1100. *Shellac. Part I. The Structure of Butolic Acid.*

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Hydrolysis of lac resin furnishes a mixture of hydroxy-acids from which 6-hydroxytetradecanoic acid has been isolated in 5—8% yield. This is considered to be identical with butolic acid, previously described as 6-hydroxypentadecanoic acid.

Crude lac consists of a resin accompanied by two colouring matters, an odoriferous principle, and a wax. The resin is probably a mixture of cross-linked polyesters largely derived from hydroxy-acids. The acids present in lac hydrolysate have been the subject of many investigations during the last forty years but little progress has been made in identifying them. The major component (~30%) is aleuritic acid (9,10,16-trihydroxyhexadecanoic acid) and this aliphatic compound is accompanied by an unsaturated, tricyclic, dibasic C_{15} dihydroxy-acid, shellolic acid. The structure of this acid has recently been elucidated,[1] but there is still uncertainty about the amount of it in lac resin and, indeed, whether it is a primary hydrolysis product. No other component has been

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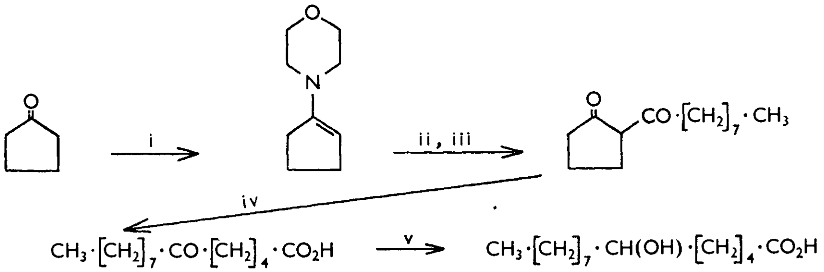
[1] Yates and Field, *J. Amer. Chem. Soc.*, 1960, **82**, 5764; Carruthers, Cook, Glen, and Gunstone, *J.*, 1961, 5251.

adequately identified though there are reports of mono-,[2] di-,[2,3] and tetra-hydroxyhexadecanoic acids,[4] of a monohydroxypentadecanoic acid (butolic),[5] of acids closely related to shellolic acid,[1,6] and of carbonyl-containing acids.[7] Estimates of the composition of lac hydrolysate suggest that it contains aleuritic and isomeric acids (30—35%), aldehydic acids (20—25%), shellolic and related water-soluble acids (20—25%), and butolic acid (~2%), with the remainder undesignated; [8] the structures of aleuritic and shellolic acid only have been known hitherto with certainty.

We hydrolysed lac resin to its component acids and submitted the derived methyl esters to a number of separation procedures, mainly chromatographic. By these means a fraction was obtained (~7%) which was shown, by thin-layer chromatography and by gas-liquid chromatography, to be almost entirely a single component. Its chromatographic behaviour, and the fact that it gave methyl tetradecanoate by iodination-de-iodination,[9] showed it to be a monohydroxytetradecanoate. The hydroxy-ester was oxidised to a keto-ester, the oximes of which, when submitted to Beckmann rearrangement, furnished amides; these were hydrolysed and two of the four possible products, nonanoic and adipic acid, were identified.[10] These must have come from 6-hydroxytetradecanoic acid.



Reagents: (i) Morpholine and toluene-*p*-sulphonic acid; (ii) $CH_3\cdot[CH_2]_7\cdot COCl-NEt_3$; (iii) HCl; (iv) K_2CO_3; (v) MeOH–HCl; $NaBH_4$; KOH.

6-Oxo- and $(\pm)$-6-hydroxytetradecanoic acid were synthesised and shown to be identical with similar products derived from the natural acid. This synthesis was achieved from cyclopentanone and nonanoic acid by adaptation of the enamine procedure described by Hünig and Lendle.[11] The 6-oxo-acid has been synthesised previously by another method,[12] but neither the $(\pm)$- nor the $(-)$-hydroxy-acid has been reported before.

The natural acid was similar in many respects to butolic acid, considered by Sen Gupta and Bose [5,8] to be 6-hydroxypentadecanoic acid. It seemed likely that these might be the same and a re-investigation, by our chromatographic procedures, of a sample of butolic acid isolated by Sen Gupta and supplied by him, showed it to be a C_{14} acid with the hydroxyl group attached to C-6.

This acid, comprising 5—8% of the hydrolysate of the lac used in this investigation, can now be included with aleuritic and shellolic acid among the constituents of lac resin of known structure.

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[2] Tschirch and Lüdy, *Helv. Chim. Acta*, 1923, **6**, 994.

[3] Gardner and Whitmore, *Ind. Eng. Chem.*, 1929, **21**, 226.

[4] Schaeffer and Gardner, *Ind. Eng. Chem.*, 1938, **30**, 333.

[5] Sen Gupta and Bose, *J. Sci. Ind. Res.* (*India*), 1952, **11**, *B*, 458.

[6] Kirk, Spoerri, and Gardner, *J. Amer. Chem. Soc.*, 1941, **63**, 1243.

