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Biochemical Studies of Some Varieties of Apples, Plums, and Grapes Grown in Minnesota

Eleanor Olds Barnes
Division of Agricultural Biochemistry

University of Minnesota
Agricultural Experiment Station

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INTRODUCTION

The quantitative composition of fruit changes with the geographical location of growth, with the season, and within fairly wide limits during the ripening process. For this reason, results of analyses of fruits grown in other parts of the country are not applicable to Minnesota fruits.

Some of the physiological and biochemical aspects of Minnesota fruits have been studied, with particular reference to the effect of physical and chemical characteristics on resistance to plant disease. Most of the new varieties of apples, plums, and grapes which have been developed at the Minnesota Agricultural Experiment Station have never been examined chemically, and the available data describing apples and grapes were collected before the importance of hydrogen-ion concentration[2] was appreciated.

Experimental work in foods makes possible increasing precision in standardization of culinary practice, establishment of criteria of quality for the production of raw materials, and evaluation of food products in terms independent of personal judgment. Such terms can be generally understood and reproduced only when expressed numerically, and to be effective they must represent the results of accurate measurement.

Exact definition of the constituents contributing to the quality of fruit can be approached only by determination of measurable chemical and physical properties. The substances which exhibit these properties, and the proportions in which they occur, may be expected to vary with accepted quality.

This bulletin is intended to supplement earlier biochemical work on fruit, to provide useful analytical data for the definition

[1] The experimental data in this bulletin were utilized by the author in a thesis for the Degree of Doctor of Philosophy presented to the Graduate School of the University of Minnesota, June 1939. The present bulletin represents an extensive revision and condensation of the thesis.

[2] In this bulletin, the older term "hydrogen-ion concentration" is used instead of the more strictly accurate "hydrogen-ion activity."

of desirable characteristics to be attained in the development of new varieties, and to measure chemical components which are contributing factors in culinary value.

REVIEW OF LITERATURE

Caldwell (10) has made the most extensive analysis of American apples, testing each year for several years juices of more than 200 varieties. Brierley (8) examined ciders of 28 varieties of Minnesota apples for mineral and organic content. In neither of these investigations was hydrogen-ion concentration determined.

Fellers (11) reported acidity values for juices of eight varieties of apples, ranging from *p*H 3.18 to 3.60, and total acidity expressed as malic acid, ranging from 1.11 to 0.38 per cent. He found the relation existing between titratable acidity and H-ion concentration reasonably constant. Some varieties appeared to contain more buffers than others.

Newton and Edwards (22) published titration curves of fruit and vegetable juices and advocated the potentiometric method and appraisal of titration curves as an excellent means of analysis in studies of fermentation and plant diseases.

Grove and Sommers (14) measured titratable acidity and H-ion concentration in 33 varieties of apples and found that "they were not placed in the same order of acidity by the two methods." As there was closer agreement in filtered juices, they concluded there were some filterable constituents which depressed H-ion concentration but not titratable acidity.

In a study of English apples, Haynes and Brown (17) attempted to estimate the salt content of apple juices from their *p*H and titratable acidity measurements. A comparison of salt content, as obtained from ash analysis, showed good agreement in juices of high acidity but poor results with those of low acidity.

Kaulbersz-Marynowska (18) conducted electrometric titrations on the juices of lemons, oranges, apples, and bananas and graphically compared the buffer coefficient curves of each fruit with that of its predominating acid. He also discussed the effect of H-ion concentration on viscosity of the juice of each fruit.

The work of Tarr (28) has shown that jellying power is correlated with *p*H and not with titratable acidity. Myers and Baker (20) related *p*H values to the hydrolysis of pectic ma-

terials, which would seem to signify that *p*H may be of considerable importance in the cooking behavior of apples.

Tests made by Richards (24) indicate that *p*H is important in sourness although, according to Harvey (16), titratable acidity contributes as much to taste as does H-ion concentration.

There is considerable diversity of opinion among different workers as to the identity of acids which are present in fruits. Bigelow and Dunbar (6) suggest that this may be due to some extent to varietal and climatic conditions, but that the most probable reason for disagreement is the inaccuracy of available methods for the determination of individual acids. They present a survey in tabular form of the acids reported to occur in fruits and include the results of analyses, by improved methods, of Fitzgerald, Johnson, and Pratt, of the Bureau of Chemistry, United States Department of Agriculture. These workers, using the uranyl acetate method, conclude that malic is the only acid occurring to any extent in plums and apples. By comparing the per cent of malic acid found by this method to the total acid found by titration and calculated as malic, they believe that most of the acids occurring in plums and apples are in the uncombined state. Willaman and Sandstrom (30) found small amounts of oxalic acid in Minnesota plums.

Nelson (21), in a study of the acids of various fruits by the ester distillation method, found in representative samples of Concord grapes 60 per cent *l*-malic acid and 40 per cent *d*-tartaric acid. The occurrence of malic acid in the grape is also pointed out by Alwood (1) who discusses the changes of acid and sugar content during the ripening process. He suggests that the reasons for decrease in titratable acidity in ripening are the formation of potassium acid tartrate caused by an influx of potassium into the fruit, the loss of malic acid through respiratory processes, and possibly the dilution of acid by an increase in the sugar and water content.

Alwood points out that as the amount of acid declines, the sugar content increases, and that the suitability of the grape for dessert purposes, for wine, or for unfermented beverages is determined largely by these two constituents. Caldwell (10) states that the palatability of a fruit or fruit juice depends on the relative proportions of acids, astringent materials, and sugars simultaneously presented to the taste nerves.

In a survey of 66 varieties of American grapes, extending over a five-year period, Caldwell (9) gives analytical data describing

grapes grown in a single vineyard in New Jersey under carefully controlled conditions. His figures show that there is a considerable yearly difference in chemical composition in a given variety. By comparison with the data of Alwood (2, 3), Caldwell proves that this range of difference is much smaller than that for the same varieties grown in more widely scattered areas.

For the grapes grown in the New Jersey vineyard, Caldwell (9) was able to prove a direct relationship between the amount of sunshine from March to September and the percentage of sugar. He found that conditions which stimulated photosynthetic activity correspondingly increased the amount of sugar and decreased the quantity of acid and astringent materials.

The importance of the relative proportions of acid and sugar in determining the desirability of grapes is also discussed by Shoemaker (26), who presents data concerning sugar, acid, and juice color of 120 varieties grown at Wooster, Ohio.

Although European grapes are generally considered as containing no sucrose, analyses of grapes of American origin show sucrose to be present in appreciable but variable quantities in some varieties and entirely absent in others. Gore (12), in examination of 66 varieties, found sucrose absent in 43, occasionally present in 10, and always present in 13 varieties. Hartmann and Tolman (15) found no sucrose in pure Concord juice in analyses of several hundred samples over a three-year period. Caldwell (9) believes that in some degree the presence of sucrose indicates immaturity of grapes although it is often found in the fully ripe fruit.

In a series of studies entitled "Biochemistry of Plant Diseases" by Willaman and others (30, 31, 32), some analyses of varieties of Minnesota plums are presented. The only available data describing sugar and acid in Minnesota grapes were published by Green (13) in 1892. He reported analyses by H. Snyder, which showed, in 18 varieties, a range of acidity, expressed as per cent tartaric, of 1 per cent to 2 per cent; of total sugars, as dextrose, of 8.8 per cent to 16.6 per cent.

MATERIALS AND METHODS

The Material

APPLES—Apples for this study were furnished by the Division of Horticulture, University of Minnesota Agricultural Experiment Station. They were produced in the summer of 1935 at the

Station Fruit Breeding Farm near Excelsior, Minnesota and were held until needed in the storage cellar at the University Farm at approximately 5° C.

The apples were picked, as nearly as possible, at the same stage of maturity, that is market ripe. No attempt was made to test them at a definite period of ripening or to report the conditions under which they were grown because great diversity in type of apple, stage of maturity, and growing conditions was desired for study of the relations of hydrogen-ion concentration, total acidity, and the buffer system.

PLUMS AND GRAPES—The plums and grapes for this study were also furnished by the Division of Horticulture, University of Minnesota Agricultural Experiment Station. These, except the "Waneta" and "Kaga" plums which were developed at the South Dakota Agricultural Experiment Station, had been developed as a part of the fruit breeding program designed to produce special varieties particularly adapted to Minnesota's climatic conditions. Many of the superior varieties have been given names by which they are known commercially.

The plums were of two general types:

1. Minnesota hybrid plums: These hybrids are chiefly of the native wild plum, *(Prunus Americana)*, and the Japanese plum, *(Prunus salicina)*. They include—La Crescent, Waneta, Underwood, Monitor, Redwing, Superior, Tonka, and Kaga.

2. Sand cherry hybrids: These hybrids were developed from Minnesota hybrid plums or cherries and the sand cherry, *(Prunus Besseyi)*. These include—St. Anthony, Nicollet, and Zumbra.

The grapes were hybrids of Beta grapes (selected wild variety) and eastern dessert types such as Concord and Delaware.

Twenty-five different samples of plums, representing 11 varieties, were picked in 1936 on August 10, 13, 18, and 25. Plums of each variety were obtained in the green state and at one or two later stages of ripening.

The grapes were all picked at approximately the same state of maturity. Samples of four varieties were picked August 28, 1936. On August 30, 1938, grapes of seven additional varieties were obtained together with samples of the same varieties taken in 1936.

Shortly after picking, the fruit was taken to the Biochemistry building at the University Farm. The plums and grapes were removed from the stems, packed in sealed glass jars, and stored

at approximately —15° C. It is believed that storage at this low temperature inhibited any appreciable biochemical changes from taking place while the fruits were in storage prior to analysis.

Preparation of Material for Analysis

APPLES *(Raw Juice)*—Whole apples were washed and dried, cut in pieces, placed in a filter cloth, and the juice expressed in a heavy steel hand press. Because considerable pulp passed through the filter cloth, it was necessary to strain the juice through a muslin bag in a potato ricer. In order to obtain as uniform a sample as possible, and to avoid, in titration, volume errors due to solid material, the juice was centrifuged for 10 minutes.

