Tetrahedron. Vol. 30, pp. 867 to 874. Pergamon Press 1974. Printed in Great Britain

CHEMISTRY OF LAC RESIN—VI[a]

COMPONENTS OF SOFT RESIN[b,c]

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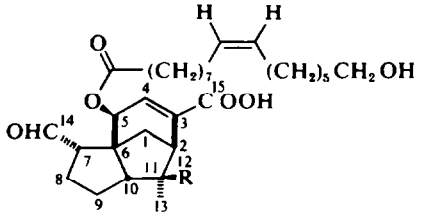
(*Received in the UK* 7 *August* 1973; *Accepted for publication* 30 *August* 1973)

Abstract—From the soft resin fraction of *Palas* seedlac, we have succeeded in isolating four, essentially pure acid esters, which together constitute the bulk of the soft resin. We have termed these acid esters, jalaric ester-I, jalaric ester-II, laccijalaric ester-I and laccijalaric ester-II and, have assigned to these, structures **2**, **4**, **1** and **3** respectively.

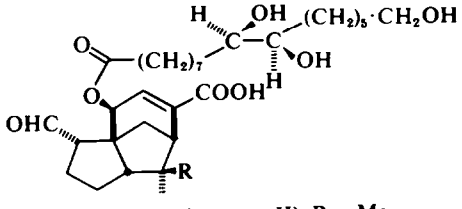
We have already described the gross separation of *Palas* seedlac resin into "hard" and "soft" resin fractions.[1] Nature of the 'hard resin' has been discussed earlier[2,3] and we report now on the isolation and characterization of major constituents of the 'soft resin', which by virtue of its method of isolation,[1] is acidic in character.

This work was primarily undertaken to see if soft resin will contain inter-esters of substantially lower molecular weight than those found in hard resin Such a finding is expected to shed further light on the structure of the "pure lac resins".[2,3] TLC of the soft resin showed that four components are predominating, of which two (R_f 0·40, 0·15) are major. By a judicious combination of fractional solvent precipitation and chromatography it has been possible to isolate (Fig 1) these constituents in an essentially pure state. Table 1 records some characteristics of these compounds.

From UV absorption (Table 1) of these compounds it became clear that all four compounds contain a terpene lac acid moiety[2] and further, from a comparison of the $E^{1\%}_{1cm}$ values (Table 1) of these compounds with the average $E^{1\%}_{1cm}$ value (~ 202) of terpenic lac acids,[2] it appeared most likely that the terpenic acid moiety constitutes approx. half of the molecule. By following the methods developed earlier[2,3] for probing the structure of the "pure lac resin", it has been possible to establish the structures of these compounds (decreasing R_f values) as **1**, **2**, **3** and **4** respectively. These structures are fully supported by their PMR spectra. Structures **3** and **4** are further borne out by partial synthesis. In the following pages we summarise the evidence supporting these conclusions.



1 (laccijalaric ester – I): R = Me
2 (jalaric ester – I): R = CH_2OH



3 (laccijalaric ester – II): R = Me
4 (jalaric ester – II): R = CH_2OH

Structure

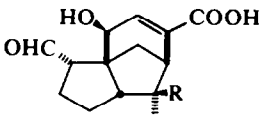
Jalaric ester-II. This compound (colorless foam), which could be comparatively easily isolated, was investigated first. By virtue of its method of isolation, it is an acid. Its IR spectrum (Nujol) shows bands for OH (3300 cm^{-1}, broad) and apparently several overlapping absorptions (1675–1740 cm^{-1}) in the C=O region, besides C=C absorption (1630 cm^{-1}). Room temperature saponification (5 hr)[1] yielded primarily jalaric acid (**5**), as detected by paper chromatography,[1] as the water-soluble acid. Simultaneous Ag_2O oxidative-base hydrolysis gave a product, which after CH_2N_2 esterification, was shown by TLC[1] to essentially consist of methyl aleuritate[5] (**12**), and dimethyl epishellolate[4] (**7**) with minor amounts of dimethyl shellolate[4] (**9**). Jones oxidation, followed by alkaline hydrolysis and esterification (CH_2N_2) yielded a product, which was analyzed by column chromatography-GLC, as discussed in detail earlier[2,3] for "pure lac resin". In this way, the product from this sequence of reactions was shown to be dimethyl pimelate, dimethyl aze-

*Part V: *Tetrahedron* **26**, 4387 (1970).
[b]Communication No. 1771, National Chemical Laboratory, Poona.
[c]In part, abstracted from the Ph.D thesis of A. N. Singh (Poona University, 1971).

