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CHEMISTRY OF LAC RESIN—IV

PURE LAC RESIN—1: ISOLATION AND QUANTITATIVE DETERMINATION OF CONSTITUENT ACIDS*†

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Abstract—From the "hard resin" of *Palas* seedlac, an essentially pure lac resin fraction (termed, pure lac resin) has been isolated by the solvent precipitation method. Since, some of the constituent acids of lac resin could not be estimated (as Me esters) by GLC, owing to decomposition on GLC columns, a semi-quantitative method for their estimation, involving short-term hydrolysis, followed by oxidation (CrO_3), esterification and GLC estimation of products, has been developed. It is shown that "pure lac resin" molecule is derived from three molecules of aleuritic acid, five molecules of jalaric (shellolic) acid and one molecule of laccijalaric acid.

WE HAVE already described the gross separation of seedlac resin into "hard" and "soft" resin fractions.[1] Both of these fractions are fairly complex mixtures of several polyester species. We now describe the isolation, in ~12% yield, of a sub-fraction of "hard" resin, which appears to be *essentially* homogenous and has been termed "pure lac resin". This fraction, which from its method of isolation corresponds to the major part of lac resin of high molecular weight, is considered to constitute the "backbone" of seedlac and has been subjected to further structural investigations with a view to throwing light on the nature of the lac resin.

Pure lac resin

No serious effort appears to have been made to obtain homogeneous polyester fractions of lac resin. A few authors[2–4] who attempted purification of lac resin, used as the starting material, shellac, which is much more complex than "hard resin"[1] and, by solvent extraction[2] or urea adductation[3] or temperature-based fractional precipitation from an acetone solution,[4] obtained fractions showing considerable overlap of various physico-chemical characteristics. For the present investigation we started with *palas*§ hard resin, the preparation of which has already been described.[1] After considerable exploratory work (including attempted column chromatography over silica gel, ion-exchange resin and gel-filtration) a procedure involving fractional precipitation[6] (solvent system: benzene–dioxan) could be successfully worked out (Fig 1). The separation was monitored by TLC, determination of neutralization equivalents and TLC/paper chromatography of acids resulting from saponification. The relevant data for the initial twelve fractions (*vide* Experimental) is given in Table 1

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§ *Palas* (host tree: *Butea monosperma* Lamk.) seedlac, which accounts for the bulk of Indian lac,[5] has been selected as the standard raw material (unless stated otherwise) for all of our present and future work pertaining to the chemistry of lac resin.

TABLE 1. INITIAL FRACTIONATION OF *PALAS* HARD RESIN BY FRACTIONAL PRECIPITATION FROM DIOXAN SOLUTION WITH BENZENE

Fraction No.	% of hard resin	Neutralization equivalent*	Physical appearance	Remarks
1	10	1390	Brown powder	Pool A ; all the three fractions leave ash on ignition
2	6·5	1220	„ „	
3	3·5	1060	„ „	
4	7	1050	Buff coloured powder, with a reddish tinge	Pool B ; no buolic acid (TLC[1]) after saponification
5	24	1030	„	
6	12	1000	„	
7	5	940	„	
8	14	905	Light cream-coloured powder	Pool C ; no butolic acid (TLC[1]) after saponification.
9	3	960	„	
10	3	930	„	
11	4	780	Dark brown gum	Pool D ; gives butolic acid (TLC) after saponification.
12	5	610	„	

* Neutralization equivalents determined in ethanol-tetrahydrofuran (1:1); accuracy: ±5%

to show the extent of separation ; it may be noted that only fractions 11 and 12 showed (TLC[1]) butolic acid after saponification. Based on their TLC behaviour and neutralization equivalent, the various fractions were grouped into four pools. Pool B, accounting for ~50% of hard resin was subjected to further purification (Fig 1) to ultimately give, what we have termed, "pure lac resin", in ~12% yield, based on hard resin. The product, a pale coloured amorphous powder,* has the following characteristics: m.p. 102–104°, $[\alpha]_D^{30}$ +63·4 (EtOH); UV, λ_{max}^{EtOH} 225 mμ ($E_{1\,cm}^{1\%}$, 134); IR (KBr), 3448 cm^{-1} (OH), 1724, 1250 cm^{-1} (COOR), 1631 cm^{-1} (olefinic linkage); molecular weight (Osmometric method[8]), 2095 ±110; neutralization equivalent, 990 ±50.

Constituent acids of pure lac resin

Room temperature saponification (5 hr)[1] of pure lac resin gave an hydrolysate containing aleuritic (I), jalaric (II), laccijalaric (VI), shellolic (V) and epishellolic acids (III), as revealed by the paper chromatography[1] of resulting acids; no butolic acid (6-hydroxy-tetradecanoid acid) was detected. This finding was confirmed by an extended hydrolysis (~30°, 10 days)[1] of pure lac resin and identifying the products by paper chromatography and, after esterification (CH_2N_2), by TLC[1]; a typical thin layer chromatogram is shown in Fig 2.

