

SOME DERIVATIVES OF *p*-SULPHOCINNAMIC ACID.

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THE action of fuming sulphuric acid upon cinnamic acid was first thoroughly studied by Rudnew,¹ who isolated from the sulphonation mixture, two acids: one, the now well-known *p*-sulphocinnamic acid, which is the principal product of the reaction; and the other, an isomer which he called a meta-compound. Since that time the true *m*-sulphocinnamic acid has been prepared synthetically by Kafka,² and as its properties do not agree with those of the acid described by Rudnew, it is probable that the latter is an ortho-compound.

Rudnew's method of isolating these acids from the sulphonation mixture was the familiar one of treating the products of the reaction with barium hydroxide. The sulphonic acids were then separated from each other, and from the masses of barium sulphate produced, by crystallization from water. This method is tedious at best, and when one only wishes to prepare the para acid (as in the present investigation) it is better to take advantage of the fact (apparently heretofore overlooked) that this acid crystallizes spontaneously from the sulphonation mixture upon appropriate dilution with water. The *p*-sulphocinnamic acid used in this investigation was prepared in accordance with the following procedure. 150 grams of fuming sulphuric acid (containing 15 per cent. to 20 per cent. anhydride) are placed in a flask and 50 grams of finely ground cinnamic acid are introduced in small portions with constant shaking. The temperature rises during the reaction, and the quantities of cinnamic acid added are so regulated that the flask in which the sulphonation takes place shall not become uncomfortably warm to the hand. At the close, the reaction becomes sluggish, and may be concluded by heating for fifteen or twenty minutes on the water-bath. At this point the mixture should not be dark brown in color and should smell only faintly of sulphur dioxide. When cold, it is diluted with about three times its volume of water, and allowed to stand over night. If crystals of the *p*-sulphocinnamic acid are at hand, they should be added as soon as the diluted acid has become cold. Crystalliza-

¹ Rudnew: *Ann. Chem. (Liebig)*, **173**, 8.

² Kafka: *Ber. d. chem. Ges.*, **24**, 746.

tion then begins almost at once—usually at the bottom of the flask—but proceeds very slowly. It is seldom complete in less than ten hours, but at the end of that time the contents of the flask usually seem entirely solidified. It is usually best to determine the proper amount of dilution by experiment, with small portions, as different sulphonations, under apparently identical conditions, sometimes require slightly different treatment. The crystals thus obtained are filtered off and dried by suction. They are sufficiently pure for most purposes. A perfectly pure product is best obtained by dissolving the crude acid in water, precipitating the acid barium salt by means of a solution of barium chloride, purifying this by crystallization, and finally decomposing it with the calculated amount of sulphuric acid. On evaporation, the acid is obtained in the long four-sided prisms described by Rudnew. He describes these crystals as stable in the atmosphere,—an observation which I cannot confirm, possibly on account of the greater dryness of the American climate. The crystals which I obtained were very large and well formed, often showing beautiful twin-formation, but they weathered rapidly on exposure to the air. The acid was characterized by the preparation of the amide described by Palmer,¹ and by the crystalline form of the acid barium salt described by Rudnew, which crystallizes in beautiful long needles very difficultly soluble in cold water.

Previous investigators do not seem to have noticed the fact that this acid forms very insoluble acid salts with a number of the aromatic amines, and these salts offer a more convenient means of characterizing this acid than either of the methods mentioned above. Only the aniline salt was analyzed. This may be prepared by treating a solution of the acid, or any of its more soluble salts, with a solution of aniline hydrochloride. A crystalline precipitate appears at once, and on recrystallization from hot water, the salt shows a marked tendency to form large radially arranged aggregates. These crystals melt at 246° (uncorrected) and their composition is established by the following analysis.

Calculated for $C_{15}H_{15}O_3NS$: C, 56.08 per cent.; H, 4.67 per cent.; N, 4.35 per cent. Found: C, 56.07 per cent.; H, 4.82 per cent.; N, 4.77 per cent.