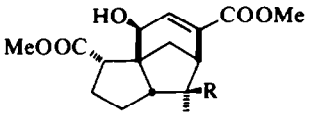
Table 1. Some characteristics of "soft resin" components

	Laccijalaric ester-I (1)	Jalaric ester-I (2)	Laccijalaric ester-II (3)	Jalaric ester-II (4)
R_f (TLC)*	0·90	0·65	0·40	0·15
Physical state	gum	gum	Foam	Foam
Molecular formula	$C_{31}H_{48}O_6$	$C_{31}H_{48}O_7$	$C_{31}H_{50}O_8$	$C_{31}H_{50}O_9$
$[\alpha]_D^{CHCl_3}$	+65·3	+68·6	+65·6	+69·6
UV: λ_{max}^{EtOH} nm (ϵ)	~216 (7350)	~216 (6350)	~216 (7500)	~216 (6200)
$E_{1cm}^{1\%}$	123	119	137	109

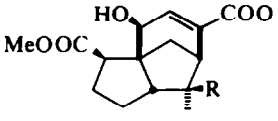
*Solvent system: C_6H_6—EtOAc—AcOH: 20–80–3; Solvent front: 10 cm; adsorbent: silica gel (0·3 mm layers); temp.: ~27°.



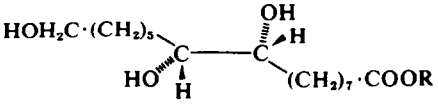
5: R = CH_2OH
6: R = Me



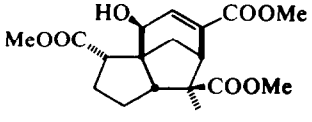
7: R = CH_2OH
8: R = Me



9: R = CH_2OH
10: R = Me



11: R = H
12: R = Me



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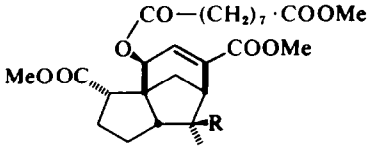
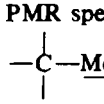


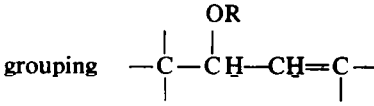
14: R = COOMe
15: R = Me

late and the hydroxy triester (**13**)[3] in approximate molar ratios of 1:1:1. These data are consistent with the formulation of this compound, which we name jalaric ester-II, as **4**.

Structure **4** could be confirmed as follows: Jones oxidation of this compound, followed by esterification with CH_2N_2, yielded a product, which was separated by SiO_2 gel chromatography into dimethyl pimelate and another ester analysing for $C_{28}H_{40}O_{10}$ [M^+, *m/e* 536; $(M\text{-}CH_3OH)^+$, *m/e* 504] and, clearly recognized as **14** from its spectral characteristics. Thus, its mass spectrum displays the expected fragmentations depicted in **16**. Its PMR spectrum (CCl_4) shows signals assignable to



—Me (3H, s, 1·33 ppm), four COOMe (3H singlets at 3·53, 3·62, 3·66 and 3·70 ppm), and the

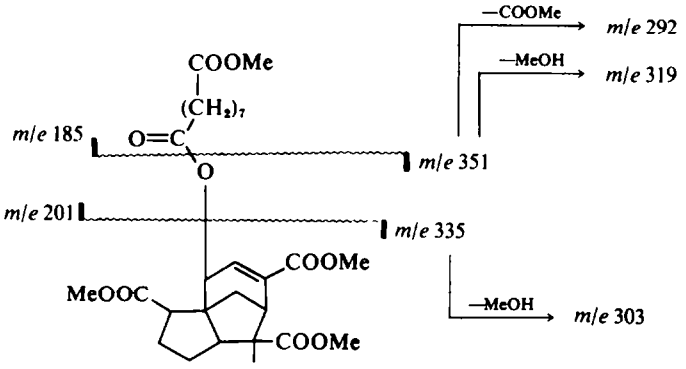


grouping (1H, doublets at 5·78 and 6·36 ppm, each with J = 2·5 Hz) characteristic[4] of all the known terpenic lac acids. Finally, a synthetic sample of **14**, prepared by condensation of acid chloride of monomethyl azelate with the hydroxy triester (**13**), was found to be completely identical (IR, PMR, Mass) with the sample obtained by the above degradation from natural jalaric ester—II (**4**).

A partial synthesis of jalaric ester-II is described later.

Laccijalaric ester-II. By following exactly the methods and techniques exploited for settling the structure of jalaric ester-II, as described above, laccijalaric ester-II was shown to be an inter-ester derived from laccijalaric acid (**6**) and aleutitic acid (**11**) and to possess the structure **3**. The partially degraded ester **15** was also synthesised in a like manner.

Jalaric ester-I and laccijalaric ester-I. When subjected to the action of Ag_2O-NaOH, jalaric ester-I yielded a product, which after CH_2N_2 esterification,



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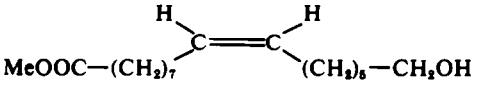

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was separated by column chromatography into dimethyl epishellolate (and minor amounts of dimethyl shellolate) and an unsaturated fatty acid ester. This fatty ester was recognised from its spectral data (IR, PMR, Mass) as methyl 16-hydroxy-*cis*-9-hexadecenoate (**17**). Identification of **17** was completed by its comparison (PMR, Mass) with an authentic sample of its *trans*-isomer.*[6] The presence of this acid (**17**) as a minor constituent of shellac hydrolysate has been noted earlier[7] and the compound has been synthesised.[8] In view of the inter-esterification pattern observed in **3** and **4** this compound is assigned structure **2**.

