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CHEMISTRY OF LAC RESIN—V

PURE LAC RESIN—2: POINTS OF LINKAGE OF CONSTITUENT ACIDS*†

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Abstract—Pure lac resin has been oxidized and then hydrolysed to furnish a mixture of products, which were carefully separated and identified. This information has enabled the authors to determine the points of attachment of constituent lac acids in the pure lac resin.

IN PART IV,[1] it has been demonstrated that a molecule of pure lac resin is derived from three molecules of aleuritic acid (I), five molecules of jalaric acid (VI)/(*epi*shelloic/shelloic acid) and one of laccijalaric acid (VII). In this communication we report on the work leading to the determination of points of linkage of these acids.

The first approach, which proved abortive, envisaged methylation of free hydroxyls in pure lac resin, followed by hydrolysis of the methylated resin—a sequence of reactions commonly, successfully employed in carbohydrate chemistry[2] for similar purposes. As a first step permethylation of aleuritic acid (I) and dimethyl *epi*-shellolate (VIII) with CaO–MeI in dimethyl sulphoxide (DMSO)[3] was investigated. However, even under the optimum conditions (*vide* Experimental) reached by us, permethylation of aleuritic acid was incomplete, as methyl 9,10,16-trimethoxy-palmitate (V) was formed in ~28% yield (GLC), other products being methyl aleuritate (10%), monomethyl ether II (15%), dimethyl ether III (33%) and dimethyl ether IV (14%). Under the same conditions of methylation, dimethyl epishellolate gave only a low yield of monomethyl ether (IX). In view of these results this line of approach was abandoned.

Oxidation-hydrolysis of pure lac resin

Attention was next diverted to oxidation of lac resin with Jones reagent[4] with the object of oxidising any free α-glycol linkage, secondary and primary hydroxyls and aldehydic functions and then subjecting the oxidised resin to base hydrolysis to get recognisable fragments. This method appeared to be all the more attractive and reliable because, the results of Jones oxidation of individual lac acids were already available from an earlier investigation.[1]

Points of linkage of two aleuritic acid units. Pure lac resin was oxidised with Jones reagent and the gummy product esterified (CH_2N_2) and the resulting product vacuum distilled (~160°/2·5 mm) to collect the total volatile products (~13% on weight basis). GLC of this material showed it to contain one major component (~80%), identified (GLC, IR) as dimethyl pimelate. In another experiment, the oxidised product was

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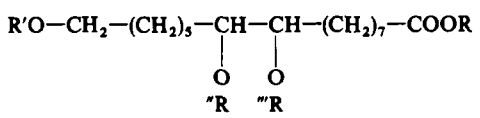
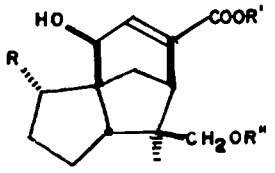
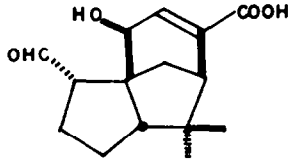


I: R = R′ = R″ = R‴ = H
II: R = Me; R′ = H; R″ = H (Me); R‴ = Me (H)
III: R = R″ = R‴ = Me; R′ = H
IV: R = R′ = Me; R″ = H (Me); R‴ = Me (H)
V: R = R′ = R″ = R‴ = Me



VI: R = CHO; R′ = R″ = H
VIII: R = COOMe; R′ = Me; R″ = H
IX: R = COOMe; R′ = R″ = Me



VII

first hydrolysed and then esterified and the volatile fraction (~24%) collected as above. This fraction was shown by GLC and IR to consist of ~36% of dimethyl pimelate and ~50% of dimethyl azelate; the unidentified components (two) had the same retention time as the two by-products formed during the Jones oxidation of aleuritic acid.[1] Table 1 shows the yields, corrected yields and molar yields, obtained by utilising the factors and method already discussed.[1]

TABLE 1. SUMMARY OF RESULTS OF BREAKDOWN OF ALEURITIC ACID RESIDUES IN PURE LAC RESIN ON JONES OXIDATION

Reaction	Weight yield (%)		Corrected yield (%)*		Molar yield	
	Pimelate	Azelate	Pimelate	Azelate	Pimelate	Azelate
1. Pure resin—Jones oxidation-esterification-distillation	10·7	—	13·9	—	1·8	—
2. Pure resin—Jones oxidation-hydrolysis-esterification-distillation	8·8	12·2	11·4	15·6	1·5	1·8

* Corrected for actual yields obtained from aleuritic acid after Jones oxidation.[1]

It is clear from Table 1 that one mole of pure resin yields after oxidation ~2 moles of pimelic acid and after oxidation-hydrolysis ~2 moles of pimelic acid and ~2 moles of azelaic acid. These results require that of the three units[1] of aleuritic acid in pure lac resin, two must be linked through the carboxylic group and all the three hydroxyls (I) must be free. This also implies that the third unit of aleuritic acid must be linked, at least, through one of the α-glycol hydroxyls. More precise information on this unit could be obtained from experiments described below.

