[CONTRIBUTION FROM THE SHELLAC RESEARCH BUREAU OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Shellolic Acid and Similar Acids[1]

BY PHILIP M. KIRK,[2] PAUL E. SPOERRI AND WM. HOWLETT GARDNER

Shellolic acid is the only constituent of the zoochemical resin, lac, for which a cyclic structure has been suggested.[3] The acid has attracted a great deal of attention, since several investigators have assumed that its presence in lac may have important biochemical and chemical significance.[3b,4c] This acid was first isolated by Harries and Nagel[3a] in 1922 from the hard portion of the resin in lac. They first completely removed aleuritic acid from the mixture of acids obtained by saponifying the hard resin. The remaining acids were then converted to their methyl esters, and dimethyl shellolate was separated by crystallization from a diethyl ether solution of the resulting mixture of esters.

Other investigators have been unable, however, to obtain these constituents[5] by performing the operations carried out by Harries and Nagel. Consequently other methods for separating the acids have been developed. These methods in most instances, however, have yielded products of entirely different properties from those of shellolic acid. Bhattacharya,[5a] for example, could obtain at first only a lactone-acid melting at 90°. When he finally succeeded in isolating small amounts of shellolic acid (m. p. 200°), it was from fractions containing aleuritic acid. From various fractions of the resin, instead of shellolic acid Weinberger and Gardner obtained an amorphous powder of constant composition represented by the formula $C_{16}H_{32}O_5$. They named the amorphous product "lacollic lactone" but they were unable to prepare any crystalline derivatives.

This article describes how it was possible to obtain consistently from shellac and other lacs, shellolic acid in amounts equal to those isolated by Nagel and his co-workers.[3b] This was accomplished by using a modification of the procedure employed by Weinberger and Gardner[5c] in obtaining "lacollic lactone." No one has as yet succeeded, however, in separating shellolic acid directly from any mixture of lac acids. It was found that it was always necessary first to convert the acids to their methyl esters in order to isolate this constituent, although small amounts of other crystalline products of a similar nature were obtained in this study from mixtures of lac acids.

It is well known that resin acids frequently isomerize in the presence of mineral acids.[6] Nagel and his co-investigators had used hydrogen chloride as the catalyst for esterifying his lac acids. We therefore studied the effect of other methods of esterification. Dimethyl shellolate was obtained from the mixtures of esters in all experiments. The amounts of dimethyl shellolate isolated were much larger when hydrogen chloride was used, but this may have been due to more complete esterification. It would seem reasonable therefore that shellolic acid is very probably one of the constituents of some of the inter-esters composing the natural lac resin.[7]

The total amount of shellolic acid present in lac must be relatively small. Several different lacs were used for this study, and the greatest quantity isolated in any experiment was 3.6% of the lac resin. Nagel and Mertens obtained from 2.8 to 4.0%, based upon the total lac resin. Such agreement between investigators is excellent.

This amount of shellolic acid was approximately half of the fraction of acids the lead salts

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(1) This communication is part of a doctoral thesis presented by Philip M. Kirk to the Graduate Faculty of the Polytechnic Institute of Brooklyn, June, 1939. Paper XV in the series of Nature and Constitution of Shellac. Presented before the Division of Paint and Varnish Chemistry at the 98th Meeting of the Society, Boston, Mass., September, 1939. Contribution No. 53 from the Shellac Research Bureau and No. 60 from the Department of Chemistry of the Polytechnic Institute of Brooklyn. This research was sponsored by the United States Shellac Importers Association. Original manuscript received July 13, 1940.

(2) Shellac Research Fellow 1936–1939. Present address: Research Laboratories of the American Cyanamid Company, Stamford, Conn.