The percentage of aleuritic acid in the hydrolysate was readily estimated by the periodic acid method discussed earlier,[1] to be 36 ±1%. It is clear from the above that the balance (~65%) is represented by terpenic acids. This conclusion is fully corroborated by an independent estimation of total terpenic acids. Since, all the terpene acid components of lac resin have an αβ-olefinic carboxyl chromophore (λ_{max}^{EtOH} 220–230 mμ, ε 5600–7000; see Table 2), UV absorption of pure lac resin in the 220–230

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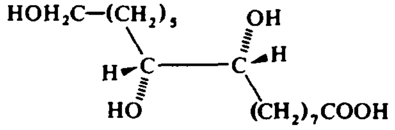
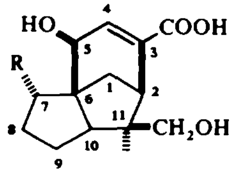
* Further purification by gel-filtration of its tetrahydrofuran soln through Sephadex LH-20 proved abortive because, though a colourless product was readily obtained, TLC of the product showed extra spots.

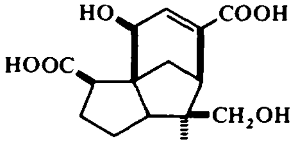
Sephadex LH-20 (M/s. Pharmicia Fine Chemicals, Uppasala) is recommended for gel filtration in organic solvents and is considered useful for the molecular weight range 100–4000.[7]



I



II : R = CHO
III : R = COOH
IV : R = CH$_2$OH



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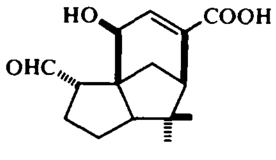

VI

mμ region (in which aleuritic acid is essentially transparent) can be utilized to estimate the number of terpene acid residues. As already stated, pure lac resin shows λ_{max}^{EtOH} 225 mμ, $E_{1\,cm}^{1\%}$ 134. When this is compared with the average $E_{1\,cm}^{1\%}$ (202) of lac acids (Table 2), a 67% content of terpene acids follows.* A further confirmation of these results follows from the estimation of individual lac acids constituting the pure lac resin, described below.

Chromic acid oxidation of individual lac acids

The next point to be established was the quantitative determination of the various terpene acids in the hydrolysate of pure lac resin. Obviously, the method of choice would be the GLC of the methyl esters of these acids. However, two difficulties barred this approach. Firstly, it is known[9] that the reaction of jalaric acid (II) with diazomethane is quite complex, leading to a number of products. Secondly, attempted GLC of pure dimethyl shellolate/dimethyl *epi*shellolate (on 0·25% SE 30 or 1% Silicone QF supported on 60–80 mesh Chromosorb W) showed multiple peaks, indicating decomposition under these conditions. It was suspected that hydroxyl groups in shellolic (V)/*epi*shellolic acid (III) could be responsible for transformation on GLC columns† and hence it was decided to oxidize these functions and then standardize their estimation in terms of GLC of the major oxidation product. This necessitated a study of oxidation of *all* the lac acids obtained by hydrolysis of pure lac resin, in order to arrive at the most appropriate reaction conditions and obtain reference samples of the oxidation products. Chromic acid (Jones reagent[11]) appeared to be the choice oxidizing agent as this should convert jalaric (II), *epi*shellolic (III) and *epi*laksholic acids (IV) to the same (major) product, *viz.* the keto tricarboxylic acid (XII), thus simplifying analysis, as of these three acids (II, III, IV) only jalaric acid is considered[9] to be the primary lac acid.

Jones oxidation of dimethyl *epi*shellolate furnished a neutral (27%) and an acidic

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* It is, of course, assumed that interesterification of different lac acids has no effect on absorptivity of various components and the absorptivity of the resulting polyester is purely additive.

† As an alternative approach silylation[10] of lac acids and GLC of the resulting derivatives is being investigated.