Points of linkage of terpene acids and the third aleuritic acid unit. Pure lac resin was oxidised (Jones reagent), hydrolysed (KOH aq) and then esterified (CH_2N_2). The total esters, thus obtained, were chromatographed over silica gel and the various

fractions grouped into six pools, by virtue of their identical behaviour on TLC. These results are summarised in Table 2.

All fractions in pool A were liquids and were examined by GLC. Fractions 13 and 20 were found (GLC, IR) to be essentially homogeneous and corresponded to dimethyl azelate and dimethyl pimelate respectively. Other major fractions were found to be essentially mixtures of these two compounds.

Pool B was rechromatographed to obtain the major component (R_f 0·71) which was identified (GLC, IR) as dimethyl *epi*laccishellolate (X).[5] The minor component, from its R_f value (0·77),[6] is considered to be dimethyl laccishellolate.[5]

Pool C yielded a crystalline compound (m.p. 134–135°), readily identified (m.p., mixed m.p. and IR) as the ketolactone (XI) obtained earlier[1] by the CrO_3 oxidation of dimethyl *epi*shellolate.

TABLE 2. POOLED FRACTIONS FROM OXIDATION-HYDROLYSIS – ESTERIFICATION OF PURE LAC RESIN

Pool	Frac. No.	Solvent used for elution	Weight (%)	TLC behaviour*
A	1–20	C_6H_6	23·5	Single elongated spot: R_f 0·82
	21–26	5% EtOAc in C_6H_6		
B	27–36	5% EtOAc in C_6H_6	12·8	Two spots: R_f 0·77, 0·71
C	37–40	5% EtOAc in C_6H_6	12·4	Two spots: R_f 0·71, 0·66
	41–48	10% EtOAc in C_6H_6		
D	49–67	10% EtOAc in C_6H_6	26·5	Two spots: R_f 0·66, 0·62
E	68–78	25% EtOAc in C_6H_6	19·3	Three spots: R_f 0·51, 0·42, 0·35
	79–87	50% EtOAc in C_6H_6		
F	88	EtOAc	5·5	Complex mixture

* Solvent system: benzene-EtOAc-acetone, 7:4:4; temp: 28°; the underlined R_f value indicates the major component.

Pool D, after rechromatography afforded a solid (m.p. 131–132°; R_f 0·62), analysing for $C_{18}H_{24}O_7$ and showing the following structural features: CHOH (IR: 3400, 1130 and 1117 cm^{-1}; PMR: 1 H doublet at 277 c/s, J = 2·5 c/s), CH=C—COOMe (UV: λ_{max} 225 mμ, ε 6000; IR: 1725 and 1653 cm^{-1}; PMR: 1 H doublet at 380 c/s, J = 2·5 c/s), COOMe (IR: 1740 and 1725 cm^{-1}; PMR: 3 H singlets at 206, 212 and 216 c/s), and one quaternary Me (PMR: 3 H singlet at 78 c/s). In view of these features, the compound has been assigned structure XII and, this has been confirmed by its Jones oxidation to the already reported[1] keto triester (XIII).

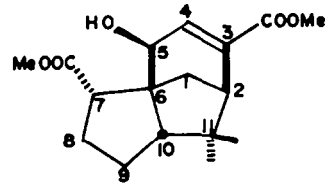
Rechromatography of pool E yielded a crystalline solid (m.p. 151–152°; R_f 0·35) and two gums (R_f 0·42, 0·51). The solid was readily identified (mixed m.p., IR, TLC) as dimethyl *epi*shellolate (VIII) and one of the gums (R_f 0·42), from its IR and R_f values,[5] essentially dimethyl shellolate (C_7 epimer of VIII). The second gum (R_f 0·51) is clearly aliphatic [IR: $(CH_2)_n$ 730 cm^{-1}; PMR: $(CH_2)_n$ 82 c/s] showing bands for CHOH (IR: 3400 cm^{-1}; PMR: 1 H multiplet at 240 c/s), CH_2OH (IR: 3400 cm^{-1}; PMR: multiplet centred at 212 c/s), COOMe (IR: 1740 cm^{-1}; PMR: 3 H singlet at 217 c/s) and a keto function (IR: 1700 cm^{-1}, shoulder). From these data this compound was assigned structure XIV/XV. Chemical confirmation of this was obtained

