

CHANGES IN THE COMPOSITION OF PRUNES DURING PROCESSING

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Production figures show that approximately 210,000 tons of dried prunes are produced annually on a world-wide basis with California producing approximately 75% of the total. Since the time prune trees were first planted around 1855 in the San Jose area, the past 108 years have seen a succession of improved techniques and equipment unparalleled in many other crops. Most of these are of relatively recent origin. In 1932, a product was commercially produced for the first time which today accounts for the usage of 27-30% of the crop. This product is prune juice, the water extract of dried prunes. While considerable data on the composition of fresh prunes and of the dried fruit are available in the literature, data derived from the water extract of these fruits is very limited. Sufficient data also are lacking on the changes which take place during the drying of prunes.

The present study was carried out to obtain information on the changes which occur during dehydration of French prunes, of juices experimentally extracted from the resulting dried fruit and the determination of variations occurring in commercially manufactured prune juices and concentrates.

To study changes which take place during dehydration, samples for analysis were taken of the fresh fruit and after the fruit had been dehydrated to 55%, 73% and 85% solids. Experimental juice samples were prepared from the dried fruit, both by battery diffusion and disintegration processes which simulated those used in industry. Commercial prune juice and concentrate samples were collected from the manufacturers of these products as well as samples obtained from retail sources in various parts of the United States. It was possible in the majority of the samples to find out from the manufacturer whether the product was the result of diffusion

or disintegration processes. For purposes of comparing data obtained on various samples, results will be discussed by the components analyzed for.

As prunes are known to have a relatively high concentration of sugars, analyses were carried out to determine which were present in the fresh fruit and what changes took place, if any, during the drying and subsequent extraction. Chromatographic analyses showed glucose, fructose, sucrose and melezitose were found in the fresh fruit. Glucose and fructose were in very large amounts, sucrose in moderate quantities and melezitose in rather small amounts. The following table shows the changes which took place during dehydration as well as ranges of data collected on dried fruit in 1933 by Mrak and co-workers.

	<u>% Reducing Sugars</u>	<u>% Total Reducing Sugars</u>	<u>% Sucrose*</u>
Fresh Prunes	40.84	53.42	11.95
Dehydrates Prunes			
55% Solids	43.71	53.97	9.75
73% Solids	49.30	54.07	4.50
85% Solids	51.28	54.58	3.14
Mrak et al. (1933)	43.31 - 64.37	50.15 - 65.11	0.74 - 6.84

*The figures given for sucrose also include the small amounts of melezitose found.

The hydrolysis of sucrose during dehydration reduces the amount from over 22% of the total reducing sugars found in the fresh fruit to approximately 6% in prunes dried to 15% moisture. Juices experimentally prepared from this fruit show that by the third extraction, using the battery diffusion method, no sucrose remained. When the disintegration process was used, approximately .25% sucrose remained which was completely hydrolyzed by further heating.

It is interesting that the sugar breakdown product hydroxymethylfurfural (HMF) was found only in the juices which were prepared experimentally and commercially but not in

the experimentally dried prunes nor in commercially stored dried prunes (82 per lb.) which had been kept for 8 months. In addition to HMF only glucose and fructose generally were found.

A second detailed study was made on the changes in composition of the amino acids present since one pathway by which browning may occur in dried fruits is by the Maillard reaction. This reaction involves simple sugars and amino acids. Twelve amino acids were found to be present in the fresh fruit, present in relatively large amounts were the amino acids; asparagine, aspartic acid and arginine while alanine, proline and gamma amino butyric acid were found in somewhat lesser amounts. Glutamic acid, glutamine and serine were found in relatively small amounts while valine, glycine and cystine were present in only trace amounts. When these fruits were dehydrated to 55% solids, asparagine and cystine no longer could be detected while glutamic acid and glutamine were in much smaller amounts than in fresh fruit. Further dehydration to 73% solids resulted in the disappearance of glutamine and reductions in the amount of glutamic acid. No changes appeared in relative amounts of the other amino acids. Glutamic acid was reduced still further when prune dehydration was carried to 85% solids.

When experimental juices were prepared, it was found that glutamic acid was absent when the battery diffusion method was used while traces of this amino acid could still be found when juice was prepared by the disintegration method. With one exception, commercial juice and concentrate samples had a similar amino acid composition to that of the experimental juices. The exception was the finding of trace amounts of asparagine in some of the commercial samples whereas this amino acid had disappeared during the experimental dehydration of prunes to 55% solids.

The protein content of commercial samples was found to vary from approximately 3.2 to 4.5 (see Table 1). Differences between samples prepared in a similar manner were very small.

