Calc. for $NH(C_6H_5)CO.CO_2(NH_4)$: total N, 15.38%. Found: 15.36%.

Ammonium Phenylpropiolate.—Phenylpropiolic acid, which contains a triple bond, is the first acid of its type whose ammonium salt has been studied in this laboratory. There is no record of the salt having been made elsewhere. It was precipitated in an ether solution of the free acid. A little heat was developed during the saturation with ammonia, which is an unusual occurrence with ether solutions. The salt is a pure white powder, having a slight odor. It is somewhat soluble in ethyl alcohol, very soluble in methyl alcohol, and insoluble in chloroform, acetone, benzene and ether. An aqueous solution is neutral for about 2 hours, after which time it slowly hydrolyzes and gives an acid reaction. Moist air causes it to lose ammonia, but in dry air at 50° it remains unchanged for about 1 hour before it begins to lose ammonia slowly. The salt is not hygroscopic.

Calc. for $C_6H_5C\vdots CCO_2(NH_4)$: N, 8.59%. Found: 8.62%.

Work is still in progress in this laboratory on the ammonium salts of organic acids.

ST. LOUIS, MO.

[CONTRIBUTION FROM THE DIVISION OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA.]

AN OPTICAL METHOD FOR THE DETERMINATION OF MALIC AND TARTARIC ACIDS IN THE SAME SOLUTIONS.[1]

BY J. J. WILLAMAN.

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Introduction.

For several years the question of optical methods for malic and for tartaric acids has been before the conventions of the Association of Official Agricultural Chemists. Such progress was made in the case of malic acid that a polariscopic method was incorporated in the official methods of the Association in 1916.[2] The method involves the increase in optical activity caused by uranyl acetate, a reaction first observed by Walden.[3] A method for tartaric acid was not so successfully evolved, although its optical activity is likewise strongly increased by uranyl acetate.[4]

Where both acids occur in the same solution, a special problem arises. There is no way now known by which they can be separated quantitatively; hence any method for their determination must depend upon

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[1] Published with the approval of the Director as Paper No. 111, Journal Series Minnesota Agricultural Experiment Station.

[2] "Methods of Analysis," *J. Assoc. Off. Agr. Chemists*, 1916.

[3] Walden, "Über ein neues, die Drehungsgrösse steigerndes Mittel.," *Ber.*, [3] 30, 2889–2895 (1897).

[4] P. B. Dunbar, "The Determination of Tartaric Acid," *U. S. Dept. Agr. Bur. Chem. Circ.*, 106 (1912).

two factors applied to the same solution. In 1911, Yoder[1] suggested, but did not work out in detail, that when these two acids are present in the same solution, the titre and the optical activity as increased by uranyl acetate would give data for calculating the amount of each acid. The difficulty here, of course, is in having only these two acids present and in the free state. In 1912, Dunbar[2] published a method for these two acids, employing the activated rotatory power together with either the amount of oxalic acid formed by the permanganate oxidation of these acids, or the amount of permanganate reduced. The method has been unsuccessful in the hands of other workers, due, no doubt, to the fact that in natural products there are always other substances present which reduce permanganate and form oxalic acid. At the 1913 meeting of the Association of Official Agricultural Chemists, Gore[3] reported an attempt to use two optical activators, uranyl acetate and ammonium heptamolybdate. The former increases the negative rotation of *l*-malic acid and the positive rotation of *d*-tartaric acid; the latter reverses the direction of rotation of *l*-malic, giving a strong positive rotation for both acids. Gore found, however, that linear relations do not exist between the amount of acid present and the optical activity, especially in the case of the tartaric acid. Hence the proposed method was untenable. He concluded his discussion with the statement, "No method for the estimation of the two acids in the presence of each other by polarimetric means alone is in sight at present."

It occurred to the writer, however, that whether strictly linear relations existed or not, a given set of conditions could be chosen and adhered to in constructing tables or curves with known amounts of pure malic and tartaric acids, which curves could then be used for the determination of unknown quantities of these acids. The method herein described has such an origin. Nothing new is claimed for any of the processes; but the combination of processes chosen has resulted in a new, simple, and satisfactory optical method for the determination of malic and tartaric acids in natural products.