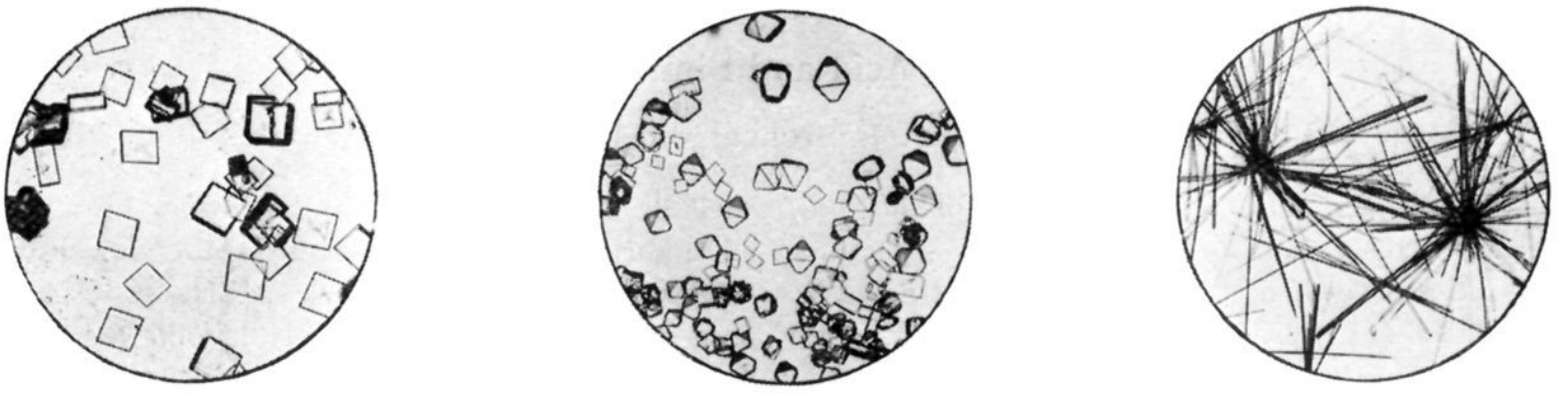
(3) (a) C. Harries and W. Nagel, *Ber.*, **55B**, 3855 (1922). (b) W. Nagel and W. Mertens, *ibid.*, **70**, 2173 (1937); **72**, 985 (1939). (c) W. Nagel and E. Baumann, *Wiss. Veroffentl. Siemens-Konzern*, **11**, 99 (1932).

(4) (a) W. H. Gardner, "The Chemistry of Shellac as Compared to Other Natural Resins," paper presented before the Amer. Assoc. Advancement Sci., Richmond, Va., Dec. 27, 1938. (b) R. Bhattacharya and A. J. Gibson, *Oil Colour Trade J.*, **94**, 1584 (1938). (c) R. Bhattacharya and B. S. Gidvani, *J. Soc. Chem. Ind.*, **57**, 285 (1938). (d) B. S. Gidvani and R. Bhattacharya, Bull. 3, London Shellac Research Bu., London (1939). (e) C. E. Barnes, *Ind. Eng. Chem.*, **30**, 449 (1938).

(5) (a) R. Bhattacharya, *J. Soc. Chem. Ind.*, **54**, 82T (1935); **55**, 309 (1936). (b) B. B. Schaeffer and W. H. Gardner, *Ind. Eng. Chem.*, **30**, 333 (1938). (c) H. Weinberger and W. H. Gardner, *ibid.*, **30**, 454 (1938).

(6) S. Palkin, *J. Chem. Education*, **12**, 35 (1935).

(7) (a) W. H. Gardner, Ann. Rept., Shellac Research Bureau, Polytechnic Institute of Brooklyn (1937–38). (b) W. H. Gardner, *Modern Plastics*, **17**, 94, 98 (1939).



1 2 3

Fig. 1.—1, shellolic acid; 2, dimethyl shellolate; 3, shellolyl dihydrazide.

of which were insoluble in alcohol. The remaining portion of this fraction was definitely a mixture of similar dibasic acids. Fractional crystallization of various mixtures of these acids from very dilute aqueous solutions yielded limited amounts of five different crystalline products, although the amounts were too small for purification in other solvents. All but one of the products had different physical properties from shellolic acid. Four of the products consisted entirely of hexagonal crystals like dihydroshellolic acid. Only crystals of the fifth were cubic like shellolic acid. Elementary analyses and the crystalline form suggest that these products may be the following: Two isomeric CH_2-homologs of dihydroshellolic acid (m. p. 166 and 226°), an isomer of shellolic acid (m. p. 238°), and two isomers of dihydroshellolic acid (m. p. 226 and 245°). Even if these products were impure fractions of shellolic acid the total amount would still be less than investigators have assumed from previous limited evidence.[3a,4b,4c]

