Influence of Desamerization on the Quality of a Jam Based on Grapefruit

Lagha Benamrouche, Samira*+●; Zhira, Benkaci

Département de Biologie, Faculté des Sciences, Université M'Hamed Bougara, Boumerdès 035000, ALGÉRIE

ABSTRACT: *This work consists of studying the influence of the desamerization of the albedo on the composition, the antioxidant potential, and the sensorial quality of the jam, based on the grapefruit. Salt, heat, and water are considered driving elements in the operation of desamerization process. The desamerization was carried out by different concentrations of NaCl relative to the fresh weight of the fruit (0.3125%, 0.625%, 1.25% 2.5%, and 5 %). The result of the various analyzes shows that the desamerization does not influence the rate of sugars and pectins, decreases the titratable acidity and the protein contents, and increases the ash contents. With regard to antioxidants, the results show that desamerization decreases vitamin C levels, carotenoids, and phenolic compounds. Concerning the sensory analysis of the jams, the results show that the salt significantly reduces the bitterness of the jams. The hedonic analysis shows that the tasters preferred significantly the desamerized jam NaCl 5% to all the other samples.*

KEYWORDS: *Grapefruit, jam; Desamerization; Composition; Antioxidant activity; Sensory analysis.*

INTRODUCTION

The large *Rutaceae* family includes trees called citrus. In international conventions, we group under the term citrus certain numbers of species of the genus *Citrus* which includes: oranges, easy peelers (mandarins, clementine, kumquats, bigarade, ... etc.), lemon and lime (lemon green), grapefruit and pomelo [1].

Citrus fruits are eaten mostly raw or in juice form because of their nutritional and antioxidant properties. The most known antioxidants are carotenoids (especially β-carotene), ascorbic acid, tocopherols (vitamin E), and polyphenols. These include flavonoids, tanins, and phenolic acids [2]. Citrus fruits include grapefruit (*Citrus maxima* L.); it is citrus rarely consumed fresh because it is very acidic, its juice is used for the preparation of cocktails, jams, and marmalades, and its peels are used for the preparation of candied fruit mixes.

Grapefruit peels are characterized by their high content of dietary fiber (pectin, cellulose, and polysaccharides), minerals, vitamins, and secondary metabolites with significant antioxidant potential (carotenoids, essential oils, and phenolic compounds). The presence of certain flavonoids (Neohesperidine, Naringin, ...) in its peels gives the fruit a bitter taste, which is felt in the jam preparations based on this fruit and limits its uses [3].

Bitterness is a characteristic of the taste of many citrus species and therefore constitutes an advantage

*****To whomcorrespondenceshouldbeaddressed.
+E-mail:Laghasamira@gmail.com & s.lagha@univ-boumerdes.dz
● OtherAddress:Laboratoire de Recherche Technologie Douce, Valorisation, Physicochimie des Matériaux Biologiques et Biodiversité, Faculté des Sciences, Université UMB, Boumerdès 35000, ALGÉRIE
1021-9986/2022/1/109-120 12/$/6.02

or a disadvantage depending on the quality sought. The slight bitterness is an advantage for the preparation of tonic drinks with a therapeutic effect. However, the exaggerated bitterness of canneries is considered a serious disadvantage for their marketing. There are not many processes of desamerization of the juice, already bitter or at risk of becoming bitter by the presence of precursors. According to *Dupaigne* [4], dialysis makes it possible to modify the composition of citrus juices by removing certain constituents; the simplest constituents pass first (metals, organic acids), while the bitter constituents have too high a molecular weight. Selective absorption, by polyamide powders, has been used in clear juices to decrease the polyphenol content of the juice and thus correct astringency. According to *Dupaigne*[5], the desamerisation of citrus products by the enzymatic route makes it possible to partially hydrolyze bitter compounds into residues that are hardly bitter or absolutely tasteless; but this action is often accompanied by unintended effects on fruit products, due to the pectolytic or oxidasic power of the enzyme mixture used. The use of more specific enzymes such as hesperidinase and naringinase allows better control of their effects.

According to Huet [6, 7], bitter substances are much more abundant in inedible parts, such as albedo or mesocarp, than in juice cells. In this context, we have tried to remove the bitter taste from the peel, taking inspiration from the desamerization of olives by salt brine. The objective of our work is to study the influence of the desamerization of mesocarp on the composition, the antioxidant potential, and the sensorial quality of the grapefruit jam.

EXPERIMENTAL SECTION

Collection of samples

Grapefruit (*Citrus maxima* L.) was harvested in the Boumerdes region (regions located Northeast of Algiers, Algeria). Harvesting was done randomly from several trees belonging to the same variety during the month of February 2019.

White sugar (99.9% purity) SKOR brand produced by CEVITAL and iodized refined salt (99.9% purity) produced by ENASEL were purchased from the market.

Desamerization of peels and preparation of jams

Desamerization

The desamerization of the peels is carried out according to the modified *Lagha-Benamrouche et al.* [8] protocol. Salt, heat, and water are considered driving elements in the operation of desamerization process. In this study the salt factor was variable; five salt levels were fixed during this operation. They correspond to the five percentages: 0.3125, 0.625, 1.25, 2.5, and 5% of salt taken according to the weight of the fruit (which corresponds to the following salt concentrations: 20, 10, 5, 2.5, and 1.25 g NaCl/L of water for 406± 13.25g of fruit or 200 ± 10.13g of peels).