when CrO_3 oxidation of this gum, followed by esterification, yielded a material, shown by GLC to essentially consist of equimolar quantities of dimethyl pimelate and dimethyl azelate. Further support has been obtained by synthesis of XIV/XV and, this is described in a separate section. A decision in favour of XIV could be made as follows:

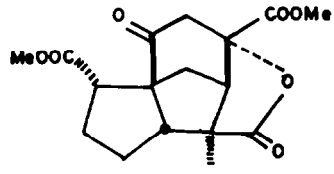
Of the structures XIV and XV, only XV is capable of yielding dimethyl azelate after periodic acid cleavage and esterification. Hence, the pure lac resin was oxidized (Jones), hydrolysed, further oxidized with $NaIO_4$ and then esterified and, the total esters vacuum distilled. Since, the distillate showed dimethyl pimelate and dimethyl azelate in the same ratio as had been obtained earlier (Table 1) without the periodate oxidation step, alternative XV can be ruled out.

No pure compound could be isolated from pool F, which besides showing (TLC) traces of VIII and XIV, apparently contains several byproducts from the oxidation-hydrolysis-esterification sequence.

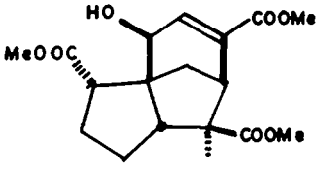
The above results clearly reveal the points of linkage of various constituent lac acids of pure lac resin. However, in order to find out the number of units of one type having the same points of attachments, it is necessary to get a quantitative picture of the above results. In order to do this, oxidation-hydrolysis of pure lac resin was



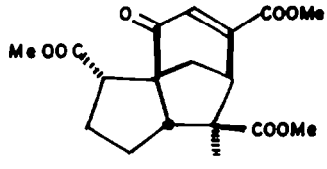
X



XI



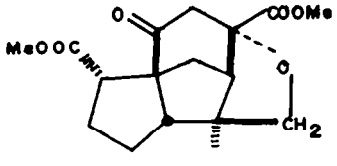
XII



XIII

$HOH_2C \cdot (CH_2)_5 \cdot C(=O)-CH(OH)-(CH_2)_7 \cdot COOMe$ XIV

$HOH_2C \cdot (CH_2)_5 \cdot CH(OH)-C(=O)-(CH_2)_7 \cdot COOMe$ XV



XVI

repeated and the resulting product was now esterified with MeOH–H_2SO_4 instead of diazomethane.* It has already been noted[1] that dimethyl *epi*shellolate (VIII) and dimethyl shellolate are not amenable to GLC analysis (decomposition on column) and now we find that compound XIV also behaves likewise. Hence in order to estimate various products by GLC, it was found essential to remove VIII and XIV by column chromatography before carrying out a GLC analysis; the estimation of VIII and XIV could be carried out subsequently after further oxidation-esterification to keto triester XIII (for dimethyl *epi*shellolate) and dimethyl pimelate, dimethyl azelate (for XIV) as already demonstrated earlier for a similar situation.[1]

Table 3 summarizes the results of these estimations. The column, corrected yield (%), gives values for yields extrapolated to 100% yield and includes the molecular weight term; the conversion factors, based on yields (oxidation-esterification) actually

TABLE 3. ESTIMATION OF PRODUCTS FROM OXIDATION-HYDROLYSIS – ESTERIFICATION OF PURE LAC RESIN

No.	Compound[a]	RRT[b]	Weight yield (%)	Corrected[c] yield (%)	Molar ratio
1	Dimethyl azelate	—	15·5	13·7	2·1
2	Dimethyl pimelate	—	10·3	9·2	1·6
3	Dimethyl *epi*laccishellolate (X)	1	9·1	9·2	1·0
4	Keto ether (XVI)	1·4	6·2	9·9	1·0
5	Keto triester (XIII)	1·66			
6	Hydroxy triester (XII)	1·92	22·4	30·6	2·9
7	Dihydroxy-keto[d] palmitate (XIV)	(azelate)	10·6	9·4	1·4
		(pimelate)	6·3	5·6	1·0
8	Dimethyl[d] *epi*shellolate (VIII)	(Keto triester)	7·5	12·1	1·2
9	Unidentified	—	11·9	—	—