Juice from Cooked Apples: Apples were washed and dried, stem and flower ends removed, sliced into pieces approximately one-fourth inch thick, one-half their weight of distilled water added, and cooked in a covered container for 20 minutes at a moderate temperature. The juice was then strained through a muslin bag and placed in a corked flask to cool to room temperature.

Apples for Subsequent Sugar Determination: Representative apples of each variety were cut into slices approximately 8 mm. thick without removing either skin or core. Aliquots of these slices were then preserved by heating to boiling with 95 per cent ethanol to which a small amount of ammonium hydroxide had been added to neutralize any acidity and thus to prevent hydrolysis. The samples so prepared were stored in sealed glass containers until used for analysis.

PLUMS AND GRAPES—As previously indicated, the plums and grapes were stored in the proper condition at approximately —15° C. In preparing the juices for analysis, the frozen fruit was placed in stoppered glass containers and allowed to stand overnight at room temperature. The juice was then pressed out in a cone-shaped colander with a fitting wooden pestle, strained through cheesecloth, and centrifuged for 10 minutes.

As a precaution against oxidation of astringent materials or hydrolysis of sucrose, fruit used for determination of sugar and tannin was never allowed to thaw overnight. The samples were brought from the refrigerating room as needed, and the juice expressed as soon as the fruit was sufficiently soft.

Apparatus and Analytical Methods

Specific gravity, hydrogen-ion concentration, titratable acidity, reducing sugars, and total sugars were determined on all samples. In addition the weight of the dried alcoholic precipitate was determined on the raw juices from 33 varieties of apples and on the cooked juices from 13 apple varieties. The total astringency and the astringent non-tannins were also determined on the juices of 25 plum and 15 grape samples.

Specific gravity was determined by weighing a calibrated glass plummet in air and in the juice and making the appropriate calculations.

The hydrogen-ion concentration and titratable acidity were determined electrometrically by means of the quinhydrone electrodes and an L&N potentiometer, the systems under investigation being first checked to ensure the absence of other oxidation-reduction systems which would affect the recorded potentials [cf (7) and (27)]. In the case of the plum juices a composite sample was titrated against the glass electrode as an additional precaution against stray oxidation-reduction systems.

Titratable acidity was taken to be equivalent to the requirement of sodium hydroxide necessary to bring the system to $p\mathrm{H} = 7.0$. Buffer curves were constructed by adding increments of standard alkali or acid to an aliquot of the juice and by recording the equilibrium hydrogen-ion concentration after each addition. In order that all curves drawn might be readily compared, the buffer curves are plotted with the ordinate axis in units of 0.04 gram equivalent of acid (or alkali) per liter of juice.

Fruit-ash + fruit-acid buffer curves were studied in order to ascertain how nearly such curves might simulate the normal buffer curves. The apple series was prepared as follows:

A composite sample of approximately 400 ml. of the juice of five different varieties of apples was prepared. The specific gravity was determined, the alcohol precipitate dried and weighed, and samples were titrated with base and acid. The remainder of the sample (312.35 grams) was precipitated with alcohol, the alcohol evaporated, the material concentrated on a steam bath and dried in an oven. It was then charred and ashed, using the alcohol-glycerol mixture of the method suggested by Hertwig and Bailey and applied to plant tissues by Rogers (25).

The ash was transferred quantitatively to an Erlenmeyer flask and made up to the original volume of juice from which it was obtained, with a malic acid solution of the same normality

as that of the juice. The H-ion concentration of the resulting solution was lower than that of the juice because of the combination of the acid with the bases of the ash. Weighed portions of crystalline malic acid were added successively until the original *p*H of the juice was reached. This solution was titrated in the usual way, as were portions of the solution of ash made up to higher and lower normalities of malic acid than that which simulated the original juice.

Similar ash-acid buffer curves were made in the plum and grape series. In these instances the whole juice, representing a composite sample of the juices of each variety, was ashed and then the ash taken up with a malic acid solution of the same normality and volume as the original juice from which the ash had been obtained. Proper adjustment with solid malic acid brought the ash-acid system to the required *p*H following which titrations were made. In the case of the grape composite a duplicate series was made when tartaric acid replaced the malic acid.

The alcohol precipitate was determined on the apple juices by pipetting 25-ml. portions of juice into two beakers, each containing 75 ml. 95 per cent alcohol. The beakers were covered with watch glasses and allowed to stand in a refrigerator for 24 hours. The alcohol was decanted through previously weighed filter papers, and the papers containing the precipitate were unfolded and placed on watch glasses in a drying oven (60° C.) for 36 hours. They were then dried in a vacuum oven at 60° C. and 25 mm. mercury pressure for 12 hours, removed to a desiccator, cooled, and weighed quickly to the nearest milligram. As it was impossible to dry the precipitate to a constant weight, this arbitrary method was used.

For the sugar determinations the prepared apple samples were crushed in the alcoholic solution and the alcoholic liquor filtered off. The residue was thoroughly extracted with fresh alcohol, the alcoholic filtrates were combined, the alcohol removed by evaporation, and the residue made up to volume for clarification and reduction.

The clarification, reduction, and inversion procedures were run on the plum and grape juices as expressed from the freshly thawed fruits.

Clarification of the juices was made with saturated, neutral lead acetate solution, the excess lead was removed with potassium oxalate, and reducing sugars determined by the Quisumbing and Thomas (23) method under exactly controlled con-

ditions of time and temperature and volume. The cuprous oxide was filtered on asbestos in Gooch crucibles, washed, dried, and weighed as cupric oxide after oxidation in an electric muffle.

Total sugars were determined as above after inversion with 1 per cent HCl at 80° C. for 30 minutes.

The tentative method of the Association of Agricultural Chemists (5) for the determination of tannin in tea was used for estimation of tannin in plum and grape juice. Although admittedly unsatisfactory so far as absolute results are concerned, this titration method is rapidly carried out, and the data are useful for comparative purposes.

For the determination of "astringent non-tannins" (Caldwell's term), a 100.00-ml. aliquot of the diluted juice was shaken for 10 minutes with a mixture containing 50.00 ml. of a 2½ per cent gelatin solution made up in saturated NaCl, 100.00 ml. of a solution of saturated NaCl acidified with H_2SO_4, and 10 grams of kaolin. The precipitate was allowed to settle and the supernatant liquid decanted through quantitative filter paper. 25 ml. of the filtrate were titrated with the $KMnO_4$. The difference between this titration and that of the blank is the measure of astringent non-tannins. The true tannins, which are removed by the gelatin, are calculated by difference.

THE EXPERIMENTAL DATA AND RESULTS

The experimental data resulting from these studies are given in tables I through X in the appendix and in figures 1 through 8.

Titratable Acidity and Hydrogen-Ion Concentration

As shown in table I, the acidity of the 33 varieties of Minnesota apples ranged from *p*H 3.03 to 5.40 (H-ion concentration from 9.33×10^{-4} to 3.98×10^{-6}); titratable acidity varied from 1.45 to 0.026 per cent, expressed as malic acid.

When the data were treated statistically, a significant correlation (r=0.9265) between titratable acidity and hydrogen-ion concentration was found to exist. Calculation of the correlation coefficient was made by the Harris formula:

$$r_{xy} = \frac{[\Sigma xy/N] - \overline{x}\,\overline{y}}{\sigma_x \sigma_y}$$

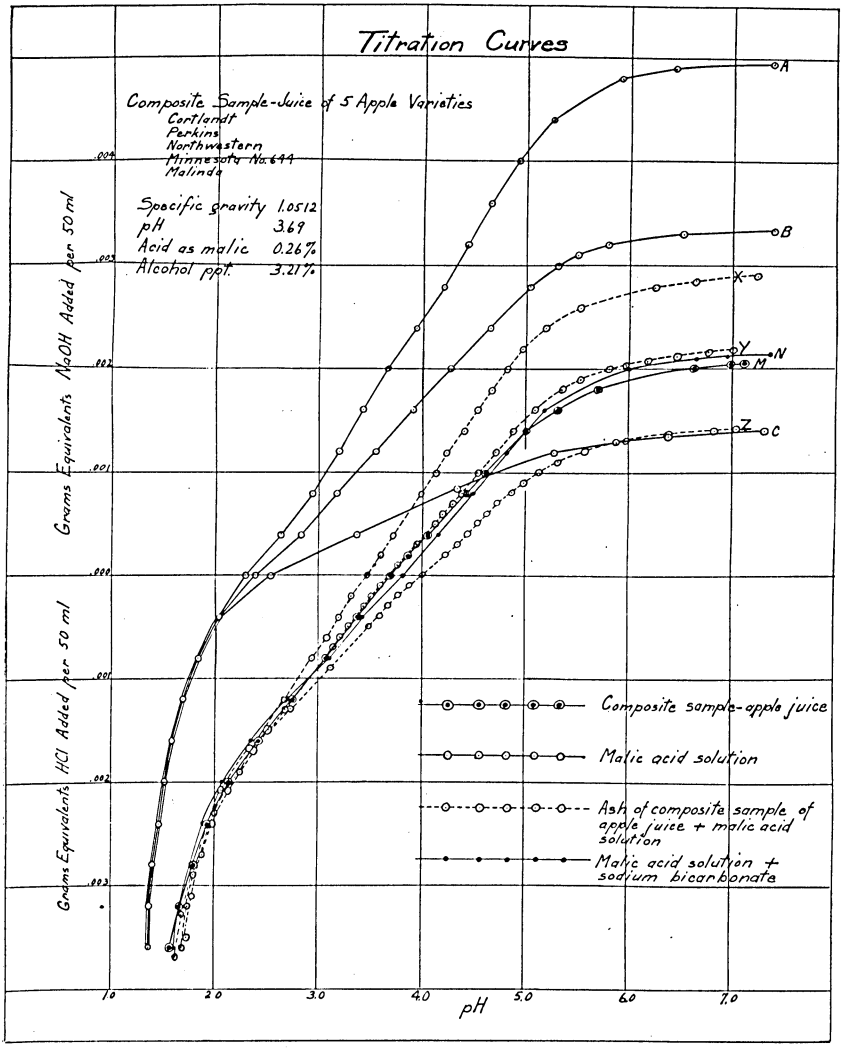

FIG. 1. BUFFER CURVE OF A COMPOSITE SAMPLE OF APPLE JUICE IN COMPARISON WITH MALIC ACID, MALIC ACID-SODIUM MALATE, AND MALIC ACID-APPLE JUICE ASH

This high correlation is in interesting contrast to the following statement of Askew (4) in a publication entitled, "pH Values and Titratable Acidity of Apple-Juices," "The pH value of apple-juice does not seem to bear any definite relation to the total acidity as determined by titration."

