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The Glucose-Fructose Ratio of California Grapes

by

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The importance of the total fermentable sugar in grape musts is universally recognized. The final alcohol content of unfortified wines depends primarily on the initial sugar content. For the production of high quality raisins JACOB (1942) has shown that the sugar content of the grapes prior to drying should be at least 22° Balling. For table grapes WINKLER (1932) has shown that above a certain minimum sugar content the balance of sugar and acidity is more important than the sugar content alone.

The sugars present in grapes are largely glucose (dextrose) and fructose (levulose). There are two aspects of the sugar content which have not received adequate attention. First, fructose is much sweeter than glucose. Fifteen per cent fructose is approximately equal in sweetness to 22.8 per cent glucose and to 17.8 per cent sucrose. The relative sweetness changes slightly with concentration, according to CAMERON (1947) so that at higher concentrations the difference in sweetness is not so great, but at lower concentrations the differences are even larger. Second, most yeasts ferment glucose more rapidly than fructose but rapidly ferment both in mixtures. Other yeasts, e.g., the so-called Sauternes strain or Dubourg yeast, ferment fructose more rapidly than glucose and complete the fermentation slowly, if at all. For a review of the literature to 1954, see AMERINE (1954).

These facts are of particular interest to viticulturists. In the production of grape juice from grapes grown in cool climates use of grapes high in fructose would result in sweeter tasting musts at lower total sugar contents. On the other hand, for grapes grown in warm climatic regions where sugar production is frequently too high for balanced grape juice high-glucose varieties would yield less sweet and better-balanced musts. Since it is apparently the sweetness-to-acid taste which is important a wide range of fructose to titratable acidity relationships is possible.

It is also obvious that with the usual varieties of yeast high-glucose varieties would be useful in the production of sweet table wines (of the German *Auslese* or French Sauternes types), since the glucose is slowly fermented by such strains of yeast and would permit better control of the rate and extent of fermentation.

The data to 1922 on the fructose/glucose ratio are summarized by VON DER HEIDE and SCHMITTHENNER (1922) and to 1954 by AMERINE (1954). The general conclusion has been that in unripe grapes glucose predominates, that at maturity the ratio is about 1, and that in overripe grapes fructose constitutes the major sugar. Little data on this ratio in different varieties harvested at approximately the same degree of maturity from the same climatic region are available. GENEVOIS and RIBÉREAU-GAYON (1947), for example, state simply that at maturity the two sugars are generally present in equimolar quantities. PEYNAUD (1947) reported the usual decrease in glucose/fructose ratio during the ripening of five Bordeaux varieties based on grams per 100 berries: the ratio at maturity varied from 0.91 to 0.94 in 1938 and from 0.93 to 0.96 in 1937 in one region and from 0.93 to 1.02 (in four varieties only) in another region in 1938. Several varieties when subjected to 35° C for four or five days showed decreases in the glucose/fructose ratio. This was true on a per berry or per ml of juice basis. This experiment should be repeated although PEYNAUD indicates that it is based on considerable previous experimentation. His and previous data show slight but distinct difference in the ratio from one season to the other.

In an extensive study of the fructose and glucose contents of Hungarian grapes SZABO and RAKCSÁNYI (1935) showed that at the beginning of the ripening of the grapes glucose predominated. During ripening fructose increased more rapidly than glucose, until in overripe grapes it amounted to 56 per cent of the total reducing sugars. Fructose equaled or exceeded glucose when the total sugar was about 17 per cent. In unripe grapes SIDERSKY (1942) reported a glucose/fructose ratio of above 1, but this varies with variety and origin. ESPINOZA (1943) showed the glucose to decrease from 86 per cent of the total reducing sugar to about 47 per cent during ripening. In thirty varieties the ratio at maturity varied from 0.87 to 0.96, average 0.90. According to VON DER HEIDE and SCHMITTHENNER (1922) an abundant source of experimental information about the relative proportions between glucose and fructose in grapes is summarized in the German *Weinstatistik* [see FRESENIUS, Z. anal. Chem. **27** (1880) to **43** (1904)]. They also mention that K. WINDISCH [*Werden des Weines* (1906)] investigated 60 different musts of the 1903 vintage season and found 13 to have about equal proportions of both sugars, 13 having more glucose than fructose and 34 with more fructose than glucose.

In grape concentrate GAROGLIO and BARINI BANCHI (1940) found glucose and fructose in about equal amounts but they used a polarimetric procedure.