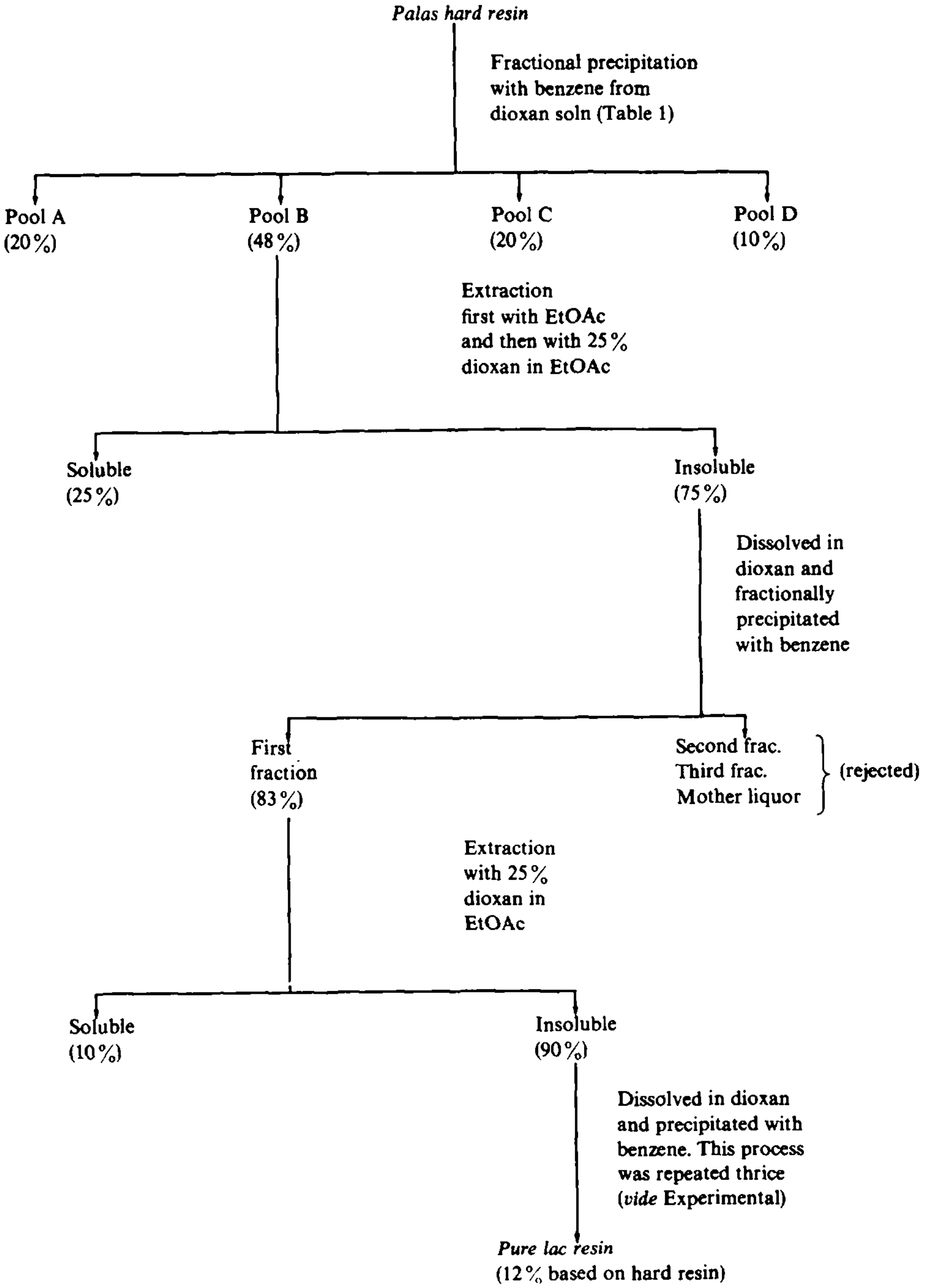


Fig 1. Isolation of pure lac resin from *Palas* "hard resin".

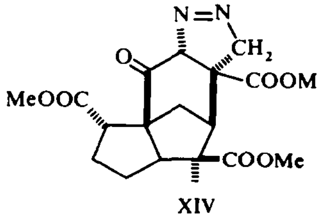
TABLE 2. UV ABSORPTION OF LAC ACIDS AND THEIR METHYL ESTERS

No.	Compound	Acid		Me ester	
		λ_{max}^{EtOH}	ε	λ_{max}^{EtOH}	ε
1	Jalaric	220	6200	—	—
2	Shellolic	230	6200	230	6400
3	*Epi*shellolic	227	6000	230	6050
4	Laccijalaric	217	7400	—	—
5	*Epi*laccishellolic	223	5000	226	5600
6	Aleuritic	—	(ε_{225}, 35)	—	—