[7] Sen Gupta, *J. Sci. Ind. Res.* (*India*), 1955, **14**, *B*, 86; Kamath, Proc. Symposium on Lac and Lac Products, Namkum Bihar, 1956, p. 68.

[8] Young, " Shellac," Angelo Bros. Ltd., Calcutta, 1956, p. 75; Sen Gupta, Proc. Symposium on Lac and Lac Products, Namkum Bihar, 1956, p. 72.

[9] Matic, *Biochem. J.*, 1956, **63**, 168.

[10] Gunstone, *J.*, 1952, 1274.

[11] Hünig and Lendle, *Chem. Ber.*, 1960, **93**, 909.

[12] Keskin, *Rev. Fac. Sci. Univ. Istanbul*, 1952, **17**, *A*, 344 (*Chem. Abs.*, 1954, **48**, 10,618).

EXPERIMENTAL

Light petroleum is the fraction of boiling range 40—60°. Gas–liquid chromatography was carried out at 150° or 200° with a Pye Argon chromatograph and 4 ft. columns packed with Apiezon L (10%) or the fluorinated silicone, QF-1, (10%) on Celite. Relative retention times are reported as " carbon numbers." [13] In thin-layer chromatography the adsorbent was silica gel G (Merck) and the developing solvent a mixture of ether, light petroleum, and methanol (50 : 48 : 2); the separated components were detected by exposure of the plate to iodine vapour.

Isolation of Butolic Acid.—Butolic acid has been isolated from lac esters by a number of chromatographic procedures, one of which is described here. Its methyl ester is eluted from neutral alumina with ether, immediately after a small amount of non-hydroxy-esters, and from silica by 7 : 3 benzene–ether.

" Super Blonde Shellac " (200 g.) was hydrolysed by aqueous-alcoholic N-sodium hydroxide (1·1 l.) during 16 hr. The solution was not heated and care was taken to see that the temperature did not exceed 30° at any time. The free acids were liberated by passing the alkaline solution through a column of ion-exchange resin (Zeo-Karb 225) and were recovered by removal of solvent in a rotary-film evaporator at $\not>$40°. Methylation was effected by boiling methanolic hydrogen chloride.

The mixed esters (116 g.) were placed on a column of alumina (750 g.; previously treated with ethyl acetate [14]). Ether (4·5 l.) eluted half of the esters and these were re-chromatographed on a similar column; successive 1-l. portions of ether eluted 1·2, 7·2, 2·5, 3·2, and 3·6% of the original esters. The second fraction was almost pure methyl butolate, a little of which was also present in the third fraction.

Methyl butolate, $[\alpha]_D^{19}$ −0·9° (*c* 6 in EtOH, *l* 2 dm.), had " carbon numbers " of 15·8 (Apiezon L) and 18·0 (QF-1). On a column containing only 2½% of Apiezon L the carbon number was 16·2. The methoxy-ester had a " carbon number " of 15·1 on Apiezon L. Hydrolysis of methyl butolate gave (−)-*butolic acid*, m. p. 58—58·5° (from light petroleum) (Found: C, 68·4; H, 11·4. $C_{14}H_{28}O_3$ requires C, 68·8; H, 11·6%).

6-Oxotetradecanoic acid was obtained by oxidation of this acid with chromic anhydride in acetic acid. After crystallisation from light petroleum it melted at 70—71° (lit., 71·5° [12]) (Found: C, 68·9; H, 10·8. Calc. for $C_{14}H_{26}O_3$: C, 69·3; H, 10·8). The semicarbazone had m. p. 129—131° (lit.,[12] 130°) (Found: C, 60·4; H, 9·8; N, 14·0. Calc. for $C_{15}H_{29}N_3O_3$: C, 60·2; H, 9·8; N, 14·0%). Methyl 6-oxotetradecanoate showed a " carbon number " of 15·4 (Apiezon L).

(±)-Butolic acid, m. p. 61·5—63° (from light petroleum), was obtained from the oxo-ester by reduction with sodium borohydride and subsequent hydrolysis.

Conversion of Methyl Butolate into Methyl Tetradecanoate.—Methyl butolate (52 mg.) was heated at 100° with iodine (270 mg.) and red phosphorus (620 mg.) for 1 hr. The excess of iodine was removed under reduced pressure and the residue, dissolved in ether, was washed successively with water, sodium hydrogen sulphite solution, and water. The iodinated ester (67 mg.) remaining after removal of the solvent was refluxed for 4 hr. with methanolic 5% hydrogen chloride (5 ml.) and activated zinc (~200 mg.). This metal was prepared as required by refluxing zinc dust (1 g.) with methanol (5 ml.) and hydrogen iodide (0·1 ml.) for 5 min., decanting the solvent, and washing the residue thoroughly with methanol. The organic product, recovered by ether-extraction, was undistinguishable from methyl tetradecanoate in its chromatographic behaviour (Apiezon L).

