Structural Investigation of Lac Resin. Part XI.[1] The Role of Acetalisation in Resin Formation, and the Configuration of Jalaric Acid

By **G. B. V. Subramanian,* Javed Iqbal, K. N. Ganesh,** and **N. Sriram,** Department of Chemistry, University of Delhi, Delhi-110007, India

The alkali-stable linkage in shellac has now been recognised as acetalic in nature, in the light of the formation of dioxolans from *threo*-9,10,16-trihydroxyhexadecanoic (aleuritic) acid and the terpene aldehydes of shellac. A method of estimation of the extent of acetalisation is presented. The minor terpene constituents of shellac have now been identified as of the oxo-ether type, previously prepared from the major components. Evidence correlating the configuration of 2-*epi*-shellolic acid with that of the major aldehydic acid is presented.

ALTHOUGH it is generally accepted that lac resin is a polyester [2] formed from terpenes possessing the cedrene skeleton [3,4] and *threo*-aleuritic acid (9,10,16-trihydroxyhexadecanoic acid), we have shown in our earlier papers that (i) alkaline hydrolysis of the processed commercial superblonde shellac or of the pretreated hard resin did not release either the terpene acids or the aleuritic acid completely,[5,6] (ii) the 9- and 10-hydroxy-groups of aleuritic acid are involved in alkali-stable linkages,[7] and (iii) a large part of the aleuritic acid remains in the combined form in the primary gum obtained after treatment with aqueous 20% sodium hydroxide.[8] As one of the main terpenes of shellac is the aldehydic acid jalaric acid, the likelihood of the vicinal glycol system in aleuritic acid

[1] Part X, G. B. V. Subramanian, N. Sriram, V. S. Chauhan, J. Iqbal, and K. N. Ganesh, *J.C.S. Perkin I*, 1976, 967.
[2] A. N. Singh, A. B. Upadhye, V. V. Mhaskar, S. Dev, A. V. Pol, and V. G. Naik, *Tetrahedron*, 1974, **30**, 3689.
[3] R. C. Cookson, N. Lewin, and A. Morrison, *Tetrahedron*, 1962, **18**, 547.
[4] P. Yates and G. F. Field, *Tetrahedron*, 1970, **26**, 3135; P. Yates, P. M. Burke, and G. F. Field, *ibid.*, p. 3159.
[5] R. Madhav, T. R. Seshadri, and G. B. V. Subramanian, *Indian J. Chem.*, 1967, **5**, 182.
[6] H. Singh, R. Madhav, T. R. Seshadri, and G. B. V. Subramanian, *Tetrahedron*, 1967, **23**, 4795.
[7] T. R. Seshadri, N. Sriram, and G. B. V. Subramanian, *Indian J. Chem.*, 1971, **9**, 524, 528.
[8] V. S. Chauhan, N. Sriram, G. B. V. Subramanian, and H. Singh, *J. Chromatog.*, 1973, **84**, 51.

being involved in dioxolan ring formation with the aldehydic function of the terpene has now been investigated. In view of the well known stability [9] of dioxolans and 1,3-dioxans, the 9- and 10-hydroxy-groups would be expected to be preferred for acetalisation rather than the 16-hydroxy-group of aleuritic acid (to give an acyclic acetal). An attempt was therefore made to study the equilibrium by titration with periodic acid in acetic acid or dioxan. Model acetals prepared from piperonal and *threo*-aleuritic acid were unstable to periodic and acetic acids and yielded various results depending on the reaction conditions. The stability of sugar acetals to sodium periodate [10] suggested the use of the latter in the present case; indeed titrations were successfully carried out with this reagent in dioxan solution. Table 1 summarises the results obtained under a wide variety of conditions, including those which may be operative during processing as well as hydrolysis of shellac.