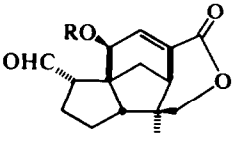
In a like manner, laccijalaric ester-I has been shown to possess structure **1**.

Partial synthesis. Synthesis of laccijalaric ester-II and jalaric ester-II from the respective constituent acids has been realized. Problem of synthesis, for example of jalaric ester-II (**4**) is essentially that of selective protection of free hydroxyls of **4** in the constituent acids, jalaric acid (**5**) and aleuritic acid (**11**), followed by esterification and regeneration of blocked groups without affecting the new ester linkage. After considerable unsuccessful probing reactions involving the use of 2,3-dihydropyran,[9] trityl chloride[9] or boric acid,[10] the aim was realised as under.

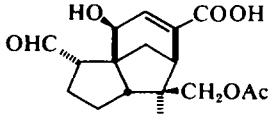
In view of the known[11] chemistry of shellolic acid (*cf* **9**) it was anticipated that jalaric acid (**5**) should yield the lactone **18** which should be susceptible to facile hydrolysis. In practice, it was found that a short exposure of jalaric acid to Ac_2O and NaOAc in refluxing benzene resulted in the formation of the desired δ-lactone (**18**) besides small amounts of δ-lactone acetate (**19**) and jalaric acid and monoacetate (**20**). As expected δ-lactone could be readily cleaved by a short treatment with $NaHCO_3$ in aqueous dioxane. This property was, then exploited for the partial synthesis of jalaric ester-II (**4**). The three hydroxyl groups in aleuritic acid (**11**) were best protected as formates and, the triformyl aleuritic acid (**21**), obtained by exposure of aleuritic acid to formic-acetic anhydride[12], was converted to the corresponding acid chloride (**22**) by oxalyl chloride. Interaction of this acid chloride with the jalaric acid δ-lactone (**18**) in benzene containing some pyridine gave the required ester (**23**). This, on treatment with $NaHCO_3$ in aqueous dioxane at water-bath temperature for 0·5 hr, yielded, besides small amounts of jalaric and aleuritic acid, the required inter-ester (**4**) as the major product. This was found to be completely identical (TLC, IR, NMR) with the naturally occurring jalaric ester-II.

Partial synthesis of laccijalaric ester-II (**3**) was achieved, on similar lines, from triformyl aleurityl chloride (**22**) and laccijalaric acid (**6**).

PMR spectra. PMR spectra of the inter-esters (**1–4**) were studied in DMSO-d_6 and the spectra are completely in accord with the assigned structures. Table 2 gives a summary of PMR spectral charac-



18: R = H
19: R = Ac



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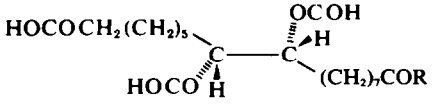


21: R = OH
22: R = Cl

*An authentic sample of *cis*-isomer could not be obtained, whereas the *trans*-isomer was readily on hand. As expected, the mass spectra of the two isomers were virtually identical, while the PMR and IR spectra showed the expected differences [See e.g. C. Y. Hopkins, *Progress in Chem. of Fats and Other Lipids* **8** (part 2), 213 (1965)].

Table 2. PMR spectral characteristics of inter-esters from soft resin and those of their component acids

Compd.	Signal (ppm) assignment*‡							
	Terpene moiety					Aliphatic moiety		
	(multiplicity, J in Hz) C—C(—C)—CH₃ (s)	CH₂OH	CHOR (d, ~2·5)	C=CH (d, ~2·5)	CHO (d, ~2)	CH₂OH	CHOH	CH=CH (t, 5)
Laccijalaric ester-I (1)	0·88, 1·01		5·80	6·43	9·70	3·35		5·31
Jalaric ester-I (2)	1·03	3·13	5·80	6·41	9·71	3·35		5·33
Laccijalaric ester-II (3)	0·88, 1·00		5·77	6·41	9·73		3·10 – 3·50†	
Jalaric ester-II (4)	1·05	3·13	5·80	6·40	9·73		3·10 – 3·50†	
Laccijalaric acid (6)[5]	0·87, 0·98		4·51	6·51	9·71			
Jalaric acid (5)[5]	1·03	3·15	4·52	6·48	9·70			
Aleuritic acid (11)							3·10 – 3·6†	
Methyl 16-hydroxy-*cis*-9-hexadecenoate (17)						3·51		5·30

*Except for 17 for which CCl_4 solution was used, all other spectra were run in DMSO-d_6.
‡In case of multiplets, position given is that of the centre; s = singlet, d = doublet, t = triplet.
†4H, overlapping signals assigned to CH_2OH and two CHOH.