The peels of the fruit are cut into pieces and then immersed in one liter of saltwater for 4 hours and then preheated with the salt for five minutes after boiling. After each preheating, a fresh salt solution would replace immediately the heated solution. The operation is repeated 4 times at 4hour intervals. The last preheating is done in water without salt, thrice, to eliminate the auxiliary. The experiment is repeated 3 times for each concentration of salt.

Cooking

The drained peel and the cleaned fruit quarters are cut into small pieces and the seeds are put in a small muslin bag. Weigh the fruits and take the same weight of water and 1.5 weights of sugar to prepare the syrup. The fruits and the small muslin are added and the whole is cooked for 45 to 50 minutes. During the boiling, temperature and sugar concentration was checked. This treatment is stopped when the concentration reaches 60–65°Brix using a refractometer [8].

Chemical composition and physicochemical parameters

Chemical composition and some physicochemical parameters were analyzed (moisture content and solids content [9], pH, and titratable acidity [10]). The total sugar content was determined according to the method of *Dubois et al.* [11], the reduction of Fehling's liquor by sugars makes it possible to determine the reducing sugars, and the hydrolysis of the defecated solution in acidic and hot medium allowed us to determine the total sugars (reducing sugars+ hydrolysable sugars) and to deduce indirectly the rate of non-reducing sugars (total sugars-reducing sugars) [12].

The pectin content of the jams is determined according to the protocol described by *Multon* [13]. The proteins were determined according to the method of *Bradford* [14] and the ash content is determined by the destruction of any organic matter under the effect of the high temperature (550°C for 3 to 5 hours) and the obtaining of a white or greyish-white powder [15]. The determination of the Na^+ ion was carried out by Atomic Absorption Spectrophotometry (AAS) [16] while the determination of chlorides was carried out by the method of Charpentier Volhard described by ISO [17].

Antioxidants and antioxidant activity

Antioxidants

The ascorbic acid content is determined according to the method *Tillman's* [18]. The carotenoid contents are determined according to the modified AOAC (1997) method (cited by *Rodriguez-Amaya and Kimura* [19]).

As regards the phenolic compounds, 10 g of jam are extracted by maceration with 100 mL of methanol-water (800:200, V/V) at room temperature for 24 hours with magnetic stirring. The extract is filtered and then concentrated in an oven with aeration at 40°C until complete evaporation of the organic solvent and then reconstitute in pure methanol. Total polyphenols are quantified according to *Meyers et al.* [20], and the condensed tanins are determined by the vanillin method described by *Ba et al.* [21]. The contents of hydrolysable tanins are determined according to the method of *Mole and Waterman* [22].

The contents of flavonols and flavonoids are respectively determined according to *Kumaran and Karunakaran* [23] and *Bahorun et al.* [24] by direct dosing with aluminum chloride.

Antioxidant activity

In this study, the antioxidant activity of jams was evaluated using two methods: the reducing power (potassium ferricyanide method [25]) and the scavenging activity of the free radical DPPH [26]. Quercetin and gallic acid were used for comparison.

Sensory analysis

We carried out a sensory evaluation in order to classify the jams in order of bitterness intensity and to determine the presence or absence of significant differences in the degree of bitterness appreciation. We applied the multiple pair-wise comparisons of sums of ranks to determine which pairs of samples differ from each other. We also applied a hedonic scoring test to assess the consumer's degree of appreciation of the product.

(1) Grading test

The subject's task (35 trained subjects) consists in presenting him with a series of coded jams and asking him to classify them in order of intensity of bitterness. The samples are presented simultaneously by increasing (or decreasing) the intensity of the analyzed characteristics [27].

(2) Hedonic test

We use categories ranging from « likes a lot» to « do not like at all» through «neutral» with a variable number of intermediate categories. For each sample, the tasters select the category corresponding to their degree of appreciation. Compared to the classification test, it has the advantage of not requiring the simultaneous evaluation of all the products studied, but it supposes a good sensory memory of the scale of notation. Codified products are presented to a panel of 35 subjects. Each subject receives the samples in cups coded with three digits. The order of presentation of samples is random [27].

Statistic study

Experiments were conducted in three parallel measurements and results were expressed as mean ± Standard Deviation (SD).The statistical analysis is carried out using the software STATISTICA 5.5. For the biochemical and antioxidant results, we analyzed the one-factor variance followed by a Tukey HSD Test.

For the results of the sensory analysis, we applied the test of multiple comparisons in pairs of the sums of the rows. For the results of the hedonic analysis, the categories are converted into numerical notations ranging from 1 to 9, where 1 corresponds to "does not like at all" and 9 "loves a lot". The scores for each sample are presented in tabular form and analyzed by means of the variance analysis.

RESULTS AND DISCUSSIONS

Physicochemical analyzes

The physicochemical characteristics of the jams analyzed are illustrated in Table 1. The pH did not differ significantly ($P>0.05$) from one jam to another; it ranges

Table 1: Effect of desamerization on the physicochemical characteristics of jams.

