Radiation Physics and Chemistry 124 (2016) 208–211

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Comparison of the ionizing radiation effects on cochineal, annatto and turmeric natural dyes

Helio M. Cosentino [a], Patricia Y.I. Takinami [b], Nelida L. del Mastro [b,*]

[a] Mackenzie Presbyterian University, R. da Consolação 930, 01302-907 SP, Brazil
[b] Center of Radiation Technology, IPEN-CNEN/SP, Av. Prof. Lineu Prestes, 2242, 05508-900 SP, Brazil

HIGHLIGHTS

- Comparison of radiosensitivity of food colors was performed.
- Carmine showed the highest resistance to radiation.
- Annatto and turmeric behaved sensitive to radiation when diluted.
- Turmeric was the most affected by ionizing radiation.

ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form
23 September 2015
Accepted 28 September 2015
Available online 5 October 2015

Keywords:
Food colors
Ionizing radiation
Carmine
Annatto
Turmeric

ABSTRACT

As studies on radiation stability of food dyes are scarce, commercially important natural food grade dyes were evaluated in terms of their sensitivity against gamma ionizing radiation. Cochineal, annatto and turmeric dyes with suitable concentrations were subjected to increasing doses up to 32 kGy and analyzed by spectrophotometry and capillary electrophoresis. The results showed different pattern of absorbance versus absorbed dose for the three systems. Carmine, the glucosidal coloring matter from the scale insect *Coccus cacti* L., Homoptera (cochineal) remained almost unaffected by radiation up to doses of about 32 kGy (absorbance at 494 nm). Meanwhile, at that dose, a plant-derived product annatto or urucum (*Bixa orellana* L.) tincture presented a nearly 58% reduction in color intensity. Tincture of curcumin (diferuloylmethane) the active ingredient in the eastern spice turmeric (*Curcuma longa*) showed to be highly sensitive to radiation when diluted. These data shall be taken in account whenever food products containing these food colors were going to undergo radiation processing.

1. Introduction

Useful colors of plant or animal origin have been known for a long time and not only are still widely used but also the use of natural-type food colors continues to increase (Downham and Collins, 2000).

Carmine was used extensively before the advent of synthetic coloring materials. Since then it has been used only when a natural pigment is required in the food industry, for cosmetics and pill coatings and water-soluble drug preparations. The coloring principle of the extract is carminic acid, a hydroxyanthraquinone linked to a glucose unit, comprising 10% of the cochineal and 2–4% of its extract (Fig. 1). Treatment of carminic acid with an aluminum salt produces carmine, the soluble aluminum lake. Carmine is normally 50% or more carminic acid. Typical applications are at a dosage levels ranging from 0.1 to 0.5% (FAO, 2014). Carminic acid and particularly carmine aluminum lake are permitted and widely used in the food industries in North and South America and Western Europe. In Japan, carminic acid rather carmine is employed by the food industry.

Among natural colorants, extracts obtained from annatto have been used in many processed foods, especially dairy products. Annatto, a plant-derived product, is the carotenoid-based dye extracted from the seeds of the tropical tree *Bixa orellana*, known as *achiote* in Spanish and *urucum* in Portuguese. The pigment is made up of bixin (both *cis* and *trans*) with traces of norbixin, bixin dimethyl ester and other apocarotenoids, several of them lycopene cleavage products (Giuliano et al., 2003). Bixin which is a carotenoid with two carboxylic groups, one of which is esterified, is the major pigment present in annatto extract (Fig. 2). Norbixin, which is derived from bixin by hydrolysis of the ester group, is also

* Corresponding author.
E-mail address: nlmastro@ipen.br (N.L. del Mastro).

http://dx.doi.org/10.1016/j.radphyschem.2015.09.016

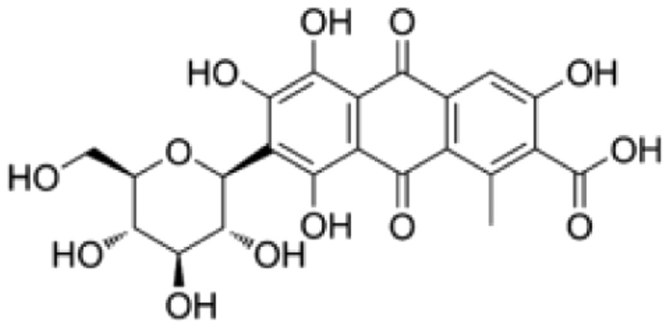

Fig. 1. Chemical structure of carminic acid (*Source*: Merck Index, 11th Edition, 1850).

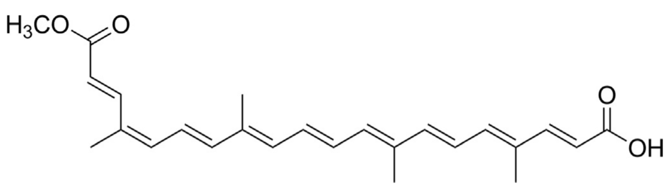

Fig. 2. Chemical structure of bixin (*Source*: http://ntp.niehs.nih.gov/testing/status/background/execsumm/b/bixin/index.html#selection).

sold as a food pigment, and this molecule is water soluble, whereas bixin is oil-soluble.