product. The neutral compound (m.p. 133–135°, $C_{17}H_{20}O_7$), from its spectral characteristics (UV: no λ_{max} between 210–270 mμ. IR: no OH absorption; COOMe 1730 cm^{-1}; γ-lactone 1780 cm^{-1}. PMR: quaternary Me, 3H singlet at 80 c/s; two COO$\underline{\mathrm{Me}}$, 3H singlets at 221 and 233 c/s; $\mathrm{O{=}C{-}C\underline{H}_2{-}\overset{|}{\underset{|}{C}}{-}}$, an AB quartet centred at 185 c/s, J_{AB} = 18 c/s, $\delta_B - \delta_A$ = 26 c/s) was readily recognized as the keto-lactone (VII), arising from an internal Michael addition in the expected oxidation product (VIII). The acidic product, on interaction with diazomethane yielded two products. One of these (m.p. 123–124°), though showing λ_{max}^{EtOH} 246 mμ (ε, 7000) expected of an αβ-unsaturated ketone and three COO$\underline{\mathrm{Me}}$ signals in its PMR spectrum (3H singlets at 216, 220 and 232 c/s) cannot be the desired product IX, in view of the absence of any olefinic proton signal in its PMR spectrum; the PMR spectrum, instead, shows an extra 3H singlet at 120 c/s, readily assignable to a vinylic Me (further deshielded by the adjacent carbonyl function). In view of this, the compound is formulated as X, understandably arising from the diazomethane addition product (pyrazoline, XI; *vide infra*) of IX, by loss of nitrogen and reorganization. The second product analyses for $C_{19}H_{24}O_7N_2$ (M^+, m/e = 392) and melts with decomposition at 126–127°; the melt on cooling solidifies to a product, m.p. 115–117°, identified (IR) as X. Hence, this compound should be the pyrazoline XI.*

Exactly parallel results were obtained with dimethyl shellolate, both at the Jones oxidation stage and subsequent esterification of the acidic part with diazomethane.

* The alternative formulation (XIV) stands ruled out, in view of the structure of the decomposition product (X) and the fact that its PMR spectrum displays the —CH_2—N=N— signal as an eight-line, 2H multiplet located between 272–332 c/s, which clearly represents the AB part of an ABX system and this is compatible only with XI. The stereochemistry (XI) shown for the pyrazoline ring, follows from the expected α-attack[12]; its circular dichrogram is fully consistent[13] with this stereochemistry.



XIV

XIV

The ready addition of diazomethane to an αβ-olefinic carbonyl system to give pyrazolines is well-known[14]; however, the pyrazoline XI, appears to be exceptionally labile and slowly passes into X, even at room temp.

To by-pass the complications mentioned above, action of methanol containing sulphuric acid, on the ketolactone (VII) and the keto acid (VIII) was investigated. Both gave the same product, *viz.* keto triester (IX, UV: λ_{max}^{EtOH} 240 mμ, ε 7700. IR: C=O 1724, 1695 cm^{-1}; C=C 1613, 787 cm^{-1}. PMR: $-\underset{|}{C}=C\underline{H}-$, 1H singlet at 397 c/s; $COOC\underline{H}_3$, three 3H singlets at 215, 219 and 231 c/s; one quaternary methyl, 3H singlet at 88 c/s) contaminated to a small extent (GLC; <5%) with its C_7-epimer (XIII). This greatly simplified matters. Thus, *epi*shellolic acid (III) on Jones oxidation, followed by esterification of the total product with MeOH–H_2SO_4 gave a material, readily amenable to analysis by GLC and this way shown to consist of IX (84%), XIII (5%) and two other unidentified products. The estimation of *epi*shellolic acid, thus, can be carried out in terms of the keto ester IX.

This method, that is Jones oxidation followed by esterification with MeOH–H_2SO_4, was next applied to *epi*shellolic acid (III), jalaric acid (II), laccijalaric acid (VI) and aleuritic acid (I). The results have been summarized in Table 3. It may be noted that jalaric acid gave a rather unsatisfactory yield of keto triesters (IX, XIII), a number of byproducts were formed; however, the major product was the expected keto ester IX. In connection with the oxidation of aleuritic acid, it may be mentioned that chromic acid is known[15] to cleave α-glycols.

Table 3. Oxidation-esterification of lac acids

No.	Acid	Product	
		Total yield (%)	GLC analysis: compd (%)
1	*Epi*shellolic	60	IX (84%) + XIII (5%) + two unidentified (11%)
2	Jalaric	66	IX (54%) + XIII (11%) + six unidentified (35%)
2	Laccijalaric	75	XV (70%) + XVI (20%) + one unidentified (10%)
4	Aleuritic	85	dimethyl pimelate (42%) dimethyl azelate (49%) two unidentified (9%)

Estimation of constituent acids

The sequence, oxidation-esterification-GLC analysis, described above for individual lac acids, was next applied to the lac acid mixture obtained after 48 hr alkaline hydrolysis of pure lac resin. The resulting total methyl esters were first separated into benzene-eluted (54%) and 5% EtOAc in benzene-eluted (45%) fractions by column chromatography and, each fraction, then, analysed by temperature-programmed GLC (Figs 3, 4), identification of the various constituents being carried out by the peak-accentuation method using authentic samples in mixed chromatograms. By taking into account the composition of each eluate and the relative proportions of these (benzene and 5% EtOAc in benzene eluates) eluates, the weighted total for each constituent was arrived at and further corrected for actual yields obtained with pure acids. In this way, ultimately, approximate molar ratios for each constituent could be obtained (of course, the unidentified products, also obtained during Jones oxidation of pure lac acids, were ignored). These results have been summarized in Table 4.