This seems a conclusion of doubtful accuracy, inasmuch as only three varieties of apples were examined.

Although it has been shown that jellying power has a higher correlation with pH than with titratable acidity, the usual com-

mercial practice is to "adjust" acidity by the titration method. The correlation between hydrogen-ion concentration and titratable acidity may explain the successful use of this practice.

Comparison of results with the juices of raw and cooked apples of the same variety (table II) shows close agreement in *p*H and titratable acidity, and almost perfect similarity in the shape of titration curves (figure 3). With a few exceptions, total acidity and H-ion concentration were slightly lower in the juice of cooked apples. Some difference in titratable acidity might be expected because of dilution of the juice with water added for the cooking of apples. Also the amount of evaporation probably varied both during the cooking process and during the straining of the juice. The small decrease in H-ion concentration after cooking might be explained by loss of CO_2.

Some effects of increasing the length of the storage period on the acidity of apples are shown in table III. As no measurements were made before November 1, 1935, all apples tested were in storage for some length of time. On apples of seven varieties, analyses were made on two different dates, from six to nine weeks apart. The data indicate that a general decrease in H-ion concentration and titratable acidity has taken place. In one variety, King David, the *p*H was the same at the second testing, and in another, Windsor Chief, the titratable acidity was slightly higher. Some variation in results of these measurements was to be expected, however, because it could not be certain that the apples for the second tests were from the same tree or were picked at the same time.

As shown in table VI, the acidity of juice from 25 samples, representing 11 varieties of Minnesota plums at different stages of ripening, ranged from *p*H 2.88 to *p*H 3.38 (H-ion concentration from 1.32×10^{-3} to 4.17×10^{-4}). The titratable acidity, expressed as malic acid, and calculated from the volume of 0.20058 *N* NaOH required to bring a measured volume of juice to *p*H 7, ranged from 1.09 per cent to 2.22 per cent.

When the data were treated statistically, a correlation ($r = 0.6198$) was found to exist between hydrogen-ion concentration and titratable acidity.

Table VII shows the range of acidity of the juices of grape varieties. The correlation between hydrogen-ion concentration and titratable acidity (as malic) was found to be 0.9213. It is interesting to note that these correlations are much higher for apples and grapes than for plums.

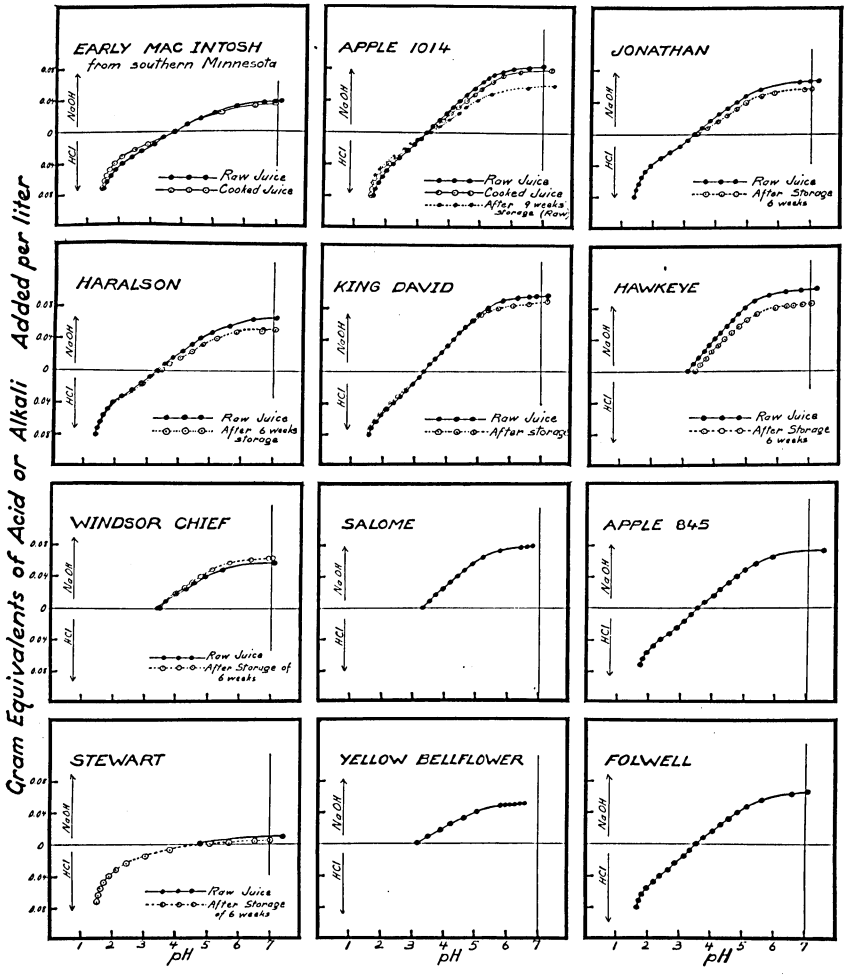

FIG. 2. BUFFER CURVES OF THE JUICES OF CERTAIN VARIETIES OF MINNESOTA APPLES

All samples of grapes were picked in 1938, with the exception of four samples which are designated on the table as having been taken in 1936. The acidity of juice of the 1936 crop is noticeably lower than that of juice of the same varieties picked in 1938. The summer of 1936 had higher temperatures and more sunshine than did 1938, which had a cool summer with considerable rain. This is in agreement with the results of Caldwell (9) who found an inverse relationship between acidity and amount of sunshine.

For the preparation of jelly, fruit is usually chosen which is just ripe or slightly under-ripe, at which stage the largest amount

of pectin is present in acid fruits. The optimum *p*H for the formation of jelly is reported by Tarr (28) to be 3.46. Inspection of the *p*H values for both grapes and plums explains one common reason for jelly failures.

Titration Curves

Titration curves for 33 varieties of Minnesota apples are shown in figures 2 to 4, in which *p*H values are abscissae. Gram equivalents NaOH per liter in steps of 0.04 are ordinates above the "x" axis and gram equivalents of HCl in steps of 0.04 below. Each plotted point on the graph represents a potentiometric measurement of *p*H.