Experimental Study of Factors Involved.

The development of the method involved two phases: first, the ascertaining of whether a given set of necessary conditions will always give the same results, and second, the search for that combination of conditions and processes that will give results satisfactory from the standpoints of accuracy, ease of manipulation, and applicability to materials from

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[1] P. A. Yoder, "A Polarimetric Method for the Determination of Malic Acid and its Application in Cane and Maple Products," *J. Ind. Eng. Chem.*, 3, 563–574 (1911).

[2] P. B. Dunbar, "The Determination of Malic and Tartaric Acids in the same Solution," *U. S. Dept. Agr. Bur. Chem. Circ.*, 105.

[3] Gore, *J. Assoc. Off. Agric. Chemists*, 1, 120–130 (1915).

varied sources. The first point was answered affirmatively by a review of the published experiences of the various workers in this field, and by some preliminary trials by the writer. The second point necessitated a careful study of all the factors which affect the optical activities of the acids under the proposed treatment. The simplest way to explain the choice of details finally decided upon is to enumerate and discuss each factor separately.

1. **Kind of Activator.**—A number of compounds of uranium, tungsten, molybdenum, boron, titanium, etc., have been found which increase the optical activity of certain organic compounds. Uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$, and ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, were chosen for the present work, because (1) they give very marked increases in the rotatory power of malic and tartaric acids, (2) they have been worked with enough to show their applicability to the method in hand, and (3) they can be obtained as pure salts fairly readily. Yoder[1] found uranyl nitrate to be inferior to the acetate because of the mineral acid produced by hydrolysis.

2. **Kind of Acids Affected.**—Walden[1] showed that it is the optically active, dicarboxylic oxy-acids that are affected by these metals; other oxy-acids, however, are not excluded. Thus malic and tartaric are markedly affected; citric[2] is to a certain degree, and any considerable quantity of it will interfere with the present method; lactic[3] is affected very slightly, but not enough to interfere; a few aromatic acids are affected, but are not commonly found in natural products. Hence citric acid is the only one to be guarded against in applying the present method.

3. **Effect of Substances Other than Acids.**—Yoder[1] found that sugars in concentrations up to five times that of the malic acid do not interfere; Dunbar and Bacon[4] found that normal solutions of sucrose and invert sugar give slightly lower readings in the presence of uranyl acetate. In the present method the sugars are excluded by removing the acids as the barium salts. Ammonium sulfate increases the readings with molybdenum and decreases those with uranium. Although ammonium sulfate is not present in appreciable amounts in natural products, it is present in the following method, due to excess of the salt after decomposing the barium malate and tartrate. In establishing the curves, therefore, with known amounts of the two acids, the same excess of ammonium sulfate was used in each case as would be present in determining an unknown.

4. **Reaction of the Medium.**—Yoder[1] found that two equivalents of mineral acid completely destroy the effect of uranyl acetate, that or-

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[1] *Loc. cit.*

[2] H. C. Gore, *J. Assoc. Off. Agric. Chemists*, 1, 480–484 (1915).

[3] *Ibid.*, 120–130 (1915).

[4] P. B. Dunbar and R. F. Bacon, "The Determination of Malic Acid," *U. S. Dept. Agric. Bur. Chem. Circ.*, **105** (1912).

ganic acids had a much slighter effect, and that free alkali disturbed it but little. Walden[1] used four equivalents of potassium hydroxide to overcome the acidity of one equivalent of uranyl nitrate. Gore[2] found that if the malic and tartaric acids are neutralized previous to treatment, higher readings are obtained. He also found that the addition of acetic acid to the neutralized malic and tartaric acids gave higher readings. Two cc. of glacial acetic acid per 100 cc. of solution gave maximum readings with uranium; but with molybdenum 6 cc. of acetic acid are required for malic acid and over 16 cc. for tartaric acid before maximum readings are obtained. No explanations have been offered for this behavior of acetic acid in connection with these uranium and molybdenum complexes. In the present method it was decided to employ 6 cc. of acetic acid per 100 cc. of solution of neutralized acids. This is too much for the maximum uranium readings and too little for the molybdenum; but it is the best average that could be struck. Any divergence from maximum polariscope readings will occur in the curves of knowns and unknowns alike.