[a] All terpene compounds, include minor amounts of their C_7-epimers, which were detected by TLC/GLC

[b] Relative retention times in terms of dimethyl *epi*laccishellolate; column; 20% silicone SE 30; temp: 280°; gas: 30 ml/min

[c] Corrected for actual yields obtained with pure lac acids and after ignoring unidentified products. Correction factor used for hydroxy triester, 2·0; for other factors see Ref 1

[d] Estimated after further oxidation (*vide* text)

obtained with pure lac acids, have been described.[1] The molar ratios have been derived in the usual manner. During this estimation, one new product was detected and identified as the keto ether (XVI), already described[1]; traces of its C_7-epimer were also detected.

From the results reported in Table 3, it is clear that of the three aleuritic acid units, two must be linked only through the COOH group (XVII), while the third unit must have C_{16} and C_9 hydroxyls linked (XVIII). It may be noted that these conclusions are consistent with the earlier results (Table 1) obtained by a slightly different procedure. Formation of dimethyl *epi*laccishellolate requires that laccijalaric acid must have the C_5-OH linked, while the C_7-aldehyde must be free (XIX) or involved in an acid-sensitive linkage (e.g. acetal). The mode of linkage of the five jalaric (*epi*shellolic) acid

* Since we find that, in at least some jalaric acid (epishellolic acid) units, C_5 hydroxyl is free (isolation of keto lactone XI), it is necessary to avoid diazomethane, which has been demonstrated[1] to add to keto esters, such as XIII. Moreover, MeOH–H_2SO_4 has been shown[1] to convert keto lactone (XI), which decomposes during GLC, into the triester XIII, which can be estimated by GLC.

units are also clear (XX–XXII) and these along with conclusions reached earlier for other acids are summarized in Fig 1. Since, the various terpene lac acid derivatives obtained in the present work have α-configuration at C_7 (structures as depicted in this communication) and the corresponding epimeric compounds were detected to a small extent only, the most preponderant configuration (7α) has been shown in Fig 1.