TABLE 1

Results of periodate estimations

	Reactants	% Glycol
1	*threo*-Aleuritic acid	101.7
2	*threo*-Aleuritic acid + $HClO_4$	93.8
3	*threo*-Aleuritic and 2-*epi*-jalaric acids + $HClO_4$	8.4
4	*threo*-Aleuritic acid heated to melting (105 °C) in the absence of catalyst	101.7
5	*threo*-Aleuritic and 2-*epi*-jalaric acids heated to melting (105 °C) in the absence of catalyst	42.6
6	*threo*-Aleuritic acid in aq. N-NaOH (30 °C; 1 h) and neutralised with HCl	98.0
7	*threo*-Aleuritic and 2-*epi*-jalaric acids in aq. N-NaOH (30 °C, 1 h) and neutralised with HCl	88.5
8	Solution of *threo*-aleuritic and 2-*epi*-jalaric acids in water heated to boiling for 5 min	77.0
9	Methyl *threo*-aleuritate and piperonal + $HClO_4$	72.6

In all cases titrations were carried out under analogous conditions (i) with the reagent only, (ii) with aleuritic acid and the reagent, (iii) with the aldehyde and the reagent, and (iv) with aleuritic acid, the aldehyde, and the reagent. In the experiments involving aleuritic acid in dioxan solution with an acid catalyst ($HClO_4$) under anhydrous conditions, esterification could be a competing reaction, and the measured extent of acetalization may thus be less than the actual value. However, it was found that under the above conditions esterification was marginal (*ca.* 6%), the primary process being acetalisation. In all other control experiments employing only aleuritic acid, the glycol function was estimated correctly.

The most noteworthy feature was the ease with which acetalisation takes place, even in aqueous solution without an acid catalyst. All resin samples are thus likely to exist as equilibrium mixtures, the extent of acetalisation depending on the nature of the sample and the treatment it has undergone. The erratic behaviour of shellac samples and the changes brought about by various treatments reported by earlier workers [11] may be accounted for on the basis of the degree of acetalisation.

According to Sukh Dev *et al.*,[12] the aldehydic acids are the primary acids of lac resin, the corresponding alcoholic and acid components arising from Cannizzaro-type reactions during hydrolysis by strong alkali. Hydrolysis of the commercial, superblonde shellac under the conditions used by these authors, as well as under milder conditions to minimise the above reaction, followed by esterification–acetalisation with methanolic hydrogen chloride and chromatography on silica gel gave a number of compounds. The known dimethyl shellolate (I), dimethyl 2-*epi*-shellolate (II), methyl laksholate (III), and methyl 2-*epi*-laksholate (IV) were isolated pure, the 2-*epi*-shellolate being the major product. The two oxo-ethers (V) and (VI), earlier obtained [3,4] by oxidation of (I) and (II) respectively with manganese dioxide were also obtained, as shown by direct comparison with synthetic samples (m.p., mixed m.p., and i.r. and n.m.r.).

TABLE 2

New products from the hydrolysis of superblonde shellac by mild alkali

	N.m.r. data [δ ($CDCl_3$); *J* in Hz]						
	CMe (3 H, s)	CH_2·O	OMe (s)	CO_2Me (3 H, s)	RO·C*H*·OMe	HO·C*H*·CH:C	HO·CH·C*H*:C
Methyl 10β,12-epoxy-13-hydroxy-12-methoxycedr-8-en-15-oate (IX)	1.15	3.28br	3.42 (3 H)	3.82	4.80 (2 H, d)		7.00 (d)
Methyl 12,12-dimethoxy-8,13-epoxy-2β*H*-10-oxocedran-15-oate (VIII)	1.15	3.66 (s)	3.22 (3 H), 3.30 (3 H)	3.78	4.14 (*J* 9.0)		
Methyl 8,13-epoxy-10,12-dioxo-2β*H*-cedran-15-oate (XIX)	1.15	3.66 (s)		3.80	9.80 (d) (CHO)		
Methyl 10β,13-dihydroxy-12,12-dimethoxy-2β*H*-cedr-8-en-15-oate (VII)	1.15	3.30 (2 H)	3.30 (6 H)	3.75	4.10 (*J* 7.5)	4.75 (d)	6.70 (d)

The new compounds listed in Table 2 were characterised by spectral and analytical data in the case of crystalline components.

Although no hemiacetal was isolated, the aldehydic components were present in equilibrium with the corresponding dimethyl acetals. The acetals were readily

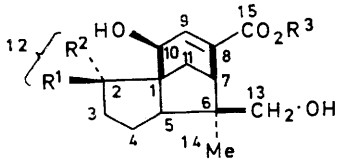
[9] 'Chemistry of the Ether Linkage,' ed. S. Patai, Interscience, New York, 1967, ch. 7.