Jams	pH	Acidity(g CAE /l)	Brix (%)	Moisture (%)
Bitter	2,92± 0,015[c]	35,22±3,20[a]	65,33±0,289[ab]	33,000±0,793[c]
DJ NaCl 0,3125%	3,05±0,015 [a]	28,15±2,01[b]	64,50±0,50[cd]	34,045±0,491[b]
DJ NaCl 0,625%	2,98±0,047 [abc]	29,08±3,85[b]	63,83±0,289[d]	34,526±0,603[a]
DJ NaCl 1,25%	3,00±0,052[ab]	29,49±1,85[b]	65,00±0,00[bc]	33,489±0,465[bc]
DJ NaCl 2,5%	3,00± 0,070[ab]	29,21±0,69[b]	66,00±0,50[a]	32,811±0,614[c]
DJ NaCl 5%	2,95±0,012[bc]	28,81±3,21[b]	65,50±0,50[ab]	33,609±0,463[bc]

CAE: Citric Acid Equivalents, DJ: Desamerized Jam.
Values with the same letter in each column show no significant difference (P> 0.05). Results are ranked in descending order: a> b> c> d.

from 2.92 to 3.05. These results comply with the standard required by the Codex Alimentarius (pH≤3.5). At a pH of 3.3, the pectin molecules do not repel because they are no longer loaded; it is gelling. Our results are higher than those found by *Lagha-Benamrouche et al.* [8]. The latter reported pH values between 2.80 and 2.87 for the bitter orange jam and its desamerized jams with almost the same process undertaken in this study. This can be explained by the nature of the fruit and its degree of acidity.

Titratable acidity provides information on the number of organic acids present in a sample. From our results, we find that the bitter jam is significantly (p≤0.05) considered to be the most acidic (35.22g/L). The acidity decreases with the desamerization and does not differ significantly (P>0.05) between the desamerized jams. It ranges from 28.15 g/L to 29.49 g/L. Our results are consistent with those of *Lagha-Benamrouche et al.* [8], the latter also note a decrease in titratable acidity during desamerization from 34.33g/L for bitter jam of bigarade to 24.33- 27.84 g/L for desamezised jams. The decrease in titratable acidity can be explained by the entrainment of organic acids with the water of desamerization [8].

Brix levels of jams are generally similar (p>0.05), they are between 63.83 to 66.00%. (Table 1). This can be explained by the good practice and the precision in the measurements during the preparation of the jams. Sugar adds consistency and bulk to the product and also promotes gelling [28].

The results shown in Table 1, show overall that the moisture does not vary significantly (P> 0.05) between jams, except for DJ NaCl 0.625%, which seems to be significantly (p≤0.05) the more humid. Moisture has a direct relationship with the shelf life of jams; the more moist the jam, the longer its shelf life [29].

Chemical composition of jams

The chemical composition of the jams studied is illustrated in Table 2. The ash contents vary significantly (p≤0.05) between the jams. The contents increase proportionally with the increase of the salt concentration used for the desamerization. Thus, the highest content was found for DJ NaCl 5% and the lowest content was found for DJ NaCl 0.3125%. This increase may be due to the dissolution of NaCl in the medium thus giving the Na^+ and Cl^- ions, which are mineral salts. Our result is consistent with that of *Lagha-Benamrouche et al.* [8] and supports this proportionality. The results of the determination of the Na^+ and Cl^- ions confirm this result (the contents go from 1.273 ± 0.033 to 1.612 ± 0.087 mg /100g for the Na^+ ion and from 2.58± 0.025 to 2.91 ± 0.057mg/100g for the Cl^- ion, respectively for DJ NaCl 0.3125% and DJ NaCl 5%). Salt is necessary for the proper functioning of the organism (4g/day) but overconsumption (more than 12 g/day) could be harmful, thus promoting high blood pressure and the development of cardiovascular diseases. The European Food Safety Authority (EFSA) recommends a maximum intake of 6 g of salt (2400 mg of sodium) per day, while the World Health Organization (WHO) sets a target of 5 g of salt (2000 mg sodium) maximum [30].

The results in Table 2 show no significant differences (P> 0.05) in the pectin content of the jams. The contents vary from 1.525 to 1.560%. The results show that the desamerization does not seem to affect the pectin content of the jams. This result is in agreement with that of Lagha-Benamrouche et al. [8]. The comparison of our data with those of these same authors shows that the pectin content of grapefruit jam is twice as high as that of bigarade (1.540% to 1.560% against 0.55% to 0.59%). This difference in results can be justified by the thickness of the

Table 2: Effect of desamerization on the chemical composition of jams.

	Bitter	DJ NaCl 0,3125%	DJ NaCl0,625%	DJ NaCl 1,25%	DJ NaCl 2,5%	DJ NaCl5%
Ashes(g/100g FM)	0,18 ^{f}±0,005	0,26 ^{e}±0,004	0,34 ^{d}±0,008	0,37 ^{c}±0,002	0,47 ^{b}±0,003	0,64 ^{a}±0,008
Na^+(mg/100g)	1,058^{f}±0,018	1,273^{e}±0,033	1,339^{d}±0,017	1,472^{c}±0,008	1,537^{b}±0,011	1,612^{a}±0,087
Cl^-(mg/100g)	2,373^{f}±0,011	2,589^{e}±0,025	2,653^{d}±0,019	2,781^{c}±0,011	2,824^{b}±0,008	2,921^{a}±0,057
Pectins(g/100 g FM)	1,540 ^{a}±0,026	1,543 ^{a}±0,021	1,557 ^{a}±0,02	1,560 ^{a}±0,170	1,525 ^{a}±0,048	1,550 ^{a}±0,044
Proteins(g BSA E /100 g FM)	0,658 ^{a}±0,017	0,589 ^{b}±0,008	0,507 ^{c}±0,004	0,423 ^{d}±0,006	0,363^{e}±0,004	0,299 ^{f}±0,002
Total sugars(g G E /100g FM)	138,056 ^{a}±6,310	136,389 ^{ab}±3,368	132,222 ^{ab}±1,273	128,333 ^{b}±5,833	126,389 ^{b}±6,028	114,722 ^{c}±0,962
Reducing sugars(g GE/100 g FM)	38,637 ^{a}±0,765	37,840 ^{a}±1,194	37,821 ^{a}±0,555	37,152 ^{a}±2,514	37,353 ^{a}±0,706	38,153 ^{a}±0,998
Non-Reducing sugars(g/100 g FM)	31,912 ^{a}±4,950	33,162 ^{a}±3,755	30,385 ^{a}±1,551	28,086 ^{a}±1,419	31,145 ^{a}±5,806	33,384 ^{a}±3,410