Curcumin (diferuloyl methane) is a bright orange-yellow crystalline powder used as food coloring. It is the product obtained by solvent extraction of turmeric i.e., the ground rhizomes of *Curcuma longa* L. (*Curcuma domestica* Valeton) and purification of the extract by crystallization. Curcumin is chemically a diarylheptanoid, which incorporates several functional groups (Fig. 3). The ring systems, which are phenols, are connected by two α, β unsaturated carbonyl groups. The diketones form stables enols and are readily deprotonated to form enolates, so, the α, β carbonyl groups undergoes nucleophilic addition. In a way, that sort of compound could indicate a good radical scavenging capacity (Duque et al., 2013).

There are numerous reports in the literature about environmental applications of ionizing radiation like bleaching of dyes solutions, some of them from our own laboratory (Borrely et al., 1998). On the other hand, decontamination of food by ionizing radiation is a safe and efficient process for the elimination of potentially pathogenic bacteria (Farkas, 1998). The processes of cochineal insects, urucum seeds and turmeric roots imply a number of phases from the field to the industry where high risks of contamination do exist. Then, the aim of this work was to establish and compare the radiosensitivity of natural food colors: carmine (cochineal), annatto (urucum) and turmeric (curcumin) using spectrophotometry and also capillary electrophoresis.

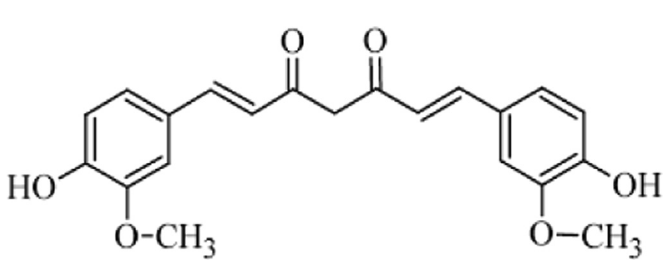

Fig. 3. Chemical structure of Curcumin (*Source*: http://tools.niehs.nih.gov/cebs3/ntpviews/index.cfm?action=testarticle.properties&cas_number=458-37-7).

2. Experimental

2.1. Material

Cochineal carmine: as powder, aluminum-calcic lake, minimum of 52% dry weight carminic acid; as tincture, minimum of 3 g/100 ml carminic acid as ammoniac solution, pH 10.2–10.8, soluble in water.

Urucum dye: as powder, minimum of 30% dry weight of norbixin (expressed as total carotenoids), soluble in water.

Curcumin: as powder, minimum of 30% dry weight of curcuminoids; as tincture, minimum of 30% of curcuminoids in a hydroalcohol solution.

For each one of the food colors a series of samples were prepared as follows:

Carmine powder commercially available containing 5% humidity; commercially available liquid carmine tincture and two tincture dilutions at 5% and 10% v/v.

Commercially available liquid tinctures of urucum and curcumin and their dilutions at 50%, 10% and 5% v/v.

Sample preparations were made according to Codex (1975) and Brazilian norms carmine (Brasil, 1996a) urucum (Brasil, 1996b) and curcumin (Brasil, 1996c). All samples were analyzed in triplicate (spectrophotometry) or duplicate (capillary electrophoresis) and the results expressed as mean and standard deviation.

2.2. Irradiation

Samples (4 concentrations from each food color) were gamma irradiated in a Co-60 Gammacell 220 (AECL), dose rate about 5.2 kGy/h with doses of 0, 1, 2, 4, 8, 16 and 32 kGy, dose uniformity factor: 1.13.

2.3. Spectrophotometry

A VARIAN, model 280, UV/vis was employed.

2.4. Capillary electrophoresis

Capillary electrophoresis separates ions based on their electrophoretic mobility with the use of an applied voltage. It is dependent upon the charge of the molecule, the viscosity, and the atom's radius. The rate at which the particle moves is directly proportional to the applied electric field; neutral species are not affected. Capillary electrophoresis is used most predominately because it gives faster results and provides high-resolution separation (Camilleri, 1997). A BECKMAN P/ACE 5510 (Beckman Coulter Instruments, Fullerton, CA, USA) equipment was utilized with a silica capillary tube, 75 pm internal diameter and 47 cm length model P/ACE 5510, equipped with a variable UV–vis, software for data acquisition and treatment (Beckman P/ACE System Gold Software). Determinations were made at 25 °C under a ddp of 25 kV and injection rate of 0.5 psi/s.

3. Results and discussion

3.1. Carmine

In Table 1 are shown the variation of absorbance at 494 nm due to the application of different absorbed doses for all the carmine samples: original carmine powder, and 5%, 10% and 50% aqueous solutions. The hydroxyanthraquinone absorption spectrum corresponding to most diluted samples showed notorious decrease, but as a rule, carmine samples remained quite stable against radiation treatment. It was reported that carminic acid extracts, the