5. **Amount of Activator to be Used.**—Yoder[1] found that 1.25 equivalents of uranium for each molecule of malic acid gave the maximum readings. According to Walden's[1] hypothesis that the uranium molecule enters at the hydroxyl group, one equivalent should be sufficient; but even under optimum conditions it never is. With molybdenum 3 molecular equivalents are necessary. The interesting fact of these ratios is that both more and less of the activator than is necessary for maximum readings gives a marked decrease in the reading. This is strikingly shown in Gore's graphs.[2] Therefore, in working with an unknown amount of either organic acid, it is quite impossible to add the correct amount of activator for maximum rotations. Yoder[1] used 0.7 g. uranium acetate in 25 cc. of solution; Dunbar and Bacon[3] in their methods saturate their solutions with powdered uranyl acetate, which usually requires from 2 to 3 g. for 25 cc. of solution. Gore[1] found it easier to employ a standard solution of uranyl acetate and of ammonium molybdate. A solution is also used in the Official Method.[4] It has the advantage of giving a definite amount of salt, and giving it in solution immediately; it requires 2 or 3 hours of shaking to saturate a solution with uranyl acetate, and then the amount that dissolves depends somewhat upon the amount of malic and tartaric acids present. In the present work it was decided to use standard solutions of the two activators, of such strength that 10 cc. will furnish 0.8

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[1] *Loc. cit.*

[2] H. C. Gore, Twenty-ninth Meeting of Assoc. Off. Agric. Chemists, *U. S. Dept. Agr. Bull.*, **162**, 63–71 (1913).

[3] *U. S. Dept. Agr. Bur. Chem. Circ.*, **105**, 106 (1912).

[4] *J. Assoc. Off. Agric. Chemists*, **1916**.

g. uranyl acetate and 1.0 g. ammonium molybdate, respectively. This will provide about 1.25 equivalents of uranium and 3 equivalents of molybdenum for 0.2 g. of combined malic and tartaric acids in a 25 cc. aliquot. Thus in all determinations 10 cc. of each of the activating solutions are added to 25 cc. aliquots of acid solution; in some cases it will be above and in some below, the amount required for maximum readings, but the difference will likewise obtain in the curves from known amounts of acids.

6. Amount of Malic and of Tartaric Acid Present.—Gore[1] made the most exact study of the effect of concentration on the specific rotation of the activated acids. He corroborated the previous workers in that the specific rotations of malic acid were practically the same for concentrations up to 2.0 g. per 100 cc. With tartaric, however, the case is different, a marked fall in the specific rotation occurring at lower concentrations. It was this lack of linear relations that led him to abandon the proposition for a quantitative method. In the present method lack of linear relations can be completely ignored, as the curves constructed from known amounts of the two acids in question give the rotations, under established conditions, of all combinations of the two acids up to 0.8 g. of malic acid and 0.6 g. of tartaric acid per 100 cc. Amounts of each acid from 0.1 to 0.6 g. are the most convenient to work with and give the most satisfactory results.

7. Kind of Light.—White light gives slightly higher polariscope readings than sodium light. The writer used the light from a carbon-flame lamp in the construction of the accompanying curves, because it happened to be more convenient. Any light, however, can be used, if each individual using the method standardizes his whole procedure, as is discussed in the paragraph, "Standardization of Conditions."

8. Time of Standing.—The uranium and molybdenum complexes with the organic acids in question undergo a very interesting series of changes in optical activity. Yoder[2] took the polariscope reading as soon as the uranyl acetate was dissolved; he says that standing a few hours has no effect, but several days causes a lowering. Dunbar[3] says that the time to reach a maximum reading increases with higher concentrations of tartaric acid; that for 0.5 g. per 100 cc. the maximum is attained in one hour, and that after this time there is a gradual decrease to a constant after two or three days. He recommends the addition of sodium acetate; although it lowers the reading, it causes the maximum to be reached more quickly, and the reading is then constant. The official method calls for a period of 5 hours, or preferably 10, to elapse before taking the reading. Some trials by the writer showed that the two acids and the two activators behaved rather dissimilarly in their fluctuations of optical

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[1] *J. Assoc. Off. Agric. Chemists,* 1, 120–130 (1915).