BSA E: Bovin Serum Albumin Equivalents, DJ: Desamerized Jams,FM: Fresh Matter, GE: Glucose Equivalents.Values with the same letter in each row show no significant difference (P>0.05). Results are ranked in descending order: a> b> c> d> e> f.

albedo layer of grapefruit compared to that of bigarade (where the pectins are mainly located).

Protein levels differed significantly ($p \leq 0.05$) between jams. They range from 0.299 g/100g (DJ NaCl 5%) to 0.658 g/100g (bitter jam). The decrease in the protein content of jams is proportional to the increase in the salt concentration used for desamination. This decrease can be explained by the precipitation of proteins in the presence of high salt concentration. NaCl has the effect of lowering the ionic forces between the protein structures; the higher the NaCl content, the more the protein bonds become weakened (where the NaCl will "take its place" by the ionic interactions) and the protein loses its solubility and thus precipitates [31].

The comparison of our results with those obtained by *Lagha-Benamrouche et al.* [8] for bigarade jam (0.485 g/100g for DJ NaCl 2.5% to 0.98 g/100g for bitter jam), confirms our result (decrease in protein levels by desamerization) and also shows that bigarade jam is richer in protein than grapefruit jam. This high protein content may be related to the richness of the fruit in these compounds. However, the protein content of fruits decreases during their transformation. *Pavlova et al.* [32] report a decrease in the protein content of the pulp when processed into the jam from 1.76 to 0.48% for raspberry and from 1.82 to 0.27% for peach.

The total sugar content did not differ significantly (P>0.05) between bitter jam, DJ NaCl 0.3125% and DJ NaCl 0.625%, and between DJ NaCl 1.25 and DJ NaCl 2.5%. This is the DJ NaCl 5% which contains significantly ($p \leq 0.05$) less total sugars compared to other jams. The results of the reducing sugars assay (Table 2) indicate that the contents do not differ significantly (P>0.05) between the jams. The contents range from 37.152 g/100g (DJ NaCl 1.25%) to 38.637g/100g (bitter jam). The same result is observed for non-reducing sugars. The contents range from 28.086 g/100g MF (DJ NaCl 1.25%) to 33.384 g/100g MF (DJ NaCl 0.3125%). The reducing and non-reducing sugars contents of our jams are higher than those found by *Lagha-Benamrouche et al.* [8] for bigarade jams (20.53 to 35.02 g/100g and 26.22 to 13.34 g/100g, respectively). This can be justified by the high total sugar content of our jams and by the inversion of sucrose into glucose and fructose (reducing sugars) during cooking favored by the acidity of jams [33].

Antioxidant content

The antioxidant contents of the jams studied are illustrated in Table 3. The results of the assay show that the contents of phenolic compounds decrease significantly ($p \leq 0.05$) between jams.

Table 3: Effect of desamerization on the antioxidants of jams.

	Bitter	DJ NaCl 0.3125%	DJ NaCl 0.625%	DJ NaCl1.25%	DJ NaCl 2.50%	DJ NaCl5%
Total phenol (g GAE/100g FM)	56,956 ^{a}±8,326	52,652 ^{ab}±15,931	36,842 ^{b}±18,470	15,937 ^{c}±4,799	13,267 ^{c}±2,334	8,687 ^{c}±2,689
Flavonoids (g QE /100g FM)	0,526 ^{a}±0,076	0,416 ^{b}±0,017	0,383 ^{bc}±0,008	0,325 ^{c}±0,009	0,244 ^{d}±0,017	0,212 ^{d}±0,007
Flavonols (g QE /100g FM)	0,573 ^{a}±0,115	0,409 ^{b}±0,014	0,410 ^{b}±0,017	0,359 ^{bc}±0,009	0,275 ^{cd}±0,003	0 ,235 ^{d}±0,002
Proantho-cyanidins (g CE/100g FM)	4,264 ^{a}±0,069	1,900 ^{b}±0,023	1,870 ^{b}±0,030	1,564 ^{c}±0,041	1,447 ^{d}±0,036	1,088 ^{e}±0,009
Hydrolyzable tanins (g TAE/100g FM)	0,398 ^{a}±0,195	0,185 ^{b}±0,002	0,184 ^{b}±0,002	0,156 ^{b}±0,002	0,154 ^{b}±0,002	0,126 ^{b}±0,002
Carotenoids (mg BCE/g FM)	7,125 ^{a}±0,460	5,406 ^{b}±0,610	2,103 ^{c}±0,312	1,677 ^{cd}±0,060	1,582 ^{cd}±0,026	1,169 ^{d}±0,051
Vitamine C (mg AAE/100g FM)	2,919 ^{a} ±0,051	2,767 ^{a}±0,111	2,611 ^{a} ±0,226	2,257 ^{a}±0,143	1,804 ^{b}±0,159	1,584 ^{b}±0,289

