$OH. This will also explain the formation of two acids on Ag_2O oxidation of jalaric acid, as epimerization of jalaric acid at the centre α to the aldehyde function, under the alkaline conditions of silver oxide oxidation, is understandable. Thus, the major product of Ag_2O oxidation of jalaric acid must be formulated as III (*epi*shellolic acid*).

TABLE 2. PMR SPECTRAL CHARACTERISTICS OF DIMETHYL SHELLOLATE AND RELATED COMPOUNDS

Compound	Signal (c/s)* assignment				
	 $C{-}C(C)(C){-}\underline{Me}$†	COO$\underline{Me}$†	C$\underline{H}$OH	 $C{=}C{\diagdown}H$	C$\underline{H_2}$OH (C_{11})
Dimethyl shellolate	72	225 227·5	271 (d, *J* = 2·5)	397·5 (d, *J* = 2·5)	199 (bq, *J* = 11·5)
Dimethyl *epi*shellolate	72	221 227	289 (d, *J* = 2·5)	402 (d, *J* = 2·5)	197 (bq, *J* = 11·5)
Methyl laksholate	71	225	281 (d, *J* = 2·5)	396 (d, *J* = 2·5)	197 (bq, *J* = 12)
Methyl *epi*laksholate	68	224	281·5 (bd, *J* = 2·5)	397 (d, *J* = 2·5)	196 (vbs)

* In case of multiplets position given is that at the centre; d = doublet, bd = broadened doublet, bq = broadened quartet of AB type, vbs = broad singlet; *J* in c/s.

† All 3H singlets.

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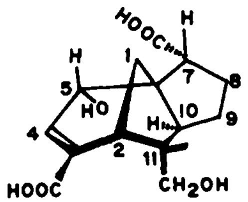
* An acid, m.p. 238° and considered to be isomeric with shellolic acid has been described by Kirk *et al.*[19]

* At this stage of our work, Cookson *et al.*[1c] described isolation and chemical characterization of *epi*shellolic acid (m.p. 232–233°). In a later publication[1d] its PMR spectrum was discussed. Our preliminary communication on jalaric acid appeared soon after this.



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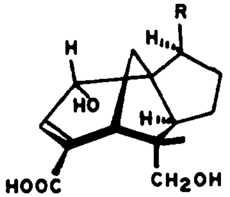


III, R = COOH

IV, R = CHO

V, R = $COCH_3$

Oxidation of jalaric acid with peracetic acid, conditions under which epimerization at α to a carbonyl function is considered unlikely, gave only *epi*shellolic acid (III). Hence, jalaric acid must be represented by IV. Since the absolute configuration of (+)-Shellolic (II) acid has been deduced, IV should also represent the absolute stereochemistry of (+)-jalaric acid.

At the time of our preliminary communication, PMR spectrum of jalaric acid could not be investigated because of its solubility characteristics and its failure to give a normal Me ester with CH_2N_2 (*vide infra*). We have now been able to study the PMR spectrum of jalaric acid in DMSO-d_6. The spectrum which is shown in Fig. 1 fully

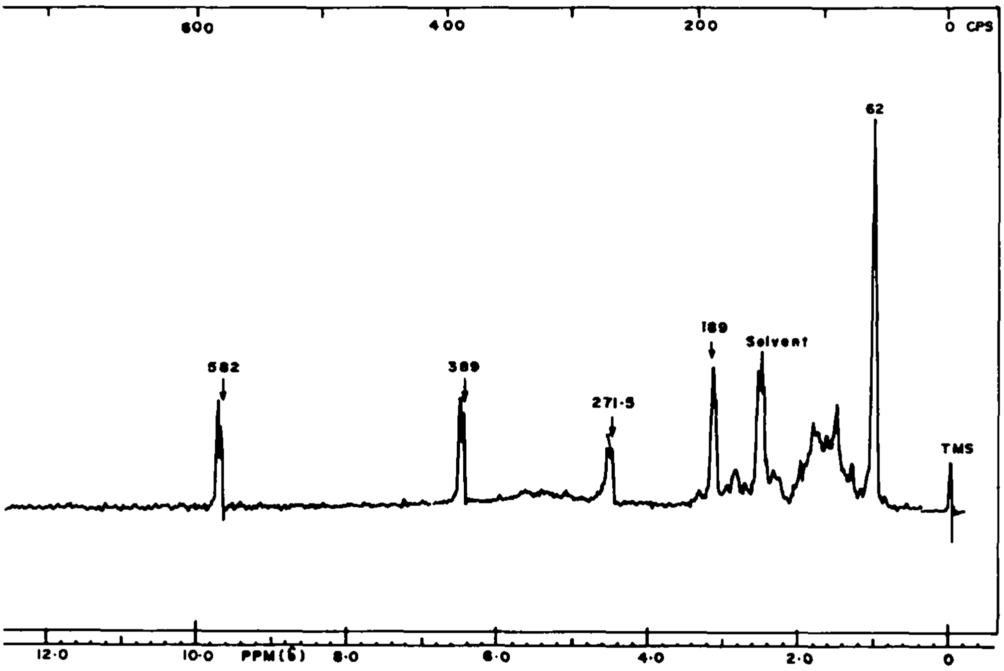
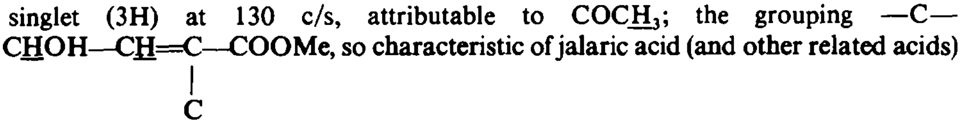