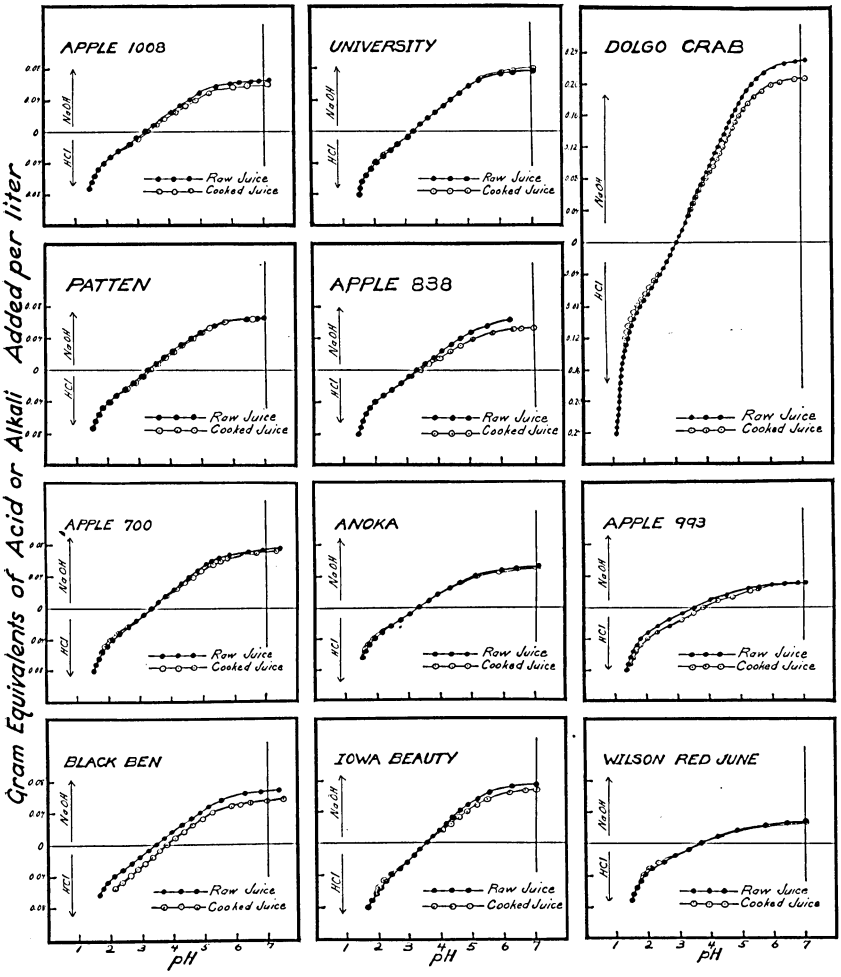

FIG. 3. BUFFER CURVES OF THE JUICES OF CERTAIN VARIETIES OF MINNESOTA APPLES

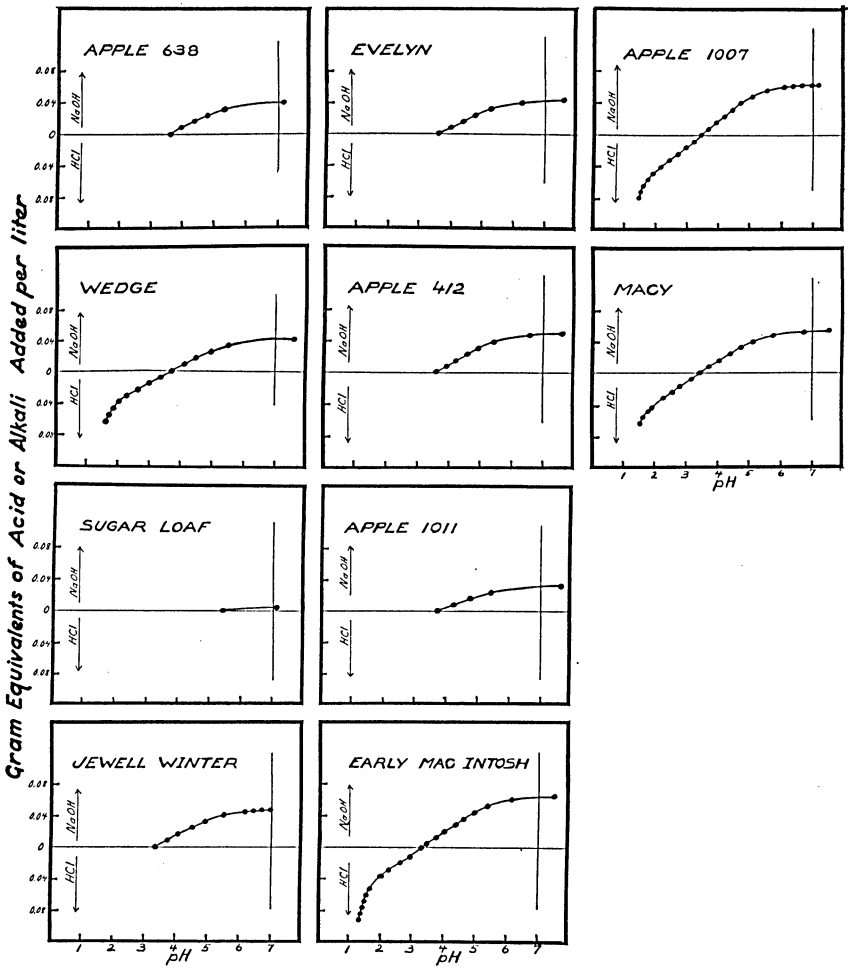

FIG. 4. BUFFER CURVES OF THE JUICES OF CERTAIN VARIETIES OF MINNESOTA APPLES

Titration curves for all samples of grapes and plums are shown in figures 5 and 6. The portions of curves lying in the alkaline range should be considered only as approximations since measurements by the quinhydrone method are known to be inaccurate above *p*H 7. There is some discrepancy between values obtained in this region by quinhydrone and glass electrode methods, but the quinhydrone electrode measurements are not so greatly in error as to be valueless.

The Buffer System of Apple Juice

In figure 1 have been plotted titration curves A, B, and C, for malic acid solutions of different normalities. Comparison of these

curves with those of apple juice shows, as would be expected, that malic acid solutions are less highly buffered than is apple juice.

Curve N is a titration curve of a solution of malic acid and its sodium salts obtained by adding $NaHCO_3$ to a malic acid solution. In apples, the potassium rather than the sodium salt predominates (19), but the buffer effect would be similar.

Curve M represents values obtained by titration of a sample composited from the juice of five different varieties of apples. The *p*H of the juice was 3.69 and the titratable acidity, expressed as per cent malic acid, was 0.32 per cent.

The addition of the ash of a measured volume of the composite sample, to a malic acid solution of like volume and of the same titratable acidity as the juice from which the ash was obtained, shifted the *p*H from 2.50 (*p*H of the malic acid solution) to 4.60. To bring 50.00 ml. of this solution to the *p*H of the original juice (3.69), 100 mg. of crystalline malic acid were required. The resulting mixture was a simulation of the composite sample of apple juice, with respect to H-ion concentration, titratable acidity, and ash content. Curve Y is the titration curve of this solution.

Curves X and Z are titration curves of the ash-malic acid solution to which 50 mg. and 150 mg. malic acid have been added, in contrast to the 100 mg. added for the solution represented by curve Y.

Comparison of curves M and Y show that H-ion concentration, titratable acidity, and buffer value are practically identical in the apple juice sample and in the solution of malic acid containing the ash of the apple juice. It may, therefore, be concluded that the buffer action of apple juice is due chiefly to malic acid with its salts.

Citric acid is the only other organic acid reported to occur in apples in any appreciable amount. Haynes and Brown (17) have shown that titration curves of citric acid and its salts closely resemble those of the malic acid-salt system.

Curve N representing the titration of a malic acid-sodium salt solution is similar to the titration curve of the apple juice although it does not agree as closely as does the curve of the malic acid-ash solution.

According to Small [27 (p. 335)], the organic acids and their salts in cell sap are important:

1. "as very effective buffer substances capable of keeping the reaction of the sap within the limits of the range which the adjacent cytoplasm can endure without injury,