[2] *Loc. cit.*

[3] *U. S. Dept. Agr. Bur. Chem. Circ.,* 106 (1912).

activity. Some of the experiments are presented in Table I. Since apparently no period could be chosen which would give the absolute maximum for all combinations of the two acids and the two activators, 3 hours was arbitrarily chosen as the time to elapse between the addition of the activator and the taking of the polariscope reading.

TABLE I.—EFFECT OF TIME OF STANDING ON THE OPTICAL ROTATION OF MALIC AND TARTARIC ACID SOLUTIONS TREATED WITH AMMONIUM MOLYBDATE AND URANYL ACETATE.

Acids present in 100 cc. solution.		Length of time of standing.								
Malic. G.	Tartaric. G.	8 min. V°.	1 hr. V°.	2 hrs. V°.	3 hrs. V°.	5 hrs. V°.	7.5 hrs. V°.	10 hrs. V°.	15 hrs. V°.	27 hrs. V°.
With ammonium molybdate.										
1.034	1.000	32.0	..	52.00	51.87	..	51.75	51.60	..	..
1.034	1.000	..	..	..	..	..	51.80	51.80	51.70	52.25
1.034	0.900	..	..	..	50.35	..	49.50	49.64	49.70	..
1.034	0.900	..	..	..	..	..	49.55	49.83	49.85	..
1.020	0	..	32.82	31.60	31.50	31.77	..	..	..	..
0.270	0	..	8.01	7.34	..	7.50	..	..	..	..
0	0.980	..	28.63	..	26.80	26.88	..	..	..	..
0	0.200	..	5.31	5.17	..	5.18	..	5.25	..	..
With uranyl acetate.										
1.034	1.000	—6.90	..	—6.80	—6.71	..	—6.55	..	..	..
1.034	1.000	..	..	..	..	..	—6.55	—6.65	—6.60	—6.55
1.034	0.900	..	..	—7.25	—7.16	..	—7.04	—7.03	..	..
1.034	0.900	..	..	..	..	..	—7.04	—7.14	—7.14	—7.33
0.270	0	..	—4.55	—4.84	..	—4.73	..	—4.94	..	..

9. **Effect of Temperature on Polarization.**—Yoder[1] states that there is a decrease of 0.03° Ventzke for each increase of 1° C. The temperature can thus vary several degrees either side of 20° without any appreciable effect on the polarization.

10. **Effect of Sunlight.**—Sunlight appears to have a destructive effect on the acid complexes of uranium,[2] hence the solutions must be kept in the dark before polarizing.

11. **Isolation of the Acids.**—In order to avoid the presence of as many substances as possible other than malic and tartaric acids, it is necessary to effect a separation of them. Various methods of separating them as the lead or barium salt have been suggested, the most satisfactory of which is the one adopted in the official method for malic acid.[3] The juice is first neutralized with ammonia, in order to prevent crystallization of acid tartrate when alcohol is added. The pectins are then removed by two volumes of alcohol, excess of barium acetate added, and then 95% alcohol up to 14 volumes (about 89%). This gives not only

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[1] *Loc. cit.*

[2] Gore, *J. Assoc. Off. Agric. Chemists*, 1, 480–484 (1915).

[3] *Ibid.*, 1 (1916).

practically complete removal of the malic acid, but also tartaric and citric acids. Hence the latter acid, as mentioned in Section 2, must be absent from the material. A trial by the writer showed that the above procedure separated tartaric acid so completely that the filtrate from the barium tartrate, after evaporation of the alcohol and treatment with uranium and molybdenum in the usual way, gave readings of 0° in the polariscope. Therefore, this procedure is adopted in the present method.