[10] R. Barker and D. L. MacDonald, *J. Amer. Chem. Soc.*, 1960, **82**, 2301.

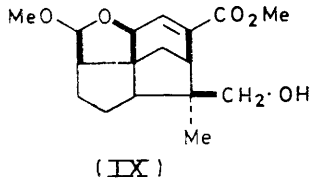
[11] P. K. Bose, K. Sankaranarayanan, and S. C. Sen Gupta, 'Chemistry of Lac,' Indian Lac Research Institute, Ranchi, Indian, 1963, ch. 9 and references cited therein.

[12] M. S. Wadia, R. G. Khurana, V. V. Mhaskar, and S. Dev, *Tetrahedron*, 1969, **25**, 3841.

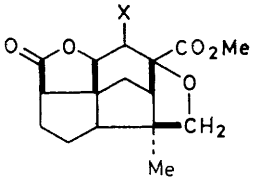
hydrolysed in the presence of dilute mineral acids to the corresponding free aldehydes, as shown by n.m.r. spectra. However, ether saturated with hydrochloric acid hydrolysed the acetal (VIII) only partially, giving free aldehyde and acetal in the ratio 1 : 3 (g.l.c.). The configuration of (VIII) was shown by Jones oxidation to the corresponding acid, followed by esterification and g.l.c., which



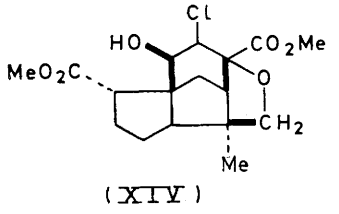
(I) $R^1 = CO_2Me, R^2 = H, R^3 = Me$
(II) $R^1 = H, R^2 = CO_2Me, R^3 = Me$
(III) $R^1 = CH_2{\cdot}OH, R^2 = H, R^3 = Me$
(IV) $R^1 = H, R^2 = CH_2{\cdot}OH, R^3 = Me$
(VII) $R^1 = H, R^2 = CH(OMe)_2, R^3 = Me$
(X) $R^1 = CO_2H, R^2 = R^3 = H$
(XI) $R^2 = R^3 = H, R^1 = CHO$
(XIII) $R^1 = R^3 = H, R^2 = CO_2H$
(XV) $R^1 = H, R^2 = CHO, R^3 = Me$
(XVIII) $R^1 = R^3 = H, R^2 = CHO$



(IX)



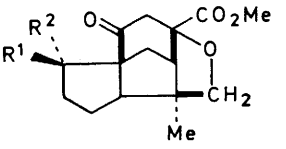
(XIII) X = Cl
(XVI) X = Br



(XIV)

the lactone (XIII), thereby confirming the assignment. In all three cases the reaction proceeded smoothly to give a single product almost quantitatively, thereby excluding the possibility of epimerisation.

We have earlier [1] used the differences in the chemical shift of the allylic proton at C-10 to distinguish between C-2 epimeric terpenes, in $CDCl_3$ [the difference was not



(V) $R^1 = CO_2Me, R^2 = H$
(VI) $R^1 = H, R^2 = CO_2Me$
(VIII) $R^1 = H, R^2 = CH(OMe)_2$
(XVIII) $R^1 = H, R^2 = CH_2{\cdot}OH$
(XIX) $R^1 = H, R^2 = CHO$

indicated the product to be the oxo-ether of dimethyl 2-*epi*-shellolate.

Compound (IX) must have arisen from one of the two jalaric acids (C-2 epimers). The intramolecular oxide ring formation suggested that the parent aldehydic acid should have the same stereochemistry as shellolic acid (X) at C-2. Hence the parent acid appears to be jalaric acid (XI). This acid was not well characterised, since it was a minor component in the total resin and attempts at direct isolation were unsuccessful. The formation of (IX) was erratic in most of the experiments. However this product was different from the major aldehydic acid reported by Sukh Dev *et al.*,[12] which we have now isolated as a pure methyl ester, subsequently hydrolysed to the free acid. Thus the major aldehydic acid which the above workers designated jalaric acid is configurationally related to 2-*epi*-shellolic acid and not to shellolic acid. Another set of experiments carried the same implication. Whereas shellolic acid can readily form a γ-lactone, the epimer (XII) cannot. Sodium hypochlorite converted dimethyl shellolate into the previously known chloro-lactone acid,[3] which was subsequently esterified to give a chloro-lactone methyl ester (XIII). On the other hand dimethyl 2-*epi*-shellolate gave the dimethyl ester (XIV). Similar treatment of the major aldehydic acid followed by esterification gave the diester (XIV) and not observed in $(CD_3)_2SO$]. The spectrum of methyl 2-*epi*-jalarate (XV) was more similar to that of dimethyl 2-*epi*-shellolate than to that of dimethyl shellolate (Table 3).

