The portion not soluble in benzene was dissolved in dilute acetic acid and precipitated with concentrated hydrochloric acid. The process was repeated till clean, white, blunt needles were obtained, which melted sharply at 256°. These were dried over sulphuric acid in an atmosphere containing a little hydrochloric acid gas, and then in vacuum.

Calculated for $C_{17}H_{20}O_2NCl$:	C, 66.9; H, 6.6; N, 4.6; Cl, 11.6.
Found:	C, 66.4; H, 6.8; N, 4.8; Cl, 11.6.

This substance is then the hydrochloride of β,γ-diphenyl-δ-aminovaleric acid. Up to the present time a sufficient yield has not been secured to enable a careful study of derivatives of the substance to be made.

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THE NITRATION OF β-p-TOLYLGLUTARIC ACID.

BY S. AVERY AND FRED W. UPSON.

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Early in the spring of 1902 the senior author collected all of the unpublished work done under his direction on the aromatic glutaric acids. After the usual delay in the hands of the editor, this work appeared in the July number of the *American Chemical Journal*[1] with no mention of the date when it was received. A part of the ariticle related to the nitration of β-phenylglutaric acid.[2] In the meantime there appeared an article on the same subject by Schroeter and Meerwein,[3] received by the editor of the *Berichte*, May 27th, and published with the usual promptness. The two articles appeared simultaneously in America, though, of course, Schroeter and Meerwein's work was seen first by European readers. The results obtained were essentially the same in both cases. The nitration product obtained in the greater quantity proved to be β-*p*-nitrophenylglutaric acid, m. p. 237°. The product obtained in smaller quantity was described as follows:[4] "This product has not as yet been investigated, but is probably β-*ortho*nitrophenylglutaric acid. Under the conditions of nitration given, the amount of this compound formed does not exceed ten per cent. of the phenylglutaric acid used." It may be added that Meerwein and Schroeter[5] have since shown this product to consist of a mixture of the *ortho*nitro and *meta*nitro acids. The *ortho*nitro acid is of especial interest because of the possibility of converting it into quinoline derivatives, but on account of their technical priority,

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[1] *Amer. Chem. J.*, **28**, 48.

[2] Avery and Beans, *Amer. Chem. J.*, **28**, 55.

[3] *Ber.*, **35** 2073 (compare also statement of Meerwein & Schroeter, *Ber.*, **36**, 2670).

[4] *Amer. Chem. J.*, **28**, 55.

[5] *Ber.*, **40**, 1586.

and the larger amount of work that they had already accomplished, it seemed proper to relinquish the field to Meerwein and Schroeter, reserving only in agreement with them the study of the nitration of *p*-tolylglutaric acid, the synthesis of which had recently been effected by Avery and Parmelee.[1] As the glutaric acid had apparently yielded only *para*-nitro and *ortho*nitro products, it seemed probable that the *p*-tolylglutaric acid would yield a much greater proportion of the corresponding *ortho* compound, and that this might form a satisfactory substance from which to start in the synthesis of certain quinoline derivatives. Though this expectation was somewhat diminished by the recent work of Meerwein and Schroeter, yet the subject seemed to be of sufficient interest to warrant a thorough investigation of the nitration products of *p*-tolylglutaric acid.

Experimental Part.

β-*p*-Tolylglutaric acid, made as directed by Avery and Parmelee,[1] was treated with fuming nitric acid as previously described[2] in the work with β-phenylglutaric acid. As practically no nitration took place, the procedure was modified to the following: The tolylglutaric acid was added slowly to ten times its weight of fuming nitric acid kept below a temperature of 10°. The mixture was kept at approximately this temperature for several hours and then allowed to stand at room temperature (about 21°) for three days. At the end of this time the mixture was poured into ice-water, with the precipitation of crystals. After several recrystallizations from a mixture of acetic ester and petroleum ether, and finally from hot water, the melting point remained constant at 182°–183°.

The analysis gave: C, 46.1; H, 3.9; N, 9.1.
Calculated for $C_{12}H_{12}O_8N_2$: C, 46.1; H, 3.9; N, 9.0.
Titration: 0.1600 gram required 10.15 cc. 0.1 *N* sodium hydroxide.
Calculated for 2 acid hydrogens in above formula 10.24 cc.
The silver salt contained Ag, 41.0. Calculated for $C_{12}H_{10}O_8N_2Ag_2$, Ag 41.0.