The fractions of shellac, KIB and KID[8] which were obtained by separating the resin with solvents, yielded but one-sixth to one-half of the above amounts of shellolic acid. It was from these fractions of lac that Weinberger and Gardner[5c] obtained the greatest quantities of their so-called "lacollic lactone." There can be no doubt that this lactone was a mixture, but it must not be overlooked that the analytical results of Weinberger and Gardner showed it to contain a much larger percentage of carbon than has shellolic acid. This can be readily explained by assuming the mixture to contain a relatively large proportion of C_{16}-dibasic acids, such as were apparently obtained in small amounts from dilute aqueous solutions of the mixture of dibasic acids from these fractions. The $C_{16}H_{24}O_6$ acid listed above as melting at 226° formed a lactone-ester upon esterification. This would indicate that some of the dibasic acids might readily form lactones as the results of previous authors have indicated.

Properties of Shellolic Acid.—The various preparations of dimethyl shellolate obtained in this investigation were identical in properties with those described by Harries and Nagel.[3a] Mixtures of different proportions of our ester and a sample of the esters which Nagel[3b] had kindly sent to us showed no change in melting point (149–150°). However, amorphous products of indefinite composition were obtained from dimethyl shellolate when Harries and Nagel's procedure[3a] was employed for preparing the acid. Pure shellolic acid was found to undergo change when heated or treated with mineral acids. It was too soluble in alcohol to be recrystallized from this solvent. Hence, a new procedure was developed for preparing this acid from its ester. Samples of the purified acid and one received from Nagel melted sharply with decomposition at 206°. Various mixtures of the two showed no signs of melting below this temperature although Harries and Nagel[3a] have reported that shellolic acid melted at 200° and decomposed at 204°. A thermometer calibrated and certified by the United States Bureau of Standards was used for these determinations. A photomicrograph of the crystals of this acid is shown in Fig. 1.

A yield of 91% of the theoretical amount of the dihydrazide was obtained from the ester when the procedure described in the experimental part was used. The dihydrazide melted at 246° after purification. The German investigators[3a] reported a yield of 80% by their method. Their product melted at 243 to 244°.

Both shellolic acid and its dimethyl ester were readily hydrogenated when Adams platinum oxide catalyst was used. The purified dihydro-

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(8) B. B. Schaeffer, H. Weinberge and W. H. Gardner, *Ind. Eng. Chem.*, **30**, 451 (1938).

shellolic acid produced melted at 157 to 158°. The preparation of this acid and some of its derivatives will be described in a subsequent paper.

Slightly less than one-half of the theoretical amount of ammonia was recovered as a product of the Curtius series of reactions. A substance which showed the usual qualitative tests for an amino-acid was obtained in minute amounts as the final product. Such a product could not be produced if shellolic acid has the structure postulated for it by Nagel and Mertens.[3b] Further study of this series of reactions is being undertaken at the present time.

Dimethyl shellolate was recovered unchanged when an attempt was made to prepare the semicarbazone and phenylhydrazone derivatives of shellolic acid using the methods of Kamm.[9]

Experimental Part

The methods used for obtaining the solvent fractions of lac, and the lead salt fractions of lac-acids, were essentially the same as described by Weinberger and Gardner.[5c] The alkali salts of the lac-acids when freed from sodium carbonate were dissolved in 1.5 liters of water for each 100 g. of original material taken for saponification, instead of the 2.4 liters used by previous investigators.