TABLE 3

N.m.r. data (δ; J in Hz)

	Solvent	$CH_2{\cdot}OH$	$CH{\cdot}OH$ (1 H, d)	C:CH (1 H, d)
Dimethyl shellolate	$CDCl_3$	3.36br (q)	4.56 (J 2.5)	6.66 (J 2.5)
	$(CD_3)_2SO$	3.18 (s)	4.60 (J 2.5)	6.43 (J 2.5)
Dimethyl 2-*epi*-shellolate	$CDCl_3$	3.28br (q)	4.80 (J 2.5)	6.69 (J 2.5)
	$(CD_3)_2SO$	3.18 (s)	4.60 (J 2.5)	6.53 (J 2.5)
Methyl 2-*epi*-jalarate	$CDCl_3$	3.30br (q)	4.75 (J 2.5)	6.72 (J 2.5)
	$(CD_3)_2SO$	3.16 (d)	4.55 (J 1.5)	6.55 (J 1.5)

During reduction of the aldehyde or ester function [1] at C-2 with borohydride no appreciable epimerisation takes place. The absolute stereochemistry of shellolic acid has been well established through spectra, reactions, and an *X*-ray analysis of the bromo-lactone methyl ester [13,14] (XVI). Hence we consider that the major aldehydic

[13] R. C. Cookson, A. Melera, and A. Morrison, *Tetrahedron*, 1962, **18**, 1321.
[14] E. J. Gabe, *Acta Cryst.*, 1962, **15**, 759.

acid of lac resin should be termed 2-*epi*-jalaric acid (XVII).

Methyl 2-*epi*-jalarate, in the presence of moisture, is in equilibrium with the corresponding hydrate as shown by the n.m.r. spectrum, which contains a characteristic acetal doublet (δ 4.00—4.30) and an aldehydic signal corresponding to less than one proton.

Neither shellolic acid nor 2-*epi*-shellolic acid has a tendency to epimerise to any appreciable extent, even in strongly alkaline aqueous solution. However, whereas mild alkaline hydrolysis of the resin yielded 2-*epi*-shellolic acid as the primary product along with 2-*epi*-jalaric acid, strong alkaline hydrolysis gave shellolic acid as the primary product, with 2-*epi*-shellolic acid becoming relatively minor. In earlier work [7] involving a preliminary borohydride reduction of the hard resin followed by strong alkaline hydrolysis a much greater yield of 2-*epi*-laksholic acid rather than laksholic acid was obtained. The hydrolysis results may be summarised as follows. Although various groups of workers have speculated that the resin samples contain nearly 40% each of aleuritic and terpene acids, the amounts actually isolated by alkaline hydrolysis were always *ca.* 20 and 5—10%, respectively. Apparently the remainder was present as acetals. The terpene acids, both aldehydic and non-aldehydic were usually isolated from the aqueous mother liquors after hydrolysis. Under mild hydrolytic conditions, in the absence of Cannizzaro reactions, the products were obtained without epimerisation. On strong alkaline hydrolysis that part of the 2-*epi*-jalaric acid with a free aldehyde function disproportionates, with epimerisation to yield shellolic acid as a primary product. 2-*epi*-Shellolic acid itself has an independent existence in the resin along with 2-*epi*-jalaric acid.

We have earlier shown by g.l.c. analysis [8] the presence of at least five minor terpene components in the strong alkaline hydrolysate of shellac, in addition to the previously reported primary acids. As we now have evidence for the presence of compounds of the oxo-ether type from mild hydrolysis, g.l.c. of the gums from the hard resin (prepared from superblonde shellac) hydrolysate was carried out (on 10% SE-30). The presence of this group of compounds was confirmed, but some of them were not well separated, as shown by an analysis of the pure synthetic samples, *e.g.* (V) and (XVIII). Hence the presence or absence of all the oxo-ethers could not be confirmed. The hydroxylated terpenes were not eluted under the conditions used.