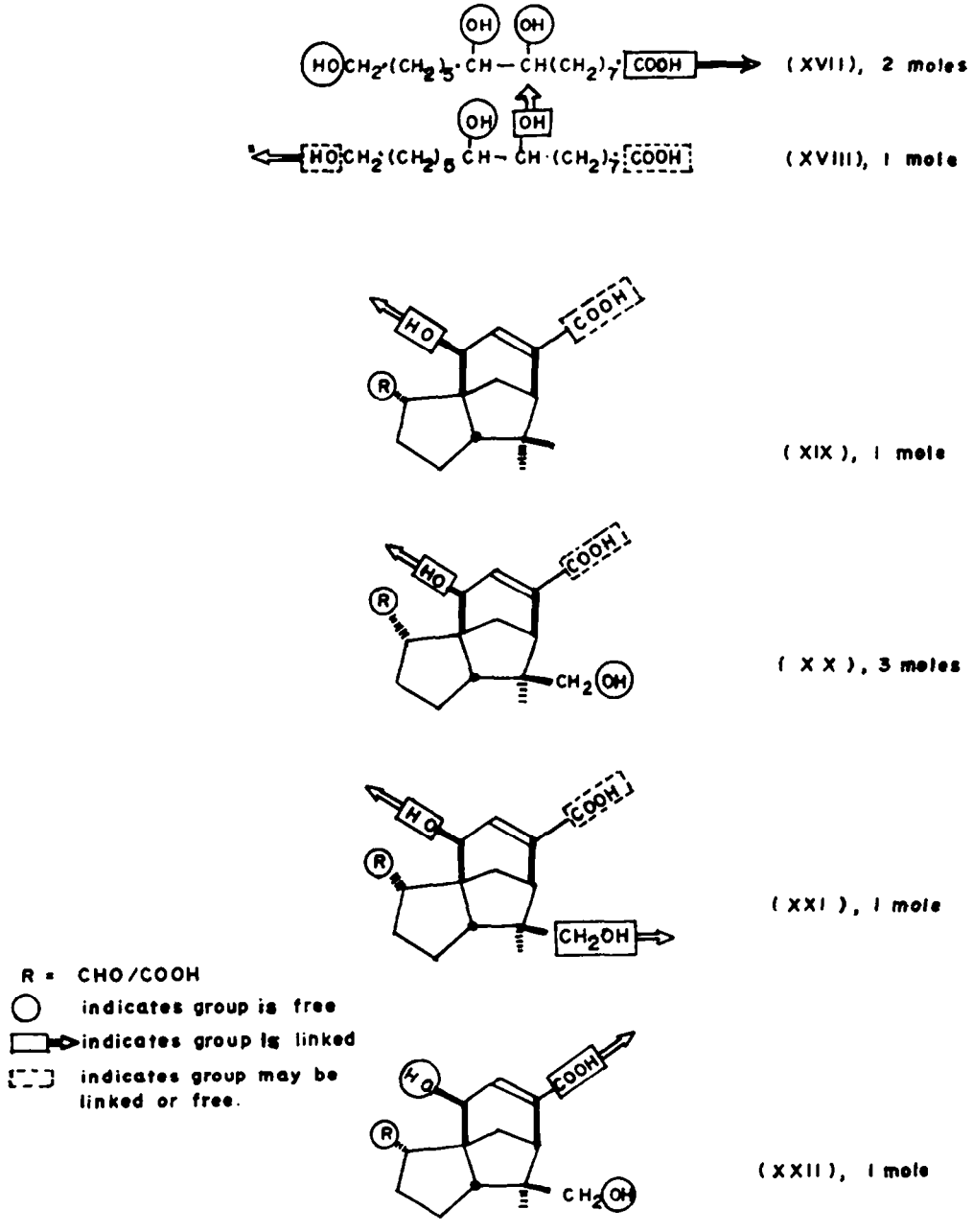


FIG 1 Points of linkage of Constituent acids of pure lac resin.

Furthermore, since only approximately half of the terpene acids from hard resin have aldehyde group,[6] the group at C_7, in Fig 1, has been depicted by R (= aldehyde or carboxyl).

Work is now in progress on the "soft resin" of lac with a view to isolating compounds having only two or three constituent acids. Attempts are also being made to devise methods for selective cleavage of pure lac resin with a view to establish the sequence of linkage of constituent acids.

Partial synthesis of methyl dihydroxy-keto-palmitate (XIV/XV)

The recently described procedure of Cohen and Tsuji[7] for converting oxiranes into α-ketols has been utilised for effecting a partial synthesis of XIV/XV. Methyl 16-hydroxy-Δ^9-hexadecenoate,[8] readily obtainable from aleuritic acid, was epoxidised (perbenzoic acid) and the crude product treated with DMSO in presence of $BF_3 \cdot Et_2O$. Three products, identified spectroscopically as methyl 16-hydroxy-9(or 10)-oxo-palmitate (19%), an α-ketol (15%), and methyl aleuritate (8%) could be isolated. The α-ketol, which is expected to be a mixture (XIV, XV) was found to have spectral characteristics (IR, PMR) and TLC behaviour indistinguishable from that of the product from oxidation-hydrolysis-esterification of pure lac resin.

EXPERIMENTAL

For general remarks see Part IV[1] of this series.

Action of MeI–CaO *in DMSO on aleuritic acid*

To a soln of aleuritic acid (m.p. 100–101°; 1·5 g) in dry DMSO (45 ml), CaO (10 g) and MeI (35 ml) were added and the mixture stirred at room temp (~30°) for 96 hr and then worked up as usual and the product (1·3 g) chromatographed over Al_2O_3/II (20 cm × 2·2 cm) with TLC monitoring (solvent: C_6H_6–EtOAc–acetone, 7:4:2; temp 30°):

Frac. 1	Hexane	250 ml × 8	0·290 g; essentially single spot with R_f 0·58
Frac. 2	50% C_6H_6 in hexane	250 ml × 4	0·140 g; essentially single spot with R_f 0·50
Frac. 3	C_6H_6	250 ml × 4	0·492 g; two spots, R_f 0·40, 0·28
	1% MeOH in C_6H_6	250 ml × 4	
Frac. 4	5% MeOH in C_6H_6	200 ml × 5	0·100 g, essentially methyl aleuritate

Frac. 1 on distillation gave a viscous liquid b.p. 230–240° (bath)/3 mm (GLC, single peak; temp 250°; gas 30 ml/min) identified as trimethyl ether of methyl aleuritate (V). IR: OH absent; COOMe 1750 cm^{-1}; PMR (CCl_4): COOMe 3 H singlet at 218 c/s; three OMe, 3 H singlets at 196, 202 and 202 c/s. (Found: C, 66·44; H, 11·38. $C_{20}H_{40}O_5$ requires: C, 66·63; H, 11·18%).

