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Chemical Study of 'Harisa', (Chili Red Pepper Sauce), Manufactured in the Libyan Arab Republic

MOHAMED I. EL-GHARBAWI¹

ABSTRACT

Two different locally manufactured 'Harisa' (Chili red pepper sauce) were studied. Chemical and physical tests showed some significant differences with respect to their constituents. One brand product was free from any added material to the natural pepper fruit pulp extract concentrated by evaporation. The other brand product contained added filling and colouring materials in addition to chemical preservative.

Some suggestions were given in this paper which could be used as a guide in the preparation of future standard specifications for the product studied.

INTRODUCTION

Chili red pepper fruits of genus (*Capsicum*), are mostly used by the Libyans in their foods as a condiment. It provides the food with a desirable color and pungent flavor. Usually, the fully ripe pepper fruits are sun-dried, crushed and sieved before use in preparing cooked food. Almost every recipe of their daily starchy or vegetable dishes contains hot pepper and tomato sauce.

Harisa, a common name for the chili red pepper sauce, is commercially produced in the Libyan Arab Republic and packed in cans or glass containers. The sauce consists essentially of a suspension of very finely divided red pepper fruit particles in a thickened spiced medium. This medium may be obtained by evaporation of the pepper fruits extracts or by adding some filling materials such as starch or soybean flour to the extract depending on the method adopted for making such a product. No standard specifications or data are available concerning these products in the Libyan Arab Republic at the time of writing this paper.

This is an attempt to determine some of the chemical characteristics of the Chili red pepper sauce products manufactured locally in Tripoli.

MATERIAL AND METHODS

Samples

Harisa samples were obtained from two different plants in Tripoli. 'El-Mansourah' brand is produced by the Libyan Plants for Canned Foods, and packed in No. 1 lacquered

¹ Mohamed I. El-Gharbawi, Department of Food Science, University of Tripoli, Tripoli, Libyan Arab Republic.

MOHAMED I. EL-GHARBAWI

tin cans. The sauce was made from sun-dried chili red pepper fruits purchased from different locations around Tripoli. The fruits were washed by soaking in running water, steamed, pulped and screened mechanically to separate flesh extract from skin and seeds. The pulp was concentrated by evaporation under vacuum. The concentrate (about 22%) was spiced by adding a mixture of powdered coriander, cumin, salt and minced garlic. The hot paste was then poured into the cans which were immediately sealed and thermally processed for preservation.

The second sample was obtained from 'Ba.Mi.Fa.' factory of Tripoli. The sauce manufactured in this plant was also made from the locally produced sun-dried red pepper. The fruits were washed and stored in a vinegar-sorbic acid solution for a few months. The soft fruits were then minced and passed through a colloidal mill to produce a homogeneous paste. Blanched potatoes were mashed and mixed with pepper paste, spiced and coloured artificially. The mixture was then mechanically sieved to obtain a homogeneous product which was chemically preserved and packed in glass containers.

Chemicals

All chemicals used in this study were analytical reagent grade. Isopropanol was of spectro-photometric grade. The capsaicin used as a standard was obtained from Merk Company, Germany.

Moisture determination

The water content of the samples was determined at 70°C in a thermostatically controlled vacuum oven according to the method described by Jacobs (7).

Total acidity

About 5 grams of sauce were diluted with 100 ml of CO_2 -free distilled water and treated with activated carbon for colour removal. Titration was carried out with 0.1 N NaOH using phenolphthalein as indicator. The total acidity was calculated as citric acid.

Reducing sugars

Samples were diluted with distilled water, clarified with neutral lead acetate and the reducing sugars were determined in deleaded filtrates by Lane-Eynon method (1).

Starch determination

About 5 grams of pepper sauce were thoroughly defatted with light petroleum and then with 95% ethanol and air-dried. The dried sample was rewetted with ammonia-free water and heated on a water bath for 30 minutes. The sample was cooled to 55°C for three hours. The mixture was then transferred quantitatively to a 250 ml volumetric flask and made up to volume with distilled water and filtered. Two hundred millilitres of filtrate were mixed with 20 ml of HCl (Sp gr 1.125), and heated in boiling water for three hours. The solution was cooled and neutralized. The reducing sugars content in the neutralized solution was determined by the Lane-Eynon method (1). The starch content was calculated by using the following equation: dextrose $\times 0.90 =$ starch.

120

Sodium chloride

NaCl content of the sauce was determined by the silver nitrate volumetric method (1).

Artificial colours

Detection of artificial colouring materials was carried out qualitatively using wool test technique (1).

pH value

The pH values of the sauce samples were determined by PYE-pH-metre, model 78 at room temperature.

Capsaicin determination

The method used in this study for determining capsaicin in chili pepper sauce was suggested by Gonzalez and Tamarino (6). Capsaicin was extracted from the samples with isopropanol using Soxhlet extraction apparatus. The extract was decolourized with activated charcoal and the clear extract filtrate was dried under vacuum. The oil residue was dissolved in petroleum ether, washed with distilled water in a separatory funnel and the aqueous layer was discarded. The ether layer was dried and the oily residue was dissolved and quantitatively transferred into a 25 ml volumetric flask and brought to volume with isopropanol. The absorbance was read at 281 mu using the Perkin-Elmer 204 Ultra-Violet-Visible Spectro-photometre against an isopropanol blank. A standard curve for absorbancy of different concentrations of capsaicin per ml was prepared, and the quantity of capsaicin in the sauce was determined from this curve.