FIG. 1 PMR spectrum of jalaric acid (in DMSO-d_6).

supports structure IV: quaternary Me (3H, s at 62 c/s), $-C-C\underline{H_2}OH$ (2H, merging central peaks of an AB qu, centred at 189 c/s), $C\underline{H}OH$ (1H, d at 271·5 c/s, $J=2\cdot 3$ c/s), $-C{=}C\underline{H}$ (1H, d at 389 c/s, $J=2\cdot 3$ c/s), $-CH-C\underline{H}O$ (1H, d at 582 c/s, $J=2\cdot 0$ c/s).

Reaction of CH_2N_2 with jalaric acid gave a rather complex product, from which the major component could be obtained pure (m.p. 106–108°) by chromatography. As the IR spectrum of this compound showed no absorption at ~2700 cm^{-1}, it was suspected that the aldehyde function had also reacted.[20] This was confirmed by the fact that after treatment with alkaline silver oxide, followed by esterification, the compound was recovered unchanged. Its PMR spectrum, besides showing the quaternary Me (70 c/s) and $COO\underline{Me}$ (225 c/s) 3H singlets, displays another sharp singlet (3H) at 130 c/s, attributable to $COC\underline{H_3}$; the grouping  $-C-C\underline{H}OH-C\underline{H}{=}\underset{\substack{|\\ C}}{C}-COOMe$, so characteristic of jalaric acid (and other related acids) remained unchanged: doublets centred at 284 (1H, $J = 3$ c/s) and 399 (1H, $J = 3$ c/s). In view of above data and the known reaction[20] of aldehydes to give with CH_2N_2, under certain conditions, a methyl ketone, this product of reaction of jalaric acid with CH_2N_2 is formulated as V.

The three spots obtained in the paper chromatography of crude jalaric acid can now be identified as due to *epi*shellolic acid (R_f 0·43), shellolic acid (R_f 0·54) and jalaric acid (R_f 0·71).

Laksholic acid and epi*laksholic acid*

In connection with our general programme on the chemistry of lac resin, preparation of shellolic acid on a rather larger scale was required. Of the several reported procedures[7b, 7c, 19, 21–24] that described by Cookson *et al.*[7c] was adopted. Thin layer chromatography (TLC) of the crude methyl shellolate, thus obtained, always showed two more spots (R_{shellol}.[*] 0·62 and 0·31) besides those of dimethyl shellolate (R_{shellol}. 1) and dimethyl *epi*shellolate (R_{shellol}. 0·83). By repeated chromatography, it was possible to get pure esters corresponding to these two spots. Base hydrolysis of these esters yielded crystalline compounds of m.p. 181–183° (ester: R_{shellol}. 0·62 and 201–203° (ester: R_{shellol}. 0·31).

Laksholic acid. The acid of m.p. 181–183°, which we have termed laksholic acid,[†] analyses for $C_{15}H_{22}O_5$ and titrates for a monobasic acid. It is clearly a hydroxy (IR :OH 3440, 3220, 1098, 1080 and 1040 cm^{-1}), αβ-unsaturated carboxylic acid [IR: C=O 1680 cm^{-1}; C=C 1650 cm^{-1}; Me ester, λ_{max} 230 mμ, ε 6600; IR ($CHCl_3$): C=O 1700 cm^{-1}]. The presence of an αβ-unsaturated carboxylic function, at once, suggested that the new acid may belong to the shellolic acid group of lac acids. This conclusion is fully corroborated by the PMR spectrum of its Me ester, which displays two 1H doublets centred at 281 and 396 c/s and assignable (Table 1) to the grouping VI, so very characteristic of this group of lac acids.