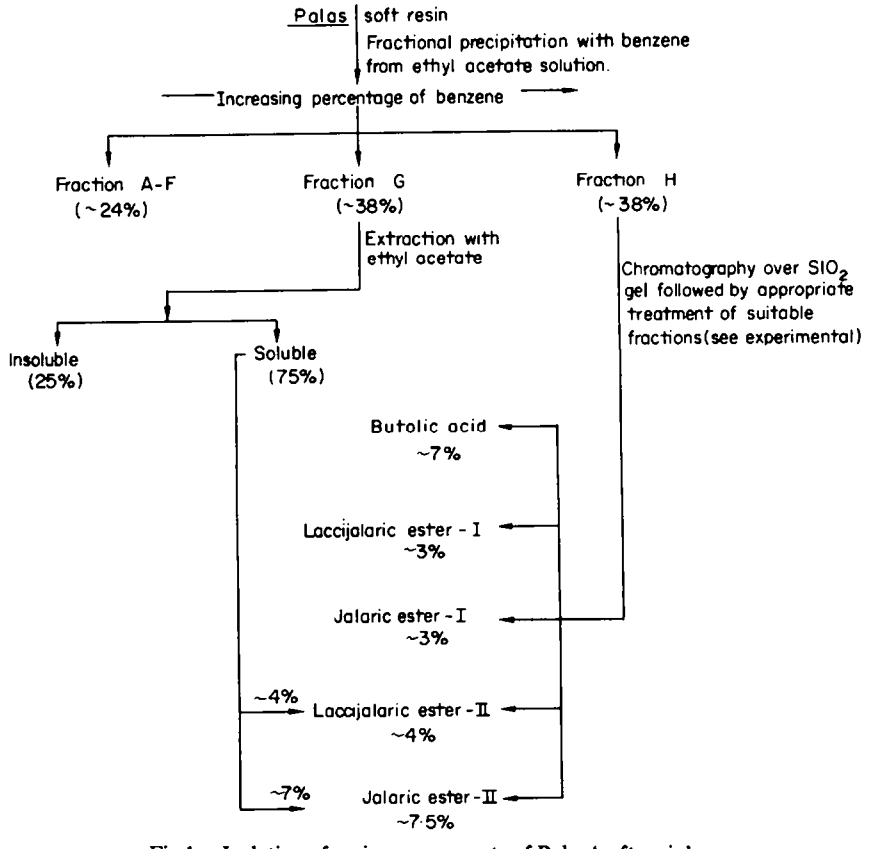
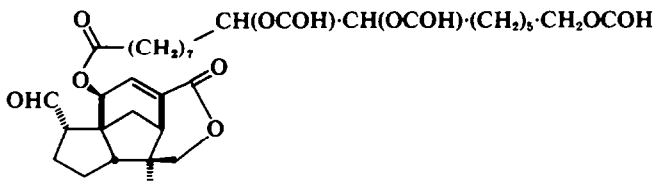


Fig 1. Isolation of major components of Palas 'soft resin'.



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teristics of these compounds as well as those of their component acids.

EXPERIMENTAL

All m.ps and b.ps are uncorrected. Light petroleum refers to the fraction b.p. 40–60°. Optical rotations were measured in $CHCl_3$ at room temp (22–30°).

Silica gel for column chromatography was −100/+200 mesh, and was washed with hot distilled water till sulphate-free, dried, activated at 125–130° (6–8 hr) and standardised.[13] TLC was carried out on silica gel layers (0·3 mm) containing 15% gypsum; visualization agent: conc. H_2SO_4 or iodine vapour. Mixed solvent composition is by volume.

The following instruments were used for spectral/analytical data: Perkin-Elmer spectrophotometer, 350 (UV); Perkin-Elmer infracord, 137E(IR); Varian Associates A-60 spectrometer (PMR; TMS as internal standard); CEC mass spectrometer, 21-110B (Mass; 70 eV, direct inlet system); Aerograph model A-350-B (GLC; 150 cm × 0·5 cm Al columns packed with 20% silicone SE-30 on Chromosorb W of 60-80 mesh, H_2 carrier gas). In the mass spectrum ten important ions are given.

Isolation of 'soft resin' components. Palas soft resin[1] (50 g) was dissolved in EtOAc (600 ml) by slight warming and the soln allowed to stand at 30° for 1 hr. The insoluble material (fraction A, 1·9 g) was removed by decantation, and to the clear soln, benzene (100 ml) was added with stirring when precipitation just started. After allowing it to stand at 30° for 1 hr, the ppt (fraction B, 1·7 g) was separated by decantation. This procedure was repeated 3 times with 100 ml portions of benzene and the fourth time with 200 ml of benzene to give four more fractions: fraction C (1·4 g), fraction D (1·2 g), fraction E (1·5 g) and fraction F (3·6 g). Finally, the clear soln was set aside at 10 ± 1° for 24 hr and fraction G (19 g) separated by decantation. The final clear soln was freed of solvent, at 40 mm, to give a gum (18·4 g) as the fraction H. Both fractions G and H were further processed for the isolation of major components (Fig 1). Details are given below for processing of fraction H.