AAE: Ascorbic Acid Equivalents, βCE: β carotene Equivalents, CE: Catechin Equivalents, FM: fresh matter, DJ: Desamerized Jams, GAE: Gallic Acid Equivalents, QE: Qercetin Equivalents.
Values with the same letter in each row show no significant difference (P> 0.05). Results are ranked in descending order: a> b> c> d.

The decrease is proportional to the increase in the salt concentration used for desamerization. Levels increased from 56.956 mg GAE/g for bitter jam to 8.687 mg GAE/g for DJ NaCl 5% for total phenols, 0.526 mg QE/g to 0.212 mg EQ/g for flavonoids and 0.573 mg EQ/g to 0, 235 mg EQ/g for flavonols. For tanins the levels increased from 4,264 mg EC/g to 1,088 mg EC/g and from 0,398 mg TAE/g to 0,126 mg TAE/g for proantho-cyanidines and hydrolyzable tanins, respectively.

Our result is in agreement with that of *Lagha-Benamrouche et al.* [8], these latter also note this decrease which can be explained by the fact that the phenolic compounds are water-soluble; the presence of salt causes their entrainment, by the phenomenon of osmosis, with the mesocarp wash water during the desamerization. Despite the loss of polyphenols by the dimerization process, mesmerized grapefruit jam remains a good source of phenolic compounds. It contains more total polyphenols than strawberry and orange jam (8.687 to 52.652g GAE/100g versus 0.7 to 0.75mg QE/100g for strawberry jam and 44mg GAE/100g for jam orange, respectively, according to *Danijela et al.* [34] and *Rababah et al.* [35]).

Carotenoid contents (Table 2) did not vary significantly (P> 0.05) between jams, except for bitter jam, DJ NaCl 0.3125%, and DJ NaCl 0.625%. Overall, our results show that the carotenoid content decreases with increasing salt concentration used for desamerization. Carotenoids are fat-soluble; they are often bound to proteins or other molecules [36]. The precipitation of proteins by the salt can lead to the loss of carotenoids which may explain this decrease. The carotenoid contents of grapefruit jams are much higher than those found by *Lagha-Benamrouche et al.* [8] for jams of bigarade (7.125 to 1.169 mg βCE/g against 1.42 to 0.21 mg βCE/g, respectively). This can be explained by the richness of grapefruit in these compounds.

The jams analyzed have vitamin C contents between 2.919 and 1.584 mg/100 g. *Lagha-Benamrouche et al.* [8] report vitamin C levels between 17.19 to 33.17 mg / 100 g for bigarade jams. This can be explained by the richness of bigarade peels on vitamin C compared to grapefruit and other fruits. *Lagha-Benamrouche* [37] reports vitamin C levels of bigarade peels in the order of 9.12 mg AAE/g FM.

Antioxidant activity

Analysis of the reducing power of the extracts at the concentration of 1 mg/mL leads to absorbances between 0.845 and 0.416 (Fig. 1).

As can be seen, it is the bitter jam that shows the highest absorbances and therefore the most pronounced reductive power. On the basis of the reduction capacity, the jams are classified in descending order of following: bitter jam> DJ NaCl 0.3125%> DJ NaCl 0.625%> DJ NaCl 1.25%> DJ NaCl 2.5%> DJ NaCl 5 %. These results also show that the reducing power of jams is significantly higher ($p \leq 0.05$) than that of standards tested at 0.02 mg/mL: quercetin and gallic acid (respective absorbances: 0.447 and 0.29), except for the DJ NaCl 2.5% which has

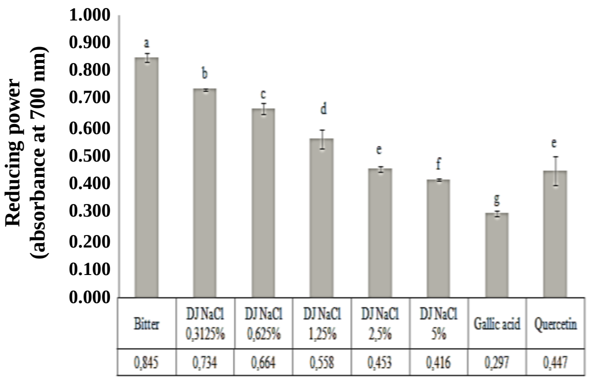

Fig. 1: Reducing power of jams at 1 mg/mL, quercetin and gallic acid at 0.02 mg/mL.

DJ: Desamerized Jams, FM: Fresh Matter. Values bearing the same letter showed no significant difference (P>0.05). The results are sorted in decreasing order: a > b > c > d > e > f > g.