We have no evidence at present enabling us to define unambiguously whether the oxo-ethers are formed during processing of crude shellac (a patented process,* which does not appear to involve any bleaching step) or are present in the parent resin itself. However, we have excluded the possibility of their formation during alkaline hydrolysis through model experiments carried out on shellolic and 2-*epi*-shellolic acids, with an alkali concentration ranging from 4 to 20%. We further suggest that the allylic hydroxy-group may have to remain unesterified to some extent in some of the resin fractions for the oxo-ethers to be present in the alkali hydrolysate.

* Angelo Bros., Calcutta, India.

EXPERIMENTAL

T.l.c. of methyl esters was carried out in chloroform–methanol (96 : 4) and of the free acids in toluene–ethyl formate–formic acid (5 : 4 : 1) on silica gel plates. Aldehydic components were detected with 2,4-dinitrophenylhydrazine reagent and other components by spraying with aqueous 50% sulphuric acid followed by charring. G.l.c. analyses were carried out with a Perkin-Elmer F-11 gas chromatograph (10% SE-30 on Chromosorb P; column temp. 250 °C; injection port temp. 250 °C; carrier gas N_2 at 40 ml min^{-1}; chart speed 2.0 in min^{-1}).

Estimations with Periodate.—All estimations were carried out with solutions in dioxan, by using aqueous solutions of sodium periodate (0.1M), sulphuric acid (6N), and potassium iodide (20%). In experiments involving perchloric acid as catalyst the components were kept at 30 °C for 2½ h before addition of periodate. The reaction mixtures were kept in contact with periodate at 30 °C for 40 min to effect the glycol fission. A typical procedure is given below.

Estimation 3. *threo*-Aleuritic acid (150 mg) and 2-*epi*-jalaric acid [12] (300 mg) were dissolved in dioxan and treated with perchloric acid (70%; two drops) at 30 °C for 2½ h. The mixture was then treated with sodium periodate (10 ml) during 40 min, after which potassium iodide (15 ml) and aqueous sulphuric acid (10 ml) were added and the mixture was titrated against 0.208N-sodium thiosulphate (starch indicator). A blank experiment was carried out under analogous conditions without the aleuritic acid.

Estimation 7. *threo*-Aleuritic acid (150 mg) and 2-*epi*-jalaric acid (300 mg) were dissolved in aqueous sodium hydroxide (4%; 10 ml); the mixture was kept for 1 h at 30 °C, neutralised with aqueous hydrochloric acid (1 : 1), then dissolved in dioxan (10 ml) before estimation.

Estimation 8. *threo*-Aleuritic acid (150 mg) and 2-*epi*-jalaric acid (300 mg) were dissolved in distilled water (20 ml); the mixture was boiled for 5 min, cooled to 30 °C, dissolved in dioxan (10 ml), and estimated.

Estimation 5. *threo*-Aleuritic acid (100 mg) and 2-*epi*-jalaric acid (200 mg) were melted together at 105 °C, cooled to 30 °C, and dissolved in dioxan (10 ml) before estimation.

Hydrolysis of Superblonde Shellac.—Superblonde shellac (75 g) was dissolved in ice-cold aqueous sodium hydroxide (1.75N; 375 ml); the solution was stirred for 5 h at 20—22 °C, after addition of benzene to form an inert surface. It was then acidified with ice-cold phosphoric acid (1 : 1) and kept overnight at 0 °C. The gummy residue that separated was filtered off and the solution was extracted with ethyl acetate (3 × 75 ml). The extract was evaporated and the residual gum (9 g) was esterified with methanolic hydrogen chloride at 10 °C. The gummy product was chromatographed over silica gel (300 g) in benzene containing increasing proportions of ethyl acetate.