12. **Standardization of Conditions.**—A perusal of the above eleven sections makes it evident that many factors may affect the rotatory power of solutions of malic and tartaric acids containing uranyl acetate or ammonium molybdate. It is also obvious that the directions, reagents, and conditions used by the writer in the construction of his graphs must be rigidly adhered to by all other users of the method if his rotations are to be duplicated. Some of the reagents and conditions, however, may be difficult to duplicate in some laboratories. Therefore, it is strongly recommended by the writer that each worker adopt conditions and reagents as near as possible to those listed here, and then standardize his procedure against known amounts of malic and tartaric acid. This can best be done by using, say, 0, 0.3 and 0.8 g. per 100 cc. of each acid alone and in combination with a similar series of the other. These 9 determinations, applied to the curves given herein, will indicate the correction to be made on each subsequent polariscope reading on unknown material before using that reading on the graphs. Those factors which are likely to be subject to change in different laboratories, and which can be changed without jeopardizing the method (provided they are incorporated in the above standardization) are as follows: the kind of light used with the polariscope, the length of time of standing before polarizing, the temperature at which the polarization is made, and the purity of the uranium and molybdenum salts (in other words, the amounts of the activating materials used).

Method in Detail.

The following solutions are required: (1) Standard alkali for titration; (2) ammonium hydroxide, approximately normal; (3) glacial acetic acid; (4) ammonium sulfate, 20 g. per 100 cc. of solution; (5) about 10% barium acetate in 50% alcohol; (6) ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, 10.00 g. per 100 cc. of solution; (7) uranyl acetate, $UO_2(C_2H_3O_2)_2.2H_2O$, 8.00 g. per 100 cc. Both this compound and the molybdate should be the purest obtainable, and the solutions filtered perfectly clear before using. Heat will aid the solution of the uranyl acetate.

The details of the method follow: Most of them are taken directly from the official method for malic acid, or from the processes worked out by Gore and his associates.

An amount of the sample that, judged by titration or by previous experience, will probably furnish at least 0.1 g. of either acid, and not more