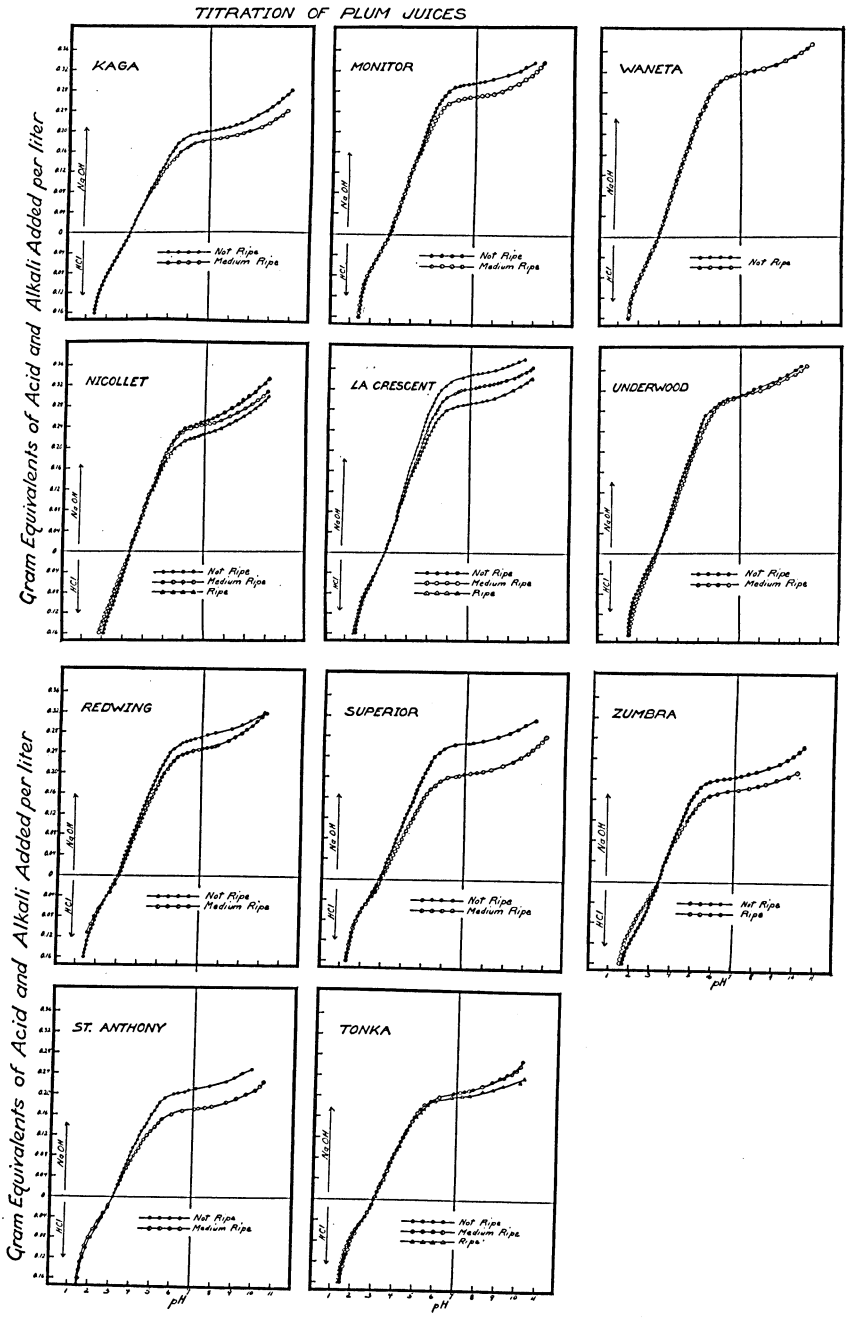

FIG. 5. BUFFER CURVES OF CERTAIN VARIETIES OF MINNESOTA PLUM JUICES

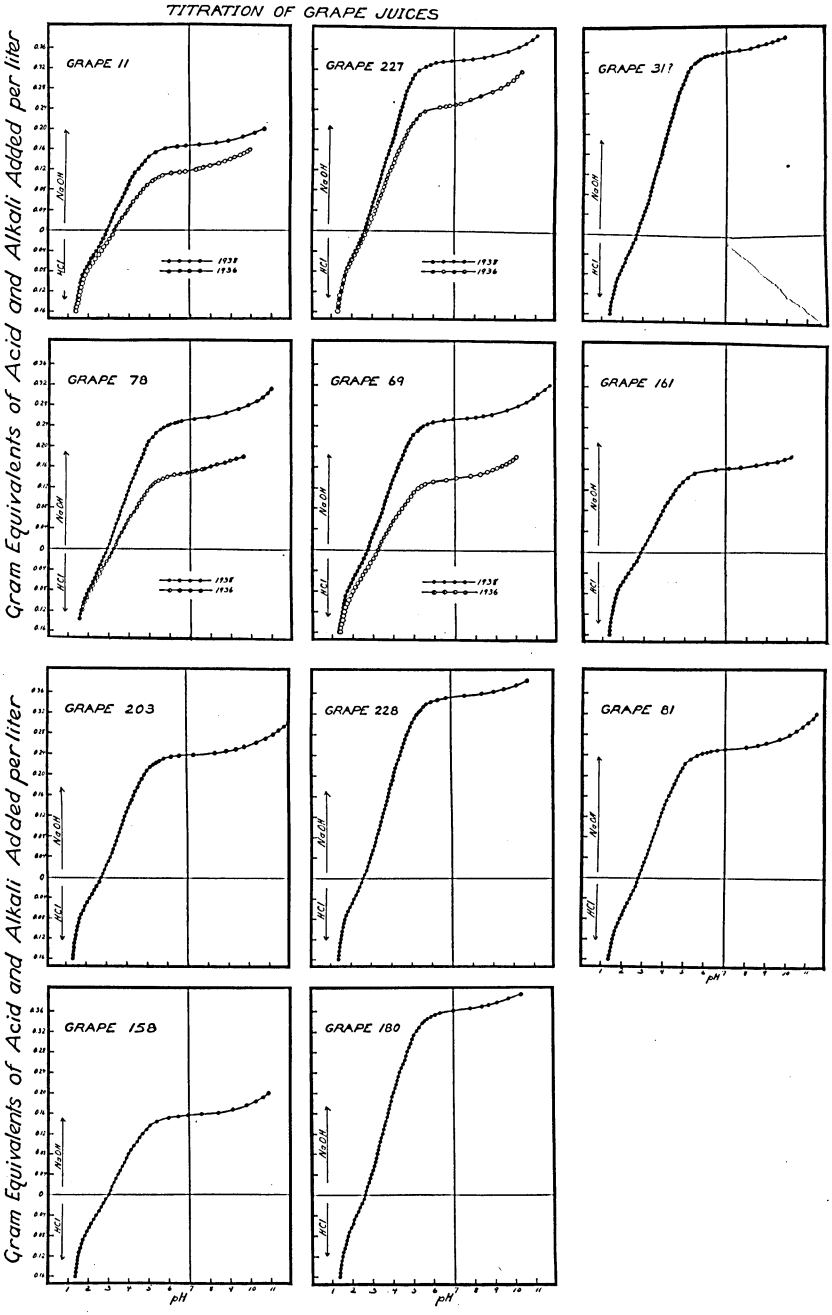

FIG. 6. BUFFER CURVES OF CERTAIN VARIETIES OF MINNESOTA GRAPE JUICES

2. "as acids producing the various degrees of H-ions which determine the relative activity of enzymes in an enzymatic mixture."

Consideration of the titration curves and buffer indexes (29) of all the varieties of apples tested shows the curves to be markedly similar in form. Some juices are more highly buffered than others, chiefly because of their higher total acidity. All show their maximum buffer capacity in the range of *p*H 2.5 to 5.0, with a sharp decrease between *p*H 5 and 6, becoming almost zero at *p*H 7. Below *p*H 2.5 there is a rapid rise in the buffer index as the "so-called buffer value of a water plus strong acid system takes effect" [27 (p. 362)].

It might be expected that the points of maximum buffering would be at *p*H 3.48 and 5.11, the *p*K values of malic acid, and that the curve should show a depression between these points. However, the hydrogens of the two carboxyl groups of malic acid ionize so close together that no depression can be distinguished and the curve maintains a level between the maximum points.

The Buffer Systems of Plums and Grapes

Figure 7, in which are presented titration curves of composite samples of plum and grape juice, of malic and tartaric acids, and of solutions of fruit ash dissolved in acid, offers interesting possibilities for speculation.

In the first graph, curves 1 and 2 cannot be compared directly because of the difference due to the buffer salts in the juice; however, they have some similarity in form. Curve 3 is what might be expected when some of the malic acid has formed salts with the bases of the ash.

Curve 4 shows rather unexpected results. Between *p*H 3 and 5, it closely approximates curve 1. Below *p*H 3 and above *p*H 5, it resembles the malic acid curve more than that of plum juice. Evidently there are substances in the juice which titrate as acid but do not furnish as many hydrogen-ions in certain regions as does malic acid, or there are ionizable salts, other than malic acid salts, which repress acid ionization. There is also the possibility that malic is not the only important acid in plums although the literature seems to disprove it. Perhaps the fact that the salt-malic acid system only partially accounts for the plum titration curve may be related to the lower correlation between hydrogen-ion concentration and titratable acidity obtained for plums than for apples and grapes

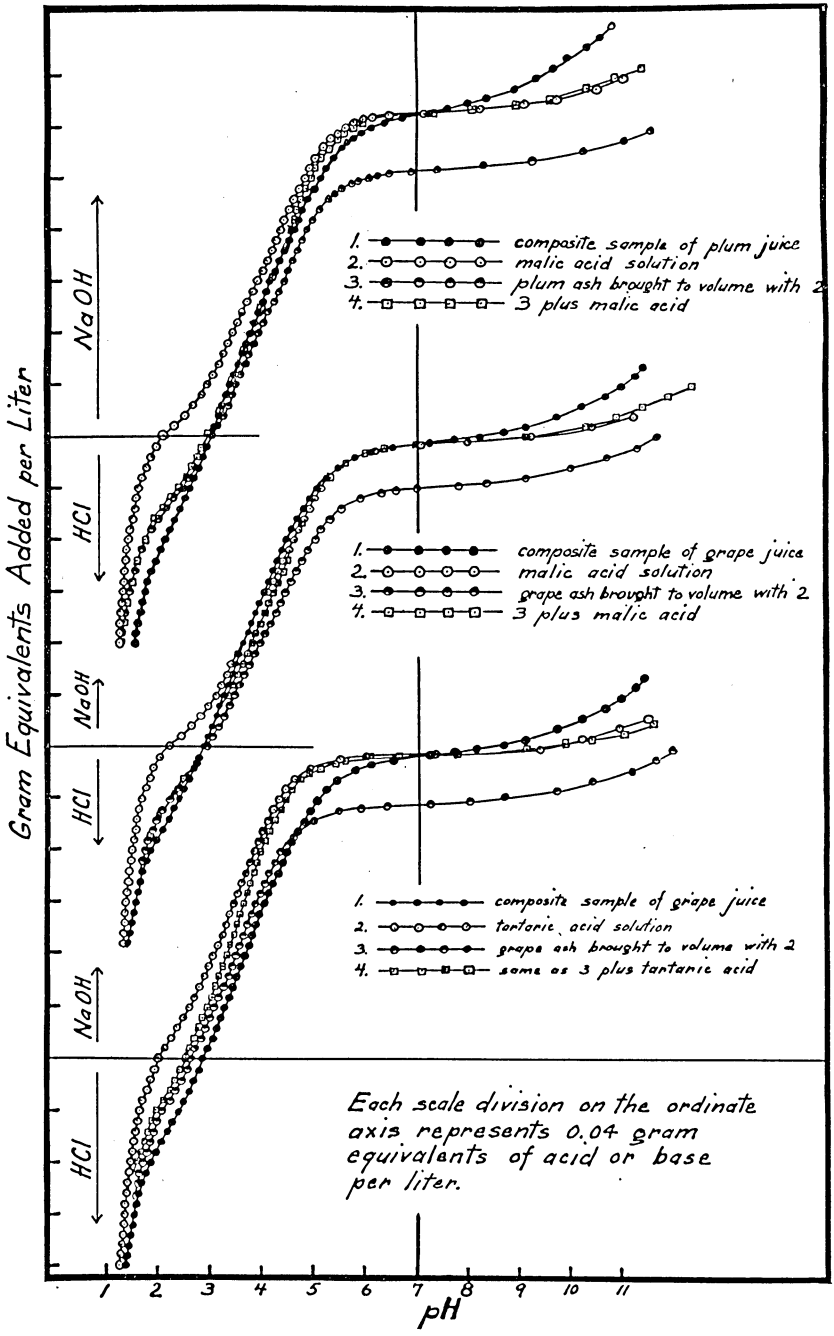

FIG. 7. BUFFER CURVES OF COMPOSITE SAMPLES OF PLUM JUICES AND GRAPE JUICES IN COMPARISON WITH MALIC AND TARTARIC ACID SOLUTION AND ARTIFICIAL JUICE-ASH ORGANIC-ACID BUFFER CURVES

Consideration of the two lower graphs of figure 7 leads to the conclusion that neither the malic acid-salt system nor the tartaric acid-salt system completely agrees with that of grape juice. Of the two, the malic acid-grape ash solution is more similar.

Figure 8, in which a mixture of malic and tartaric acids have been employed to bring a low acid composite sample of grape juice to the same titratable acidity as a high acid sample, presents rather convincing evidence that the two acids do occur together in the Minnesota grapes, and that they probably occur in approximately the ratios in which the acids were added.

These results cannot be interpreted to mean that a malic and tartaric acid-salt system will exactly simulate that of grape juice because this experiment was performed with the grape juice itself and not its ash; however, examination of the two lower sets of curves in figure 7 indicates that a close approximation to grape juice should be shown by such a system.

SUGARS—The results of sugar analyses in the whole apple are reported in table V and in the plum and grape juices in tables VIII and IX. The apple data show only total reducing sugars after inversion. The range here is from 9.76 per cent to 4.68 per cent. If this series can be taken as a representative year, it is apparent that the varieties tested form a very uniformly-graded series of sugar values.

Brierley (8) in 1919 reported a series of analyses of the ciders of Minnesota apples with particular reference to the utilization of the ciders for the production of cider vinegar. His values for total sugars ranged from 5.39 to 10.43 per cent. Table V shows that whereas none of the present series of analyses exceeded the maximum total sugars of Brierley's series, there are three samples which were below his minimum.

Brierley points out that a total sugar content of 8 per cent or more is usually regarded as necessary to produce vinegar of legal strength and that in general Minnesota apples do not have a high enough sugar content to justify their indiscriminate use for vinegar manufacture. The present series of analyses confirms this conclusion since 28 of the 33 varieties show a sugar content below 8.0 per cent, and 21 of those varieties have total sugars of less than 7.0 per cent.