Frac. 2 purified by inverted dry column chromatography (IDCC)[9] on silica gel gave IV; IR: OH 3410 cm^{-1}; COOMe 1734 cm^{-1}; PMR (CCl_4): COOMe 3 H singlet at 218 c/s; two OMe 3 H singlets at 197 and 202 c/s (OMe in methyl ω-methoxy stearate appears at 196 c/s). (Found: C, 65·43; H, 11·03. $C_{19}H_{38}O_5$ requires: C, 65·86; H, 11·05%).

Frac. 3 after purification by IDCC on silica gel yielded III; IR: OH 3315 cm^{-1}; COOMe 1735 cm^{-1}; PMR (CCl_4): COOMe 3 H singlet at 218 c/s; two OMe 6 H singlet at 202 c/s. (Found: C, 65·72; H, 11·24. $C_{19}H_{38}O_5$ requires: C, 65·86; H, 11·05%). The other component isolated as a gum (150 mg; GLC, single peak; temp: 250°; gas 30 ml/min) was identified as II; IR: OH 3350 cm^{-1}; COOMe 1740 cm^{-1}; PMR (CCl_4): $COOCH_3$ 3 H singlet at 218 c/s; OMe 3 H singlet at 202 c/s; CHOMe 1 H multiplet centred at 171 c/s; CH_2OH 2 H multiplet centred at 211 c/s. (Found: C, 64·77; H, 10·73. $C_{18}H_{36}O_5$ requires: C, 65·02; H, 10·92%).

Frac. 4 on crystallization from acetone furnished a substance m.p. 70–71° identified (IR, mixed m.p.) as methyl aleuritate.

Action of MeI–CaO *in DMSO on dimethyl epishellolate*

Dimethyl epishellolate (2 g) in dry DMSO (30 ml) was treated with CaO (10 g) and MeI (30 ml) and the gummy product (1·9 g) chromatographed over Al_2O_3/II (21 cm × 2·3 cm) with TLC monitoring (solvent system: C_6H_6, EtOAc, acetone, 7:4:4, temp 30°). C_6H_6 eluate (500 ml) gave a product (75 mg) which after IDCC and crystallization from C_6H_6-hexane (1:1) furnished prisms m.p. 105–106° and was identified as the monomethyl ether of IX; λ_{max}^{EtOH} 227 mμ, ε 6200; IR: OH 3390 cm^{-1}; COOMe 1694 cm^{-1}; C=C 1627, 803 cm^{-1}; PMR ($CDCl_3$): $-\underset{|}{\overset{|}{C}}-Me$, 3 H singlet at 76 c/s; OMe, 3 H singlet at 192 c/s; two COOMe, 3 H singlets at 220 and 225 c/s; $-CH=\underset{|}{C}-COOMe$, 1 H doublet ($J$ = 2·5 c/s) at 394 c/s and $-\underset{|}{C}-CH_2-O$, degenerate AB quartet at 186 c/s. (Found: C, 64·1; H, 7·8. $C_{18}H_{26}O_6$ requires: C, 63·88; H, 7·74%).

Determination of points of linkage of two aleuritic acid units in pure lac resin

Pure lac fraction (4 g) in acetone (1200 ml) was oxidized with Jones reagent (60 ml; 14 g CrO_3 in 42 ml H_2O containing 11·6 ml conc H_2SO_4) at ~30° for 24 hr. Usual work up gave a gummy product (3·5 g) which was used in the following experiments.

(a) The gummy product (425 mg) in EtOH (10 ml) was esterified with etherial CH_2N_2 and the resulting product distilled at 2·5 mm from an oil bath (150–160°). The distillate (70 mg) was analysed by GLC (Column: 20% tung oil polymer; temp: 200°; H_2 press 10 p.s.i.) and consisted of one major component (80%). The distillate was chromatographed over silica gel/IIB (13 cm × 1 cm); 5% EtOAc in C_6H_6 (50 ml × 5) eluted in the later fractions pure dimethyl pimelate (mixed GLC, IR).