Fraction H (17·0 g) was chromatographed over silica gel/IIA (42 cm × 5·5 cm) with TLC monitoring (solvent: C_6H_6-EtOAc-AcOH: 20-80-3).

Laccijalaric ester-I (1). Fracs. 1,2 were mixed and triturated with warm light petroleum (100 ml × 5) to remove butolic acid. The residue was extracted with C_6H_6 (50 ml × 5), the extracts freed of solvent to give a gum (2·43 g) which was again triturated with light petroleum (15 ml × 4). The insoluble portion (1·5 g) on chromatography over silica gel/IIA (23·5 cm × 2 cm) gave in 10% EtOAc in C_6H_6 eluates (250 ml × 8) laccijalaric ester-I (0·456 g; R_f 0·74; solvent: C_6H_6-EtOAc-AcOH: 30-70-1).

Jalaric ester-I (2). Frac. 4 (2·0 g) was rechromatographed over silica gel/IIA (26 cm × 3 cm). Material (1·08 g) eluted with 35% EtOAc in C_6H_6 (250 ml × 5) was essentially pure jalaric ester-I, which was further purified by inverted-dry-column-chromatography (IDCC)[14] over silica gel/IIB using C_6H_6-EtOAc-AcOH (20-80-3) as solvent system, to give jalaric ester-I (0·467 g).

Laccijalaric ester-II (3). Frac. 6 (1·4 g) was rechromatographed over silica gel/IIA (21·5 cm × 2 cm) and the material (0·908 g) eluted with later 40% EtOAc in C_6H_6 fractions (500 ml × 4) was further purified by another similar chromatography, followed by charcoal treatment to furnish laccijalaric ester-II (0·70 g).

Jalaric ester-II (4). Frac. 9–12 (1·5 g) were mixed, charcoaled in EtOAc (50 ml) and the clear soln filtered through a column of silica gel/IIA (21 cm × 1·5 cm), which was washed with EtOAc (600 ml). The filtrate and washings were combined and freed of solvent to give a white foam (1·30 g; jalaric ester-II).

Oxidations with silver oxide

General procedure. 10% NaOH aq (25 ml) was added to finely powdered $AgNO_3$ (1·0 g) and the mixture was stirred at room temp (~28°) for 10 min. To this reagent a soln of the lac ester (0·8–1·0 g) in dioxane (20 ml) was added in

Frac. 1	5% EtOAc in C_6H_6	2·0 l	0·62 g; essentially
	10% EtOAc in C_6H_6	2·5 l	components of R_f 0·9
Frac. 2	25% EtOAc in C_6H_6	1·5 l × 4	5·72 g; mixture of lac dye and components with R_f 0·9
Frac. 3	50% EtOAc in C_6H_6	1·5 l × 2	1·62 g; mixture of components with R_f 0·65 and 0·75
Frac. 4	50% EtOAc in C_6H_6	1·5 l × 3	2·08 g; major component, R_f 0·65
Frac. 5	75% EtOAc in C_6H_6	1·5	1·31 g; mixture
Frac. 6	75% EtOAc in C_6H_6	1·5 l × 2	1·4 g; essentially single component, R_f 0·4
Frac. 7	75% EtOAc in C_6H_6	2·5 l	0·51 g; mixture.
Frac. 8	EtOAc	1·5 l × 3	1·05 g; mixture.
Frac. 9	EtOAc	1·5 l × 2	
Frac. 10	1% MeOH in EtOAc	1·5 l	1·51 g; rich in component
Frac. 11	5% MeOH in EtOAc	2·0 l	with R_f 0·15.
Frac. 12	15% MeOH in EtOAc	2·0 l	

one lot and the mixture stirred for 20 min during which the oxidation was complete (as tested by DNP reagent). The mixture was left overnight (14 hr), the precipitated Ag filtered off and thoroughly washed with water. The filtrate, washings were combined, acidified with 1N HCl and extracted with EtOAc to yield total acid mixture, which was esterified (CH_2N_2 in ether).

Products from jalaric ester-II. TLC (solvent: toluene-EtOAc-acetone: 7-4-4) of the product showed spots for methyl aleuritate (R_f 0·22) and dimethyl epilaccishellolate (R_f 0·35).

Products from laccijalaric ester-II. This product, on TLC (solvent system, as above) displayed spots for methyl aleuritate (R_f 0·22) and dimethyl epilaccishellolate (R_f 0·71).