Acid Sodium Salt.—In the preparation of sulphocinnamic acid,

¹ Palmer: *Am. Chem. J.*, 4, 163.

as above described, a somewhat larger yield may be obtained by pouring the mother-liquor from the crystals of free acid into a saturated solution of sodium chloride. The acid sodium salt then separates out, and may be purified by crystallization from water. As this salt has not been heretofore described, the following analytical data are appended:

Calculated for $C_9H_7O_5SNa, 2H_2O$: Na, 8.04 per cent.; H_2O , 12.59 per cent. Found: Na, 7.93 per cent.; H_2O , 12.59 per cent. at 110° .

p-Sulphodibromhydrocinnamic Acid.—*p*-Sulphocinnamic acid absorbs two equivalents of bromine with great readiness, even in aqueous solution. For this purpose, the acid is dissolved in just enough cold water to make a clear solution, and the calculated amount of bromine is added in portions of about a cubic centimeter with constant shaking. Any excess of bromine is finally removed by a current of air. A large part of the bromine addition product now separates as a fine, white, crystalline powder, and an almost quantitative yield may be obtained by evaporation of the mother-liquor in the cold. The first portions of the acid to be precipitated are very pure, but, for purposes of analysis, the acid was recrystallized from water, and then air-dried.

Calculated for $C_9H_5Br_2S, 2H_2O$: C, 25.15 per cent.; H, 2.83 per cent.; Br, 37.20 per cent.; S, 7.54 per cent.; H_2O , 8.25 per cent. Found: C, 25.21, 25.22, 25.38 per cent.; H, 2.85, 3.00, 2.79 per cent.; Br, 37.15, 37.65, 37.32 per cent.; S, 7.93, 7.77, 7.59 per cent.; H_2O , 6.05, 7.73, 6.68 per cent.

One hundred parts of saturated solution at 20° contain from 53 to 57 parts of solid acid.

It is evident from the above, that the acid does not give up quite all its water of crystallization at 110° , but continued heating at a higher temperature results in slight decomposition as shown by a brown discoloration of the material.

Barium Salt.—The most characteristic inorganic salt of this acid is the acid barium salt, which is precipitated when a solution of the acid is treated with barium chloride. It crystallizes in short colorless needles.

Calculated for $C_{18}H_{14}O_{10}S_2Br_4Ba, 4H_2O$: C, 21.98 per cent.; H, 2.24 per cent.; S, 6.36 per cent.; Br, 32.55 per cent.; Ba, 13.94 per cent.; H_2O , 7.32 per cent.

Found: C, 21.64 per cent.; H, 2.40 per cent.; S, 6.64 per cent.; Br, 32.52 per cent.; Ba, 14.37 per cent.; H₂O, 8.10 and 7.34 per cent.

100 parts saturated solution contain 2.7 parts of solid salt.

Copper Salt.—When concentrated solutions of the acid are treated with a concentrated solution of copper sulphate, a white precipitate is obtained. This may be recrystallized from water, and then forms small wart-like aggregates of a pale greenish white color, which show some tendency to decompose when half dry, but which, when perfectly dry, are quite stable. The substance is evidently an acid salt.

Calculated for C₁₈H₁₄O₁₀Br₄S₂Cu, 2H₂O: Br, 36.63 per cent.; S, 7.32 per cent.; Cu, 7.28 per cent.; H₂O, 4.12 per cent.

Found: Br, 35.38, 35.10 per cent.; S, 7.25, 7.39 per cent.; Cu, 7.11, 7.43 per cent.; H₂O, 4.50 per cent. at 110°.

The results for bromine can hardly be considered satisfactory, but the salt is not well characterized, and another analysis did not seem worth while. It is very soluble in water.

Sodium Salts.—The acid sodium salt was prepared by the action of bromine upon the acid sodium salt of *p*-sulphocinnamic acid. It is a white crystalline powder.

Calculated for C₉H₇O₃BrSNa, 3H₂O: Br, 34.48 per cent.; S, 6.90 per cent.; Na, 4.95 per cent.; H₂O, 11.63 per cent.

Found: Br, 34.76 per cent.; S, 7.30 per cent.; Na, 5.21 per cent.; H₂O, 11.69 per cent.

The neutral sodium salt was prepared by treating a solution of the free acid with sodium hydroxide until the solution was neutral to phenolphthalein. This salt crystallizes in needles very soluble in water.

Calculated for C₉H₆O₃Br₂SNa₂, 4H₂O: H₂O, 14.03 per cent. Found: H₂O, 14.02 per cent.

Ammonium Salt.—When a solution of the free acid is treated with an excess of ammonia and evaporated in a desiccator over sulphuric acid, crystals appear which probably consist of the neutral ammonium salt, but an analysis was impracticable, as the salt is not stable, and the products of decomposition have not yet been determined. They will be an object of subsequent study.