Elution with pure benzene (6 × 500 ml) gave dimethyl 8,13-epoxy-10-oxo-2β*H*-cedrane-12,15-dioate (VI) (150 mg), which crystallised from ethyl acetate–petroleum as needles, m.p. 149—150° (lit.,[3] 151°), identical with a synthetic sample (g.l.c. t_R 24.0 min). Elution with 1% ethyl acetate in benzene (8 × 500 ml) gave *methyl* 10β,12-*epoxy*-13-*hydroxy*-12-*methoxycedr*-8-*en*-15-*oate* (IX) (200 mg), which crystallised from ethyl acetate–petroleum; m.p. 138—140°, $[\alpha]_D$ +53° (MeOH) (Found: C, 66.3; H, 7.8. $C_{17}H_{24}O_5$ re-

quires C, 66.2; H, 7.9%), $\lambda_{max.}$ (MeOH) 230 nm (ε 6 600), $\nu_{max.}$ (KBr) 3 540s, 1 681s, and 1 608s cm^{-1}.

Elution with 2% ethyl acetate in benzene (4 × 500 ml) gave dimethyl 8,13-epoxy-10-oxocedrane-12,15-dioate (V) (g.l.c. t_R 25.5 min) (50 mg), which crystallised from ethyl acetate–petroleum; m.p. 118—120° (lit.,[3] 122.5—124.5°). Elution with 4% ethyl acetate in benzene (3 × 500 ml) gave *methyl* 8,13-*epoxy*-12,12-*dimethoxy*-10-*oxo*-2βH-*cedran*-15-*oate* (VIII) (g.l.c. t_R 19.0 min) (100 mg), which crystallised from ethyl acetate–petroleum; m.p. 130° (Found: C, 63.3; H, 7.8. $C_{18}H_{26}O_6$ requires C, 63.9; H, 7.7%), $\nu_{max.}$ (KBr) 1 724s cm^{-1}. Elution with 10% ethyl acetate in benzene (10 × 500 ml) gave dimethyl 10β,13-dihydroxycedr-8-en-12,15-dioate (dimethyl shellolate) (I) (6.00 mg), m.p. 152° (lit.,[3] 151—152°). Elution with 15% ethyl acetate in benzene (15 × 500 ml) gave dimethyl 2-*epi*-shellolate (1 g), m.p. 151—153° (lit.,[3] 151—152°).

Elution with 18% ethyl acetate in benzene gave methyl 10,13-dihydroxy-12,12-dimethoxy-2β*H*-cedr-8-en-15-oate (VII) (400 mg) as a gum (t.l.c.-pure; positive dinitrophenylhydrazine test). Elution with 20% ethyl acetate in benzene gave *methyl* 10β,13-*dihydroxy*-12-*oxo*-2βH-*cedr*-8-*en*-15-*oate* (XV) (*methyl* 2-epi-*jalarate*) (2 g), m.p. 60° (Found: C, 64.7; H, 6.7. $C_{16}H_{22}O_5$ requires C, 65.3; H, 7.4%), $\nu_{max.}$ (KBr) 3 510s, 1 709s, and 1 634s cm^{-1}. Elution with 25% ethyl acetate in benzene (6 × 500 ml) gave methyl 10β,12,13-trihydroxycedr-8-en-15-oate (III) (methyl laksholate) (100 mg), m.p. 122—124° (lit.[1] 124°). Elution with 50% ethyl acetate in benzene (4 × 500 ml) gave methyl 2-*epi*-laksholate (IV) (50 mg), m.p. 124° (lit.,[1] 124°).

Acidic Hydrolysis of Acetals.—The oxo-aldehyde dimethyl acetal (VIII) (40 mg) in dioxan (2 ml) was hydrolysed with aqueous sulphuric acid (2N; 5 ml; 4 h) at room temperature. The mixture was extracted into ethyl acetate (3 × 10 ml). Removal of solvent left a gum (25 mg) identified as methyl 8,13-epoxy-10,12-dioxo-2β*H*-cedran-15-oate (XIX) by g.l.c. (t_R 11.5 min) and spectral data.

The dimethyl acetal of methyl 2-*epi*-jalarate (VII) (50 mg) on similar hydrolysis gave methyl 2-*epi*-jalarate.

Acidic Hydrolysis of the Acetal (IX).—The acetal (IX) (80 mg) on prolonged hydrolysis with aqueous sulphuric acid (20 ml; 2N) in dioxan solution (1 ml) for 24 h at 30 °C followed by extraction with ethyl acetate and removal of the solvent gave jalaric acid (XI) as an amorphous powder, m.p. 140°.