TABLE 4. ESTIMATION OF PRODUCTS OF OXIDATION OF TOTAL LAC ACIDS FROM PURE LAC RESIN

No.	Product	GLC peak No.	Yield (%)			Yield after correction*		Molar ratio
			C_6H_6 fraction	EtOAc-C_6H_6 fraction	Weighted total	Corrected weighted total	Corrected percentage	
1	Dimethyl azelate	④	41	—	22·55	28·97	18·93	2·70
2	Dimethyl pimelate	②	31	—	17·05	22·79	14·89	2·44
3	Keto triesters (IX, XIII)	⑭,⑮	9	52	28·35	66·12	43·21	3·81
4	Keto ethers (XVII, XVIII)	⑫,⑬	negligible	19	8·55	19·94	15·18	1·25
5	Keto diesters (XV, XVI)	⑩,⑪	8	13	10·25	13·03	9·922	1
6	Unidentified	—	11	16	13·25	—	—	—

* Corrected for actual yields obtained with pure lac acids (*vide* Table 3), factors being 1·28, 1·30, 2·33 and 1·50 for dimethyl azelate, dimethyl pimelate, (IX, XIII, XVII and XVIII), and (XV and XVI) respectively.

TABLE 5. SOME CHARACTERISTICS OF PURE LAC RESIN AND A POLYMER THEORETICALLY DERIVED FROM ONE MOLE OF LACCIJALARIC ACID, FIVE (SIX) MOLES OF JALARIC ACID AND THREE MOLES OF ALEURITIC ACID

Property	Pure lac resin	Molecule theoretically derived from	
		3 moles of aleuritic acid 5 moles of jalaric acid 1 mole of laccijalaric acid	3 moles of aleuritic acid 6 moles of jalaric acid 1 mole of laccijalaric acid
Molecular weight	2095 ±110	2432	2692
% Aleuritic acid	36 ±1%	37·5	33·88
% Terpenic acids*	67%	68·05	72·14

* In terms of jalaric acid

It may be noted that the first two products (Table 4) originate from aleuritic acid, while the keto triesters and the keto ethers must have their origin in jalaric/*epi*-shellolic acid (for convenience sake isomerism at C_7 is ignored) and, the keto diesters (XV, XVI) result from laccijalaric acid (stereochemistry and oxidation level of C_7 substituent is ignored). Thus, it follows from these results (Table 4) that base hydrolysis of pure lac resin yields, for every one mole of laccijalaric acid (VI), approximately three moles of aleuritic acid (I) and five moles of jalaric/*epi*shellolic acid. Now, if these nine molecules of acids are interesterified (with loss of eight molecules of water), a polymer will result, which must have the characteristics shown in Table 5. This table also gives the values *actually* found for the pure lac resin and, for another polymer theoretically derived in a slightly different fashion (six molecules of jalaric acid rather than five). It is thus clear from this comparison that the pure lac resin molecule can reasonably be considered as having been derived from three molecules of aleuritic acid, five molecules of jalaric acid (*epi*shellolic/shellolic) and one of laccijalaric acid.

EXPERIMENTAL

For general remarks see Part III[1] of this series. IR spectra were recorded as smears (liquids) or Nujol mulls (solids) on a Perkin-Elmer Infracord, model 137E. PMR spectra were taken in 10–20% soln in $CDCl_3$ or CCl_4 with TMS as the internal standard, on a Varian A-60 spectrometer; signals are recorded in c/s relative to TMS as zero.

GLC was carried out on Aerograph model A-350-B using 150 cm × 5 mm column packed with 20% silicone SE-30 on Chromosorb W (60–80 mesh), using H_2 as the carrier gas.

TLC was carried out with silica gel containing 15% plaster of Paris; visualization agent: conc H_2SO_4 or iodine vapour.