Amide.—*p*-Sulphocinnamic acid and its salts react vigorously

with phosphorus pentachloride. The acid chloride thus formed has not been isolated, but the reaction-mixture was poured into dilute ammonia with the object of preparing the amide. A product was thus formed which crystallizes from hot water (in which it is soluble only with difficulty) in bulky scales. These melt sharply at 208° (uncorrected) and decompose just above the melting-point with evolution of bromine. This substance is doubtless the diamide in which both hydroxyl groups of the acid are replaced by amido-groups, although the analytical results (especially for nitrogen) have never been entirely satisfactory. The yield is poor—never better than 10 per cent. of the material used. Other less well-characterized products sometimes appear, and the amide seems to undergo some decomposition in the treatment with hot water necessary for recrystallization.

Calculated for $C_6H_{10}O_3N_2BrS$: N, 7.25 per cent.; Br, 41.45 per cent.; S, 8.29 per cent.

Found: N, 8.22 per cent.; Br, 41.18 per cent.; S, 8.44 per cent.

Salts with Organic Bases.—When the acid is treated with aniline hydrochloride in aqueous solution, a white crystalline precipitate is obtained. Salts of most of the aromatic amines seem to behave in a similar way. Among those tried were aniline, dimethyl aniline, diethyl aniline, quinoline, α - and β -naphthyl amine, phenylene diamine, and diphenyl amine. It should be noted that neither pyridine nor any of the aliphatic amines yield similar precipitates, so far as tried. Most of the salts of the aromatic amines thus obtained crystallize well, and the aniline, dimethyl aniline, and diethyl aniline salts also melt sharply. They therefore furnish the most convenient method of characterizing the acid. The three salts just mentioned are all acid salts, as is shown by the analyses given below; the others probably have similar composition, but were not analyzed. All may be crystallized from hot water, the dimethyl aniline salt producing the best-formed crystals.

Aniline salt, white needles, melting-point 192° .

Calculated for $C_{15}H_{15}O_3NBr_2S$: Br, 33.27 per cent.; S, 6.65 per cent.; N, 2.91 per cent.

Found: Br, 33.52, 33.43 per cent.; S, 7.01, 6.82 per cent.; N, 3.05, 3.27 per cent.

One part of salt dissolves in 67 parts of water at room temperature.

Diethyl aniline salt, melting-point 160°.

Calculated for $C_{18}H_{23}O_5NBr_2S$: C, 42.45 per cent.; H, 4.28 per cent.; N, 2.61 per cent.; Br, 29.80 per cent.; S, 5.96 per cent.

Found: C, 42.25 per cent.; H, 4.19 per cent.; N, 2.80 per cent.; Br, 29.63, 29.89 per cent.; S, 6.14, 6.13 per cent.

Dimethyl aniline salt, clear prisms melting at 150°.

Calculated for $C_{17}H_{19}O_5NBr_2S$: C, 41.02 per cent.; H, 3.73 per cent.; N, 2.75 per cent.; Br, 31.44 per cent.; S, 6.29 per cent.

Found: C, 40.59 per cent.; H, 3.89 per cent.; N, 3.25 per cent.; Br, 31.09 per cent.; S, 6.31 per cent.

Action of Silver Nitrate upon p-Sulphodibromhydrocinnamic Acid.—When an aqueous solution of the free acid or its salts is treated with a solution of silver nitrate, a precipitate is formed. This is sometimes curdy, but when both solutions are concentrated, a separation of short needle-like crystals is sometimes observed. This may be a silver salt of the organic acid, but, if so, it is extremely unstable, and in a few minutes at longest, the precipitate consists entirely of silver bromide. In dilute solutions in the cold, it may be determined by a rough titration that precipitation ceases when one molecule of silver nitrate has been added to one of the acid. Salts of lead and mercurous mercury act in this respect like silver. The result, in any case, seems to be a splitting-off of one molecule of hydrobromic acid from the side-chain, resulting in the formation of a *p*-sulphobromcinnamic acid. This acid has not yet been isolated, and even the salts are difficult to obtain. When silver nitrate is used to remove the hydrobromic acid, the nitric acid set free by the reaction seems to have an oxidizing action upon the new product formed. The substitution of other salts for silver nitrate has hitherto involved somewhat similar difficulties. On one occasion, when the acid sodium salt of *p*-sulphodibromhydrocinnamic acid had been treated with dilute silver nitrate solution, the silver bromide produced filtered off, and the filtrate evaporated in a vacuum desiccator over sulphuric acid; crystals were obtained, for whose purity no guarantee could be given, but the analytical data presented below would seem to indicate the presence of an acid sodium salt of *p*-sulphomonobromcinnamic acid. Nothing conclusive is claimed for the results.

