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Constituents of Shellac: Part I—Butolic Acid

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A modified procedure for the fractionation of the constituent acids of shellac is described. Shellac is subjected to alkaline hydrolysis at room temperature when sodium aleuritate separates out; from the filtrate barium, zinc and lead salts of other constituent acids are prepared by successive precipitations. A monohydroxy pentadecanoic acid, $C_{15}H_{30}O_3$, m.p. 54°-55°C., designated butolic acid, has been isolated from the alcohol-soluble but water-insoluble barium salt.

SHELLAC has been shown[1-6] by a number of investigators to comprise several polyhydroxy acid units. It is assumed that these acids are present in shellac as lactides[1] or as inter-esters[7,8]. The isolation of aleuritic acid[1,3,4,6-9], $C_{16}H_{32}O_5$, m.p. 100°-101°C., and shellolic acid[1,3,5,6,9,12], $C_{15}H_{20}O_6$, m.p. 206°C., from shellac has been described by various workers. Weinberger and Gardner[8] obtained a lactone, $C_{16}H_{24}O_5$, m.p. 90°-91°C., instead of shellolic acid which they named lacolic lactone. They also claimed to have separated kerrolic acid, $C_{16}H_{32}O_6$, a tetrahydroxy palmitic acid, m.p. 132°C., and an isomer of aleuritic acid, m.p. 89°-90°C. Later, the investigations of Kirk and others[5] indicated that lacolic lactone was largely composed of isomers of a CH_2-homologue of dihydroshellolic acid. They further claimed to have isolated isomers of shellolic acid in small amounts.

Aleuritic acid is the only constituent of shellac whose structure has been definitely established as 9: 10: 16-trihydroxypalmitic acid[1,10,11]. According to Gidvani[9], it is present in shellac to the extent of 43 per cent. An oxidized tricyclic sesquiterpene structure has been suggested for shellolic acid by Nagel and Mertens[12]. According to Wright[6], shellolic acid constitutes 6·4 per cent of shellac. The remaining known acids are present to the extent of 5-6 per cent[5,8].

About 55 per cent of the constituent acids of shellac have so far been isolated in pure form. With a view to investigating the nature of the remaining unknown acids and also to correlate the available data, work on the constitution of shellac was taken up in these laboratories.

The procedure followed in the present investigation is an adaptation of the methods employed by earlier workers[1,3,4,8]. Shellac was subjected to alkaline hydrolysis and sodium aleuritate separated from the hydrolysate; the barium, zinc and lead salts of the other constituent acids were then successively prepared from the filtrate.

A portion of the barium salt (Ba I, Ba II and Ba III), soluble in hot absolute alcohol but insoluble in water, yielded (0·5 per cent on the weight of shellac), on decomposition with acid, a monohydroxy monobasic acid (m.p. 54°-55°C.). This new acid, designated as butolic acid, may also be present in other fractions not yet fully investigated.

Butolic acid is soluble in methyl and ethyl alcohols, acetone, ether, chloroform, ethyl acetate, benzene and warm petroleum ether and hexane. It does not decolourize dilute bromine solution in chloroform and is optically inactive. Analytical data for butolic acid and the probable monohydroxy acids as well as their parent saturated acids are given in Table 1.

The mixed melting points of the acids were: butolic acid + 11-hydroxymyristic (convolvulinolic) acid, 45°-47°C.; reduced butolic acid + reduced aleuritic acid, 46°-47°C.

Comparative data on the melting points of butolic, synthetic 11-hydroxypentadecanoic and convolvulinolic acids and their derivatives are given in Table 2.

The mixed melting point of keto butolic acid and 11-ketopentadecanoic acid was 63°-64°C.

From the analytical data given in Tables 1 and 2, it is evident that butolic acid is a monohydroxy pentadecanoic acid, not identical with 11-hydroxypentadecanoic acid.