Dimethyl Shellolate (a).—One hundred grams of the finely powdered dry lead salts was suspended in 1 liter of a 3% solution of hydrogen chloride in anhydrous methyl alcohol. The lead salts reacted immediately to form lead chloride and the solution assumed a faint yellow color. The mixture was allowed to stand for three days at room temperature and was agitated occasionally. The white precipitate of lead chloride was then removed by filtration and the alcoholic solution was carefully neutralized with a solution of sodium hydroxide in methyl alcohol using brom thymol blue as indicator. The precipitate of sodium chloride was removed and the filtrate evaporated to a sirup at 50 to 60°, under reduced pressure. This sirup was dissolved in a small amount of chloroform. The chloroform solution was washed with a 10% aqueous solution of sodium carbonate, dried with anhydrous calcium sulfate, filtered, and evaporated to dryness at 50 to 60°. The amorphous mixture of esters was dissolved in a small amount of diethyl ether and the solution was allowed to evaporate spontaneously at room temperature. Crystallization was induced by scratching the sides of the beaker with a stirring rod. The solution was then placed in a refrigerator maintained at 10° for twelve hours. The crystals were removed by filtration, and the filtrate was kept at 10° until no more crystals were obtained. The solution was then allowed to evaporate to dryness and a reddish tan viscous residue remained which contained only small amounts of dimethyl shellolate. The balance of dimethyl shellolate was recovered by dissolving the residue in a small amount of diethyl ether, treating the solution with decolorizing carbon, removing the ether and extracting the residue with small portions of low boiling ligroin (boiling range 38 to 50°). Small amounts of shellolic acid, and of the homolog melting at 226° were recovered from the sodium carbonate solution used in purifying the original chloroform solution of the esters.

(**b**) Thirty-five grams of lead salts (41.5% Pb) which had been dried at 110° for twenty-four hours, was suspended in 250 ml. of an aqueous solution containing 7.431 g. of sodium carbonate. The lead carbonate which was formed was removed by filtration and the filtrate evaporated to dryness. The last traces of moisture were removed from the sodium salts in a vacuum desiccator over phosphorus pentoxide.

Three grams of sodium salts was placed in a Parr sulfur bomb, and 5 ml. of anhydrous methyl alcohol and 7 ml. of pure, freshly distilled methyl iodide added. The mixture was heated for three hours at 90 to 100°. After cooling, the bomb was opened and the contents filtered. Crystals of dimethyl shellolate separated after several hours; yield, 0.3 g.

(**c**) Three and four-tenths grams of sodium salts was dissolved in water, and a solution containing 3.41 g. of silver nitrate was slowly added. The silver salts which precipitated were removed by filtration and dried in the dark. Two and a half grams of the silver salts was then suspended in freshly distilled methyl iodide and heated under a reflux for six hours. After thoroughly washing the resulting solution with sodium carbonate, crystals of dimethyl shellolate separated; yield, 0.3 g.

Shellolic Acid.—One gram of dimethyl shellolate (m. p. 150 to 151°) was refluxed for three hours with 15 ml. of 1 *N* aqueous sodium hydroxide, and an exact equivalent (15 ml.) of 1 *N* sulfuric acid was added to the resulting solution. The perfectly clear solution was then placed in a vacuum desiccator and evaporated under reduced pressure over phosphorus pentoxide. When the volume had been reduced to one-third, the fraction of colorless crystals was separated and washed with small amounts of water. Two other fractions were obtained in the same manner. All melted at 206°; yield, 87%.

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 60.81; H, 6.82; acid no., 379. Found: C, 60.47, 60.60; H, 6.88, 6.77; acid no., 374, 374.

A sample of 0.65 g. of shellolic acid was dissolved in 10 ml. of 5% solution of hydrogen chloride in methyl alcohol and allowed to stand at room temperature. Crystals of dimethyl shellolate readily formed in chloroform solution in which the reaction products were dissolved. This product was identical in composition and melting point (150°) with the dimethyl shellolate obtained from the mixture of esters. A yield of 82% of the theoretical amount of ester was obtained.

Anal. Calcd. for $C_{17}H_{24}O_6$: C, 62.92; H, 7.47; sapon. no., 339.4; mol. wt., 330. Found: C, 63.10, 63.22; H, 7.68, 7.46; sapon. no., 340, 340; mol. wt. (Rast), 328, 330, 324; sp. rot. $[\alpha]^{20}_{D}$ +36°.

Shellolyl Dihydrazide.—4.5 g. of pure dimethyl shellolate was dissolved in 15 ml. of methyl alcohol and carefully added to 25 ml. of a 50% aqueous solution of hydrazine hydrate, and the reaction mixture was refluxed for thirty minutes. Shellolyl dihydrazide crystallized when the

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(9) O. Kamm, "Qualitative Organic Analysis," John Wiley & Sons, New York, N. Y., 2nd ed., 1932, p. 155, 170.

solution was cooled. The crystals were separated and recrystallized from hot water.