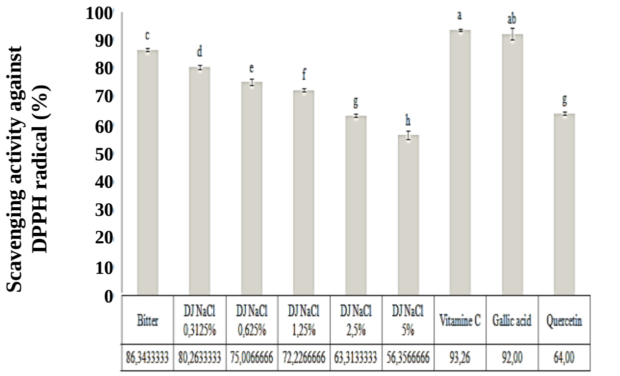

Fig. 2: Mean antioxidant activity against DPPH radical of jams and vitamin C at 1 mg/mL and standards (gallic acid and quercetin) at 40µg/mL.

DJ: Desamerized Jams, DPPH: 1,1-diphenyl 1-2-picrylhydrazyl. Values bearing the same letter showed no significant difference (P>0.05). The results are sorted in decreasing order: a > b > c > d > e > f > g > h.

a similar reduction capacity (p> 0.05) to that of quercetin which is significantly (p≤0.05) more reductive than the DJ NaCl 5%.Our experimental data show that grapefruit jam reduction capacities are slightly higher than those obtained by Lagha-Benamrouche et al. [8] for jams of bigarade (absorbances between 0.805 and 0.556).

The values of the anti-radical activity for the extracts studied (at a concentration of 1 mg/mL) vary between 86.34% and 56.35% (Fig. 2). Bitter jam has the highest anti-radical activity. The latter is significantly lower (p≤0.05) than those of vitamin C and gallic acid but significantly (p≤0.05) higher than that of quercetin, which shows an antioxidant activity similar to DJ NaCl 2.5%. Depending on the anti-radical activity, the jams are classified in following order: bitter jam> DJ NaCl 0.3125%> DJ NaCl 0.625%> DJ NaCl 1.25%> DJ NaCl 2.5%> DJ NaCl 5%. These results show that the antioxidant potential is inversely proportional to the salt concentration used for the desamerization. This can be explained by the loss of compounds with antioxidant potential as already observed during their quantification. The comparison of our results with the bibliographic data leads us to say that grapefruit jam has greater antioxidant activity than that of bigarade which was 22.48% to 56.23% [8] and to that of cherry, apricot, and fig (10.06%, 9.95%, and 8.96%, respectively), according to *Rababah et al.* [35].

Correlation

The coefficients of correlation between the antioxidant capacities of the jams and the contents of bioactive compounds are illustrated in Table 4.Significant positive correlations (p≤0.05) were observed between the levels of bioactive compounds (polyphenols, flavonoids, flavonols, hydrolysable and condensed tanins, Vitamin C and carotenoids) and the antioxidant activities evaluated by the methods of reducing power and the inhibition of the DPPH radical (the correlation coefficients vary between 0.702 and 0.994). Similar results were observed by *Lagha-Benamrouche* and *Madani* [2] and *Lagha-Benamrouche et al.* [8].

Sensory analysis

Rankings according to the degree of bitterness

The classification of jams according to the degree of bitterness is a descriptive method. It is used to qualify product differences by establishing a "sensory profile" f or each of them. To process the data from the ranking tests first, we calculated all the differences between the sums of the ranks of the products taken from 2 to 2. Then, in a second step, we read the critical value at the intersection of the column (products) and line (subjects) on the table of Newell and Mac Farlane corresponding to risk α ≤ 5%. Any calculated difference between products equal to or greater than this critical value means that the corresponding products may be considered different.

Table 4: Correlation matrix between the levels of bioactive compounds and the antioxidant activities of jams.

	TP	F	FOL	PAC	HT	VC	Car	RP	DPPH
TP	1								
F	0,944*	1							
FOL	0,892*	0,988*	1						
PAC	0,773*	0,881*	0,926*	1					
HT	0,751*	٠,859*	0,906*	0,998*	1				
VC	0,941*	0,966*	0,929*	0,735*	0,702	1			
Car	0,923*	0,900*	0,870*	0,869*	0,858*	0,816*	1		
RP	0,970*	0,994*	0,969*	0,843*	0,819*	0,977*	0,905*	1	
DPPH	0,924*	0,979*	0,956*	0,803*	0,772*	0,983*	0,860*	0,879*	1

*TP: Total polyphenol, F: Flavonoids, FOL : Flavonol, PAC : ProAnthoCyanidins, VC: Vitamin C, Car: Carotenoids, RP: Reducing Power, DPPH :1.1-diphenyl 1-2-picrylhydrazyl, * : significant Correlation ($P < 0.05$).*

Table 5: Multiple comparisons by pair of the sums of rows for the degree of bitterness of the jams.

Samples	Effectif (n)	Sums of ranks	Differences in the ranks between the possible pairs	Critical value for p≤ 0.05 and Effective = 35 Number of products = 6	Groups
Bitter (1)	35	36	(2)-(1) = 62* (3)-(1) = 93* (4)-(1) = 88* (5)-(1)=108* (6)-(1)=162*	45	A
DJ NaCl 0.312% (2)	35	98	(6)-(2) = 100* (5)-(2) = 46* (4)-(2) = 26 (3)-(2)=31	45	B
DJ NaCl 0.625% (3)	35	129	(6)-(3) = 69* (5)-(3) = 15 (3)-(4) = 05	45	BC
DJ NaCl 1.25% (4)	35	124	(6)-(4) = 74* (5)-(4) = 20	45	BC
DJ NaCl 2.5 % (5)	35	144	(6)-(5) = 54*	45	C
DJ NaCl 5 % (6)	35	198	–	–	D

*DJ: Desamerized Jam, *: Significant at the $p \leq 0.05$ level.*

The results in Table 5 show that the calculated value for desamerized jam and bitter grapefruit jam are greater than the critical value. The difference in bitterness perceived between these jams is significant. The tasters find that the desamerized jams are perceived as less bitter ($p < 0.05$). The bitter jam is therefore classified in a group different from the others, namely the group (A).