In plum juice, the range of total sugar after inversion, expressed as invert sugar, was from 5.13 per cent in the unripe Kaga to 10.43 per cent in the ripe La Crescent. In grape juice,

the percentage of sugar varied from 9.75 per cent in No. 228 to 17.29 per cent in No. 81.

The increase in reducing power after inversion, calculated as sucrose, ranged from 0 to 0.27 per cent. These small values might well be attributed to experimental error were they not all in the same direction—an increase in reducing capacity following inversion. The fact that the differences were greater than the error between duplicate determinations leads to the conclusion

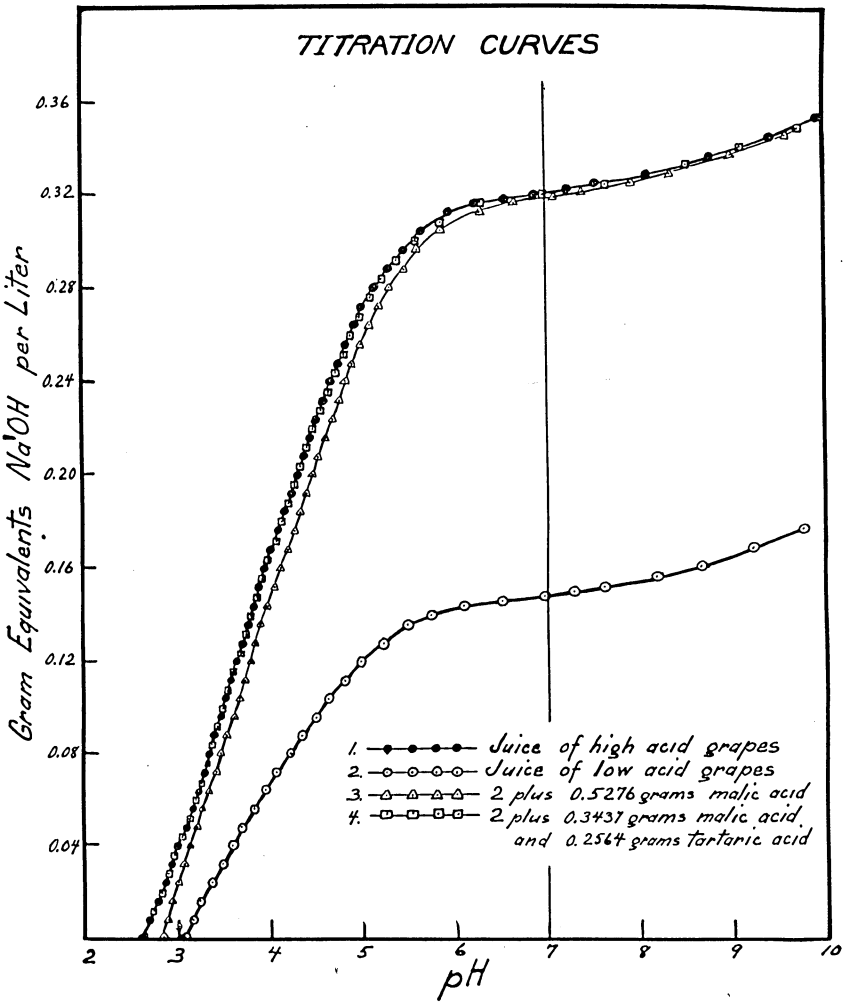

FIG. 8. BUFFER CURVES OF HIGH-ACID AND LOW-ACID GRAPE JUICES AND ARTIFICIAL ADJUSTMENT OF THE LOW-ACID JUICE TO THE HIGH-ACID JUICE RANGE

that, whether or not due to sucrose, there was generally a small but real increase in reducing sugars after inversion for the juices examined.

Statistical treatment of the data showed no significant correlation between total sugars and per cent acid as malic when all samples of all varieties were considered:

For plum juice, $r = 0.1834$
For grape juice, $r = -0.3712$

It is evident from comparison of the acid and sugar data for the different maturities of the same variety that sugar and acid have a marked tendency to vary inversely; that is, as the fruit ripens, the sugar increases and the acid decreases.

The Alcohol Precipitate of Apple Juices (crude pectin)

In table IV are given the results of the alcohol precipitation. The figures represent the per cent weight of the dried alcohol precipitate on the weight of the juice from which the precipitate was obtained. The method aids in evaluating juices as to high or low pectin content and serves to give some estimate of jellying capacity. It is of interest to note that the per cent alcohol precipitate obtained from the juice of raw apples is similar to that from the juice of cooked apples. Undoubtedly the length of the storage period and the pressure used in extracting the juice have some bearing on the pectin content of the raw juice. Jelly was made from the raw juice of a few varieties of these apples and it was found to be excellent in flavor and texture although the color was unattractive.

Total Astringents, Astringent Non-Tannins, and Tannins in the Juice of the Plums and Grapes

Examination of tables VIII and IX shows the relatively high percentage of astringent substances in plums as compared with grapes.

When the data were treated statistically, the following correlations were found to exist:

Between total astringents and total acid,

plum juice $r = 0.6100$
grape juice $r = 0.7817$

Between tannins and total acid,

plum juice $r = 0.5725$
grape juice $r = 0.2598$

Relative Proportions of Acid, Sugar, and Astringent Substances in the Plum and Grape Juices

Inasmuch as palatability of a fruit juice is greatly influenced by the relative proportions in which acid, sugar, and astringent substances occur, as well as by the absolute quantities of those substances, the method of Caldwell (10) has been followed, in which ratios between these substances are calculated.

In table X are given the ratios for plum and grape juices. The acid: sugar ratio is obtained by dividing the per cent sugar by per cent acid; the acid:astringency ratio by dividing per cent total astringents by per cent acid; the astringency:sugar ratio by dividing per cent sugar by per cent total astringents.

Although no criterion for the most desirable combination of acid, sugar, and total astringency seems to be available, some measure of optimum proportions between sugar and acid may be obtained from the data of Hartmann and Tolman (15), who found an average acid:sugar ratio of 1:15 in 104 samples of commercial Concord grape juice. If this acid:sugar ratio may be accepted as a standard, only four of the grape samples examined meet the optimum requirement. Three of these four were from grapes of the 1936 crop.

SUMMARY

Measurements of *p*H and titratable acidity (to *p*H 7.00) were made electrometrically on the juices of 33 varieties of Minnesota apples. Specific gravity was determined for all juices. Their approximate pectin content was estimated from the weight of the dried alcohol precipitate. For 13 varieties, *p*H and titratable acidity were measured on the juice of cooked apples; on the juice of 7 varieties, the same measurements were made on two dates from 6 to 9 weeks apart. The buffer system of apple juice was studied and buffer index values were calculated.

Electrometric titrations to determine *p*H and titratable acidity were carried out on 25 different samples of plums, representing 11 varieties at various stages of maturity, and on 15 different samples of grapes of the same maturity, including 11 varieties from the 1938 crop and 4 of the same varieties from the 1936 crop. Experiments were performed to study the acid-salt systems in the juice of plums and grapes. On the juices of all samples were made measurements of specific gravity, reducing sugars, total sugars after inversion, total astringent substances, and as-

tringent non-tannins. Acid:sugar, acid:astringency, and astringency:sugar ratios were calculated.

It is evident from these studies that:

1. The buffer systems of the fruits studied are largely determined by (a) the predominant organic acids which are present and (b) the character of the ash constituents in the juices. Mixtures of organic acids and fruit ash can be prepared which closely reproduce the acid-base titration curves of the fruit juices.

2. Marked variations were found in the chemical composition of the fruit juices derived from selected fruit varieties developed at the Fruit Breeding Station of the University of Minnesota.

The ranges in *p*H, per cent acid, total sugars, sucrose, total astringent substances, and tannins as they were found are shown in table XI.

Correlations were found as follows:

Between hydrogen-ion concentration and titratable acidity,

apple juice $r =$ 0.9265 plum juice $r =$ 0.6198
grape juice $r =$ 0.9213

Between total sugars and per cent acid as malic,

plum juice $r =$ 0.1834 grape juice $r = -0.3712$

Between total astringents and total acids,

plum juice $r =$ 0.6100 grape juice $r =$ 0.7817

Between tannins and total acid,

plum juice $r =$ 0.5725 grape juice $r =$ 0.2598

The *p*H of juice of cooked apples agreed closely with the *p*H of the raw juice.

Extending the storage period, reduced the acidity of the juice of apples.

The per cent alcohol precipitate, which ranged from 0.88 to 5.60 per cent of the raw juice, furnished a rough estimate of the pectin content of the apples.

To what extent some of the differences in composition are due to varietal and genetic characteristics, or on the other hand to environmental or climatic influences, it is impossible to ascertain from the present data. It is believed, however, that certain of the data represent true varietal differences and, as such, may assist the horticulturist or the consumer in evaluating the fruit for specific purposes. For example, grape #81, with 17.29 per cent to total sugars, appears to be far above the average of the grapes analysed; just as grape #228, with only 9.75 per cent total sugars is definitely below the average.

Similarly there are marked differences in the plums with respect to sugar content, acid content, and total astringency or tannins which may well be responsible for the ultimate use or desirability of these plums for specific purposes.

The data reported in this bulletin are admittedly of the survey type. They suggest, however, the desirability of carrying out similar studies over several crop seasons. Such studies should (a) assist in separating environmental and seasonal factors from genetic behavior, (b) indicate those varieties which exhibit a relatively stable constitution insofar as fruit composition is concerned, and (c) perhaps indicate genetic combinations which will assist the fruit-breeder in developing varieties of fruits suitable for specific purposes. In this last connection grape #81 may again be taken as an illustration. If a desirable grape with a sugar content stabilized at approximately 17 per cent can be grown in Minnesota, it might well provide raw material for a local wine industry.

