Summary

1. A method has been described for the analysis of carbon and hydrogen in organic compounds containing arsenic.
2. A method has been described for determining carbon, hydrogen and mercury in organic compounds of mercury.
3. A comparison of the results for mercury obtained gravimetrically and by the combustion method indicates the superiority of the latter with regard to both speed and accuracy.

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THE PHYSICAL PROPERTIES OF MALEIC, FUMARIC AND MALIC ACIDS

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The authors[1,2] have described the production of maleic and fumaric acids and the conversion of these acids into *i*-malic acid. Very little of any of these materials has in the past been available to investigators. In our work on these acids we have thoroughly searched the literature for physical properties, and some of the constants which are lacking have been determined under our direction. Much, however, remains to be done and now that the various materials are available in quantity to any investigator, we feel that the presentation of these results, incomplete though they are, will serve to stimulate further investigations in this field.

Melting Points

A careful series of tests indicated a value of 52.6° corrected for maleic anhydride. This is in very good accordance with results found by Anschütz,[3] Volhard[4] and Ossipoff,[5] who obtained results of 53°, 53° and 52°, respectively, but quite different from those of Dorn[6] and Tanatar[7] who obtained much higher results.

Pure *i*-malic acid melts sharply in both open and sealed capillary tubes at 128.5° to 129°. When the capillary was allowed to cool and then reheated, a value of 117° was obtained. A third repetition gave a figure of 114°. The length of time the capillary is held at the elevated temperature affects the melting-point lowering, which is due to the formation of malo-malic acid. Although the first reduction of melting point from 128.5° to 117° was greater than the second lowering, that is, from 117° to 114°,

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[1] Weiss and Downs, *J. Ind. Eng. Chem.*, **12,** 228 (1920).

[2] Weiss and Downs, THIS JOURNAL, **44,** 1118 (1922).

[3] Anschütz, *Ber.*, **12,** 2280 (1879).

[4] Volhard, *Ann.*, **268,** 255 (1892).

[5] Ossipoff, *Compt. rend.*, **109,** 311 (1889).

[6] Dorn, *Ann.*, **188,** 87 (1877).

[7] Tanatar, *ibid.*, **273,** 32 (1893).

we do not believe that the results obtained on the first heating are seriously in error, as the conversion to malo-malic acid below the melting point is comparatively slow. The most recent prior determination by Dunstan and Thole[8] checks our figures exactly, although among earlier investigators, Pictet[9] and Walden and Lutz[10] obtained markedly lower results, while Walden,[11] Pasteur,[12] Skraup[13] and Lloydl[14] gave figures from 1° to 4° higher. The small amounts available to the earlier investigators and the difficulties of purification, however, lead us to the conclusion that our own value is more nearly correct although a determination under conditions which would insure absolute prevention of formation of malomalic acid would be of interest.

Our own tests of pure maleic acid showed a melting point of 130° to 130.5° which is in close accord with the published determinations of Kempf,[15] 130–130.5°, Keiser and McMaster,[16] 131°, and Pelouze,[17] 130°.

With pure fumaric acid we obtained a result of 284° which is a fair check on the only reported determination we were able to find, that is, 286–287° in a sealed capillary made by Michael.[18]

Boiling Point

A review of the literature shows that the boiling point of maleic anhydride is given as 196,°[19,6] 200°[20] and 202°.[3,4] Anschütz in another paper[21] gives the boiling point as 82° under 14 mm. pressure. In connection with our own work, vapor-pressure determinations were made on pure maleic anhydride. These determinations were made by the dynamic method, and the amounts volatilized at various temperatures by saturated nitrogen were carefully noted. At 72°, 100°, 130° and 160° the vapor pressures found were 6.5, 23.6, 60.0 and 180.0 mm. of mercury, respectively. A curve was plotted, using temperatures as ordinates, the logarithms of the vapor pressures as abscissas, and the boiling point of Anschütz[3] and Volhard[4] of 202°; a straight line was obtained with the 72° point at 7.6 mm. instead of 6.5 mm. observed and the 100° point at 20.9 mm. instead

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[8] Dunstan and Thole, *J. Chem. Soc.*, **93,** 1815 (1908).

[9] Pictet, *Ber.*, **14,** 2648 (1881).

[10] Walden and Lutz, *ibid.*, **30,** 2795 (1897).

[11] Walden, *ibid.*, **29,** 1692 (1896).

[12] Pasteur, (a) *Ann. chim.*, [3] **34,** 30 (1852); (b) *Ann.*, **82,** 324 (1852).

[13] Skraup, *Monatsh.*, **12,** 107 (1891).