Products from jalaric ester-I. The total ester mixture (0·82 g) was chromatographed on silica gel/IIA (25 cm × 2·2 cm) with TLC monitoring (solvent: C_6H_6-EtOAc-acetone: 7-4-2). The chromatogram was developed and eluted by using increasing amount (0–50%) of EtOAc in benzene. Material (230 mg) eluted with 20-30% EtOAc in benzene (250 ml × 4), on recrystallisation from benzene furnished dimethyl epishellolate[1] (**7**; 85 mg, prisms, m.p. 152–153°). Fractions eluted with benzene (150 ml), 5% EtOAc in benzene (100 ml × 10) and 10% EtOAc in benzene (100 ml × 5) were mixed and the product (400 mg, R_f 0·72) rechromatographed over 15% $AgNO_3$-silica gel IIB[15] (27 cm × 1 cm) with TLC monitoring ($AgNO_3$-silica gel layers: solvent: C_6H_6-EtOAc: 2-1). Material (244 mg, R_f 0·5) eluted with 10% EtOAc in benzene (100 ml × 6) was distilled to give **17** (165 mg), b.p. (bath) 230°/3 mm; IR (smear): OH 3400, 1060 cm^{-1}; C=O 1735 cm^{-1}; Mass: *m/e* 284 (M^+), 266, 252 (100%), 234, 185, 137, 123, 109, 95,81. (Found: C, 71·4; H, 11·1. $C_{17}H_{32}O_3$ requires: C, 71·8; H, 11·3%).

Products from laccijalaric ester-I. This product (1·1 g, TLC, two major spots, R_f 0·65, 0·72; solvent: C_6H_6-EtOAc-acetone: 7:4:2) was worked up essentially as described above for jalaric ester-I to finally give **8**[5] (103 mg, needles from hexane, m.p. 92–93°; R_f 0·65) and **17** (115 mg).

Chromic acid oxidations

Jalaric ester-II. The compound (2·4 g) in acetone (50 ml) was treated dropwise with stirring, at room temp (~28°), with Jones reagent[16] (4 g CrO_3 in 12 ml H_2O containing 3·6ml H_2SO_4) till a brownish-red colour persisted (13 ml). After 24 hr at room temp the mixture was worked up in the usual manner by EtOAc extraction to give a gum (2·15 g) which was further used in the following two experiments.

(i) The above gummy product (450 mg) was hydrolysed with 10% KOH aq (5 ml) at ~30° for 48 hr and the total acids isolated in the usual manner and esterified with diazomethane in ether. The total esters (450 mg) were chromatographed over silica gel/IIA (20 cm × 1·5 cm) with TLC monitoring (solvent: C_6H_6-EtOAc-acetone: 7-4-4). Benzene (1 litre) and 5% EtOAc in benzene (250 ml × 2) eluted material (164 mg) which was distilled at 160° (bath)/2·5 mm and the distillate shown by GLC to consist of dimethyl pimelate (40%) and dimethyl azelate (50%). Material (210 mg; TLC, essentially single spot with R_f 0·62) eluted with 10% EtOAc in benzene (250 ml × 4) and 20% EtOAc in benzene (250 ml × 4), was purified by a further rechromatography over silica gel/IIA and the product (130 mg) recrystallised from hexane-EtOH to furnish rhombs, m.p. 132–133°, identified as **13** by comparison (mixed m.p., IR) with an authentic sample.[3]

(ii) The gummy acid (1·65 g) was esterified (CH_2N_2) and the resulting ester chromatographed over silica gel/IIA (37 cm × 2·2 cm) with TLC monitoring (solvent: 25% EtOAc in benzene). The column was developed and eluted with benzene containing increasing quantities (0–50%) of EtOAc. Material (442 mg; R_f 0·75) eluted with 5% EtOAc in benzene (500 ml) was purified by a rechromatography on silica gel/IIA (22 cm × 1 cm) and was characterised as the ester **14**, gum, $[\alpha]_D$ + 58°. IR (smear): C=O 1715–1740 cm^{-1}; C=C 1635 cm^{-1}; Mass: *m/e* 536 (M^+, < 1%), 504, 351, 335, 320 (100%), 319, 303, 292 (100%), 275, 260. (Found: C, 62·5; H, 7·6. $C_{28}H_{40}O_{10}$ requires: C, 62·7; H, 7·5%).

Laccijalaric ester-II. Laccijalaric ester-II (1·77 g) was oxidised and the product further processed in exactly the same manner as detailed above. The ester **15** was obtained as a gum, $[\alpha]_D$ + 86·4°. λ_{max}^{EtOH} 225 nm, ϵ 8000. IR(Nujol): C=O 1710–1730 cm^{-1}; C=C 1635 cm^{-1}; PMR (CCl_4): —C(Me)— (3H singlets at 0·93 and 1·09 ppm), COOMe (3H singlets at 3·61, 3·65 and 3·71 ppm), —C(H)(OR)—CH=C—COOMe (1H doublets at 5·78 and 6·48 ppm, each with J = 2·5 Hz); Mass: *m/e* 492 (M^+, < 1%), 460, 415, 308 (100%), 307 (100%), 291, 276, 275, 259, 247. (Found: C, 65·6; H, 8·3. $C_{27}H_{40}O_8$ requires: C, 65·8; H, 8·2%).