0.1996 gram substance yielded 0.1037 gram AgBr and 0.1352 gram BaSO₄.

0.2654 gram substance lost 0.0085 gram at 135°.

Calculated for $C_9H_8O_3BrSNa \cdot H_2O$: Br, 23.05 per cent.; S, 9.22 per cent.; H_2O , 5.19 per cent.

Found: Br, 22.11 per cent.; S, 9.30 per cent.; H_2O , 3.54 per cent. at 135°.

Action of Aqueous Hydrobromic Acid upon p-Sulphocinnamic Acid.—The fact that sulphocinnamic acid adds bromine in aqueous solution, rendered it probable that hydrobromic acid might be added with equal readiness. Some of the acid was therefore dissolved in concentrated hydrobromic acid. It is only soluble with difficulty in this medium, and the acid was warmed to hasten solution. A few hours later, the flask was found to be traversed in all directions by thin, needle-like crystals, whose length seemed only limited by the dimensions of the flask. These crystals were filtered off, the mother-liquor removed as much as possible by suction, and the crystals air-dried. Washing with pure water was impracticable on account of their solubility in this medium. It was supposed at first that these crystals represented the hydrobromic acid addition product sought. A bromine determination, however, showed that the bromine content was small and variable, and evidently due only to contamination from the mother-liquor.

0.1567 gram substance yielded 0.0034 gram AgBr.

0.1763 gram substance yielded 0.0068 gram AgBr.

This is equivalent to 0.92 per cent. and 1.64 per cent. Br respectively.

The possibility remained that the crystals might be unchanged *p*-sulphocinnamic acid. This seemed at first very improbable as they are very different in appearance from the large four-sided prisms with oblique ends which this acid forms when crystallized from water. A further difference existed in the fact that while the latter weathered rapidly on exposure to the air, the new crystals were very stable in the atmosphere, and only lost water over sulphuric acid. This could be accounted for if the new crystals contained less water than the old. This proved to be the case. The analysis shows that the former contain 3 molecules of water of crystallization while the latter, as described by Rudnew, contains 5. The chemical identity of the two substances was shown by dissolving the new crystals in water and adding aniline hydro-

chloride. The acid aniline salt above described, melting at 246° was precipitated.

Calculated for $C_9H_8O_3 \cdot 3H_2O$, 19.22 per cent.

Found: H_2O , 20.36 and 20.00 per cent at 110° .

The results are slightly high, but when it is remembered that these crystals contain some hydrobromic acid, which would also be lost at this temperature, they may be considered conclusive.

The above results are published on account of a temporary interruption of the work. It will, however, be again taken up, and I desire to reserve the field of the halogen derivatives of *p*-sulphocinnamic acid for some time longer.

My hearty thanks are due to my assistant, Mr. L. A. Salinger, who did most of the manipulative work, and conducted most of the analyses recorded in this paper.

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THE ANALYTICAL CONSTANTS AND COMPOSITION OF MYRTLE WAX.

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MYRTLE wax, also known as laurel wax or bayberry tallow, is a fat of minor commercial importance obtained from the fruit of *myrica cerifera*, a shrub common along the North Atlantic sea-coast and in other sections of this country. The statements regarding its composition are somewhat contradictory. The general books of reference state that it is mainly free palmitic acid with about 20 per cent. palmitin. Some state that it also contains lauric acid and others that it contains stearic and myristic acids. The first of these statements is due to Moore,¹ the second to Chevreul.²

On the other hand, the works on oil and fat analysis state that myrtle wax is a triglyceride with a small amount of free fatty acid, and give low "acid values" in support of these statements. Benedict³ states that it is composed mainly of palmitin with some myristin and stearin. Lewkowitsch⁴ says that in addition to the

¹ *Am. J. Sci. and Arts*, 2nd series, **33**, 313.

² *Compt. rend.*, **20**, 38.

³ "Analyse der Fette," 3rd ed., p. 535.

⁴ "Chemical Analysis of Oils, Fats, and Waxes," p. 542.