(b) The gummy product (305 mg) was hydrolysed with KOH aq (3 ml, 10%) at 30° for 48 hr and the acids isolated after the usual work up were taken up in EtOH (10 ml) and esterified (etherial CH_2N_2). The total esters (310 mg) were distilled at 2·5 mm (bath temp: 150–160°) to give a product (89 mg) which on GLC analysis (as above) was found to contain dimethyl pimelate (36%) and dimethyl azelate (50%). Chromatography over silica gel/IIB (15 cm × 1 cm) afforded in C_6H_6 eluate (10 ml × 7), pure dimethyl azelate (mixed GLC, IR) in the later fractions. Pure dimethyl pimelate was isolated from the tail fractions of the 5% EtOAc in benzene fractions (10 ml × 9), and identified by mixed GLC and IR.

Oxidation-hydrolysis-esterification (CH_2N_2) *of pure lac resin*

The gummy product (2·5 g) was treated with KOH aq (25 ml 10%) at 30° for 48 hr and the total acids, isolated in the usual manner, were dissolved in EtOH (50 ml) and esterified (etherial CH_2N_2). The total esters (2·15 g) were chromatographed over silica gel/IIB (18·5 cm × 3·2 cm) and the column was eluted with C_6H_6 and EtOAc in C_6H_6 mixtures. The various fractions with TLC monitoring (solvent: C_6H_6–EtOAc–acetone, 7:4:2: temp 30°) were grouped into six pools as summarized in Table 2.

Pool B (260 mg) was rechromatographed on silica gel/IIB (19 cm × 1 cm) 5% EtOAc in C_6H_6 (100 ml × 5) eluted a compound (58 mg) which on crystallization (hexane) gave needles m.p. 93–94°, identified as X.

Pool D (536 mg) after rechromatography on Al_2O_3/II (18 cm × 1 cm) yielded in 0·5% MeOH in C_6H_6 eluate (25 ml × 7), a product (198 mg), which on crystallization from hexane–EtOH (4:1) furnished rhombs m.p. 131–32°, identified as XII. (Found: C, 61·42; H, 6·86%. $C_{18}H_{24}O_7$ requires: C, 61·35; H, 6·86%). This compound (160 mg) was oxidized with Jones reagent (3 ml) which on usual work up followed by esterification (MeOH–H_2SO_4) gave a gummy product (130 mg GLC, 95% pure; temp: 250°; gas 30 ml/min). Chromatography of the product on silica gel/IIB (10 g; 16 cm × 1 cm) gave in the C_6H_6 eluates (50 ml × 5) a pure compound (51 mg) identified (IR, mixed GLC) as XIII.

Pool E (391 mg) was rechromatographed on Al_2O_3/II (17 cm × 1 cm) using TLC monitoring (solvent system: C_6H_6, EtOAc, acetone, 7:4:4). 0·5% MeOH in C_6H_6 eluates (50 ml × 3) afforded a mixture A, separation of which is described below. Early 1% MeOH in C_6H_6 fractions (50 ml × 2) gave gummy product identified (TLC, IR) as dimethyl shellolate. 2% MeOH in C_6H_6 (30 ml × 4) yielded a gummy material which after crystallization from C_6H_6 furnished prisms m.p. 150–152°, identified (IR, mixed m.p.) as dimethyl *epi*shellolate.

PLC purification (solvent system: C_6H_6, EtOAc 80:20) of mixture A gave the major component (R_f 0·51) as a gum (86 mg), identified by its spectral properties as XIV/XV. (Found: C, 63·92; H, 10·32.

$C_{17}H_{32}O_5$ requires: C, 64·52; H, 10·19%). This compound (XIV/XV) (60 mg) was oxidized with Jones reagent (2 ml). Usual work up followed by esterification (etherial CH_2N_2) afforded a liquid (50 mg) which was distilled at 160° (bath)/2·5 mm and, the distillate on GLC analysis (as above) was found to contain dimethyl pimelate (~40%) and dimethyl azelate (~45%).

Sodium metaperiodate oxidation of oxidized hydrolysed pure lac resin

To a soln of oxidized hydrolyzed pure lac resin (465 mg) in MeOH (10 ml) was added at room temp (~28°) with stirring, an aqueous soln of $NaIO_4$ (3 ml, 12%). Stirring was continued for 30 min and the product worked up in the usual manner to afford mainly an acidic portion (450 mg) which was taken up in EtOH (20 ml) and esterified (etherial CH_2N_2). The total esters were distilled (~155°/2 mm). GLC analysis of the distillate showed it to contain dimethyl pimelate (~35%) and dimethyl azelate (~52%).