Esterification of monomethyl azelate with hydroxy triester (**13**)

Preparation of **14**. Monomethyl azelate[17]* (0·4 g) in dry benzene (25 ml) containing dry pyridine (0·5 ml) was converted to the corresponding acid chloride with oxalyl chloride (1·5 ml) in the usual manner. To the resulting acid chloride, freed of solvent and excess oxalyl chloride, was added a soln of **13**[3] (0·6 g) in benzene (25 ml) containing pyridine (0·5 ml). The mixture was refluxed (12 hr) and worked up in the usual manner to give a gum (0·88 g), which was purified by chromatography (*vide* details given under chromic acid oxidation) to give **14** (0·61 g) identical in all respects (TLC, IR, PMR, Mass, $[\alpha]_D$) with the sample obtained from CrO_3 oxidation of jalaric ester-II.

Esterification of monomethyl azelate with dimethyl epilaccishellolate (**8**)

Preparation of **15**. A similar condensation of monomethyl azelate (0·258 g) and **8**[5] (0·314 g) gave after chromatography over silica gel/IIA, **15** (0·327 g; eluted with 2% EtOAc in benzene), identical in all respects (TLC, IR, PMR, Mass) with the sample obtained from laccijalaric ester-II by CrO_3 oxidation.

Partial synthesis of jalaric ester-II (**4**)

Jalaric acid δ-lactone (**18**). Jalaric acid (2·2 g), Ac_2O (8 ml) and NaOAc (0·5 g) were refluxed in benzene (170 ml) for 20 min. The reaction was quenched by pouring into water (200 ml), stirred and let stand for 1 hr to complete decomposition of Ac_2O. The benzene layer was separated, the aqueous phase extracted with EtOAc (60 ml × 3) and the organic extracts combined, and sepa-

*The half ester was more conveniently obtained by Jones oxidation of methyl aleuritate.

rated into acidic (0·6 g) and neutral (1·7 g) parts by 5% $NaHCO_3$ aq.

Neutral material on TLC showed two spots of R_f 0·72 and 0·60 (major) (solvent: C_6H_6-EtOAc-AcOH: 6-30-1). The material was chromatographed on silica gel/IIA (25 cm × 1·8 cm), the column being eluted with benzene containing increasing proportions of EtOAc. 10% EtOAc in benzene (100 ml × 3) eluted *δ-lactone acetate* (**19**; foam, 0·15 g; R_f 0·72); IR(Nujol): C=O 1710–1760 cm^{-1}; PMR ($CDCl_3$): $-\underset{|}{\overset{|}{C}}-\underline{Me}$ (s, 1·23 ppm), CO$\underline{Me}$ (s, 2·17 ppm, $-\underset{|}{\overset{|}{C}}-\underline{CH_2}-O-\overset{\overset{O}{\|}}{C}-$ (2H, s, 4·17 ppm), $-\underset{|}{\overset{|}{C}}-\underline{CH}(OR)-\underline{CH}=\underset{|}{\overset{|}{C}}-\overset{\overset{O}{\|}}{C}-O-$ (2H, m, 5·9 ppm), $-\underset{|}{\overset{|}{CH}}-\underline{CHO}$ (d, 9·77 ppm, J = 1·5 Hz). (Found: C, 67·4; H, 6·9. $C_{17}H_{20}O_5$ requires: C, 67·1; H, 6·6%). 15% EtOAc in benzene (100 ml × 8) eluted the required *jalaric acid δ-lactone* (**18**; foam, 1·21 g; R_f 0·60). λ_{max}^{EtOH} 217 nm, ϵ 4300. IR ($CHCl_3$): C=O 1700-1750 cm^{-1}; PMR ($CDCl_3$): $-\underset{|}{\overset{|}{C}}-\underline{Me}$ (s, 1·2 ppm), $-\underset{|}{\overset{|}{C}}-\underline{CH_2}-O-\overset{\overset{O}{\|}}{C}-$ (2H, s, 4·17 ppm), C$\underline{H}$OH (1H, d, 4·77 ppm, J = 1 Hz), $-C=\underline{CH}-$ (1H, d, 5·99 ppm, J = 1 Hz), $-\underline{CH}-\underline{CHO}$ (d, 9·79 ppm, J = 2·5 Hz). (Found: C, 68·9; H, 7·2. $C_{15}H_{18}O_4$ requires: C, 68·7; H, 6·9%).

The acidic part was chromatographed (silica gel/IIA, 20 cm × 1·8 cm; benzene + increasing amounts of EtOAc), when 15% EtOAc in benzene (100 ml × 6) eluted 0·42 g of a foam, characterised as **20**; IR ($CHCl_3$): C=O 1690–1735 cm^{-1}; C=C 1640 cm^{-1}; PMR ($CDCl_3$): $-\underset{|}{\overset{|}{C}}-\underline{Me}$ (s, 1·13 ppm), OCO$\underline{Me}$ (s, 2·02 ppm), $-\underset{|}{\overset{|}{C}}-\underline{CH_2}-OAc$ (2H, ill-resolved q, 3·87 ppm), C$\underline{H}$OH (bs, 4·7 ppm), $-C=\underline{CH}-$ (bs, 6·7 ppm), $-\underline{CH}-\underline{CHO}$ (bs, 9·72 ppm). (Found: C, 62·7; H, 7·3. $C_{17}H_{22}O_6$ requires: C, 63·3; H, 6·9%).