Since the new acid is monocarboxylic, it became obvious from its elemental analysis and what has been stated earlier, that the difference between shellolic

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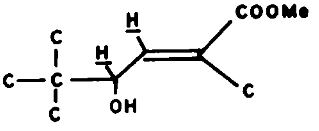
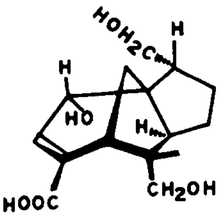
[*] R_{shellol}. $=R_f$ of compound divided by that of dimethyl shellolate; solvent system: 7:4:4 mixture (v/v) of toluene, ethyl acetate and acetone.

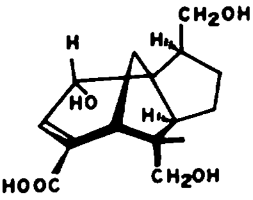
[†] From the Sanskrit word *laksha*, the root of the term lac.



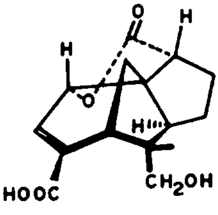
VI



VII



VIII



IX

(*epi*shellolic acid) and the new acid may as well be just the replacement of the C_7—COOH by C_7—CH_2OH. This is clearly supported by the PMR spectrum of its Me ester, which besides displaying the 2H quartet due to C_{11}—CH_2OH (Table 2), shows another set of 2H signals located between 220–230 c/s (illresolved and overlapped by the 225 c/s $COO\underline{Me}$ singlet). These data, as well as the structure of jalaric acid, discussed earlier, suggested that the new acid may be VII or VIII. Furthermore, it was suspected from its placement on the TLC, that if the two new acids represented the two trihydroxy acids (VII, VIII) corresponding to shellolic and *epi*shellolic acids (II, III), then the acid of m.p. 181–183° is in all probability VII. This has been unequivocally confirmed by its partial synthesis from shellolic acid (II). Treatment of shellolic acid with NaOAc and acetic anhydride followed by heating with water yielded the known[7a] γ-lactone (IX), which on reduction with $NaBH_4$ in diglyme[25] yielded a product, identified (m.p., mixed m.p., IR, TLC) as laksholic acid.

Epi*laksholic acid*. The methyl ester (TLC, R_{shellol} 0·31) could be isolated in only small yield, but from what has been discussed above and from its IR spectrum ($CHCl_3$; OH 3450, 1140, 1050 cm^{-1}; C=O 1700 cm^{-1}; C=C 1630 cm^{-1}), was suspected to be the Me ester of VIII. This was readily confirmed by $NaBH_4$ reduction of jalaric acid (IV) to give crystalline (m.p. 202–203°) VIII, the Me ester of which was completely identical (TLC, IR) with the product isolated from shellac hydrolysate. This acid has been termed *epi*laksholic acid.

The PMR spectrum of its Me ester is fully consistent with its structure (Table 2; the C_7—$C\underline{H}_2OH$ occurs as a doublet centred at 217 c/s, $J = 7$ c/s).

Action of alkali on jalaric acid. Kamath[13b] was the first to suggest that the acids isolated under the usual conditions of saponification need not necessarily be the primary products of hydrolysis, and, this contention led to his work on jalaric acid. Of the various secondary reactions accompanying alkali saponification he favoured "dehydrogenation", though aldol condensation and Cannizzaro reaction were also considered to contribute to some extent.[26] It is interesting to note that all the reported procedures[7b, 7c, 19, 21–24] for the isolation of shellolic acid, call for extended alkali hydrolysis.

Our results, described above, strongly suggested that shellolic acid (II) *epi*shellolic acid (III) together with their counterparts, laksholic (VII) and *epi*laksholic acids

(VIII), constitute Cannizzaro (and epimerization) products of jalaric acid. Exposure of jalaric acid to alkali (20%, 10 days, room temp.) yielded a product consisting almost entirely of the above four acids; a rough approximation* (from yields and TLC data) shows that these acids are formed in the yield (weight) ratios of 2·2 (shellolic) : 1·4 (*epi*shellolic) : 1·2 (laksholic) : 1 (*epi*laksholic). Though, Cannizzaro reaction[27] is ordinarily restricted to aldehydes that are devoid of an α-hydrogen, other aldehydes may also undergo this reaction, if the competing aldol-type condensation remains suppressed (e.g. on steric grounds[28]) and a few such cases are on record.[28, 29]

It would appear from the results disclosed in the present communication, that, of the terpenic acids of lac origin, described so far, jalaric acid (IV) may in fact be the primary acid.