TABLE 1 — COMPARATIVE DATA OF BUTOLIC AND KNOWN MONO-HYDROXY FATTY ACIDS

ACID	M.P., °C.	ACID VAL.	HYDROXYL VAL.	MOL. WT.	CARBON, %	HYDROGEN, %
Butolic acid	54-55	217·7	217·0	260·5 (Rast)	69·50	11·45
11-hydroxymyristic acid (convolvulinolic acid)	51-52	229·9	229·9	244·0	68·85	11·48
11-hydroxypentadecanoic acid	63·5-64	217·1	217·1	258·0	69·77	11·60
11-hydroxypalmitic acid	67·5-68	206·0	206·0	272·0	70·60	11·76
Reduced butolic acid	48-49	230·1	—	244·7 (Rast)	—	—
Reduced aleuritic acid (palmitic acid)	62-63	217·6	—	254·9 (Rast)	—	—
Myristic acid	53·5-54·4	245·6	—	228·4	—	—
Pentadecanoic acid	51-52·1	231·5	—	242·4	—	—
Palmitic acid	62·5-63·1	218·8	—	256·4	—	—

TABLE 2 — MELTING POINTS OF BUTOLIC AND KNOWN MONO-HYDROXY FATTY ACIDS AND THEIR DERIVATIVES

	BUTOLIC ACID, °C.	11-HYDROXY-PENTADECANOIC ACID, °C.	CONVOLVULINOLIC ACID, °C.
Acid	54-55	63·5-64	51-52
Methyl ester	27-28	29-32	31-32
Keto acid	69·5-70·5	70-71	63-64
Reduced acid	48-49	—	49·5
Ketonic acid semicarbazone	128-29	126	104

Experimental procedure

Preparation of salts of constituent acids — Angelo's dewaxed and decolourized shellac (2 kg.) was finely powdered and dissolved in caustic soda (2 litres of 20 per cent solution) and kept at room temperature for 10 days for complete hydrolysis and precipitation of sodium aleuritate. Sodium chloride (2 litres of 20 per cent solution) was then added and the solution filtered in a sintered Buchner funnel. The crude sodium aleuritate was washed with sodium chloride (1 litre of 20 per cent solution). The filtrate together with the wash liquor was concentrated to about 3 litres and kept overnight at 5°C. No further precipitation of sodium aleuritate occurred. The excess alkali in the filtrate was just neutralized with 15 per cent hydrochloric acid solution (400 cc. approximately) and ammonia (1 cc.) added. The total volume was made up to 4·5 litres. An aliquot (20 cc.) was ignited and the amount of alkali in the residue was determined. From this, the amount of barium chloride required to precipitate the acids was calculated. The barium chloride ($BaCl_2.2H_2O$, 375 g.) was added in aqueous solution in three batches representing 30, 30 and 40 per cent respectively and the precipitated barium salts (Ba I, Ba II and Ba III) obtained after each addition of barium chloride were filtered and washed with water.

The excess barium in the filtrate was removed as sulphate by the addition of sodium sulphate solution. Zinc sulphate solution (10 per cent, 800 g. of $ZnSO_4.7H_2O$) was then added in three batches of 50, 37·5 and 12·5 per cent of the total precipitant. The first two additions gave dark-coloured (Zn I) and cream-coloured zinc (Zn II) salts respectively. The filtrate after the addition of the third batch did not give any further precipitate even on keeping overnight at 5°C. It was then brought to the boiling point and filtered. The process was repeated till a little turbidity was noticed on heating. The hot water-insoluble zinc salt (Zn III) was thus separated.

The hot filtrate was then treated with solid sodium carbonate till the filtrate was alkaline to litmus. The precipitated basic zinc carbonate was filtered off and the filtrate evaporated to dryness. The residue was extracted with 95 per cent alcohol and the volume made up to 1·7 litres. The alkali content of the extract was estimated in an aliquot, and the equivalent amount of lead acetate (170 g.) dissolved in alcohol was added to the alcoholic extract. The mixture was cooled and kept overnight at 5°C. The alcohol-insoluble lead salt (Pb I) was filtered and washed with cold alcohol.

Most of the alcohol was distilled off from the filtrate and the concentrated liquor was added to a large volume of water when a white powder (Pb II) separated which was removed by filtration. The filtrate at this stage was free from organic matter.

The amounts of various salts of constituent acids obtained from 2 kg. of shellac were: crude sodium aleuritate, 575 g.; brown barium salt (Ba I), 80 g.; violet barium salt (Ba II), 77 g.; violet barium salt (Ba III), 488 g.; dark zinc salt (Zn I), 686 g.; cream-coloured zinc salt (Zn II), 275 g.; hot water-insoluble zinc salt (Zn III), 62 g.; alcohol-insoluble lead salt (Pb I), 134 g.; and alcohol-soluble lead salt (Pb II), 12 g.