Oxidation-hydrolysis-esterification (MeOH, H_2SO_4) *of pure lac resin and estimation of different products*

Pure lac resin (1 g) was oxidized with Jones reagent (15 ml) and after the usual work up the resulting gummy mass (950 mg) was hydrolyzed with KOH aq (8 ml, 20%) at 30° for 48 hr and the total acids esterified (100 ml MeOH containing 6 ml conc H_2SO_4). The ester mixture (803 mg) was chromatographed on SiO_2 gel/IIB (27 cm × 1·5 cm) and the column was eluted with C_6H_6 and C_6H_6 containing EtOAc. The various fractions were grouped into pools A, B, C, D and E with TLC monitoring (solvent system: C_6H_6, EtOAc, acetone, 7:4:4). Pools A, B and C were analysed by GLC. Pools D and E were reoxidized with Jones reagent, esterified (MeOH, H_2SO_4) and were then analysed by GLC (column: 20% silicone SE 30; temp: programmed, 150–250°, 6°/min; gas, 50 ml/min). The GLC results are summarized in Table 3.

Partial synthesis of methyl dihydroxy-keto-palmitate (XIV/XV)

(a) *Methyl 9,10-epoxy-16-hydroxy-hexadecenoate.* A $CHCl_3$ solution (50 ml) of perbenzoic acid (21 mg/ml) was added to a cooled (~10°) $CHCl_3$ soln (20 ml) of methyl 16-hydroxy-Δ^9-hexadecenoate (720 mg). The mixture was allowed to stand at ~10° for 48 hr. After usual work up the epoxide was obtained as a gum (700 mg GLC, single peak; temp: 250°; gas 30 ml/min); IR: OH 3375 cm^{-1}; COOMe 1740 cm^{-1}; PMR ($CDCl_3$): $(CH_2)_n$, broad signal at 83 c/s; $CH_2-\underset{\diagdown\,\diagup}{CH}-\underset{}{CH}-CH_2$, broad signal at 155 c/s; $CH-\underline{C}H_2-OH$, triplet (J = 6 c/s) at 214 c/s; $COO\underline{C}H_3$ singlet at 215 c/s. (Found: C, 58·8; H, 9·4. $C_{17}H_{32}O_4$ requires: C, 58·60; H, 9·26%).

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(b) *Methyl dihydroxy-keto-palmitate* (XIV/XV). To a soln of the above epoxide (670 mg) in DMSO (5 ml, freshly distilled over calcium hydride), BF_3–Et_2O (0·05 ml) was added and the mixture heated on a steam bath for 22 hr. Additional portions (0·03 and 0·02 ml) of BF_3–Et_2O were added at the end of 15 and 20 hr respectively. The reaction mixture was poured into ice water and extracted with $CHCl_3$ (30 ml × 3). The extract was washed with water (10 ml × 3), dried (Na_2SO_4) and solvent flashed off to furnish a product (650 mg), which was chromatographed on silica gel/IIB (18·5 cm × 1 cm) with TLC monitoring (solvent system: C_6H_6, EtOAc, acetone, 7:4:4; temp 30°).

Frac. 1	C_6H_6 5% EtOAc in C_6H_6	150 ml 100 ml	98 mg; mixture of two components: R_f 0·95, 0·85
Frac. 2	5% EtOAc in C_6H_6	100 ml	51 mg; mixture of two components: R_f 0·85, 0·75
Frac. 3	10% EtOAc in C_6H_6	200 ml	77 mg; essentially single spot with R_f 0·68
Frac. 4	20% EtOAc in C_6H_6	200 ml	65 mg; pure, R_f 0·51
Frac. 5	30% EtOAc in C_6H_6	200 ml × 2	67 mg; mixture of two compounds: R_f 0·51 and 0·20
Frac. 6	40% EtOAc in 200 ml C_6H_6		37 mg; pure, R_f 0·2

Frac. 3 after rechromatography (silica gel/IIB; 14 cm × 0·5 cm) furnished in 10% EtOAc in C_6H_6 eluate a homogenous product (TLC) identified by its spectral properties as methyl 16-hydroxy-9-(or 10)-oxo-palmitate. IR: OH 3340 cm^{-1}; COOMe 1740 cm^{-1}. PMR (CCl_4): $CH_2-\underline{C}H_2-OH$, 2 H triplet (J = 6 c/s) at 212 c/s; $COO\underline{C}H_3$, singlet at 217 c/s.

Frac. 4, though pure (TLC in several systems) could not be induced to crystallize. Its spectral properties led to its identification as (XIV/XV).

Frac. 6 was identified (TLC, IR) as methyl aleuritate.

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