EXPERIMENTAL

All m.p. and b.p. are uncorrected; m.p. taken on kofler hot stage. Pet. ether refers to the fraction b.p. 40–60°. All optical rotations were measured in EtOH, unless stated to the contrary.

UV spectra were taken on a Perkin-Elmer spectrophotometer, model 350, in 95% EtOH. IR spectra were recorded as smears (liquids) or Nujol mulls (solids), unless stated otherwise, on a model 221, Perkin-Elmer infrared spectrophotometer. All PMR spectra were taken on 10% solns in $CDCl_3$ (unless otherwise stated) with TMS as the internal standard on a Varian Associates A-60 spectrometer; signals are recorded in c/s relative to TMS as zero.

Alumina used for chromatography was made neutral by the HNO_3 method[30] and graded according to Brockmann.[31] TLC was carried out on silica gel (containing 15% plaster of Paris) layers, 0·3 mm thick, using the equipment and procedure already described;[32] conc H_2SO_4 or a soln of chlorosulphonic acid in AcOH (1 : 2) was used for the visualization of the spots. Paper chromatography was carried out by the ascending technique (solvent rise: 14 cm), using Whatman No. 1 paper and employing a solvent system consisting of EtOH (35 parts), n-BuOH (35 parts) and ammonia buffer (30 parts; 7·2 g of ammonium carbonate in 95 ml water and 7·5 ml NH_4OH aq of sp. gr. = 0·88); developed chromatograms were sprayed with a soln of bromophenol blue (50 mg in 100 ml water, containing 200 mg of citric acid);[17] for detection of ketonic or aldehyde compounds the paper was sprayed with a soln of 2,4-dinitrophenylhydrazine (0·4 g) in 2N HCl (100 ml).

GLC was carried out on "Aerograph" model A-350-B using a 150 cm × 5 mm column, packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh), using H_2 as the carrier gas.

Shellac used in the present work was commercial grade blond, dewaxed shellac, from Angelo Bros., Calcutta, India.

Butolic acid

Isolation. Shellac (100 g) was hydrolysed with 40Π NaOHaq (100 ml) at room temp (~30°) for 10 days, then acidified with HClaq (150 ml, 1 : 1) and extracted with EtOAc (500 ml × 2). The extract was concentrated to half the volume and dispersed on celite (200 g), dried and soxhleted with pet. ether (500 ml, 100 hr) to yield crude butolic acid fraction (14·0 g). This (4·0 g) after esterification (CH_2N_2) was fractionally distilled. The fraction b.p. 50–150°/0·4 mm (2·2 g) after saponification gave pure *butolic acid* (1·7 g) m.p. 58–59°; $[\alpha]_D^{36}$ −1·3 ($CHCl_3$; *c*, 10%). TNM test: negative. (Found: C, 69·13; H, 11·71. $C_{14}H_{28}O_3$ requires: C, 68·81; H, 11.55%).

Methyl butolate. (CH_2N_2 method): GLC, TLC pure m.p. 26–27°, b.p. 120–122°/1 mm, n_D^{30} 1·4488, $[\alpha]_D^{36}$ −2·2 ($CHCl_3$; *c*, 10%). (Found: C, 69·43; H, 11·3. $C_{15}H_{30}O_3$ requires: C, 69·72; H, 11·7%).

Jones oxidation of butolic acid. Jones reagent [3 ml; prepared from CrO_3 (0·75 g) in 10·8N H_2SO_4 (3 ml)] was added gradually at 30–35°, to a stirred soln of butolic acid (0·3 g) in acetone (5 ml), till the orange colour persisted. After stirring for 3 hr at room temp (~28°) the product was diluted with water (10 ml) and extracted with ether (3 × 30 ml). The ether soln was washed with water, dried (Na_2SO_4) and freed from solvent to yield crystals (EtOH; 0·25 g). m.p. 70–71°. (Found: C, 69·15, H, 10·63. $C_{14}H_{26}O_3$ requires: C, 69·38; H, 10·87%).

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* Under a variety of GLC conditions, esters from these acids underwent decomposition.

Methyl ester (CH_2N_2 method), m.p. 23–24°; b.p. 110–112°/1 mm; n_D^{30} 1·4419; PMR spectrum: $\underline{CH_3}—CH_2$ (53 c/s, 3H, t); $\underline{CH_2}—\underset{\underset{\displaystyle O}{\|}}{C}$ (137 c/s, 6H, m); $COOC\underline{H}_3$, (217 c/s, 3H, s).