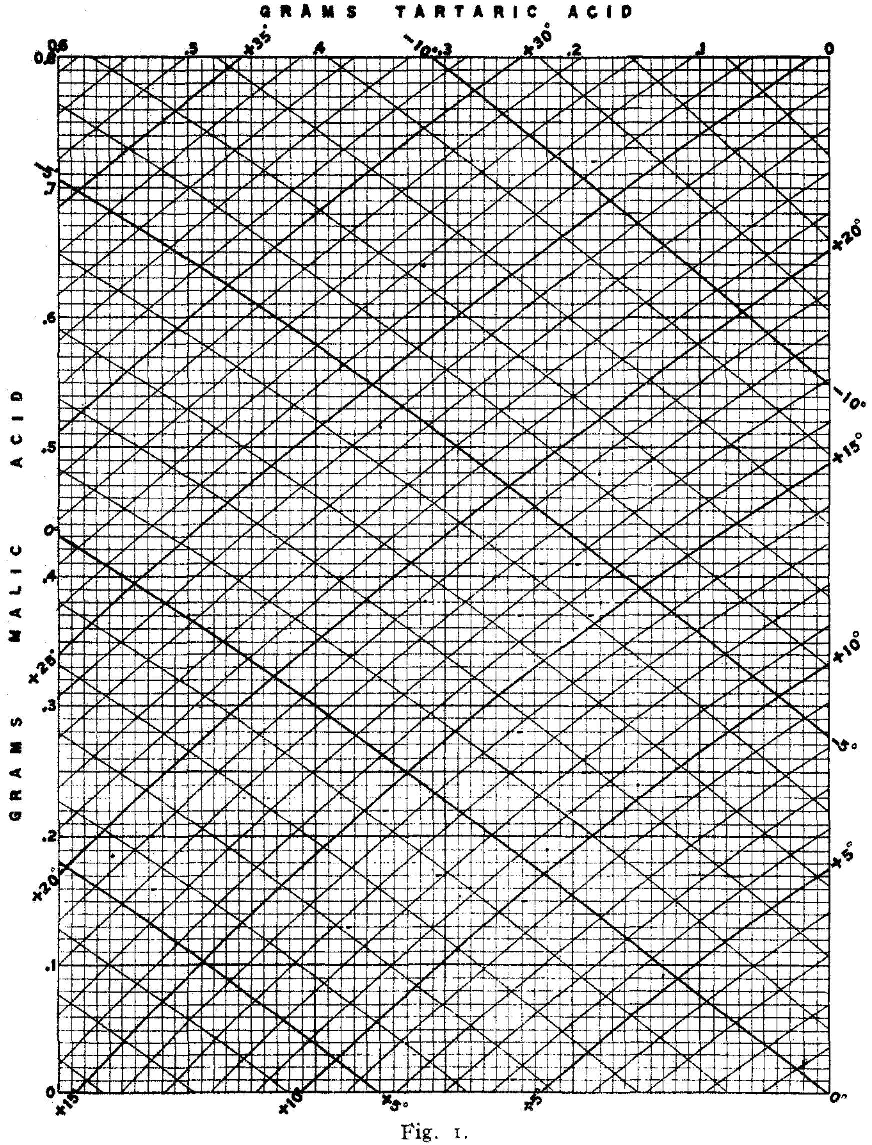

Fig. 1.

Chart for the determination of malic and tartaric acids. The curves which slant down from left to right represent the polariscope readings for combinations of malic and tartaric acids activated by uranyl acetate; the curves which slant up from left to right represent the readings with ammonium heptamolybdate. To ascertain the amount of the two acids present in a solution, obtain the optical activity of the solution as activated by uranyl acetate and ammonium molybdate, according to the prescribed method. Find the point of intersection of the curves representing these two polariscope readings; this point indicates on the abscissas the grams of tartaric acid, and on the ordinates the grams of malic acid, in 100 cc. of the solution polarized. (The original chart was constructed to include 1.0 g. of malic acid and 0.8 g. of tartaric acid. Owing to limited space on the printed page, the above abridged graph is used. The complete curve can be obtained from the author on request.)

than 0.6 g. of tartaric acid and 0.8 g. of malic acid, is neutralized with the ammonia, treated with 2 volumes of 95% alcohol, the pectins filtered off on a Büchner funnel and washed with alcohol. To the filtrate is slowly added an excess of the barium acetate solution and then enough 95% alcohol to make 14 volumes to 1 of the original solution. The precipitate of barium salts is most easily removed by centrifuging, as they filter with difficulty. If filtration must be employed, it should be done on a Büchner. The precipitate is transferred to a beaker with hot water, heated to boiling, 10.0 cc. of the ammonium sulfate solution slowly added to decompose the barium malate and tartrate; the mixture is concentrated on the steam bath to about 80 cc. volume and transferred to a 100 cc. flask. After cooling, 6 cc. of glacial acetic acid are added and the contents made up to the mark with water. It is then either filtered clear, or, more easily, centrifuged until the supernatant liquid is clear. Two 25.0 cc. aliquots of the perfectly clear solution are treated, respectively, with 10.0 cc. of the uranium acetate, and 10.0 cc. of the ammonium molybdate solution. After standing in the dark for 3 hours the solutions are polarized in a 2 dcm. tube at about 20°. Any dark green color that has been formed by reduced molybdenum can readily be dispelled by a drop of bromine water without appreciably affecting the results. The two readings are then referred to the graph, and the amounts of malic and of tartaric acids are computed according to the directions under the graph.

It was hoped in the beginning that a simple algebraic expression involving the two readings and the quantities of the two acids present could be used to calculate the results. Since the ratios are so far from linear, however, any such equations would necessarily involve also a corrective numerical factor, and this factor would change too frequently to be of use. Since the graph can be read with an accuracy of ±0.003 g. of each acid, this method of calculation brings the results within the limit of experimental error for the rest of the method.

Application of the Method.

The foregoing procedure furnishes a method applicable for all products containing *d*-tartaric acid or *l*-malic acid or both. Citric acid is probably the only interfering acid, and a scheme is in mind whereby this can be allowed for or eliminated. Highly colored solutions can be worked with only after decolorizing with bromine and neutralizing the hydrobromic acid formed with ammonia. This procedure, however, always gives low results.