The multiple paired comparisons: (DJ NaCl 0.312% - DJ NaCl 2.5%) and (DJ NaCl 2.5% - DJ NaCl 5%) shows that the value calculated for each pair is greater than the critical value. The tasters find that these jams are different ($p<0.05$) from the point of view of bitterness and classify them into different groups according to the intensity of bitterness:

Group B	Group C	Group D
(DJ NaCl 0.312%)	(DJ NaCl 2.5%)	(DJ NaCl 5%)
← More bitter		Less bitter

Table 6: Results by category of the hedonic test.

Tasters	Desamerized jams (processing)					Total tasters	Average tasters
	DJ NaCl 0.3125%	DJ NaCl 0.625%	DJNaCl 1.25%	DJ NaCl 2.5%	DJ NaCl 5%		
2		7	8	1		16	3.2
3			1	5		6	1.2
5			7			7	1.4
6		2				2	0.4
7	4		3			7	1.4
8			4			4	0.8
10	3		5	6	6	20	4
12		3				3	0.6
15		4				4	0.8
18	2					2	0.4
20				7		7	1.4
25					8	8	1.6
Total treatment	74	122	157	217	260		
Grand total						86	
Average treatment	2.1	3.5	4.5	6.2	7.4		

Highest score = 9 (Likes enormously), Lowest score = 1 = Disliked, DJ: Desamerized Jam.

For both jams: DJ NaCl 0.625% and DJ NaCl 1.25%, the calculated value is below the critical value. These two jams are placed in the same group. The multiple paired comparisons show that DJ NaCl 0.625% and DJ NaCl 1.25% jams did not significantly differ from DJ NaCl 0.3125% and DJ NaCl 2.5% jams. Both jams DJ NaCl 0.625% and DJ NaCl 1.25% are thus placed in an intermediate group between that of DJ NaCl 0.3125% and DJ NaCl 2.5%; either the BC group.

Hedonic notation test

The descriptive categories have been converted into numerical notations; the results by category of the hedonic test are given in Table 6. The coefficients F for treatment and tasters were calculated by dividing the respective AS (Average Square) values by the AS of the error. The calculated F coefficients must exceed the F coefficients in the F distribution table (significance at $p \leq 5\%$).

The coefficient F calculated for the treatment (F 29.9) exceeds the coefficient of the table (F 2.37), it was concluded that there is a significant difference ($p \leq 0.05$) between the averages of the hedonic results for the five desamerized jams. The results also indicate that the coefficient calculated for the tasters (F 14.67) exceeds the coefficient of the table (F 1.46). Such a result thus reveals a significant effect attributable to the tasters.

Analysis of the variance indicated that there were significant differences between the five desamerized jams. In order to determine which jam samples differ significantly from each other, a multiple comparison test was performed. To compare the five averages, we calculated the value of the differences for a range of 5.4, 3, and 2 averages with the following equation:

$$\text{deviation value} = Q\sqrt{\frac{AS(E)}{t}} \tag{1}$$

Where «t» is the number of individual responses used to calculate each average.

With: deviation value = Q (0.15).

The values of Q are given from the table of critical values for the Duncan multiple comparisons test ($p \leq 0.05$). When the mean difference is greater than the deviation value, the difference between these two means is, therefore, significant. The averages followed by the different letters differed significantly at the 5% probability level.

Desamerized jams	DJ NaCl0.3125%	DJ NaCl0.625%	DJ NaCl1.25%	DJ NaCl2.5%	DJ NaCl5 %
Average treatment	2.1(e)	3.5(d)	4.5(c)	6.2 (b)	7.4 (a)

Table 7: Paired comparisons of average treatments for the degree of appreciation of jams.

Sampls	Differences in means between the possible pairs	Deviation value at $p \leq 0.05$	Groups
DJ NaCl 5% (1)	(1)-(5) = 5.3* (1)-(4) = 3.2* (1)-(3) = 2.9* (1)-(2) = 1.2*	0.46 0.46 0.46 0.46	A
DJ NaCl 2.5% (2)	(2)-(5) = 4.1* (2)-(4) = 2.7* (2)-(3) = 1.7*	0.45 0.45 0.45	B
DJ NaCl 1.25% (3)	(3)-(5) = 2.4* (3)-(4) = 1*	0.43 0.43	C
DJ NaCl 0.625% (4)	(4)-(5) = 1.4*	0.41	D
DJ NaCl 0.3125% (5)	-	-	E

*DJ: Desamerized jams, *: Significant at $p \leq 0.05$, A, B,C,D, and E: are the homogeneous groups.*

The tasters favored the 5% DJ NaCl 5%, which they found less bitter, the majority of the subjects gave it a score of 8. The tasters favored the DJ NaCl 2.5 % compared to other jams. The results also show that the tasters were indifferent to DJ NaCl 1.25% and they did not like all the DJ NaCl 0.625% and the DJ NaCl 0.3125 they find that they are very bitter (Table 7).