Baeyer-Villiger oxidation of the above keto ester. A soln of the above keto ester (0·23 g) in $CHCl_3$ was added to a freshly prepared perbenzoic acid soln in $CHCl_3$ (34 ml, 0·0094 g/ml) in presence of *p*-toluenesulphonic acid (50 mg). Titration of aliquots against 0·132N $Na_2S_2O_3$ indicated required consumption (1·13 equivs) of perbenzoic acid at the end of 107 hr. After this time the reaction mixture was diluted with $CHCl_3$ (40 ml), washed with sat $NaHCO_3$aq, dried (Na_2SO_4) and freed of solvent to afford the diester (0·15 g), b.p. 100–135°/2 mm.

The diester (0·13 g) after hydrolysis (5 hr, 100°) with 10% KOHaq (5·0 ml) provided after usual work-up an acidic product (0·071 g) which furnished crystals (benzene–AcOH) m.p. 149–152° identified as adipic acid (m.p., mixed m.p., IR).

The neutral product obtained as a pleasant smelling liquid (0·031 g) b.p. 195–197°; d_4^{30} 1·4223 was identified as n-octanol (GLC, IR).

Jalaric acid

Isolation. Ice-cold 1·75N NaOHaq (1500 ml) was added to shellac (300 g). After the shellac had dissolved the reaction mixture was kept with occasional shaking for 5 hr in a bath maintained at 20–22°. The soln was acidified with ice-cold H_3PO_4aq (1 : 1, 300 ml), when a gum separated. The aqueous portion was filtered off (using fluted filter paper) and the residual gummy material was thoroughly shaken with water (450, 450 and 300 ml). The washings after filtration, together with the earlier aqueous filtrate were extracted with EtOAc (1200, 450 and 450 ml) and the solvent layer washed with water (3 × 300 ml), dried (Na_2SO_4), filtered and concentrated (to 150 ml) under *vacuo*. On keeping the concentrate at room temp a crystalline product (7·5 g) m.p. 168–172° separated. Evaporation of the mother liquors afforded a resinous mass (12·39 g).

Paper chromatography of the solid m.p. 168–172° revealed essentially a single spot (R_f 0·71). By contrast the mother liquors showed the presence of four acids (R_f 0·43, 0·54, 0·71 and 0·82) identified as *epi*shellolic, shellolic, jalaric and aleuritic acids respectively.

The acid (m.p. 168–172°, 0·2 g) dissolved in a mixture of $CHCl_3$ and n-BuOH (5 : 1, 24 ml) was chromatographed on Malinckrodt's silicic acid (40 g, 4·4 × 17 cms) to which water (24 ml) had been added:

Frac. 1	$CHCl_3$	170 ml	Negligible compound.
Frac. 2	$CHCl_3$ + 1% n-BuOH	190 ml	
Frac. 3	$CHCl_3$ + 5% n-BuOH	190 ml	
Frac. 4	$CHCl_3$ + 10% n-BuOH	190 ml	
Frac. 5	$CHCl_3$ + 10% n-BuOH	50 ml	0·116 g
Frac. 6	$CHCl_3$ + 20% n-BuOH	140 ml	
Frac. 7	$CHCl_3$ + 20% n-BuOH	50 ml	Negligible compound.
Frac. 8	$CHCl_3$ + 30% n-BuOH	140 ml	0·045 g mixture of shellolic and *epi*shellolic acids.

Fraction 5 and 6 afforded crystals (MeCN) m.p. 178–180°, $[\alpha]_D^{26}$ +36·8 (*c*, 0·7%). (Found: C, 64·4, 64·9; H, 7·3, 7·2. $C_{15}H_{22}O_5$ requires: C, 64·3; H, 7·2%). Neut. equiv. (Found: 266; requires: 280).

2,4-Dinitrophenylhydrazone (H_2SO_4 method). Yellow powder (EtOH) m.p. 241–242°; λ_{max} 335 mμ (ε 22,400). (Found: C, 54·58; H, 5·97; N, 11·6. $C_{21}H_{24}O_8N_4$ requires: C, 54·78; H, 5·25; N, 12·1%).

Oxidation of jalaric acid with silver oxide. 10% NaOHaq (4·75 ml) was added to $AgNO_3$ (0·534 g) and the mixture stirred at room temp for 45 min. After addition of dioxan (4·75 ml), jalaric acid (500 mg, m.p. 168–172°) was added in portions during 45 min with stirring at the same temp. After addition was complete the mixture was stirred for another 1 hr and the precipitated Ag filtered off, and thoroughly washed with water. The filtrate and the washings were combined, acidified with 1N HCl and extracted with EtOAc. Removal of solvent after washing and drying (Na_2SO_4) yielded a semisolid mass (380 mg, 73·1%), which furnished prisms (EtOAc) m.p. 245–248°, $[\alpha]_D^{32}$ +74·6 (*c*, 0·7%), λ_{max} 220 mμ (ε 6200). IR spectrum: OH 3443, 3333 cm^{-1}; COOH 2740, 1704, 1684 cm^{-1}; C=C 1631, 795 cm^{-1}. (Found: C 60·6; H, 6·82. $C_{15}H_{20}O_6$ requires: C, 60·81; H, 6·75%).

