liquid would then appear to be five-fourths of that of the standard. But if the prism in the standard cell had dropped 5 divisions, and the other only 2, for example, the actual lengths of columns of liquid would be 5 and 6 divisions, respectively, with the unknown having then a strength five-sixths of that of the other

In the well-known creatinine estimation, where relatively long columns are employed, such large errors are not possible, but in many other comparisons, with short columns, they doubtless actually occur. It is therefore desirable to control the zero point frequently by bringing the end of the prism in contact with the bottom of the cell and noting that the reading is at the end or zero of the scale. Care should be taken to keep the instrument away from the vicinity of steam radiators, and, in general, in a place where the temperature does not become high in summer.

Others may have had similar experiences with the Duboscq instrument, but as I have not seen them discussed in print I think it worth while to call attention to the facts in this way.

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CHEMICAL CHANGES OCCURRING DURING THE RIPENING OF THE WILD GOOSE PLUM.[1]

BY J. S. MCHARGUE.

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The beginning of the study of chemical changes that take place during the ripening of fruits dates back to the time of the phlogiston theory.

Sennebier,[2] after experimenting on a variety of fruits, supposed that they suffered a loss of phlogiston during the ripening process.

De Saussure,[3] about 1820, carried on researches on the ripening of fruits and as a result of his investigations advanced the theory that fruits act like leaves in their respiratory functions. The fallacy of his theory was later shown by Berard,[4] who carried on respiration experiments on fruits in vessels containing hydrogen, nitrogen, carbon dioxide, and *in vacuo*. In all cases he found an increase of carbon dioxide at the expense of the oxygen, and in no case the reverse change. Similar experiments were tried on fruits still attached to the tree, with the result that the fruit did not mature, but became withered and browned, showing that oxygen is necessary for the ripening of fruits. Apparently the work

[1] Read before the Lexington Section of the American Chemical Society, January 13, 1916.

[2] *J. pharm. chim.*, [2] **7**, 249 (1821).

[3] "Recherches Chemiques sur la vegetation," Paris, 1840.

[4] *Ann. chim. phys.*, [2] **16**, 152, 225 (1821).

of Berard affords us the first correct conception on the respiration of fruits.

The amount of acid in fruits and its supposed transformation during ripening has been the subject for much discussion and many theories. Among the earlier investigators it was assumed that the acid which was present in the unripe condition was transformed into sugar in the process of ripening.

In 1866 Pasteur[1] cast doubt on this theory by showing that in certain varieties of grapes the acid increased rather than diminished.

Kelley[2] also has recently shown that during the ripening of the pineapple the amount of acid increases.

In a review of the literature of more than sixty different authors on this subject, the two cases cited are the only ones in which an increase in the acidity during the ripening is recorded. All other investigations pertaining to acidity show a diminution.

However, a recent theory has been advanced which accounts for the diminution in the acidity during the ripening period by assuming that the acid undergoes decomposition, giving rise to carbon dioxide and water.

Famintzin,[3] in 1871, published the results of his study on the ripening of grapes, which offers the first satisfactory explanation on the source of the sugars which appear in the grape on ripening. Chemical and microscopical methods were used. He states that the unripe grape contains no starch but that the stems of the grape are full of starch, which disappears as the grapes ripen.

Hilger[4] confirmed the work of Famintzin and showed that the increase of sugar during a period of six days at the time of ripening was from 3.87 to 7.70% in one variety and from 5.33 to 7.71% in another, during which time the starch in the stems disappeared.

Considerable discussion has been evolved concerning what transformations tannin undergoes during the ripening process. Certain investigators have assumed that tannin is transformed into sugars; others claim that it undergoes complete decomposition and gives rise to carbon dioxide.

Lloyd,[5] in a recent publication, states that the loss of astringency in persimmons during the process of ripening is due to the union of tannin with an associated colloid of a carbohydrate nature.

The occurrence of cane sugar in fruits has been noted in a number of instances; however, no particular significance has yet been attributed to its presence.

The above remarks review briefly some of the more important theories

[1] "Weinlaube," **1870**, p. 274; also *Ann. Oenal.*, **2**, 241 (1871).

[2] *J. Ind. Eng. Chem.*, **3**, 403–405 (1911).

[3] *Ann. Oenal.*, **2**, 242 (1871).

[4] *Landw. Vers.-Stat.*, **17**, 245 (1874).

[5] *Science* (*N. S.*), **34**, 924–928 (1911).

concerning the transformations and changes taking place during the maturation and ripening of fruits in general.

Rather late in the season of 1915 the writer's attention was called by the director of this Experiment Station to the changes taking place in the ripening of the wild goose plum, and a preliminary investigation was suggested, the object of which was to trace some of the changes taking place in the later stages of maturation.

The wild goose plum (*Hortulana*) is native to North America and apparently thrives best in the central and southwest portions of the United States. The term "wild goose" is of comparatively recent origin, and according to Hedrick[1] it received the name as follows:

About the year 1850, a farmer who lived in the vicinity of Columbia, Tennessee, fired into a flock of wild geese that was passing over his farm and succeeded in bringing down a goose. In dressing the fowl a plum seed was found in its craw, which was planted with some care. In the following spring a young plant came up from the seed, which in due course of time produced a tree and bore a fruit, which excelled in many respects any variety of plum that had ever been known to grow in that vicinity. Naturally the new fruit was called the wild goose plum.

This variety of plum is well adapted to the climatic conditions of Kentucky and because of its sweet taste and large size it has become a favorite with many fruit growers in this state.

The fruit reaches maturity in the latter part of July, and in its last stages of maturation passes rather rapidly through three stages of ripening, which are apparent to both the sense of sight and to taste.