Organic acids analyses showed malic and quinic acids to be found in fresh and dried prunes and in the extracted juices as well as the commercial samples. Citric acid was

found in moderate amount in one commercial sample, however, the label indicated the addition of lemon juice. In other samples only trace amounts were detected. While only malic and quinic acids mainly were found in all samples, the proportions changed quite drastically. Malic acid was found to be much more prevalent in the fresh fruit. However, by the time the fruits were dried to 55% solids, quinic acid was already found in larger amounts than was malic. Changes which occurred in titratable acidity and in pH is shown in the following table:

	<u>pH</u>	<u>Total Acidity (% as malic dry basis)</u>
Fresh Prunes	3.80	2.24
Dried Prunes		
55% Solids	3.83	2.11
73% "	3.85	1.97
85% "	3.89	1.87

The decrease in total acidity plotted against the per cent total solids is nearly linear in its decrease. It is believed that this decrease is related to the changing proportions of malic, and quinic acid. Malic acid is a dicarboxylic acid whose dissociation constants are relatively large, whereas quinic acid is a monocarboxylic acid with a smaller dissociation constant. The total acidity of juices experimentally prepared were similar for the two methods. Ranges of pH and total acidity values obtained from commercial use and concentrate samples are found in Table 1.

Also included in Table 1, are the Brix (sugar): acid ratios which are a flavor index of sweetness-sourness relationships. This ratio which varies considerably between the various commercial samples (28.8 - 59.1) was approximately 55 for the experimentally prepared juices.

No consistent differences in commercial samples prepared by similar methods could be detected in the ash content, total alkalinity of ash, total or soluble solids. One sample of concentrate prepared by diffusion method had a rather high insoluble solids content but other commercial samples prepared by this method ranged about average in value.

SUMMARY AND CONCLUSIONS

Four sugars are found to be present in fresh prunes. These are glucose, fructose, sucrose and melezitose. The amounts of melezitose and sucrose are reduced considerably during dehydration. When juice is extracted by the diffusion process, melezitose and sucrose are hydrolyzed whereas juice experimentally extracted by the disintegration method contained both sugars in trace amounts. Neither sucrose nor melezitose were found in samples of prune juice or concentrate obtained from commercial sources. Hydroxymethylfurfural was found only when juices were extracted from the dried prunes.

Twelve amino acids were found to be present in the fresh prunes. Asparagine and cystine disappeared during the first stages of dehydration while glutamine disappeared in the latter stages. Glutamic acid was constantly reduced in amount during dehydration and was found to be present in trace amounts only in juices extracted by disintegration method. Commercial prune juices and concentrate did not contain glutamic acid regardless of the extraction method used. There were no apparent changes in the amounts of the other eight amino acids whether in fresh or dried prunes or in the juice extracted from them.

Malic and quinic acids were found to be present in fresh and dried prunes and in prune juice. Malic acid was the predominant acid in the fresh fruit, however, quinic acid became predominant after the first stages of dehydration. The total acidity was found to decrease during dehydration accompanying quite small changes in pH (increasing approximately 1/10 unit from the fresh to the dried prune). While the acidity decreased by successive leachings of the same lot of dried prunes, the over-all effect upon the juice produced by the battery diffusion method when extracts were blended was to produce a final acidity similar to that of the dried fruit. Both types of juice obtained from commercial sources were higher in acidity than the juice experimentally extracted.

With respect to the method of preparation, no consistent differences in composition were found in samples of commercially produced fruit juices. The range of values obtained in

the samples of the juices prepared by the battery diffusion method was similar to that obtained in juices by the disintegration method. Differences found between commercial and experimental juices are not great and may be expected since laboratory methods simulating commercial production cannot reproduce the conditions existing in large scale operations. The dehydration and subsequent extraction procedures strongly affect the composition of the products. The presence of trace amounts of amino acids and sugars in experimental juices and their absence in commercial juices may well be explained by the additional heating the juices received when commercially concentrated and/or bottled.

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Table 1
 COMPONENTS OF COMMERCIAL PRUNE JUICE SAMPLES
 (Per cent, Dry Weight Basis)

	Single Strength			Concentrate		
	Min.	Max.	Avg.	Min.	Max.	Avg.
Protein	3.19	4.46	3.74	3.17	4.64	3.83
Reducing Sugar*	60.67	74.39	67.92	62.91	70.38	66.28
Total Solids (wet basis)	18.20	20.67	19.59	69.76	73.35	71.94
Soluble Solids (wet basis)	17.80	20.30	19.20	69.30	72.50	71.10
Insoluble Solids (wet basis)	0.28	0.44	0.36	0.24	1.15	0.79
Organic Acids						
Quinic			5.29			
Malic			1.10			
pH	3.65	4.25	3.93	3.38	3.78	3.61
Total Acidity (as Malic)	1.64	3.42	2.31	1.83	2.95	2.25
Brix/acid ratio (wet basis)	28.80	59.10	44.00	33.60	53.60	43.00
Ash content	2.23	2.89	2.57	2.25	3.14	2.78
Total Alkalinity of Ash**	26.70	34.53	30.41	23.26	34.98	32.32

*No sucrose present

**ml IN acid/100 g sample