In another experiment, the semisolid mass obtained by oxidation (and which shows two spots on paper chromatography) was esterified (CH_2N_2) and the methyl esters (370 mg) chromatographed over Al_2O_3/II (10 g. 12 × 0·5 cms): •

Frac. 1	Benzene	100 ml	—
Frac. 2	Benzene + 1% MeOH	50 ml	0·23 g
Frac. 3	Benzene + 1% MeOH	50 ml	0·036 g
Frac. 4	Benzene + 1% MeOH	100 ml	0·025 g
Frac. 5	Benzene + 5% MeOH	50 ml	0·026 g

Frac. 2 gave prisms (benzene; 0·115 g) m.p. 140–149° which after recrystallization (EtOAc) had m.p. 151–153° (m.p. was undepressed on admixture with a sample of methyl ester prepared from the above acid of m.p. 245–248°), $[\alpha]_D^{32}$ + 51·6 (*c*, 0·9%). (Found: C, 63·23; H, 7·6. $C_{17}H_{24}O_6$ requires: C, 63·0; H, 7·5%). This was characterized as *dimethyl* epi*shellolate.*

From the mother liquors a compound m.p. 150–152° $[\alpha]_D^{32}$ +51·6 (*c*, 0·8%) could be isolated and identified as *dimethyl shellolate* by comparison (IR, TLC) with an authentic sample prepared by a known procedure.[7c]

Frac. 3 yielded prisms (benzene) m.p. 148–151°, identified as dimethyl *epi*shellolate (mixed m.p., TLC, IR).

A similar oxidation of pure jalaric acid (20 mg) gave an acid mixture whose paper chromatography showed the presence of the same two acids (shellolic and *epi*shellolic acids).

Oxidation of jalaric acid with peracetic acid. Peracetic acid [prepared by adding H_2O_2 (2·3 ml, 30%) to AcOH (7·0 ml)] was added with shaking to jalaric acid (200 mg, M.P. 168–172°). After warming for 20 min at waterbath temp the material was kept overnight. After addition of water (3 ml), the product was freed from AcOH under *vacuo* to yield a resinous mass (180 mg, 85·11%). Shellolic acid could not be detected in either the paper chromatography of the acids or the TLC of the esters.

Chromatography of the esters (300 mg) on alumina/II (6 g, 7 × 0·5 cms) furnished in the early benzene + 1% MeOH fraction the major product which crystallized from benzene to afford prisms m.p. 151–153° identified (TLC, mixed m.p., IR) as dimethyl *epi*shellolate. None of the chromatographed fractions contained dimethyl shellolate as shown by TLC.

Identical results were obtained by an oxidation of the pure jalaric acid (10 mg) though in this case dimethyl *epi*shellolate was not obtained in crystalline form.

Reaction of jalaric acid with diazomethane. Jalaric acid (5 g, m.p. 168–172°) was esterified using excess diazomethane. As the product obtained after usual work-up could not be induced to crystallize it was chromatographed on Al_2O_3/II (125g, 17 × 2·7 cms).

Frac. 1	Benzene	500 ml	0·027 g	
Frac. 2	Benzene + 1% MeOH	200 × 3	2·95 g	Mixture of 4 compds.
Frac. 3	Benzene + 1% MeOH	200 × 3	1·47 g	
Frac. 4	Benzene + 1% MeOH	200 × 3	1·3 g	Mixture of more polar compds.

Fraction 3 which was essentially pure ($R_{shellol}$ 0·66) yielded prisms (benzene, 0·29 g) m.p. 106–108°. IR spectrum: OH 3436, 3378 cm^{-1}; C=O 1698 cm^{-1}; COOMe 1684 cm^{-1}; C=C 1626, 806, 785 cm^{-1}. (Found: C, 66·6; H, 7·6. $C_{17}H_{24}O_5$ requires: C, 66·2; H, 7·8%).