[14] Lloydl, *Ann.*, **192,** 80 (1878).

[15] Kempf, *J. prakt. Chem.*, [2] **78,** 201 (1908).

[16] Keiser and McMaster, *Am. Chem. J.*, **46,** 523 (1911).

[17] Pelouze, *Ann. Pharm.*, 11, 263 (1834).

[18] Michael, *Ber.*, **28,** 1629 (1895).

[19] Kekulé, *Ann. sup.*, II, **1862,** p. 87.

[20] Perkin, *J. Chem. Soc.*, **53,** 561 (1888).

[21] Anschütz, *Ber.*, **14,** 2789 (1881).

of 23.6 mm., but with the 130° and 160° points coincident with the line. The indications are, therefore, that our figures are approximately correct. More exact determinations were unnecessary in the work we were conducting.

We also roughly determined the stability of maleic anhydride under different pressures of water vapor by placing weighed quantities of both maleic anhydride and maleic acid in separate open weighing bottles in a desiccator over definite strengths of sulfuric acid. The temperature was held constant and any changes in weight and neutralization value noted. Two strengths of acid and three temperatures were used, making 6 sets of experiments in all. In every case the anhydride changed to the acid, showing that the pressure of water vapor in these cases was above the dissociation pressure of maleic acid.

Table I

Experimental Conditions

Conc. H_2SO_4	Vapor pressure in mm. water		
%	50°	70°	90°
61.76	14.5	39	102.9
71.49	5.1	12.9	36.4

An exact determination of the dissociation pressure of maleic acid in its transition to the anhydride would be a study of great interest.

Solubility

The literature contains numerous references on the solubility of maleic anhydride, maleic, fumaric and *l*-malic acids in water, ethyl alcohol and other organic solvents. In most cases these are isolated determinations which it seems unnecessary to collate here. We have had a number of solubility determinations made by the following method.

Values were found at 25°, 40°, 60° and 100°. For the determinations of the two lower temperatures samples were placed in 60cc. stoppered bottles with distilled water so arranged as to be water-tight. They were then rotated on a rack in a thermostat under water for 24 hours at the desired temperatures. The bottles were then transferred to a holder so set in the thermostat that only the necks of the bottles projected above the water. A 25cc. sample was taken in a pipet fitted with a rubber tube and cotton filter, and brought to temperature before use, a small preliminary portion of about 5 cc. being used first to moisten the cotton and pipet. The 25 cc. of solution was allowed to run into a weighing bottle, weighed and the amount of acid present determined by titration.

In the case of the determinations at 60° and 100°, the sampling was carried on entirely under the surface of the water in the thermostat by means of an apparatus which has been described by Pawlewski.[22] This

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[22] Pawlewski, *Ber.*, **32**, 1040 (1899).

consists of a bottle provided with an air condenser, in which the solvent and solid in excess were placed. The bottle was connected by a bent glass tube to a 50–100cc. Erlenmeyer flask. Another glass tube leading from the latter was of sufficient length so that when the apparatus was immersed, the tube extended above the surface of the liquid in the thermostat. The solution was stirred until saturation was attained, when the sample was drawn from the first bottle through a cotton filter in the bent glass tube into the Erlenmeyer flask.

In the case of lighter organic solvents, the apparatus was modified so that the saturated solution was removed by pressure instead of a vacuum, and evaporation of the solvent in the process of sampling was thus avoided. The determinations in these cases were made by evaporating the solvent and weighing the solute.

TABLE II

SOLUBILITY DETERMINATIONS

Solvent	Temperature ° C.	Solubility (parts per 100 parts solvent)	
		Maleic acid	Fumaric acid
Water	25	78.8	0.70
Water	40	112.5	1.07
Water	60	148.7	2.4
Water	97.5	392.6	..
Water	100	..	9.8
95% ethyl alcohol	29.7	69.9	5.75
Ether	25	8.19	0.72
Chloroform	25	0.011	0.02
Carbon tetrachloride	25	0.002	0.027
Benzene	25	0.024	0.003
Acetone	29.7	35.77	1.72
Xylene	29.7	0.0085	0.027
Coal tar heavy solvent	29.7	0.0085	0.0343
		Solubility of maleic anhydride G. per 100 cc. of saturated solution	
Xylene	29.7	16.32	..
Coal tar heavy solvent	29.7	9.04	..
		Solubility of *i*-malic acid G. per 100 g. of	
		Solvent	Solution
Water	26	144.8	59.15
Water	50	222.0	68.95
Water	60	268.4	72.85
Water	70	332.0	76.85
Water	79	411.5	80.65

Specific Gravity of Solutions

In our work we have had occasion to determine the specific gravity of various strengths of solutions of both maleic acid and *i*-malic acid and these results are shown graphically in Fig. 1.