The substance is therefore a dinitrotolylglutaric acid. It was not found possible to form a mononitro-*p*-tolylglutaric acid by direct nitration.

On recrystallization from hot water the dinitro-β-*p*-tolylglutaric acid is obtained in the form of slightly yellow, glistening, microscopic plates, m. p. 182°. It is insoluble in petroleum ether, slightly soluble in chloroform and benzene, soluble in ethyl acetate, ether and hot water, and easily soluble in acetone and alcohol.

The anhydride is readily obtained on heating the dinitro acid with acetic anhydride. Recrystallized from glacial acetic acid this anhydride

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[1] *Amer. Chem. J.*, **28**, 49.

[2] *Ibid.*, **28**, 55.

forms hard, white, glistening plates, insoluble in chloroform, ether, alcohol, benzene and acetic ester, but soluble in acetone. The anhydride is reconverted to the acid on dissolving in an alkali and precipitating with an acid. The anhydride melts at 230–231°. This melting point is of interest since, contrary to the general rule in the case of substituted glutaric acids, it is higher than the melting point of the acid from which it is derived.

A nitrogen determination gave N 9.7. Calculated for $C_{12}H_{10}O_7N_2$, N 9.5.

The anilic acid was obtained by dissolving the anhydride in acetone and adding the molecular equivalent of aniline. It was purified by dissolving in benzene and precipitating with petroleum ether. White, microscopic needles, m. p. 169°–170°, were obtained.

A nitrogen determination gave N 10.9; calculated for $C_{18}H_{17}O_7N_3$, N 11.0.

The next matter to be investigated was the position of the nitro groups in the tolylglutaric acid. Schroeter and Meerwein[1] have found that nitro groups in the *meta* position in β-phenylglutaric acid are easily reduced by ammonium sulphide while in other positions they are more stable toward this reagent. We found that by moderate reduction with ammonium sulphide an aminonitrotolylglutaric acid was formed, and that by a greater excess of ammonium sulphide, used at a higher temperature, a very soluble product was formed, presumably the diamino acid. It was, however, not isolated.

The dinitrotolylglutaric acid is very easily reduced to the aminonitrotolylglutaric acid by observing certain precautions. It is first made alkaline with ammonia in moderate excess, heated to 70° and then treated with hydrogen sulphide without further heating. The solution becomes first red, then yellow. At this point action of the hydrogen sulphide is interrupted, the solution concentrated on the water bath and then filtered. The filtrate is evaporated to dryness, the residue extracted with acetic ester, the ester removed by evaporation and the final residue recrystallized from hot water. The yield is nearly quantitative. Long needles of a yellowish brown color, m. p. 201°.

Titration: 0.1472 gram required 10.4 cc. 0.1 *N* sodium hydroxide. Calculated for two acid hydrogens in $C_{12}H_{14}O_6N_2$, 10.4 cc. Silver Salt: Found, Ag 43.4; calculated for $C_{12}H_{12}O_6N_2Ag_2$, Ag 43.5.

The action with ammonium sulphide points strongly to the formula $CH=(CH_2COOH)_2:NO_2:CH_3:NO_2$ in the 1:3:4:5 positions in the original dinitro acid under consideration. This view is strengthened by the oxidation of the dinitrotolylglutaric acid to the dinitroterephthalic acid. Using the method of Haeussermann and Martz[2] an acid was ob-

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[1] *Ber.*, 35, 2077.

[2] *Ibid.*, 26, 2982.

tained corresponding in properties to the 1 : 3 : 4 : 5-dinitroterephthalic acid described in their article, except that it shows a slightly higher melting point, evidently on account of a slightly greater degree of purity. It does not in this respect approach the melting point of its isomers. The acid is therefore $COOH : NO_2 : COOH : NO_2 = 1 : 3 : 4 : 5$ and must have been formed from a glutaric acid having the nitro groups in the di*ortho* or di*meta* positions as related to the glutaric rest and could not have been formed from an acid of any other configuration.