The present studies were made to determine the normal glucose and fructose contents of several varieties of California grapes.

Experimental

Grapes grown at Davis were harvested during the 1957 season. The must was centrifuged and the total soluble solids (degree Balling), titratable acidity, and pH determined by the usual procedures of this laboratory (AMERINE 1955).

The glucose content was determined by applying the principle discovered by ROMIJN (1897) who first used iodine in alkaline solution for determining aldehydes. He reported quantitative oxidation of aldehydes to acids according to the equation: $I_2 + 3\,NaOH + RCHO \rightarrow RCOONa + NaI + 2H_2O$ and applied the method for estimating aldose sugars. WILLSTÄTTER and SCHUDEL (1918) also showed that under suitable conditions glucose is oxidized quantitatively to gluconic acid by alkaline iodine, whereas fructose and sucrose are not affected. However, other workers have shown that although a quantitative oxidation of the aldose sugars takes place under certain conditions, there is considerable difference of opinion regarding the influence of the various factors involved, such as time, temperature, etc., as well as the extent to which sugars other than aldoses are oxidized. LATHROP and HOLMES (1931) made an extensive study of the factors governing the oxidation by alkaline iodine of glucose, fructose, and sucrose and published a method of analysis which takes into consideration the effect of time and temperature on the rate of oxidation. A correction factor is applied in order to offset the interference of fructose. Although fructose as such is not oxidized by this method, a Lobry de Bruyn rearrangement takes place in alkaline solutions as follows:

$$\begin{tikzcd} & \text{fructose} \arrow[dl, shift left] \arrow[dr, shift left] & \\ \text{glucose} \arrow[ur, shift left] \arrow[rr, shift right] & & \text{mannose} \arrow[ul, shift left] \arrow[ll, shift right] \end{tikzcd}$$

The resulting glucose and mannose formed as a result of this rearrangement would be readily oxidized and give erroneous results as to the true concentration of glucose originally present. While RIBEREAU-GAYON and PEYNAUD (1947) noted this procedure they preferred a method based on the blue coloration of fructose with diphenylamine.

Method

In view of the foregoing discussion LOTHROP and HOLMES (1931) adopted a method for the analysis of honey which takes into consideration the major difficulties encountered in the alkaline iodine oxidation of such a system. Honey has a fructose/glucose ratio of about 1 to 1.3. Since this same ratio, with a difference of about ± 0.3, has been reported for the juice of vine-ripened grapes the method of LOTHROP and HOLMES has been adopted. The analysis was as follows: to 20 ml aliquot of the clarified solution used for the reducing sugar determination in a 250 ml Erlenmeyer flask, add 40 ml of standardized iodine solution (0.05 $\underline{N}$). Run in 30 ml of 0.1 $\underline{N}$ sodium hydroxide, stopper and let stand 10 minutes at 20° C. Acidify with 10 ml of 2 $\underline{N}$ sulfuric acid and titrate at once with standardized sodium thiosulfate (0.05 $\underline{N}$) using starch as an indicator. The weight of glucose in grams (not corrected for reduction of iodine by fructose) is found by multiplying the ml of 0.05 $\underline{N}$ iodine reduced by 0.004502. The total reducing sugar content of the juice is determined by the method of LANE and EYNON and the per cent glucose and fructose calculated. For the equations used in these calculations the original paper by LOTHROP and HOLMES (1931) should be consulted.

Typical results obtained by applying this method in determining the glucose and fructose and the recovery when these sugars were added to musts were as follows:

	Conc. %	Aliquot	Found %	Actual %
Glucose	0.5	10	0.499	0.50
Fructose	0.5	10	0.004	—
Must	—	10	0.293	—
Must + glucose	—	10 + 10	0.788	0.792
Must + fructose	—	10 + 10	0.307	0.297
Must + both	—	10 + 5 + 5	0.540	0.544

From this data the generally satisfactory recovery of glucose and the relatively small interference of fructose can be seen.

A large number of duplicate determinations were also made. The probable error of a single determination did not exceed 0.15 per cent (actual value) which can be considered quite satisfactory.