Isolation of pure lac resin. Palas "hard resin" (50 g) was dissolved at room temp (30°) in dioxan (700 ml) and the soln slowly diluted with dry benzene (450 ml) till precipitation just started. The mixture was left aside at ~30° for 0·5 hr, after which the precipitated resin (5 g, fraction 1) was collected (by decantation). To the mother liquor more benzene (50 ml) was added, the mixture set aside as above and the precipitate (3·2 g, fraction 2) collected. This operation was repeated twice by successive additions of 50 ml benzene (fraction 3, 1·8 g; fraction 4, 3·4 g) and then thrice again by addition of 100 ml benzene every time (fraction 5, 12·1 g; fraction 6, 6·1 g; fraction 7, 2·5 g). The last mother liquor was allowed to stand at 10 ± 1° for 24 hr and the solid (7·0 g, fraction 8) collected. The mother liquor was next diluted with 200 ml benzene and the precipitated resin (1·5 g, fraction 9) collected after 2 hr at ~30°. The filtrate from fraction 9 was further diluted with benzene (400 ml), allowed to stand (24 hr) at ~10° and the solid (1·5 g, fraction 10) collected. The filtrate was next diluted with more benzene (600 ml) and the separating solid (2·1 g, fraction 11) collected after 24 hr at ~10°. The final filtrate was freed of solvents at ~95°/40 mm to give a gum (2·6 g, fraction 12). The characteristics of these fractions are given in Table 1.

Fractions 4–7 were mixed (Pool B, Table 1) and the well-powdered material (24 g) extracted by mechanical stirring first with EtOAc (1200 ml × 3) and next with 25% dioxan in EtOAc (1200 ml × 3). The insoluble material was triturated with dry ether to give a granular powder (18 g). This product was dissolved (30°) in dioxan (125 ml) and then precipitated by addition of dry benzene (125 ml); after standing at ~30° for 0·5 hr, the product (15 g) was collected. This material was again extracted, as above, with 25% dioxan in EtOAc (450 ml × 3) and the insoluble product (13 g) redissolved in dioxan (125 ml) and precipitated by addition of benzene (125 ml). The ppt (11·0 g), though quite homogeneous (TLC), was reddish in colour and hence was redissolved in dioxan (150 ml); on addition of dry benzene (65 ml) a dark red ppt (1·6 g) was thrown out and this was rejected; to the filtrate more benzene (200 ml) was added and the light buff-coloured ppt (8·7 g) collected. This product (7·3 g) was again taken up in dioxan (100 ml), diluted with 45 ml benzene to remove a reddish ppt (1·1 g) and further diluted with more benzene (125 ml) and the ppt collected, triturated with dry ether and dried in vacuum at room temp to give v. pale coloured amorphous powder (5·8 g), m.p. 102–104°.

Neutralization equivalent was determined by titrating its dimethyl formamide soln (100 mg in 10 ml of solvent) against 0·0245 N NaOMe soln using thymol blue as an indicator.[16]

The mol wt was determined with Mechrolab Vapour Pressure Osmometer Model 301-A using dioxan as a solvent, in the usual manner.[17]

The above separation was monitored at each stage by TLC using two solvent systems: (i) 50% EtOAc in dioxan, (ii) 2·5% AcOH in dioxan. In the latter system, the pure lac resin has R_f 0·73 (solvent front 10 cm, 0·3 mm layers, temp 30°).

Hydrolysis of lac resin. Pure lac resin (0·5 g) was dissolved in KOHaq (12%, 5 ml) and the soln left aside at room temp (~30°) for the desired period (5 hr, 48 hr or 10 days) after which, it was acidified with H_2SO_4aq (10%) and the liberated acids extracted with EtOAc (75 ml × 3) to give 0·45–0·49 g of mixed acids, as a brown gum.

Jones oxidation of dimethyl epishellolate. To dimethyl *epi*shellolate (560 mg) in acetone (25 ml) was added, at ~30° with stirring chromic acid soln (2 g CrO_3 in 6 ml H_2O containing 1·8 ml conc H_2SO_4) till a brownish red color persisted (7 ml). After 24 hr at room temp (28°), the reaction mixture was worked up in the usual manner by EtOAc extraction and separation with acidic (gum, 395 mg) and neutral products (153 mg) by Na_2CO_3aq. The neutral product was chromatographed over silica gel (IIB; 17·5 cm × 1 cm); 10% EtOAc in C_6H_6 eluted a crystalline compound, which was recrystallized from EtOH to give pure VII (113 mg), m.p. 133–135°. (Found: C, 60·96; H, 6·31. $C_{17}H_{20}O_7$ requires: C, 60·71; H, 5·99%).

The acidic product (395 mg) in EtOH (20 ml) was esterified with excess ethereal diazomethane and the total ester mixture, isolated after 12 hr, was chromatographed over SiO_2 gel (IIB; 18·5 cm × 1 cm), with TLC monitoring (solvent: C_6H_6, EtOAc, acetone, 7:4:2).