Treatment of Acetals with Ethereal Hydrochloric Acid.—Ether (20 ml) was shaken with concentrated hydrochloric acid (5 ml) for 5 min, and the ether layer was separated. The oxo-aldehyde dimethyl acetal (VIII) (40 mg) was treated with this solution (8 ml; 12 h). Removal of the solvent after washing (to remove the acid) left a gum (35 mg). This was a mixture of unchanged acetal and the free oxo-aldehyde (XIX) (3 : 1), as shown by g.l.c.

Jones Oxidation of the Acetal (VIII).—The oxo-aldehyde dimethyl acetal (VIII) (50 mg) in dry acetone (3 ml) was treated with Jones reagent (3 ml) [from CrO_3 (2 g) in concentrated H_2SO_4 (1.6 ml) and water (6 ml)] at room temperature overnight. The mixture was extracted with ethyl acetate (25 ml) and the extract was washed with saturated aqueous sodium hydrogen carbonate (3 × 10 ml). The washings, after acidification with dilute hydrochloric acid (1 : 1), were extracted with ethyl acetate (3 × 10 ml); concentration gave a gum (25 mg) which was esterified with ethereal diazomethane, and the product was identified as the oxo-ether (VI) derivative of dimethyl 2-*epi*-shellolate by g.l.c. (pure; t_R 24.0 min).

Hypochlorite Oxidations.—Sodium hypochlorite solution was prepared by the procedure described in ref. 15. The amount of available chlorine was estimated as 9% by titration against standard sodium arsenite (potassium iodide–starch as external indicator).

Dimethyl shellolate (I) (100 mg) in dioxan (0.5 ml) was treated with sodium hypochlorite solution (1.5 ml) for 24 h at room temperature. The clear solution was acidified with ice-cold hydrochloric acid and extracted with ethyl acetate (3 × 5 ml). The extract was washed with water and concentrated. Esterification of the gummy residue with ethereal diazomethane followed by crystallisation of the product from benzene–hexane yielded 9α-*chloro*-8,13-*epoxy*-10β-*hydroxycedrane*-12,15-*dioic acid* 12,10-*lactone* 15-*methyl ester* (XIII) (80 mg), m.p. 184° (Found: C, 58.3; H, 5.9. $C_{16}H_{19}ClO_5$ requires C, 58.8; H, 5.8%), $\nu_{max.}$ (KBr) 1 727 and 1 783 cm^{-1}, δ 1.16 (s, CMe), 3.82 (s, CO_2Me), 4.10 (s, CH_2·O), 4.12 (d, *J* 11 Hz, C*H*·O·CO), and 4.52 (d, *J* 11 Hz, *CH*Cl).

Dimethyl 2-*epi*-shellolate (100 mg) on similar treatment with sodium hypochlorite followed by esterification and chromatography on silica gel gave needles of dimethyl 9α-*chloro*-8,13-*epoxy*-10β-*hydroxy*-2βH-*cedrane*-12,15-*dioate* (60 mg) (XIV), m.p. 168° (Found: C, 56.7; H, 6.4. $C_{17}H_{23}ClO_6$ requires C, 56.9; H, 6.4%), $\nu_{max.}$ (KBr) 1 690s, 1 739s, and 3 525s cm^{-1}, δ 1.13 (s, CMe), 3.7 (q, CH_2·O, overlapping with CO_2Me signal), 3.73 (s, CO_2Me), 3.83 (s, CO_2Me), 4.26 (d, *J* 2.2 Hz, C*H*·OH), and 4.55 (d, *J* 2.2 Hz, C*H*Cl).

Methyl 2-*epi*-jalarate (20 mg) on similar oxidation followed by esterification with diazomethane and chromatography gave needles of (XIV) (10 mg), m.p. 167°, identified by mixed m.p. and i.r. and n.m.r. spectra.

One of us (G. B. V. S.) thanks Lord Todd, F.R.S., for facilities and the Royal Society, Nuffield Foundation, for a bursary award. Financial assistance from the Council of Scientific and Industrial Research, India (to J. I. and K. N. G.) and Indian Petrochemical Corporation Ltd is gratefully acknowledged. We also thank the Director, Sriram Institute for Industrial Research, and Mr. A. Balyan for permission to use the gas chromatograph.

[6/122 *Received*, 19*th January*, 1976]

[15] M. S. Newman and H. L. Holmes, *Org. Synth.*, Coll. Vol. II, 1943, p. 428.