In table 1 the glucose/fructose ratios of eight table grape varieties and of eleven wine grape varieties are given. These have been calculated to 20⁰ Balling from periodical tests made during the ripening period on 10- to 30-cluster samples of fruit. In some cases the calculation is for the nearest value to this degree Balling. In some cases no samples were collected as low as 20⁰ Balling and in other cases no samples were as high as 20⁰. Ratios varied from 0.80 to 1.12. No general pattern related to ampelographical relationship appears from the data.

Table 1

Glucose and fructose contents and ratios of various varieties

Variety	Date harvested	⁰Balling	Total Acid gr.tartaric/100ml	pH pH	Glucose gr/100ml	Fructose gr/100ml	$\frac{\text{Glucose}}{\text{Fructose}}$
			Table Grape Varieties				
Alphonse Lavalée	Oct. 13	20.0	0.52	3.86	9.74	9.87	0.99
Cardinal	Aug. 16	20.0	0.44	3.76	10.23	9.30	1.10
Chasselas doré	Sept. 24	20.0	0.49	3.57	9.87	9.80	1.01
Flame Tokay	Sept. 20	20.0	0.68	3.66	9.12	10.81	0.84
Khalili	Aug. 30	14.4	0.57	3.82	6.10	6.01	1.01
Muscat of Alex.	Sept. 3	20.6	0.69	3.38	9.21	11.12	0.83
Red Malaga	Sept. 26	20.0	0.47	3.75	11.03	9.84	1.12
Thompson Seedless	Sept. 3	22.3	0.71	3.38	10.36	12.94	0.80
			Wine Grape Varieties				
Cabernet Sauvignon	Sept. 3	21.0	0.86	3.42	9.44	9.69	0.98
Delaware	Sept. 3	21.8	0.72	3.48	9.95	10.87	0.92
Gewürztraminer	Sept. 3	22.3	0.73	3.74	10.19	10.78	0.95
Folle Blanche	Oct. 16	18.3	0.81	3.30	8.31	9.22	0.90
Gamay Beaujolais	Aug. 22	20.0	0.94	3.32	9.47	8.86	1.07
Mission	Sept. 23	22.2	0.68	3.64	10.10	12.51	0.81
Palomino	Oct. 23	16.4	0.42	3.89	6.32	7.94	0.80
Sauvignon blanc	Sept. 3	20.0	1.01	3.38	8.97	10.12	0.89
Sylvaner	Sept. 3	21.1	0.95	3.48	9.38	10.95	0.86
Valdepeñas	Sept. 3	20.8	0.81	3.52	10.19	12.22	0.83
White Riesling	Sept. 3	21.2	0.76	3.35	9.63	11.54	0.83

During ripening the glucose/fructose ratio decreased in 9 of the 19 cases and increased in 10. However, the increases were negligible in 4 of the 10 samples. Nevertheless, one is certainly not justified in stating that the ratio always decreases with maturity.

At extreme over-maturity the ratio varied from 0.72 (for White Riesling) to 1.20 (for Gamay Beaujolais).

In another series of studies all the fruit of individual vines were harvested, crushed, and pressed and analyzed. This data are summarized in Table 2. The ratio is seen to vary over a rather wide range owing to differences in the rate of ripening of the fruit of different vines.

Table 2

Glucose/fructose ratio of individual vines

Variety	No. of vines	°Balling			Glucose/fructose		
		Min.	Max.	Ave.	Min.	Max.	Ave.
Carignane	13	20.8	25.5	23.5	0.94	1.12	1.02
Mission	5	21.9	24.3	23.4	0.95	1.12	1.05
Muscat of Alexandria	6	22.3	23.7	22.8	0.99	1.07	1.02
Semillon	8	21.1	23.0	21.9	1.11	1.27	1.20
Semillon	8	20.3	24.8	22.4	1.02	1.11	1.07
Thompson Seedless	5	20.5	23.8	22.7	0.85	0.96	0.92

Summary

1. Because of the high sweetness of fructose table grape varieties of high fructose content would be of interest for cold climates. For producing stable sweet table wines with ordinary yeasts high fructose varieties would be desirable. With the Sauternes strain of yeast high glucose varieties would be favored.
2. The LOTHROP-HOLMES method gave good recovery of added glucose, duplicable results, and minor interference of fructose.
3. The glucose/fructose ratio of California grapes at maturity varies over a wide range, from at least 0.80 to 1.12. There is, however, considerable variability in the ratio between different vines.
4. Further data should be obtained for a large number of varieties in order to discover as wide a range of ratios as possible. Plant breeders could then use this information in their experiments.

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