Ascorbic acid

A phosphoric acid-citric acid stabilized sample extract was titrated against a standardized dye of 2,6-dichlorophenol-indophenol as indicator. The procedure was described in the A.O.A.C. (1).

RESULTS AND DISCUSSION

'Harisa' or chili red pepper sauce is one of the major manufactured food products in the Libyan Arab Republic (5). In addition to the commercial production of this item it is commonly made by most housewives from fresh and dried pepper fruits. The sauce has widespread use in cooked vegetables and as a condiment with starchy foods, meats and fish.

The natural red colour of red pepper is due to a complex mixture of carotenoids. The major carotenoids were identified by Zechmeister and Cholnoky (10), as esters of capsanthin, capsorubin, crypxanthin and zeaxanthin. However, Curl (4) suggested that the complex mixture might contain at least six other pigments containing cyclopentane ring. Beta carotene was also identified as one of the major carotenes in the mixture (10).

The pungent flavour of the chili pepper fruit was determined by measuring the capsaicin content of the sauce. Chemically, capsaicin is: N-(3-methoxy-4-hydroxy-benzyl)-8-methylnon-6-enamide (6).

The structure of capsaicin is as follows:



Fig. 1. Capsaicin.

However, Benett and Kirby (2), Kosuge and Furuta (8), and Masada *et al.* (9), have reported that capsaicin is actually a mixture of at least five closely related vanillyl amides. Chili red pepper sauce samples used in this study were obtained from two food plants in Tripoli during summer of 1973. Sauce manufactured under El-Mansourah brand name was packed in lacquered cans and preserved by thermal treatment. Ba.Mi.Fa. factory used glass containers for packing the sauce with the addition of sorbic acid as chemical preservative.

Chemical analysis was carried out on all samples to determine some of their constituents. Table 1 shows the results obtained throughout this study for the two brands used.

The results obtained indicated that Ba.Mi.Fa. sauce showed higher values for reducing sugars, crude fiber and pH compared to corresponding values for El Mansourah sauce. In addition, Ba.Mi.Fa. samples contained about 40% added starchy filling material proved, by microscopy study, to be potato starch. On the other hand, El-Mansourah sauce was free from any added filling material.

Qualitative wool test and circular paper chromatography proved that Ba.Mi.Fa. sauce contained at least two different artificial colours to stain the filling material used and to obtain a colour comparable to that of the natural pigments of Chili red pepper.

No significant difference in capsaicin concentration was obtained between samples of the two brands investigated, although Ba.Mi.Fa. sauce contained added filling material. This lack of difference in capsaicin content might be due to the use of the entire fruit including the seeds, which contain capsaicin, by Ba.Mi.Fa. This excess of capsaicin from the seeds would, undoubtedly, be cut down by the addition of filling material in such a quantity to make the capsaicin content of the final product similar to that of the sauce made only from fruit pulp extract manufactured by the other factory (El-Mansourah brand).

Source of variation	El-Mansourah Brand	BA.MI.FA Brand
Water %	81.40	79.50
Ash %	00.90	00.68
Reducing sugars %	5.13	5.81
Starch %	00.00	9.46
Crude fiber %	1.20	1.80
Sodium chloride %	1.28	1.07
Total activity %	2.12	1.95
Ascorbic acid (mg/100 gm)	96	53
Capsaicin (mg/100 gm)	68	62
Artificial color	Nil	Present
pH	4.45	4.70

Table 1 Some characteristics of two different brands of "Harisa"; Chili red pepper sauce manufactured in Tripoli, L.A.R.

122

Values obtained for the titratable acidity, a desirable feature in thermal processing, were higher in the El-Mansourah samples compared to the other brand.

Higher values for vitamin C content were obtained for El-Mansourah brand sauce compared to the Ba.Mi.Fa. samples. This could be explained by the dilution effect on vitamin C content of the sauce by adding the filling material in the Ba.Mi.Fa. samples.

Up to the time of writing this paper, and to the best of the author's knowledge, there were no standard specifications in the Libyan Arab Republic for such products. Thus, it is recommended that consideration should be given to the chemical composition of the Chili red pepper sauce manufactured in the country when such specifications are considered.

From this study it might be advisable to classify Chili red pepper sauce products in at least two major types: first, the Chili red pepper sauce made only from red pepper pulp extract and preserved by heat, and second, the Chili red pepper sauce containing filling materials such as starch, soybean powder, vegetable extracts or any other added materials to increase the volume or improve the consistency of the product.

Both products examined are marketed under the same product name: sauce, or Harisa, at about the same price per unit weight. The word 'sauce' must be restricted to the product made from Chili red pepper pulp extract only and concentrated by evaporation and preserved by thermal treatment. Other Chili red pepper products must be given other names befitting their composition, method of preparation and method of preservation.

Finally, the author observed that both product containers lacked proper labelling which, no doubt, would mislead the consumer. Results reported, critical remarks made by the author, and suggestions submitted in this paper should be considered for future use in preparing standard specifications in the Libyan Arab Republic for such products.

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