Triformyl aleuritic acid (**21**). A soln of aleuritic acid (2·0 g) in acetic-formic anhydride[12] (20 ml), obtained by slight warming, was set aside at room temp (~26°) for ~18 hr. Removal of the excess anhydride on a water-bath under reduced pressure (40 mm) gave a solid (2·5 g) which was chromatographed (silica gel/IIA, 21·5 cm × 2 cm), when 15% EtOAc in benzene furnished pure triformyl aleuritic acid (2·3 g), m.p. 64–65° (benzene-light petrol); IR (Nujol): COOH 3150, 2650, 1690 cm^{-1}; —OCOH 1730, 1180 cm^{-1}; PMR (CCl_4): $-\underline{CH_2}OCO$ (2H, t, 4·1 ppm, J = 6 Hz), two C$\underline{H}$OCO (2H, ill-resolved broad signal, 5·07 ppm), $-CH_2OCO\underline{H}$ (1H, s, 7·94 ppm), two —CHOCO$\underline{H}$ (2$\underline{H}$, s, 8·03 ppm). (Found: C, 58·3; H, 7·8. $C_{19}H_{32}O_8$ requires: C, 58·7; H, 8·2%).

Jalaric ester-II (**4**). Triformyl aleuritic acid (0·9 g) was treated with oxalyl chloride (0·4 ml) in dry benzene (15 ml) containing dry pyridine (0·2 ml), first at room temp (15 hr) and then at reflux (20 min). Usual work-up gave the crude acid chloride, to which a soln of the jalaric acid *δ*-lactone (0·6 g) in benzene (25 ml) containing pyridine (0·2 ml), was added. After refluxing for 4·5 hr, solvent was flashed off and the residue treated with water (40 ml), acidified with HCl aq and extracted with EtOAc (40 ml × 4). Usual work up gave a gum (1·48 g), showing essentially one spot on TLC (R_f 0·8; solvent: C_6H_6-EtOAc-AcOH: 6-30-1) and, being the required ester **23**; PMR (CCl_4): two $\underline{CH_2}OCO$ (4H, s, overlapping t, 4·12 ppm), two C$\underline{H}$OCO (2H, ill-resolved signal, 5·08 ppm), $-\underset{|}{\overset{|}{C}}-\underline{CH}(OR)\cdot\underline{CH}-=\underset{|}{\overset{|}{C}}-COO$ (2H, overlapping signals, 5·85 ppm), $CH_2OCO\underline{H}$ (1$\underline{H}$, s, 7·98 ppm), two CHOCO$\underline{H}$ (2$\underline{H}$, s, 8·08 ppm), —C$\underline{H}$O (bs, 9·78 ppm).

The above ester (1·48 g), aqueous dioxane (25 ml, 1:1) and $NaHCO_3$ (1·37 g) were heated on a steambath for 0·5 hr. Solvent was rapidly removed under suction (40 mm) from a steam-bath and the residue treated with water (50 ml) and acidified with H_2SO_4 aq. Usual work-up by extraction with EtOAc (50 ml × 4) gave a product (1·2 g) which was chromatographed (silica gel/IIA, 21 cm × 2 cm; column prepared in 25% benzene in EtOAc), while monitoring with TLC (solvent: 5% AcOH in EtOAc):

Frac. 1	25% C_6H_6 in EtOAc	200 ml	
Frac. 2	EtOAc	100 ml × 4	0·4 g, mixture of aleuritic and jalaric acids.
Frac. 3	EtOAc	100 ml × 8	0·45 g, pure, R_f 0·3
Frac. 4	5% MeOH in EtOAc	100 ml × 8	0·31 g, pure, R_f 0·3

Fractions 3, 4 were combined and the product (foam) shown to be identical (TLC, IR, PMR) with the natural jalaric ester-II (**4**). (Found: C, 65·7; H, 9·1. $C_{31}H_{50}O_9$ requires: C, 65·7; H, 8·9%).

Partial synthesis of laccijalaric ester-II (**3**). Condensation of the acid chloride **22** (from 0·52 g of triformyl aleuritic acid) with laccijalaric acid (0·264 g), exactly as above, yielded a product (0·78 g) which was deformylated with $NaHCO_3$ (0·7 g) in aqueous dioxane as described for jalaric ester-II. The product (0·7 g) was chromatographed (silica gel/IIA 21 cm × 1·8 cm) with TLC (solvent: 1% AcOH in EtOAc) monitoring:

Frac. 1	25% EtOAc in C_6H_6	1 litre	0·1 g, rejected
Frac. 2	50% EtOAc in C_6H_6	100 ml × 2	0·25 g, mixture
Frac. 3	50% EtOAc in C_6H_6	100 ml × 8	0·376 g, pure, R_f 0·52
Frac. 4	25% C_6H_6 in EtOAc	100 ml × 3	0·128 g, R_f 0·4, aleuritic acid

Frac. 3 (foam) was found to be identical (TLC, IR, PMR) with the naturally occurring laccijalaric ester-II (**3**).

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