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APPENDIX

Table I. Hydrogen-Ion Concentration, pH, and Titratable Acidity in the Juice of 33 Varieties of Minnesota Apples

Variety	pH	cH	Variety	Acid as Malic
				per cent
Dolgo Crab	3.03	9.33×10^{-4}	Dolgo Crab	1.45
Hawkeye	3.16	6.92×10^{-4}	Hawkeye	0.66
Yellow Bellflower	3.20	6.31×10^{-4}	King David	0.61
#1008 (Minn.)	3.24	5.62×10^{-4}	#1014 (Minn.)	0.53
University	3.27	5.37×10^{-4}	Salome	0.50
Patten	3.30	5.01×10^{-4}	University	0.49
King David	3.32	4.79×10^{-4}	Iowa Beauty	0.47
#1014 (Minn.)	3.32	4.79×10^{-4}	#700 (Minn.)	0.47
#838 (Minn.)	3.33	4.68×10^{-4}	#845 (Minn.)	0.44
#700 (Minn.)	3.33	4.68×10^{-4}	Black Ben Davis	0.43
Jonathan	3.33	4.68×10^{-4}	Folwell	0.42
Haralson	3.35	4.47×10^{-4}	Patten	0.42
Salome	3.35	4.47×10^{-4}	Haralson	0.42
Anoka	3.35	4.47×10^{-4}	Jonathan	0.41
Early McIntosh	3.35	4.47×10^{-4}	#838 (Minn.)	0.41
Jewell Winter	3.37	4.27×10^{-4}	#1008 (Minn.)	0.41
Windsor Chief	3.42	3.80×10^{-4}	Early McIntosh	0.40
Prairie Spy (Minn. (#1007)	3.43	3.72×10^{-4}	Prairie Spy (Minn. #1007)	0.38
Black Ben Davis	3.43	3.72×10^{-4}	Windsor Chief	0.36
Macy	3.49	3.24×10^{-4}	Macy	0.34
Iowa Beauty	3.54	2.88×10^{-4}	Anoka	0.33
#993 (Minn.)	3.55	2.82×10^{-4}	#412 (Minn.)	0.32
Folwell	3.55	2.82×10^{-4}	Bellflower	0.32
#845 (Minn.)	3.55	2.82×10^{-4}	Jewell Winter	0.30
#638 (Minn.)	3.60	2.51×10^{-4}	Evelyn	0.28
Evelyn	3.60	2.51×10^{-4}	Wedge	0.25
#412 (Minn.)	3.62	2.40×10^{-4}	#638 (Minn.)	0.25
Wilson Red June	3.71	1.95×10^{-4}	McIntosh	0.24
Wedge	3.71	1.95×10^{-4}	#1011 (Minn.)	0.20
#1011 (Minn.)	3.74	1.82×10^{-4}	#993 (Minn.)	0.19
McIntosh	3.77	1.70×10^{-4}	Wilson Red June	0.18
Stewart	4.84	1.45×10^{-5}	Stewart	0.045
Sugar Loaf	5.40	3.98×10^{-6}	Sugar Loaf	0.026

Table II. Titratable Acidity and pH (Expressed as Per Cent Malic Acid) in the Juice of Raw and Cooked Apples of 13 Varieties

Variety	Raw pH	Cooked pH	Raw acid	Cooked acid
			per cent	per cent
Dolgo Crab	3.03	3.05	1.45	1.32
#1008 (Minn.)	3.24	3.33	0.41	0.38
University	3.27	3.27	0.49	0.50
Patten	3.30	3.37	0.42	0.42
#1014 (Minn.)	3.32	3.38	0.54	0.48
#700 (Minn.)	3.33	3.38	0.47	0.45
#838 (Minn.)	3.33	3.45	0.41	0.34
Anoka	3.35	3.37	0.33	0.35
Black Ben Davis	3.43	3.79	0.43	0.35
Iowa Beauty	3.54	3.59	0.47	0.44
#993 (Minn.)	3.55	3.87	0.19	0.20
Wilson Red June	3.71	3.74	0.18	0.17
McIntosh	3.77	3.72	0.24	0.22

Table III. Measurements of pH and Titratable Acidity on the Juice of Seven Varieties of Minnesota Apples on Dates From Six to Nine Weeks Apart

Variety	1st date pH	2nd date pH	Interval	1st date acid	2nd date acid
			weeks	per cent	per cent
Hawkeye	3.16	3.37	6	0.66	0.54
#1014 (Minn.)	3.32	3.45	9	0.54	0.37
King David	3.32	3.32	6	0.61	0.56
Jonathan	3.33	3.45	6	0.41	0.36
Haralson	3.35	3.50	6	0.42	0.32
Windsor Chief	3.42	3.52	6	0.36	0.40
Stewart	4.84	5.16	6	0.045	0.032

Table IV. Alcohol Precipitate*

Variety	Date	Acid	Raw Juice Ppt.	Cooked Juice Ppt.
		per cent†	per cent†	per cent†
#845 (Minn.)	Nov. 14, 1935	0.44	5.60	.....
#1014 (Minn.)	Nov. 20, 1935	0.53	.....	4.79
Sugar Loaf	Jan. 30, 1936	0.03	4.72	.....
#700 (Minn.)	Nov. 21, 1935	0.47	3.70	2.53
Yellow Bellflower	Feb. 5, 1936	0.32	2.91	.....
Dolgo Crab	Nov. 7, 1935	1.45	2.88	3.40
Early McIntosh	Nov. 6, 1935	0.40	2.86	.....
#838 (Minn.)	Jan. 24, 1936	0.41	2.77	2.24
Folwell	Nov. 14, 1935	0.42	2.67	.....
Hawkeye	Jan. 27, 1936	0.66	2.64	.....
Evelyn	Jan. 6, 1936	0.28	2.57	.....
Macy	Jan. 7, 1936	0.34	2.52	.....
Black Ben Davis	Nov. 23, 1935	0.43	2.41	2.73
Patten	Jan. 22, 1936	0.42	2.34	2.88
Jonathan	Feb. 17, 1936	0.41	2.29	.....
Jewell Winter	Jan. 28, 1936	0.30	2.25	.....
Salome	Feb. 19, 1936	0.50	2.22	.....
Windsor Chief	Feb. 3, 1936	0.36	2.17	.....
Prairie Spy (#1007)	Feb. 8, 1936	0.38	1.68	.....
#1008 (Minn.)	Feb. 10, 1936	0.41	1.65	2.62
#993 (Minn.)	Feb. 7, 1936	0.19	1.64	1.80
University	Jan. 10, 1936	0.49	1.57	1.91
Wedge	Jan. 31, 1936	0.25	1.48	.....
Iowa Beauty	Jan. 20, 1936	0.47	1.43	1.84
King David	Feb. 21, 1936	0.61	1.33	.....
McIntosh	Jan. 13, 1936	0.24	1.08	1.06
Wilson Red June	Jan. 15, 1936	0.18	1.02	1.30
Anoka	Jan. 16, 1936	0.33	0.96	1.83
Haralson	Feb. 14, 1936	0.42	0.88	.....

* Dry weight of the alcohol precipitate has been calculated as per cent of the weight of juice from which it was obtained.

† Percentages represent the means of duplicate determinations.

Table V. Per Cent Sugar in the Whole Apple

Variety	Total Sugar after Inversion	Variety	Total Sugar after Inversion
	per cent		per cent
Sugar Loaf	9.76	Minn. #412	6.71
Yellow Bellflower	8.95	Salome	6.61
Minn. #1011	8.41	Folwell	6.54
Dolgo Crab	8.32	Haralson	6.44
Jonathan	8.21	King David	6.40
Minn. #838	7.93	Minn. #993	6.29
McIntosh (southern Minn.)	7.75	Hawkeye	6.08
Early McIntosh	7.61	Evelyn	5.92
Minn. #1014	7.39	Minn. #845	5.85
Stewart	7.27	University	5.74
Wedge	7.03	Anoka	5.74
Minn. #638	7.01	Black Ben Davis	5.65
Minn. #1008	6.92	Wilson Red June	5.48
Windsor Chief	6.92	Patten	4.97
Jewell Winter	6.92	Macy	4.72
Prairie Spy (Minn. #1007)	6.86	Iowa Beauty	4.68
Minn. #700	6.72		

Table VI. Hydrogen-Ion Concentration, pH, and Titratable Acidity in the Juice of 25 Samples (11 Varieties) of Minnesota Plums

Variety	pH	cH	Variety	Acid as Malic
				per cent
Superior	2.88	1.32×10^{-3}	La Crescent	2.22
Underwood	2.89	1.29×10^{-3}	La Crescent	2.06
Monitor	2.91	1.23×10^{-3}	Waneta	2.06
La Crescent	2.93	1.17×10^{-3}	Waneta	2.05
La Crescent	2.93	1.17×10^{-3}	Underwood	2.05
Waneta	2.93	1.17×10^{-3}	Underwood	1.98
Waneta	2.94	1.15×10^{-3}	Monitor	1.90
Underwood	2.96	1.10×10^{-3}	La Crescent	1.87
La Crescent	2.96	1.10×10^{-3}	Redwing	1.73
Monitor	2.96	1.10×10^{-3}	Monitor	1.72
Redwing	2.98	1.05×10^{-3}	Superior	1.71
Superior	2.98	1.05×10^{-3}	Nicollet	1.64
Tonka	2.98	1.05×10^{-3}	Redwing	1.59
Tonka	2.99	1.02×10^{-3}	Nicollet	1.58
Tonka	3.01	9.77×10^{-4}	Nicollet	1.45
Redwing	3.06	8.71×10^{-4}	Tonka	1.34
St. Anthony	3.11	7.76×10^{-4}	Tonka	1.34
Kaga	3.11	7.76×10^{-4}	St. Anthony	1.34
Kaga	3.11	7.76×10^{-4}	Superior	1.33
St. Anthony	3.11	7.76×10^{-4}	Zumbra	1.32
Nicollet	3.32	4.79×10^{-4}	Kaga	1.30
Nicollet	3.32	4.79×10^{-4}	Tonka	1.29
Zumbra	3.33	4.68×10^{-4}	Kaga	1.18
Nicollet	3.35	4.47×10^{-4}	Zumbra	1.15
Zumbra	3.38	4.17×10^{-4}	St. Anthony	1.09

