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Nonenzymic browning during storage of white hard grape pekmez (*Zile pekmezi*)

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Abstract

Effects of storage period on hydroxymethylfurfural, pH and colour were studied in white hard grape pekmez (*Zile pekmezi*), a Turkish traditional product. Pekmez samples were stored at 20 °C for 8 months. Analysis of variance revealed significant differences in hydroxymethylfurfural, pH, *L*, *a* and *b* values ($P < 0.01$) based on storage time.

Keywords: Pekmez; *Zile pekmezi*; White hard grape pekmez; Hydroxymethylfurfural; Colour

1. Introduction

Pekmez, which has been produced for a long time in Turkey, is a traditional Turkish food. Because most of its carbohydrate is in the form of glucose and fructose, it easily passes into the blood without digestion. This is nutritionally important, especially for babies, children, sportsmen and in situations demanding urgent energy. Pekmez has an important function in the working of the brain, in which glucose is an energy source. Furthermore, pekmez confers approximately 293 kcal/100 g of energy and also has important organic acids and mineral materials. There are many publications about production, composition, standardization and health benefits of pekmez (Aksu & Nas, 1996; Batu, 1991a; Batu, 1991b; Batu, 1991c; Batu, 1993; Batu & Aktan, 1993; Batu & Yurdagel, 1993; Bozkurt, Göğüş, & Eren, 1999; Güven, 1982; Karakaya & Artık, 1990; Kayahan, 1982; Nas & Nas, 1987; Tekeli, 1965; Ustun & Tosun, 1997).

Fresh or dried grapes are particularly used in the production of pekmez, but apple, prune, watermelon, mulberry, apricot and sugar beet can also be used in pekmez production (Batu, 1991c). The raw materials and processing conditions differ geographically. Concentrated grape juice alone, up to a minimum of 65% total soluble solids, is liquid pekmez. White hard pekmez is produced by adding some gelling and bleaching agents to liquid pekmez.

Grape juice is used for the production of hard grape pekmez. Acidity is decreased with the application of $CaCO_3$-containing special white soil, or $CaCO_3$ only, and the grape juice is left to sediment. Acid-decreased and clarified grape juice is concentrated to the desired Brix degree under atmospheric pressure, or by a vacuum method. After the addition of the white of an egg, soapwort extract, former pekmez, or powdered sugar as bleaching agents, and pectin as a gelling agent, the concentrated grape juice is stirred and beaten. During this process, the penetration of air, along with the bleaching agents, causes the production of white or cream-coloured pekmez. During storage, the light colour of the product darkens because of the Maillard reaction. As an intermediate product of the Maillard reaction, that originates during production and progresses also in storage of pekmez, hydroxymethylfurfural (HMF) is an important quality index. In the Turkish Pekmez Standard (TS, 1989), maximum HMF in 1st quality product is declared as 25 mg/kg.

The purpose of this study was to evaluate HMF formation and its effects on colour during storage and also to determine the changes in pH, that affected HMF formation.

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2. Materials and methods

2.1. Materials

White hard grape pekmez samples, produced by a commercial factory in Tokat, Zile, were used. Upon production, the samples arriving to the laboratory were placed in 100 g jars and stored at 20 °C in darkness. Soluble solids, sugar, protein, total acidity, HMF, pH and colour analysis were established in samples before storage. In stored samples, HMF, pH and colour analysis were obtained at 2-month intervals.

2.2. Methods

General parameters were measured following official methods (AOAC, 1984); pH was measured with a Nel, pH-890 pH meter; titratable acidity was measured with 0.1 N NaOH up to pH 8.1 and expressed as percentage of tartaric acid; soluble solids content was measured with an ATAGO refractometer; protein was analyzed by the Kjeldahl method (N×6.25).

Colour was evaluated by measuring Hunter L (brightness, 100 = white, 0 = black), a (+, red; −, green) and b (+, yellow; −, blue) parameters by means of a reflectance colorimeter (CR 300, Chromometer, Minolta, Japan). A white tile (No: 21733001) was used to standardize the instrument.

Total sugar, invert sugar and sucrose were quantitated by the Lane-Eynon method (Cemeroglu, 1992); The hydroxymethylfurfural was determined quantitatively following the procedure described by the IFFJP (1964), based on the colorimetric reaction between barbituric acid, p-toluidine and HMF, forming a red-coloured complex. The intensity of red colour was measured at 550 nm with a JASCO UV-Visible V-560 spectrophotometer.

2.3. Statistical analysis

The data were the mean of three independent determinations and were statistically evaluated by analysis of variance (ANOVA) and the means were compared using Duncan's multiple range test at $P < 0.01$, using the MSTAT program to determine the significant differences that could be attributed to the time of storage.

3. Results and discussion

Study of the storage of pekmez was carried out over 8 months. Some compositions of samples before storage are shown in Table 1 and changes reported during storage of samples are shown in Table 2.

Because of the rich contents of sugar and protein, HMF in pekmez samples showed a significant increase ($P < 0.01$) as storage time increased (Table 2). The colour darkened; consequently L value decreased and a and b values increased parallel with the increase of HMF. These changes were found to be statistically significant ($P < 0.01$). During storage, the pH value increased until the 4th month and decreased from the 6th month; although the pH over the 8-month storage period changed actually only by approximately 0.1 pH units, this difference was found to be statistically significant ($P < 0.01$).

Higher pH values promote the development of HMF (Eskin, Henderson, & Townsend, 1971). The pH value of pekmez is higher than the original fruit because of the acid decreasing process applied during production. Consequently, the higher pH stimulates the Maillard reaction in this high sugar- and protein-containing medium.

In high soluble solids-containing pekmez samples, the HMF increased by 41.1% after 8 months of storage. This is below the maximum HMF value declared in the Turkish Pekmez Standard for the 1st quality product.

Table 1
Some components of white hard grape pekmez before storage ($n = 3$)

Component	Mean ± standard deviation
Soluble solids content (%)	83.20 ± 0.23
Total sugar (%)	76.9 ± 0.29
Invert sugar (%)	68.4 ± 0.78
Sucrose (%)	8.08 ± 0.86
Protein (%)	2.41 ± 0.28
Titratable acid (%)	2.47 ± 0.01

Table 2
Changes in colour, HMF and pH during storage of white hard grape pekmez ($n = 3$)[a]

Storage time (months)	HMF (mg/kg)	pH	L	$+a$	$+b$
0	9.03 ± 0.29c	5.53 ± 0.01d	78.50 ± 0.61a	1.10 ± 0.09d	17.38 ± 0.18d
2	10.8 ± 0.90b	5.56 ± 0.01b	69.66 ± 0.40b	2.57 ± 0.04c	18.63 ± 0.15c
4	10.9 ± 0.52b	5.57 ± 0.01a	66.60 ± 1.65c	2.91 ± 0.13bc	18.99 ± 0.33c
6	11.5 ± 0.50ab	5.55 ± 0.00c	65.91 ± 0.79c	3.22 ± 0.06b	23.52 ± 0.41b
8	12.7 ± 0.45a	5.48 ± 0.01e	64.43 ± 0.06c	4.67 ± 0.27a	24.57 ± 0.73a

[a] For a given storage period, column values with the same letter are not significantly different ($P < 0.01$).

HMF formation during storage changed colour as a difference from white-light-cream to brown and this was instrumentally established as a decrease in L value and increase in a and b values.

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