Table II gives the results of a few trials of the method, and shows what accuracy can be expected. Duplicate determinations agree very well. The recovery of added malic acid is also very satisfactory. Tartaric acid, however, gives more trouble, as ammonium tartrate is much less soluble in alcohol than ammonium malate; and natural products usually

TABLE II.—ANALYSES OF VARIOUS PRODUCTS FOR MALIC AND TARTARIC ACIDS BY THE PROPOSED METHOD.

No.	Material.	Polarizations.		Acids found.		Added acids recovered.	
		Molybdenum. V°.	Uranium. V°.	Malic. G.	Tartaric. G.	Malic. G.	Tartaric. G.
697	25.0 cc. apple juice[1]	+ 8.4	— 4.8	0.272	0.010	...	...
701	25.0 cc. apple juice	+ 8.4	— 4.8	0.272	0.010	...	...
702	25.0 cc. apple juice	+ 8.4	— 4.8	0.272	0.010	...	...
705	25.0 cc. apple juice[2]	+ 7.2	— 4.6	0.250	—0.005[3]	...	...
706	25.0 cc. apple juice	+ 7.5	— 4.7	0.258	—0.004	...	...
709	25.0 cc. apple juice + 0.300 g. malic	+17.4	—10.1	0.560	0.010	0.304	...
710	25.0 cc. apple juice + 0.300 g. malic	+17.4	—10.1	0.560	0.010	0.304	...
711	Extract of 200 g. sugar beet[4]	0.0	0.0	0	0	...	...
712	Extract of 200 g. sugar beet	0.0	0.0	0	0	...	...
721	25.0 cc. apple juice[5]	5.0	— 2.8	0.166	0.012	...	...
722	25.0 cc. apple juice	+ 5.0	— 2.9	0.170	0.010	...	...
726	25.0 cc. apple juice + 0.300 g. malic	+14.4	— 8.2	0.460	0.010	0.292	...
727	25.0 cc. Armour's grape juice[6]	+ 5.0	+ 0.2	0.088	0.125	...	...
728	25.0 cc. Armour's grape juice	+ 5.4	+ 0.2	0.088	0.133	...	...
729	25.0 cc. Armour's grape juice + 0.500 g. malic	+18.9	— 7.8	0.530	0.125	0.442	...
730	25.0 cc. Armour's grape juice + 0.500 g. malic	+19.3	— 8.0	0.541	0.126	0.453	...
731	25.0 cc. apple juice[7]	+ 3.8	— 1.9	0.120	0.020	...	...
732	25.0 cc. apple juice	+ 3.8	— 2.2	0.126	0.012	...	...
733	25.0 cc. apple juice + 0.300 g. tartaric	+10.5	+ 1.4	0.136	0.280	...	0.264

734	25.0 cc. apple juice + 0.300 g. tartaric..........	+10.5	+ 1.4	0.136	0.280	...	0.264
735	25.0 cc. apple juice + 0.800 g. tartaric..........	+22.9	+ 8.1	0.123	0.755	...	0.739
736	25.0 cc. apple juice + 0.800 g. tartaric..........	+ 4.0	— 1.2	0.108	0.050	...	0.034[8]
737	25.0 cc. apple juice[9]..........................	+ 6.8	— 4.0	0.226	0.006	...	...
738	25.0 cc. apple juice...........................	+ 6.6	— 3.8	0.219	0.005	...	...
739	25.0 cc. apple juice + 0.800 g. malic............	+29.2[10]	—17.0	1.040	0.005	0.815	...
740	25.0 cc. apple juice + 0.800 g. malic............	+29.2[10]	—17.0	1.040	0.005	0.815	...
741	25.0 cc. apple juice + 0.800 g. tartaric..........	+26.3	+ 6.0	0.230	0.770	...	0.765
742	25.0 cc. apple juice + 0.800 g. tartaric..........	+ 8.2	— 2.1	0.204	0.106	...	0.100[8]
743	25.0 cc. apple juice + 0.200 g. tartaric..........	+11.4	— 1.4	0.230	0.200	...	0.195
744	25.0 cc. apple juice + 0.200 g. tartaric..........	+11.4	— 1.4	0.230	0.200	...	0.195

[1] Wealthy apples; titre of the 25.0 cc. was 37.0 cc. 0.1 *N* alkali, equivalent to 0.248 g. malic acid.