Separation of butolic acid — The violet barium salt (Ba II) was finely powdered and extracted in a soxhlet apparatus with petroleum ether to remove adhering waxes and other impurities. It was then extracted with absolute alcohol, the solvent removed from the extract as far as possible and water added to the residue when the insoluble barium salt was obtained which was filtered and washed with water. The salt was decomposed with dilute hydrochloric acid. The precipitated butolic acid on drying melted at 53°-54°C. On decolourization and recrystallization from dilute methyl alcohol it yielded long, thin needles melting at 54°-55°C.; yield, 2·79 g.

The barium precipitate (Ba III) was similarly treated and the alcohol-soluble but water-insoluble portion decomposed with dilute hydrochloric acid when a mixture of liquid acids was obtained. The liquid acids were extracted with petroleum ether and the petroleum ether-soluble fraction crystallized from benzene and then from dilute methyl alcohol, when a further quantity of butolic acid was obtained; yield, 6·5 g.

The alcohol-soluble but water-insoluble portion of barium salt (from Ba I) treated similarly gave a further 0·6 g. of butolic acid. The total yield of butolic acid from Ba I, Ba II and Ba III was 0·5 per cent on the weight of shellac.

The microanalytical data for butolic acid along with the corresponding data for the adjacent homologous hydroxy acids are given in Table 3.

The mixed m.p. of butolic and convolvulinolic acid (11-hydroxymyristic acid) was 45°-47°C.

Methyl ester — Butolic acid (0·5 g.) was dissolved in absolute methyl alcohol (10 cc.) containing 3 per cent hydrochloric acid and allowed to stand at room temperature for four days. The solution was poured into ice-cold water and the mixture extracted with ether. The ethereal extract was washed successively with 10 per cent sodium carbonate solution and water. The ethereal solution was dried over anhydrous sodium sulphate and on removal of ether an ester (0·5 g.), m.p. 27°-28°C., was obtained.

Ketonic acid — Oxidation of butolic acid (0·5 g.) was carried out with chromic acid in glacial acetic acid solution at 50°-60°C. according to the procedure of Davis and Adams[14]. A keto acid (0·37 g.), m.p. 69·5°-70·5°C., was obtained. It contained no free hydroxyl group. Found: acid val., 226·3; mol. wt., 255·7 (Rast); required for $C_{16}H_{30}O_3$: acid val., 207·8; mol. wt., 270; required for $C_{15}H_{28}O_3$: acid val., 219·1; mol. wt., 256.

The mixed m.p. of keto butolic acid with 11-ketopentadecanoic acid (m.p. 70°-71°C.) was 63°-64°C.

Ketonic acid semicarbazone — The keto acid (0·3284 g.) was dissolved in the minimum quantity of pure ethyl alcohol, and water (5 cc.) containing semicarbazide hydrochloride (0·3450 g.) and sodium acetate (0·2950 g.) was added. There was some turbidity initially which vanished on adding a few drops of alcohol. The mixture was heated for 5 min. and allowed to stand overnight. The crystalline semicarbazone (0·36 g.) was separated and washed with alcohol and water. It melted at 128°-29°C. and decomposed at 185°C. The nitrogen content of the semicarbazone was determined indirectly by the method of Jamieson[13]. Required for $C_{16}H_{31}O_3N_3$: N, 13·42 per cent; found: N, 13·32, 13·60 per cent.

Parent acid — Butolic acid (0·5 g.) was reduced to the parent acid with hydroiodic acid and red phosphorus followed by reduction with powdered zinc and hydrochloric acid according to the procedure of Harries and Nagel[15]. The reduced acid (0·1 g.) melted at 48°-49°C. Found: acid val. (micro), 230·1; mol. wt. (micro-Rast), 243·4, 246·0.

TABLE 3 — ANALYTICAL DATA FOR BUTOLIC AND ADJACENT HOMOLOGOUS HYDROXY ACIDS

ACID	CARBON, %	HYDROGEN, %	MOL. WT.	ACID VAL.	SAP. VAL.	HYDROXYL VAL.
$C_{14}H_{28}O_3$	68·85	11·48	244·0	229·9	—	229·9
$C_{15}H_{30}O_3$	69·77	11·60	258·0	217·1	—	217·1
$C_{16}H_{32}O_3$	70·60	11·76	272·0	206·0	—	206·0
Butolic	69·40 69·60 —	11·50 11·40 —	256·6 261·7 263·2 } Rast	217·7	217·4	217·0

Similarly aleuritic acid was reduced to the parent acid, m.p. 62°-63°C. The mixed melting point of the two reduced acids was 46°-47°C.

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