As the fruit approaches maturity its color changes from a green to a slightly yellowish hue, and is more or less translucent in appearance. At this stage the fruit is sharply acid and somewhat astringent to the taste. In the course of from two to three days' time the fruit has changed from the yellowish hue to a bright pink color. The fruit at this stage is quite juicy and sweet to the taste, apparently all acidity and astringency having disappeared. It was also observed that at this stage many of the plums split or burst their skin. Usually the split was vertical rather than horizontal to the normal position of the plum. This bursting is quite pronounced in this variety of plum and has also been observed in other fruits and is in all probability due to internal pressure developed from chemical changes occurring during the ripening process.

After the plums have reached the pink or just-ripe stage, the color changes, after about 48 hours, to a dark red. The fruit at this stage has lost some of its juicy nature and the taste is decidedly less sweet.

Samples representing the fruit in the first and second stages of ripeness were collected from the tree and the sample for the third stage was ob-

[1] "The Plums of New York," p. 378.

tained by allowing some of the fruit gathered from the tree at the second stage of ripening to pass into the third, or overripe stage, under normal conditions. Determinations of acidity, reducing sugar and cane sugar were made on samples of the fruit at each of the three different stages of ripeness. Tests were also made at each of these stages for tannin. None was present as shown by the ferric chlorid test.

Table I shows the average of three determinations in each of the three different stages of ripening:

TABLE I.—SHOWING SOME OF THE CHEMICAL CHANGES OCCURRING IN THE RIPENING OF THE WILD GOOSE PLUM.

Different stages of ripening.	Acidity in terms of cc. 0.1 *N* NaOH per g. of plum.	Reducing sugar. In per cent.	Cane sugar. In per cent.	Total sugars. In per cent.
Unripe or beginning to turn yellow	3.08	5.82	0.40	6.22
	3.12	5.89	0.20	6.09
	3.19	6.04	0.65	6.69
Average	3.13	5.91	0.41	6.33
Ripe or sweet stage	2.62	6.90	3.60	10.50
	2.74	6.74	3.54	10.28
	2.72	6.93	3.70	10.63
Average	2.69	6.85	3.61	10.47
Overripe stage	2.33	9.17	0.61	9.78
	2.46	9.29	0.64	9.93
	2.40	9.02	0.46	9.48
Average	2.40	9.16	0.57	9.73

From the foregoing table it is apparent that some very marked and interesting changes take place in the acidity and in the amount of the reducing and cane sugars formed during the process of ripening of this plum. In the first place there is a decided loss in the acidity in passing from the first stage of ripening to the just-ripe stage. This loss is 14.05% of the acid found in the unripe stage. In passing from the ripe to the overripe condition there is a loss of 10.78%, which is 3.27% less than the loss in passing from the unripe to the ripe stage. The total loss in the acidity in passing from the unripe to the overripe stage was 23.32% of the acidity present in the unripe condition.

It is also interesting to note that as the acidity decreased there was a gradual increase in the amount of reducing sugar formed in each of the different stages of ripening. In passing from the unripe to the ripe stage there was an increase of 15.90% of reducing sugar formed, and in passing from the ripe to the overripe stage an increase of 33.72% and a total increase of 54.99% in passing from the unripe to the overripe stage.

The point of most interest in this investigation is the rapid formation of cane sugar in passing from the unripe to the ripe condition and its subsequent inversion in passing from the ripe to the overripe condition. In the unripe stage we have less than 0.5% of cane sugar present, whereas in the ripe stage we have as much as 3.61% of cane sugar. The cane sugar is quickly inverted and we have only a little more than 0.5% of cane sugar in the overripe stage.

From the results obtained in this investigation the following conclusions may be drawn:

First, that there is a gradual diminution in the acidity of this fruit during the ripening period and at the same time there is a more pronounced increase in the amount of reducing sugar formed.

Second, the greatest increase in total sugars occurred in passing from the unripe to the ripe condition.

Third, that cane sugar plays a very important part in the ripening of this fruit, and the idea is suggested that a fruit is just ripe when it contains the maximum amount of cane sugar.

Fourth, that this fruit contains the enzyme invertase, which is most active in passing from the ripe to the overripe stage.

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[CONTRIBUTION FROM THE ORGANIC LABORATORY, COLUMBIA UNIVERSITY, AND THE HARRIMAN RESEARCH LABORATORY. NO. 260.]

THE INFLUENCE OF CERTAIN SUBSTANCES ON THE ACTIVITY OF INVERTASE.

BY EDWARD G. GRIFFIN AND J. M. NELSON.

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Effect of Glass Beads.—Beard and Cramer[1] have shown that glass beads have an inhibiting influence on the activity of lipase, diastase and invertase, and claim that this is due to the alteration in the concentrations, produced by altering the surface energy at the larger surface of the glass beads. They found that the effect increased with the time and also with the temperature, and that a part but not all of the activity was regained when the beads were removed.

As glass is appreciably soluble in water and gives to it an alkaline reaction, it seems probable that these results were due to a change in the hydrogen-ion concentration rather than to the surface of the beads. The following experiments serve to confirm this view:

Portions of 50 cc. of a 10% cane-sugar solution with 1 cc. of invertase solution, were placed in Non-sol glass bottles with varying amounts of glass beads, and the inversion allowed to take place.

Grams of glass beads	0.0	25	50	100
Conc. of H^+	$10^{-5.9}$	$10^{-6.5}$	$10^{-7.8}$	$10^{-8.5}$
Change in rotation in 24 hrs.	0.34°	0.11°	0.06°	0.02°

[1] *Proc. Roy. Soc.*, (*B*) 88, 575 (9115).