Fraction 1	C_6H_6	10 ml × 5	10 mg
Fraction 2	C_6H_6	10 ml × 8	118 mg; single spot, R_f 0·71
Fraction 3	C_6H_6	10 ml × 2	9 mg; two spots, R_f 0·71, 0·66
Fraction 4	10% EtOAc in C_6H_6	10 ml × 4	95 mg; m.p. 120–122°; single spot, R_f 0·66
Fraction 5	10% EtOAc in C_6H_6	10 ml × 10	130 mg; two spots, R_f 0·66, 0·56
Fraction 6	EtOAc	10 ml × 5	27 mg

Fraction 2 was recrystallized from EtOH to give needles, m.p. 123–124°, identified as X. IR: C=O 1740, 1700, 1670 cm^{-1}. (Found: C, 62·58; H, 6·64. $C_{19}H_{24}O_7$ requires: C, 62·62; H, 6·64%). Fraction 4 was recrystallized from EtOH to furnish rhombs of the *pyrazoline* XI, m.p. 126–127° (dec); UV: no high intensity maximum above 210 mμ; IR: C=O 1720 cm^{-1}. PMR($CDCl_3$): $-\overset{|}{\underset{|}{C}}-$Me, 3H singlet at 91 c/s; three COOMe, 3H singlets at 215, 217 and 220 c/s; $-CH_2-N=N-$, eight line 2H multiplet located between 272–232 c/s. (Found: C, 58·60; H, 5·62; N, 7·06. $C_{19}H_{24}O_7N_2$ requires: C, 58·15; H, 6·17; N, 7·14%).

When the acidic portion (395 mg) in MeOH (40 ml) containing conc H_2SO_4 (5% v/v) was refluxed (16 hr) and worked up in the usual manner it yielded an ester mixture (380 mg), which was chromatographed over SiO_2-gel/IIB (10 g). The earlier benzene eluates yielded a crystalline product (32 mg; m.p. 119–120°, after recrystallization from ether) identified, by comparison (IR, PMR, mixed GLC) with an authentic sample (*vide infra*) as the *Keto triester* XIII (shellolate series). The later benzene eluates furnished a gum (330 mg, TLC pure) which failed to crystallize, but was characterized spectroscopically as the required *keto triester* IX (*epi*shellolate series). (Found: C, 61·40; H, 6·0. $C_{18}H_{22}O_7$ requires: C, 61·70; H, 6·33%).

When the keto lactone VII (100 mg) was likewise exposed to MeOH-H_2SO_4, it furnished keto triester IX (80 mg).

Jones oxidation of dimethyl shellolate. Dimethyl shellolate (520 mg) was oxidized with Jones reagent and the product separated into neutral (140 mg) and acidic (367 mg) portions, exactly as already described for dimethyl *epi*shellolate.

The neutral product was recrystallized from EtOH to give XIX,[18a] m.p. 149–150°; UV: no high intensity maximum above 210 mμ; IR: C=O 1790–1740 cm^{-1} (unresolved); PMR: $-\overset{|}{\underset{|}{C}}-\underline{Me}$, 3H singlet at 79 c/s; two COO$\underline{Me}$ 3H singlets at 219 and 233 c/s; $O=\underset{|}{C}-\underline{CH_2}-\overset{|}{\underset{|}{C}}-$, an AB quartet centred at 185 c/s, J_{AB} = 17 c/s, $\delta_B - \delta_A$ = 29 c/s. (Found: C, 60·15; H, 5·54. $C_{17}H_{20}O_7$ requires: C, 60·71; H, 5·99%).

The acidic product (360 mg) in EtOH was treated with excess ethereal diazomethane and the product chromatographed over SiO_2-gel (IIB, 10 g) (for details see Jones oxidation of dimethyl *epi*shellolate). Benzene containing 5% EtOAc (100 ml × 2) eluted 81 mg of a product which was crystallized from EtOH-hexane to yield needles, m.p. 105–106°, characterized as XX; UV: λ_{max}^{EtOH} 246 mμ, ε 8200. IR: C=O 1740, 1690 cm^{-1}; PMR ($CDCl_3$): $-\overset{|}{\underset{|}{C}}-\underline{Me}$, 3H singlet at 86 c/s; three COO$\underline{Me}$, 3H singlets at 216, 222 and 231 c/s; vinylic $\underline{Me}$, 3H singlet at 115 c/s. (Found: C, 62·34; H, 6·57. $C_{19}H_{24}O_7$ requires: C, 62·82; H, 6·64%). Next eluate (10% EtOAc in C_6H_6; 100 ml × 3) gave 144 mg of a solid which was recrystallized from C_6H_6-light petroleum to give XXI, m.p. 121–122° (dec); IR: C=O 1740 cm^{-1}; PMR ($CDCl_3$): $-\overset{|}{\underset{|}{C}}-\underline{Me}$, 3H singlet at 92 c/s; three COO$\underline{Me}$, 3H singlets at 219, 220 and 221 c/s; $-\underline{CH_2}-N=N-$ complex 2H multiplet located between 250–330 c/s. (Found: C, 58·50; H, 5·98; N, 6·9. $C_{19}H_{24}O_7N_2$ requires: C, 58·15; H, 6·17; N, 7·14%).