Position of the Hydroxyl Group.—Methyl butolate (50 mg.) was dissolved in acetic acid (1 ml.) and oxidised at room temperature by chromic anhydride (50 mg.) in acetic acid (1 ml.). After 1 hr., water (10 ml.) was added, the excess of oxidant was destroyed by sulphur dioxide, and the keto-ester (45 mg.) was recovered. This was refluxed for 2 hr. with hydroxylamine hydrochloride (85 mg.) and fused sodium acetate (82 mg.) in 80% ethanol (2·0 ml.). Thereafter the oximes (46 mg.) were recovered and heated to 100° with concentrated sulphuric acid (0·2 ml.) for 1 hr. to effect Beckmann rearrangement. After cooling, water (0·4 ml.) was added, and the mixture boiled to hydrolyse the amides. The resulting monobasic acid was extracted with light petroleum, and the dibasic acid subsequently with ether. After methylation, these

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[13] Woodford and van Gent, *J. Lipid Res.*, 1960, **1**, 188.

[14] Meakins and Swindells, *J.*, 1959, 1044.

were examined by gas–liquid chromatography and shown to be methyl nonanoate (Apiezon L and QF-1) and methyl adipate with " carbon numbers " of 9·0 (Apiezon L) and 11·5 (QF-1).

Synthesis of 6-*Oxotetradecanoic Acid and* (±)-6-*Hydroxytetradecanoic Acid.*—Nonanoyl chloride (6·67 g.) in dry chloroform (20 ml.) was added in 15 min. to a stirred solution of 4-cyclopent-1′-enylmorpholine[15] (5·10 g.), triethylamine (4·02 g.; distilled from sodium), and dry chloroform (40 ml.) at 35°. After a further 15 min., 6N-hydrochloric acid (20 ml.) was added and the two-phase mixture stirred vigorously for 30 min. at 35°. The chloroform layer was washed with water until the washings had pH 5—6 and the water layer, together with the aqueous washings, was neutralised with dilute sodium hydroxide solution to pH 5—6 and then extracted with chloroform. The combined chloroform extracts yielded 2-nonanoylcyclopentanone (6·35 g., 74%), b. p. 116—120°/0·4 mm., which gave a deep wine-red colour with methanolic ferric chloride.

The diketone was refluxed with 5% aqueous potassium carbonate (250 ml.) for 2·5 hr. and, after removal of neutral material by ether, the aqueous layer was acidified with hydrochloric acid: 6-oxotetradecanoic acid (4·98 g., 73%), m. p. 66—69°, was recovered. After crystallisation from light petroleum this acid (3·84 g., 41% based on the enamine) melted at 71—71·5° (lit.,[12] 71·5°) alone or mixed with oxo-acid derived from butolic acid (Found: C, 68·9; H, 10·7. Calc. for $C_{14}H_{26}O_3$: C, 69·3; H, 10·8%); its semicarbazone had m. p. 128—130° (lit.,[12] 130°) alone or mixed with a sample derived from butolic acid (Found: C, 60·4; H, 9·4; N, 14·1. Calc. for $C_{15}H_{29}N_3O_3$: C, 60·2; H, 9·8; N, 14·0). The methyl keto-ester had a " carbon number " of 15·4 (Apiezon L).

An excess of sodium borohydride (2·11 g.) was added to the keto-ester (1·0 g.) in methanol (50 ml.) in 30 min. Diluted with water and extracted with ether, the mixture furnished the hydroxy-ester (0·98 g., 98%) of " carbon number " 15·8 (Apiezon L) and 18·0 (QF-1). Hydrolysis gave the (±)-*hydroxy-acid* (78%), m. p. 65—66° (from light petroleum) alone and 63—65° when mixed with the (±)-acid derived from (−)-butolic acid (Found: C, 69·2; H, 11·6. $C_{14}H_{28}O_3$ requires C, 68·8; H, 11·6%).

Examination of a Sample of Butolic Acid Supplied by Mr. Sen Gupta.—A sample of butolic acid (70 mg.), isolated by the method of Sen Gupta and Bose,[5] was supplied by Mr. Sen Gupta. It melted at 50—55° alone and when mixed with our natural 6-hydroxytetradecanoic acid. Gas–liquid chromatography of the methyl esters showed only a peak of " carbon number " 16·2 (Apiezon L, 2½%), but thin-layer chromatography showed that the major spot due to a monohydroxy-ester was accompanied by minor spots indicating the presence of non-hydroxy- and dihydroxy-esters. This compound, degraded in the same way as our acid, gave nonanoic and adipic acid as the major mono- and di-basic acids.

We are indebted to the Indian Lac Exporters' Association (H. G. P.) and the Department of Scientific and Industrial Research (W. W. C.) for maintenance grants, to the Indian Lac Exporters' Association for a gift of shellac, and to Mr. S. C. Sen Gupta (of the Indian Lac Research Institute) for a sample of butolic acid.

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[*Received, May* 20*th*, 1963.]

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[15] Bergmann and Ikan, *J. Amer. Chem. Soc.*, 1956, **78**, 1482.