[2] Another batch of Wealthy apples; titre of 25.0 cc. was 34.3 cc. 0.1 *N* alkali, equivalent to 0.230 g. malic acid.

[3] The intersection of the two curves in the graph fell outside the chart.

[4] Titre of the sample was 15.4 cc. 0.1 *N* alkali. The acids of beets are oxalic and citric.

[5] Baldwin apples, titre of the 25.0 cc. was 21.2 cc. 0.1 *N* alkali, equivalent to 0.142 g malic acid.

[6] Titre of 25.0 cc. (using the natural indicator of the juice) was 30.5 cc. 0.1 *N* alkali, equivalent to 0.228 g. tartaric acid. Decolorized with bromine after neutralizing with ammonia.

[7] Titre of the sample was 14.2 cc. 0.1 *N* alkali, equivalent to 0.095 g. malic acid.

[8] Tartaric acid crystallized out from the acetic acid solution; it apparently lowers the malic acid value also in some way.

[9] Titre of the 25.0 cc. was 29.0 cc. 0.1 *N* alkali, equivalent to 0.194 g. malic acid.

[10] Due to an error in the amount of ammonium molybdate solution added to these, the readings are low, and the intersection of the curves on the graph falls considerably outside the chart. Assuming the uranium reading to be correct, and that there is 0.005 g. tartaric acid involved, the intersection of these two lines in the graph gives a value for malic acid of 1.040 g., which is very close to the expected amount.

contain sufficient potassium to cause the precipitation of acid tartrate when large amounts of tartaric acid are involved in an analysis. Working with purified acids, the curves were constructed for amounts of tartaric acid up to 1.0 g.; they are published through 0.8 g. only, however, since that is the limit of use in practice.

The qualitative composition of a material to be analyzed should be known since results are sometimes open to question when the point of intersection on the graph falls close to one side. As an example of this, it will be noticed that in Nos. 705 and 706, the data indicate an apparently negative amount of tartaric acid, whereas Nos. 709 and 710, from the same batch of juice, show tartaric to be present.

Although the method is not yet everything that could be desired, nevertheless it is believed that it does constitute an easy and fairly reliable means of assaying these two acids when occurring singly or together.

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THE CONFIGURATIONS OF ORGANIC COMPOUNDS AND THEIR RELATION TO CHEMICAL AND PHYSICAL PROPERTIES.

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The experimental proof[1] that in the addition of halhydric acids and halogens to acids of the acetylene series, and in the reverse elimination reactions, trans-processes are favored, showed that the then adopted configurations of all stereomeric substances, excepting those given by van't Hoff to the dibasic, unsaturated acids, had to be reversed, as they had been based on the Wislicenus hypothesis of the occurrence of cis-processes.[2] In the new classification a more marked connection between the energy-content and many of the physical properties could be traced, although certain groups of stereomers showed anomalous properties.[3] Since then, there has been very little progress made in this direction; indeed, recently, Pfeiffer[4] stated that *a priori:* "It is hardly possible to decide from the configuration which of the stereomers has the higher melting point, or represents the more stable modification."

It will be shown that it is possible to coördinate these relations and to explain the apparent exceptions, but it should be emphasized that van't

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[1] Michael, *J. prakt. Chem.*, [2] **52**, 289 (1895).

[2] *Ibid.*, 359–365. The configurations given by Pfeiffer (*Z. physik. Chem.*, **48**, 55–62 (1904)), which were based on my experimental results, were not new, as is sometimes stated in text books and papers, but were a repetition of those given in my paper (*Ibid.*, 363).

[3] Michael, *Ibid.*, 345; *Ber.*, **34**, 3644, footnote 4 (1901).

[4] *Z. physik. Chem.*, **48**, 57 (1904).