Hygroscopicity

In connection with our work on keeping-qualities of *i*-malic acid in storage we have compared the hygroscopicity of *i*-malic acid with that of tartaric and citric acids, and the results are of enough interest to be included herewith.

Approximately equal samples of the materials to be investigated were powdered and dried to constant weight in a vacuum oven at 65° and an absolute pressure of less than 25 mm. of mercury, placed in desiccators over sulfuric acid of known strength, and these were maintained at constant temperature so as to provide definite pressures of water vapor, and the experiments arranged so that the exposed surfaces were comparable.

The purity of the dried samples as evidenced by titration was for *i*-malic acid, 99.6%; citric acid, 99.3%; tartaric acid, 99.5%. Malic acid was also tested over 24.2% sulfuric acid at 20° (83% humidity) and showed a loss in weight of 0.045% in 19 days.

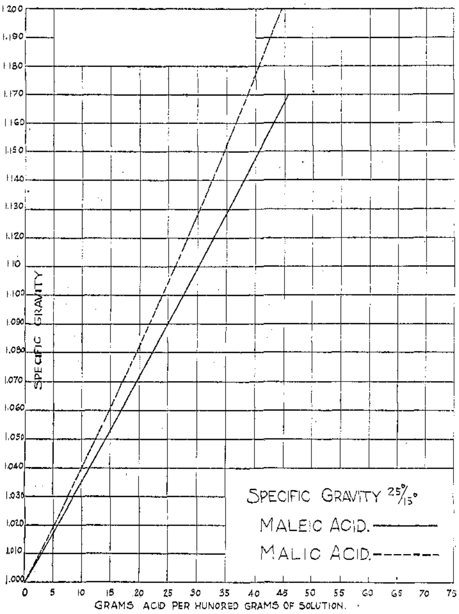

Fig. 1.

TABLE III

CUMULATIVE PERCENTAGE GAIN IN WEIGHT OVER 43.7% SULFURIC ACID (48.5% HUMIDITY AT 20°)

Acid	Days 2	3	5	19
Malic	0.07^a	0.04^a	0.08^a	0.05^a
Tartaric	0.007^a	..	0.002^a	0.000
Citric	0.06^a	..	0.20^a	0.26^a

[a] Represents loss in weight.

TABLE IV

CUMULATIVE PERCENTAGE GAIN IN WEIGHT OVER 10% SULFURIC ACID (95% HUMIDITY AT 20°)

Acid	Days 1	4	7	11
Malic	4.0	21.9	48.2	77.8
Tartaric	6.0	33.2	69.8	100.7
Citric	7.7	32.9	64.5	88.0

The indications are that pure *i*-malic acid has somewhat less tendency to absorb water under extreme atmospheric conditions than have citric and tartaric acids and that under normal atmospheric conditions there is little likelihood of trouble from absorption of water from the air by malic acid in storage.

Much of the experimental work reported in this paper was carried out by Messrs. R. M. Burns, H. P. Corson, A. E. Craver, C. W. Fisher and H. E. Williams, and we wish to express our appreciation of their interested coöperation.

Summary

As the work presented is merely a digest of data on physical properties there are no conclusions to be drawn. There are many gaps in the available data and we hope other investigators will supply much of the missing information. The stereo-isomerism of these acids makes any data on them of great theoretical interest and it is to be hoped that further and more complete studies will furnish the means by which modern ideas of intramolecular structure of compounds of this type may be clarified and amplified.

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MANNOSE FROM WHITE SPRUCE CELLULOSE

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In a recent paper[3] attention was called to the fact that mannose is present in cellulose prepared by either the Cross and Bevan method or by the sulfite process. Further investigation has shown that it is also present in the cellulose isolated from white spruce by the soda or sulfate method and that it is distributed throughout the α-, β- and γ-celluloses of the Cross and Bevan product. The quantities of mannose obtained from these different celluloses are shown in Table I. The question naturally arose as to whether the mannose is chemically combined or is present as a mannan or in the adsorbed state. Although the problem is difficult of solution, this paper contains some experimental evidence which indicates that it is probably present in the combined state, and substantiates Bertrand's[4] theory of the existence of a mannocellulose.

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[3] Sherrard and Blanco; a paper presented at the Meeting of the American Chemical Society at Birmingham, Alabama, April, 1922.

[4] Bertrand, *Compt. rend.*, **129**, 1027 (1899).