Laksholic acid and epi*laksholic acid*

Isolation. Shellac (2 kg) dissolved in 20% NaOH aq (2 l.) was kept at room temp (28°) for 11 days. The mixture was diluted with water (600 ml) and the precipitated sodium aleuritate was removed by filtration. Saturated 20% $ZnSO_4$ aq (2 l.) was added to the stirred soln till there was no further precipitation. After the precipitated Zn salts (890 g) were filtered off, the filtrate was acidified with 6N H_2SO_4. The acidified mass was then continuously extracted with ether (2 l.) for 50 hr. The solvent was distilled off in portions to yield three different crops which are gummy in nature.

Further continuous extraction of the acidified aq. material, with ether (2 l., 50 hr) yielded the fourth crop of gummy material. Table below depicts the paper chromatographic behaviour of the various crops.

Crop I	16·6 g
Crop II	17·8 g
Crop III	25·7 g
Crop IV	15·8 g

All these on paper chromatography showed 3 spots: R_f 0·43, 0·54 and 0·71. Response to 2,4-DNP spray reagent was negative.

TLC of the derived Me esters from each fraction showed four spots of varying intensity: $R_{\text{shellol.}}$ 1·0, 0·83, 0·62 and 0·31.

As these crops were similar, they were combined and esterified. The resulting esters (36·5 g were chromatographed on Al_2O_3/II (800 g, 22 × 4·5 cms).

Frac. 1	Toluene	2·0 l.	0·35 g	
Frac. 2	Toluene + 1% MeOH	3 × 2 l.	19·7g	Mixture of dimethyl shellolate and *epi*shellolate.
Frac. 3	Toluene + 5% MeOH	2 l.	6·23 g	
Frac. 4	Toluene + 5% MeOH	2 l.	4·83 g	
Frac. 5	Toluene + 5% MeOH	2 l.	0·41 g	
Frac. 6	Toluene + 5% MeOH	2 l.	2·56 g	Dark gummy material.

Fractions 4–6 were mixtures containing compounds R_{shellol}. 0·62 and 0·31.

Fraction 4 after rechromatography on Al_2O_3/II (180 g, 24 × 2·7 cms) gave one fraction (1·47 g) which was pure (R_{shellol}. 0·62). This material (0·52 g) was hydrolysed with 10% alkali (1 ml) at 100° to provide the acidic material (0·46 g) which after two crystallizations (EtOH–$CHCl_3$) had m.p. 181–183°; $[\alpha]_D{}^{32}$/ +49·4 (*c.* 0·99%). (Found: C, 63·63; H, 7·98. $C_{15}H_{22}O_5$ requires: C, 63·83; H, 7·80%). Neut. equivalent (Found: 292. Requires: 282).

Methyl ester (CH_2N_2 method): $[\alpha]_D^{32}$ +16·9 (*c*, 1·12%). Fraction 6 after rechromatography on Al_2O_3/II (20 g, 18 × 2 cms) yielded in the later toluene +5% MeOH fractions a pure fraction (R_{shellol}. 0·31) later shown to be *methyl* epi*laksholate*.

Shellolic acid monolactone (IX). Shellolic acid (1·0 g), NaOAc (fused, 1 g) and Ac_2O (22 ml) were heated at 100° for 5 hr. The reaction mixture was poured in water and heated to boiling for 1 hr. The product was extracted with EtOAc and the EtOAc layer was washed with water and dried (Na_2SO_4). Removal of solvent yielded a gum (0·93 g, ~100%). This material was chromatographed on SiO_2/Act. II, (30 g, 18 × 2 cms).

Frac. 1	Benzene	200 ml	Negligible
Frac. 2	Benze + 10% EtOAc	200 ml	0·217 g
Frac. 3	Benzene + 20% EtOAc	200 ml	0·313 g
Frac. 4	Benzene + 30% EtOAc	2 × 200 ml	0·133 g

Fraction 3 on crystallization (benzene–MeOH) yielded crystals (0·18 g, 19%) m.p. 210–212° (lit.[7a] gum). On recrystallization (benzene–MeOH) it furnished needles m.p. 221–223° (TLC and paper chromatography pure), $[\alpha]_D^{25}$ −8·56 (*c*, 1·9%), λ_{max} 229 mμ (ε 3600). IR spectrum: OH 3400 cm^{-1}; γ lactone 1761 cm^{-1}; C═O 1671 cm^{-1}; C═C 1610 and 840 cm^{-1}. (Found: C, 64·54; H, 6·61. $C_{15}H_{18}O_5$ requires: C, 64·7; H, 6·47%).