The purified product melted with decomposition at 246°. It was only slightly soluble in cold water and in alcohol, but soluble in both of these solvents at higher temperatures. It was insoluble in diethyl ether and ethyl acetate. Analysis showed it to have the expected composition.

Anal. Calcd. for $C_{15}H_{24}O_4N_4$: C, 55.52; H, 7.46; N, 17.28. Found: C, 55.36, 55.69; H, 7.38, 7.51, N (Jamieson), 17.28, 17.27.

Acknowledgment.—The authors wish to express their appreciation at this time to R. E. Kirk for the interest he has shown in this investigation and for the many helpful suggestions he has made.

Summary

1. A method has been developed for isolating shellolic acid from various lacs. This method was based upon a modification of the procedure used by Weinberger and Gardner for "lacollic lactone."

2. The various preparations of dimethyl shellolate obtained by this method were identical in properties with those described by Harries and Nagel.

3. It was shown that the total amount of shellolic acid in lac probably does not exceed 3.5 to 4%. This was about half of the fraction of acids whose lead salts are insoluble in alcohol.

4. "Lacollic lactone" was shown to be a mixture of dibasic acids. The resin fractions from which this product was obtained contained less shellolic acid than lac resin as a whole. This was interpreted as a further indication that other dibasic acids are also present as constituents of the interesters of lac resin.

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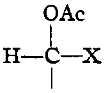
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

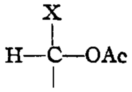
Derivatives of the Aldehydrol Form of Sugars. IV[1]

BY M. L. WOLFROM AND ROBERT L. BROWN

In previous communications from this Laboratory[1] there have been reported a number of acyl halide carbonyl addition compounds of *aldehydo*-sugar acetates. In no instance, however, were these substances isolated in the two forms predictable on stereochemical grounds.



$$\mathrm{H{-}\overset{\overset{\displaystyle OAc}{|}}{\underset{|}{C}}{-}X}$$



$$\mathrm{H{-}\overset{\overset{\displaystyle X}{|}}{\underset{|}{C}}{-}OAc}$$

Such a pair of isomers has now been obtained in the *d*-galactose structure. Their specific rotations in chloroform solution are +62° and −44° and an appreciable rotation difference is thus exhibited. This rotation difference is in contrast with the very small ones noted[1c] in other pairs of acyclic isomers likewise differing only in the configuration of carbon one. The substances will be designated[1c] α-1-chloro-*aldehydo*-*d*-galactose hexaacetate (+62°) and β-1-chloro-*aldehydo*-*d*-galactose hexaacetate (−44°).

This pair of acyclic α,β-isomers was obtained by application to the previously reported β-isomer[1a] of the zinc chloride interconversion procedure of Hudson and co-workers.[2] Both isomers exhibited a stable rotation in acetyl chloride solution but on the addition of a small amount of zinc chloride they underwent an interconversion at room temperature to an equilibrium mixture containing approximately 76.5% of the alpha isomer and 23.5% of the beta isomer. This composition is calculated upon the reasonable assumption that only these two substances are present in the equilibrium mixture. It was noted that a four-fold increase in the concentration of zinc chloride used caused no significant shift of the equilibrium point. The same equilibrium was attained when *aldehydo*-*d*-galactose pentaacetate was treated under the same conditions. In acetyl chloride alone, *aldehydo*-*d*-galactose pentaacetate underwent a slow rotation change in the opposite direction. These rotation characteristics are diagrammed in Fig. 1.

The above interconversion conditions were likewise applied to the one known form of 1-chloro-*aldehydo*-*d*-glucose hexaacetate[1b] and to *aldehydo*-*d*-glucose pentaacetate and similar optical characteristics were observed (Fig. 2). Unfortunately, the α-isomer in the *d*-glucose struc-

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[1] Previous publications in this series: (a) M. L. Wolfrom, THIS JOURNAL, 57, 2498 (1935); (b) M. L. Wolfrom and M. Konigsberg, *ibid.*, 60, 288 (1938); (c) M. L. Wolfrom, M. Konigsberg and F. B. Moody, *ibid.*, 62, 2343 (1940).

[2] Edna M. Montgomery, R. M. Hann and C. S. Hudson, *ibid.*, 59, 1124 (1937).