However, when the esterification was carried out with MeOH-H_2SO_4, the desired *keto triester* XIII was obtained: m.p. 119–120°; UV: λ_{max}^{EtOH} 240 mμ, ε 8700; IR: C=O 1730, 1685 cm^{-1}; C=C 1640 cm^{-1}; PMR ($CDCl_3$): $-\overset{|}{\underset{|}{C}}-\underline{Me}$, 3H singlet at 92 c/s; COOC$\underline{H_3}$, three 3H singlets at 221, 225 and 236 c/s; $-\underset{|}{C}=\underline{CH}-$, 1H singlet at 396 c/s.

Jones oxidation of laccijalaric acid. To laccijalaric acid (253 mg) in acetone (15 ml) was added Jones reagent (1·5 ml). Usual work up gave the acidic material (262 mg), which was methylated using MeOH-H_2SO_4 to give ester mixture (223 mg). This was chromatographed over SiO_2 gel (IIB, 10 g) and eluted with benzene. Later benzene eluates (100 ml × 2) gave 112 mg of a gum (TLC pure, solvent system, 35% EtOAc in benzene) which could not be induced to crystallization and was identified as the required XV; UV: λ_{max}^{EtOH} 242 mμ, ε 6100. IR: C=O 1748, 1724 cm^{-1}; C=C 1631 cm^{-1}; PMR (CCl_4) $-\overset{|}{\underset{|}{C}}-\underline{CH_3}$, two 3H singlets at 57 and 72 c/s; COOC$\underline{H_3}$ two singlets at 215 and 228 c/s; $-\underset{|}{C}=\underline{CH}-$, 1H singlet at 393 c/s. (Found: C, 66·95; H, 7·38. $C_{17}H_{22}O_5$ requires: C, 66·65; H, 7·24%).

Jones oxidation of aleuritic acid. Aleuritic acid (604 mg) was oxidized with Jones reagent (12 ml) and the total product (636 mg) recovered in the usual manner and esterified (MeOH-H_2SO_4). The total ester mixture (660 mg), b.p. 120–125° (bath)/0·5 mm showed four components (GLC; 20% tung oil polymer on 60–80 mesh Chromosorb W, temp 200°, hydrogen press 10 p.s.i.) with RRT of 1 (4·5%), 1·5 (42%), 2·4 (4·5%) and 3·5 (49%). The two major components were separated by column chromatography (SiO_2-gel/IIB) and identified as dimethyl azelate (C_6H_6 eluate) and dimethyl pimelate (5% EtOAc in C_6H_6 eluates) by comparison (IR, PMR mixed GLC) with authentic samples.

Jones oxidation of total acids from pure lac resin. Pure lac resin (0·5 g) was hydrolyzed as described earlier and the total acids (0·48 g) oxidized with Jones reagent (7 ml). The product (0·44 g) was esterified with MeOH-H_2SO_4 to give 0·40 g of ester mixture. A part (206 mg) was chromatographed over SiO_2-gel/IIB (15 cm × 1 cm) and the benzene (100 ml × 3; 113 mg) and 5% EtOAc in benzene (100 ml × 3; 91 mg) eluates examined by GLC (Figs 3, 4, Table 4).

Keto ethers (XVII and XVIII). Keto ether (XVIII) was prepared from dimethyl shellolate by a known[18b] procedure.

Dimethyl *epi*shellolate (0·5 g) in benzene (50 ml) was stirred and heated on a steambath (16 hr) with active manganese dioxide[19] (4 g), and worked up as usual[18b] and the neutral product (175 mg) chromatographed over SiO_2-gel/IIB (10 g). Benzene eluted a gum (120 mg), which crystallized on trituration with ether and was recrystallized from benzene–pet. ether to give XVII as colourless prisms, m.p. 149–150°; UV: no high intensity absorption max above 210 mμ; IR: C═O 1741; 1725 and 1690 cm^{-1}; PMR ($CDCl_3$): $-\overset{|}{\underset{|}{C}}-Me$, 3H singlet at 68 c/s; $COOCH_3$, two 3H singlets at 219 and 222 c/s; $-CH_2-O-$, 2H singlet at 228 c/s. (Found: C, 63·60; H, 6·80. $C_{17}H_{22}O_6$ requires: C, 63·34; H, 6·88%).

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