Sodium borohydride reduction of shellolic acid monolactone (IX) *to laksholic acid* (VII). A soln of the above lactone (0·2 g) in diglyme was added gradually to a stirred soln of $NaBH_4$ (0·2 g) in diglyme (5ml). After addition, the soln was stirred at room temp (28°) for 20 hr. The excess $NaBH_4$ was decomposed by addition of dil (1 : 1) HCl. This mixture was extracted with EtOAc and the extract was washed with water and dried (Na_2SO_4). Removal of solvent yielded a semisolid mass (160 mg, 78%) which on crystallization from EtOH–$CHCl_3$ gave crystals m.p. 179–181°, undepressed on admixture with laksholic acid.

Reduction of jalaric acid (IV) *to* epi*laksholic acid* (VIII). Several experiments were conducted to standardize the conditions. The results are summarized below:

Jalaric acid used in moles	Temp	$NaBH_4$ in moles	Time	
0·75	0°	0·75	4	Unchanged jalaric acid.
1·5	28°	1·5	8	
1·5	waterbath	1·5	2	
1·5	28°	1·5	48	DNP test −ve. Paper chromatography shows two spots R_f 0·55, 0·7.
1·5	waterbath	1·5	8	
1·5	28°	10·5	2·5	DNP test −ve. Paper chromatography shows almost single spot R_f 0·7.

The final conditions evolved were as follows. To a stirred suspension of $NaBH_4$ (1 g) in isopropanol (50 ml) was added with stirring, jalaric acid (1 g) in portions over a period of 2 hr. After addition, the reaction mixture was stirred for 15 min and then worked up to yield a gummy mass (870 mg, 86%) which furnished prisms ($EtOH-CHCl_3$) m.p. 202–203°; $[\alpha]_D$ +63·73 (*c*, 0·91%), λ_{max} 220 mμ (ε 6680); IR spectrum: OH 3300, 3250 cm^{-1}; COOH 2600, 1670 cm^{-1}; C═C 1625, 788 cm^{-1}. (Found: C, 63·47; H, 8·03. $C_{15}H_{22}O_5$ requires: C, 63·83; H, 7·83%).

Methyl ester (CH_2N_2 method): $[\alpha]_D$ + 15·7 (*c*, 1·08%), identical (TLC, IR) with that of the methyl ester ($R_{shellol}$. 0·31) from the acids of lac hydrolysate.

Treatment of jalaric acid with alkali. Jalaric acid (17 g) dissolved in 20% NaOH aq (68 ml) was kept at room temp (~28°) for 10 days. After acidification with dil HCl (1 : 1) and extraction with EtOAc (700 ml), the EtOAc layer was washed with water (3 × 35 ml) and dried (Na_2SO_4). Removal of EtOAc afforded a gummy mass (15·13 g, 86·24%). From the total methyl esters (CH_2N_2 method) 13·4 g was chromatographed on Al_2O_3/IV (400 g, 25·5 × 3 cm).

Frac. 1	Benzene	1500 ml	6·51 g
Frac. 2	Benzene	1500 ml	2·75 g
Frac. 3	Benzene + 1% MeOH	1000 ml	0·03 g
Frac. 4	Benzene + 1% MeOH	1000 ml	0·29 g pure laksholate.
Frac. 5	Benzene + 1% MeOH	1000 ml	0·62 g
Frac. 6	Benzene + 3% MeOH	3 × 1000 ml	1·24 g pure *epi*laksholate.

Fraction 1 on crystallization from EtOAc gave two crops (2·67 and 0·16 g) m.p. 149–152° and 145–149° identified as dimethyl shellolate. The mother liquors after evaporation to dryness and crystallization from benzene yielded three crops (0·18, 0·22, 0·32 g) with m.p. 147–150°, 146–150°, and 145–148° identified as dimethyl *epi*shellolate.

The mother liquor from above crystallizations showed two major sots ($R_{shellol}$. 1·0 and 0·83) and a minor spot ($R_{shellol}$. 1·38).

Fraction 5 was a mixture of methyl laksholate and *epi*laksholate in which the latter predominated.

Fraction 2 was rechromatographed on Al_2O_3/II (75 g, 17 × 2 cms).

Frac. 2a	Benzene	250 ml	negligible
Frac. 2b	Benzene + 1% MeOH	750 ml	1·54 g
Frac. 2c	Benzene + 3% MeOH	1000 ml	1·18 (pure laksholate).
Frac. 2d	Benzene + 5% MeOH	1000 ml	negligible

Fraction 2b gave after crystallization from benzene prisms (0·58 g) m.p. 147–150° identified as dimethyl *epi*shellolate.

The mother liquor from above crystallizations showed two major spots ($R_{shellol}$. 1·0 and 0·83) and a with the latter predominating.

The results of this chromatography are summarized below:

	Isolated pure (g)
Shellolate	2·83
*Epi*shellolate	1·30
Laksholate	1·45
*Epi*laksholate	1·23

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