The difficulty in deciding between the two possibilities was overcome in the following manner: *m*-Nitro-*p*-tolylaldehyde was made according to the method of Hanzlick and Bianchi[1] and converted into *m*-nitro-*p*-tolylacrylic acid ($CH_3 : NO_2 : CH : CHCOOH = 4 : 3 : 1$) by the Perkin reaction. This acid forms needles of a slightly yellow color, on recrystallization from acetic acid, m. p. 169°.

Titration: 0.1275 g. required 6.1 cc. 0.1 *N* sodium hydroxide. Calculated for one acid H in $C_{10}H_9O_4N = 6.1$ cc.

The acrylic acid was converted to the methyl ester, producing white silky needles, m. p. 109°.

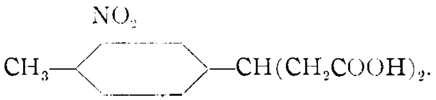
Nitrogen determination:[2] Found, N 6.5. Calculated for $C_{11}H_{11}O_4N$, 6.4.

The ester was condensed with malonic ester in the usual way and on saponification with hydrochloric acid the nitrotolylglutaric acid was obtained. This was purified by recrystallizing from dilute alcohol or dilute acetone. The crude acid may also be purified by converting to the anhydride with acetic anhydride and recrystallizing from a mixture of benzene and petroleum ether. The anhydride is reconverted to the acid by dissolving in sodium hydroxide and precipitating with hydrochloric acid. Melting point of acid 198.5°.

Titration: 0.1223 gram acid required 9.1 cc. 0.1 *N* sodium hydroxide. Calculated for two acid hydrogens in $C_{12}H_{13}O_6N$, 9.1 cc.

Silver salt gave Ag 44.78. Calculated for $C_{12}H_{11}O_6NAg_2$, Ag 44.87.

The acid is therefore



$$CH_3-C_6H_3(NO_2)-CH(CH_2COOH)_2.$$

When this acid was nitrated in the manner described in the first paragraph of the experimental part of this paper, a substance was obtained, identical in melting point, melting point of anhydride, crystal form, solubilities, and titration with the dinitro product obtained on nitrating *p*-tolylglutaric acid. It follows that the latter is of the constitution

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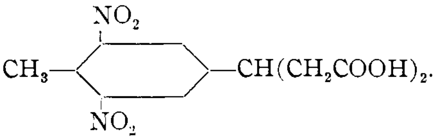
[1] *Ber.*, 32, 1288.

[2] Analysis by W. L. Hadlock.



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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

THREE NEW PRELIMINARY TESTS FOR MAPLE PRODUCTS.

BY ALBERT P. SY.

Received July 7, 1908.

The Color Test.—The literature on maple products contains very few references to the color of these products. This color is due to caramel produced during the evaporation of the sap, and to other substances the nature or composition of which is not understood. It is known that tannin is present, but in very small quantities. Caramel is insoluble in amyl alcohol, while the other coloring matters in maple products are soluble in it; they are, however, also soluble in water. In order to decrease this latter solubility, phosphoric acid is used, which causes most of the coloring matters to go into solution in the amyl alcohol. The test is made as follows: Put 15 cc. of sirup, or 15 grams of sugar and water to make 15 cc., into a test tube or narrow cylinder, add 3 cc. of pure amyl alcohol and 1 cc. of a 20 per cent. solution of phosphoric acid; mix the whole thoroughly by shaking; let stand until the alcohol separates and then note the color of the amyl alcohol layer.

The depth of color of the alcohol varies, of course, with the color of the sample taken. The test has been applied to a great many samples of maple products, of which a complete analysis was also made. A number of these samples were made by the writer and known to be pure; others were bought as pure from parties known to the writer to be producers of maple products from their own trees. In all cases the presence of maple was indicated by the color of the amyl alcohol; pure products always gave a decided brown color; adulterated samples gave from a trace of color to a light brown, according to the amount of maple product present as indicated by the results of a complete analysis. Cane sugar products colored with caramel gave no color.

The Foam Test.—This test was the result of the observation that sirups and sugars consisting mostly of cane sugar do not give any trouble and produce hardly any foam when heated and ignited for the ash determination. Pure maple products on the other hand often produce considerable foam when heated. Preliminary tests showed that a pure maple sirup diluted with water and shaken produced a persistent foam