Table VII. Hydrogen-Ion Concentration, pH, and Titratable Acidity in the Juice of 15 Samples (11 Varieties) of Minnesota Grapes

Variety	pH	cH	Variety	Acid as Malic	Acid as Tartaric
				per cent	per cent
#228	2.57	2.69×10^{-3}	#180	2.29	2.56
#180	2.62	2.40×10^{-3}	#228	2.27	2.54
#227	2.62	2.40×10^{-3}	# 31?*	2.26	2.53
# 31?*	2.67	2.14×10^{-3}	#227	2.15	2.41
#203	2.67	2.14×10^{-3}	#227 (1936)	1.61	1.80
#227 (1936)	2.74	1.82×10^{-3}	# 69	1.61	1.81
# 69	2.76	1.74×10^{-3}	# 78	1.59	1.78
# 81	2.77	1.70×10^{-3}	# 81	1.58	1.76
#161	2.88	1.32×10^{-3}	#203	1.52	1.70
# 11	2.93	1.17×10^{-3}	# 11	1.05	1.18
# 78	2.94	1.15×10^{-3}	#161	1.02	1.14
#158	3.01	9.77×10^{-4}	#158	0.98	1.10
# 69 (1936)	3.25	5.62×10^{-4}	# 78 (1936)	0.94	1.05
# 78 (1936)	3.27	5.37×10^{-4}	# 69 (1936)	0.88	0.98
# 11 (1936)	3.28	5.25×10^{-4}	# 11 (1936)	0.75	0.83

* Collecting record has some uncertainty—variety was probably #31.

Table VIII. Analyses of Representative Varieties of Minnesota Plums at Various Stages of Maturity

Variety	Specific Gravity	Acid as Malic	pH	Reducing Sugar*	Total Sugar*	Sucrose	Total Astringents	Astringent Non-Tannin	Tannin
		per cent		per cent	per cent	per cent	per cent	per cent	per cent
La Crescent									
not ripe	1.063	2.22	2.93	7.05	7.11	0.06	0.338	0.223	0.116
med. ripe	1.054	2.06	2.93	9.43	9.57	0.13	0.405	0.229	0.176
ripe	1.058	1.87	2.96	10.29	10.43	0.13	0.308	0.182	0.126
Waneta									
not ripe	1.047	2.06	2.94	7.06	7.10	0.04	0.482	0.204	0.278
med. ripe	1.050	2.05	2.93	6.59	6.64	0.05	0.530	0.195	0.335
Underwood									
not ripe	1.057	1.99	2.89	7.57	7.63	0.05	0.444	0.181	0.263
med. ripe	1.056	1.98	2.96	8.09	8.16	0.07	0.450	0.173	0.276
Monitor									
not ripe	1.050	1.90	2.91	7.46	7.56	0.09	0.297	0.133	0.164
med. ripe	1.054	1.72	2.96	8.53	8.61	0.08	0.251	0.138	0.113
Redwing									
not ripe	1.056	1.73	2.98	8.86	8.97	0.10	0.264	0.110	0.154
med. ripe	1.056	1.59	3.06	9.26	9.30	0.03	0.342	0.126	0.216
Superior									
not ripe	1.048	1.71	2.88	7.95	8.06	0.11	0.174	0.097	0.077
med. ripe	1.045	1.33	2.98	7.05	7.17	0.11	0.292	0.100	0.192
Nicollet									
not ripe	1.057	1.64	3.35	6.30	6.36	0.06	0.381	0.229	0.151
med. ripe	1.062	1.58	3.32	8.87	8.89	0.02	0.451	0.266	0.185
ripe	1.070	1.45	3.32	9.36	9.41	0.05	0.488	0.283	0.205
Tonka									
not ripe	1.050	1.34	2.99	7.86	7.93	0.06	0.254	0.111	0.143
med. ripe	1.053	1.34	3.01	9.24	9.33	0.08	0.250	0.104	0.146
ripe	1.049	1.29	2.98	7.64	7.73	0.09	0.299	0.122	0.177
St. Anthony									
not ripe	1.052	1.34	3.11	5.78	5.86	0.08	0.264	0.119	0.145
med. ripe	1.055	1.09	3.11	8.76	8.87	0.10	0.316	0.203	0.114
Zumbra									
not ripe	1.048	1.32	3.38	6.18	6.20	0.02	0.115	0.102	0.013
med. ripe	1.048	1.32	3.38	6.18	6.20	0.02	0.115	0.102	0.013
Kaga									
not ripe	1.041	1.30	3.11	5.04	5.13	0.09	0.188	0.125	0.063
med. ripe	1.048	1.18	3.11	6.82	6.98	0.15	0.162	0.117	0.045

* Calculated as invert sugar.

Table IX. Analyses of Representative Varieties of Minnesota Grapes

Variety	Specific Gravity	Acid as Malic	pH	Reducing Sugar*	Total Sugar*	Sucrose	Total Astringents	Astringent Non-Tannin	Tannin
		per cent		per cent	per cent	per cent	per cent	per cent	per cent
#180	1.054	2.29	2.62	10.62	10.62	0.00	0.120	0.106	0.014
#228	1.049	2.27	2.57	9.69	9.75	0.06	0.166	0.134	0.032
# 31?†	1.062	2.26	2.67	11.70	11.94	0.22	0.098	0.086	0.012
#227	1.062	2.15	2.62	13.43	13.73	0.28	0.132	0.111	0.021
#227 (1936)	1.064	1.61	2.74	12.53	12.55	0.02	0.107	0.090	0.017
# 69	1.057	1.60	2.76	11.65	11.65	0.00	0.109	0.071	0.038
# 78	1.063	1.59	2.94	13.09	13.09	0.00	0.102	0.085	0.017
# 81	1.075	1.58	2.77	17.09	17.29	0.19	0.111	0.107	0.004
#203	1.057	1.52	2.67	11.21	11.34	0.12	0.095	0.086	0.009
# 11	1.063	1.05	2.93	13.77	13.94	0.16	0.107	0.061	0.046
#161	1.062	1.02	2.88	13.64	13.92	0.27	0.086	0.080	0.006
#158	1.070	0.98	3.01	14.47	14.60	0.13	0.088	0.079	0.009
# 78 (1936)	1.076	0.94	3.27	14.58	14.59	0.01	0.092	0.085	0.007
# 69 (1936)	1.069	0.88	3.25	14.76	14.76	0.00	0.087	0.081	0.006
# 11 (1936)	1.068	0.75	3.28	11.68	11.69	0.01	0.083	0.076	0.007

* Calculated as invert sugar.

† Collection record has some uncertainty—variety was probably #31.

Table X. Ratios of "Acid to Sugar," "Acid to Astringency," and "Astringency to Sugar"

Variety	Acid-Sugar	Acid-Astringency	Astringency-Sugar
Grapes			
#180	1: 4.64	1:0.05	1: 88.87
#228	1: 4.30	1:0.05	1: 83.76
# 31?*	1: 5.28	1:0.04	1:121.59
#227	1: 6.39	1:0.06	1:103.94
#227	1: 7.80	1:0.07	1:117.73
# 69	1: 7.24	1:0.07	1:106.68
# 78	1: 8.23	1:0.06	1:128.97
# 81	1:10.94	1:0.07	1:155.21
#203	1: 7.46	1:0.06	1:119.87
# 11	1:13.28	1:0.10	1:130.89
#161	1:13.65	1:0.08	1:162.62
#158	1:14.90	1:0.09	1:166.10
# 78	1:15.52	1:0.10	1:158.24
# 69	1:16.77	1:0.10	1:169.07
# 11	1:15.59	1:0.11	1:140.17
Plums			
La Crescent	1: 3.20	1:0.15	1: 21.00
La Crescent	1: 4.65	1:0.20	1: 23.65
Waneta	1: 3.45	1:0.23	1: 14.73
Waneta	1: 3.24	1:0.26	1: 12.53
Underwood	1: 3.83	1:0.22	1: 17.18
Underwood	1: 4.12	1:0.23	1: 18.15
Monitor	1: 3.98	1:0.16	1: 25.48
La Crescent	1: 5.58	1:0.16	1: 33.87
Redwing	1: 5.18	1:0.15	1: 33.99
Monitor	1: 5.01	1:0.15	1: 34.37
Superior	1: 4.71	1:0.10	1: 46.32
Nicollet	1: 3.88	1:0.23	1: 16.71
Redwing	1: 5.84	1:0.21	1: 27.22
Nicollet	1: 5.63	1:0.29	1: 19.71
Nicollet	1: 6.49	1:0.34	1: 19.28
Tonka	1: 5.92	1:0.19	1: 31.23
Tonka	1: 6.96	1:0.19	1: 37.37
St. Anthony	1: 4.37	1:0.20	1: 22.23
Superior	1: 5.39	1:0.22	1: 24.53
Zumbra	1: 4.70	1:0.09	1: 53.91
Kaga	1: 3.95	1:0.14	1: 27.35
Tonka	1: 5.99	1:0.23	1: 25.84
Kaga	1: 5.92	1:0.14	1: 42.98
Zumbra	1: 6.09	1:0.09	1: 67.50
St. Anthony	1: 8.14	1:0.29	1: 28.03

* Collecting record has some uncertainty—variety was probably #31.

Table XI. Ranges in pH, Per Cent Acid, Total Sugars, Sucrose, Total Astringent Substances, and Tannins

	Plums	Grapes	Apples
pH	3.38 - 2.88	3.28 - 2.57	5.40 - 3.03
	per cent	per cent	per cent
Acid as malic	1.09 - 2.22	0.83 - 2.29	0.026 - 1.45
Total sugars |nvert	5.13 - 10.43	9.75 - 17.29	4.68 - 9.76
Sucrose	0.02 - 0.15	0.00 - 0.27	.....
Total astringency	0.104 - 0.530	0.083 - 0.132	.....
Tanin	0.008 - 0.335	0.005 - 0.046	.....