Our results converge with those of Lagha-Benamrouche et al. [8]. These later have also found that salt significantly reduces the bitterness of jams. However hedonic analysis shows that grapefruit jam is bitterer than that of bigarade. According to Lagha-Benamrouche et al. [8], the tasters preferred significantly the DJ NaCl 0.625% to all the other samples.

CONCLUSIONS

The objective of this work is to valorize the grapefruit in the form of the jam by desamerization its peels, a source of bitterness. Five salt levels were fixed during this operation; they correspond to the five percentages (0.312% -0.625% -1.25% -2.5% and 5%) of salt taken as a function of the weight of the fruit.

The results of the physicochemical parameters and the chemical composition of the jams show that the desamerization does not affect the rate of pectins and sugars but decreases significantly ($p \leq 0.05$) the acidity and the rate of proteins increase significantly ($p \leq 0.05$) in the ash content.

The results of the antioxidant assay show that desamerisation significantly decreases ($p \leq 0.05$) carotenoid, Vitamin C, and phenolic contents. On the basis of reduction capacity (ferricyanide method) and anti-radical capacity (DPPH method), jams are classified in following order: bitter jam> 0.312% NaCl CD> 0.625% NaCl CD>CD NaCl 1.25%> CD NaCl 2.5%> CD NaCl 5%. Significant positive correlations ($p \leq 0.05$) with high correlation coefficients (0.735 and 0.994) were observed between the levels of bioactive compounds (polyphenols, flavonoids, flavonols, hydrolyzable and condensed tanins, vitamin C and carotenoids) and the antioxidant activities.

Concerning the sensory analysis of the jams, the results show that the salt significantly reduces the bitterness of the jams. The hedonic analysis shows that the tasters preferred significantly the NaCl 5% to all the other samples.

Abbreviations

AAE	Ascorbic Acid Equivalents
βCEβ	carotene Equivalents
BSA E	Bovin Serum Albumin Equivalents

CAE	Citric Acid Equivalents
CE	Catechin Equivalents, DJ: Desamerized Jams, DPPH:1.1-diphenyl -2-picrylhydrazyl
FM	Fresh Matter
GAE	Gallic Acid Equivalents
GE	Glucose Equivalents
QE	Qercetin Equivalents

Acknowledgments

The authors are grateful to the Algerian Ministry of Higher Education and Scientific Research for the financial support.

Received : Jul. 20, 2020 ; Accepted : Oct. 12, 2020

REFERENCES

[1] Gautier M. La culture fruitière, "Les Production, Les Productions Fruitières". Tec & Doc, 2nd ed.; Paris, pp. 582(1993).

[2] Lagha-Benamrouche S., Madani K., Phenolic Contents and Antioxidant Activity of Orange Varieties (Citrus sinensis L. and Citrus aurantium L.) Cultivated in Algeria: Peels and Leaves. *Ind. Crop. Prod.*, **50**: 723–730 (2013).

[3] Susser A., "Great Citrus Book: A Guide with Recipes, Ten Speed Press, Berkeley", CA, US (1997).

[4] Dupaigne P., Klaversuche an Getrànken mit Polyamidpulver, *Flitssiges Obst*, **31(10)**: 504-510 (1964).

[5] Dupaigne P., La Désamerisation Des Produits D'agrumes, en Particulier Par Voie Enzymatique, *Fruits.*,**24 (9-10)**:445-451(1969).

[6] Huet R., Influence du Mode D'extraction Sur L'amertume Du Jus De Pomélo,*C. Rech.Agron.*, **11**: 83-92 (1961_a).

[7] Huet R., L'amertume Du Jus d' Orange Navel, *C. Rech. Agron.*, **11**:94-101 (1961).

[8] Lagha-Benamrouche S., Benaissa T., Sadoudi R., Desamerization of Bitter Jam: Biochemical and Sensory Quality, *J. Food Qual.*,**2**: 1-13 (2018)

[9] AOAC., "Official Methods of Analysis of the Association of Official Analytical Chemists", 16th Ed., Washington, DC: Association of Official Analytical Chemists (1995).

[10] AOAC., "Official Methods of Analysis of the Association of Official Analytical Chemists", 17th ed. Maryland. USA. pp.360 (2000).

[11] Dubois M., Colorimetric Method for Determination of Sugars and Related Substances, *Anal. Chem.*, **28(3)**: 350–356 (1956).

[12] Chidan Kumar C. S., Mythily R., Venkatachalapathy R., Chandraju S., Biomimic Conversion of Maida (polysaccharides) to Reducing Sugars by Acid Hydrolysis and its Estimation Using Standard Methods, *Int. Food Res. J.*, **21(2)**: 523–526 (2014)

[13] Multon J.L.,"Techniques D'analyses et de Contrôle Dans Les Industries Agroalimentaires", Ed. Tec et Doc, Lavoisier,Vol IV. pp. 121-137 (1991)

[14] Bradford M.M., A Rapid And Sensitive Method for the Quantification of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding, *Anal. Biochem.*,**72**: 248-254 (1976)

[15] AOAC., "Official Methods of Analysis of the Association of Official Analytical Chemists", 17thed. Gaithersburg, USA. pp. 480 (2002).

[16] ISO., "International Organization for Standardization, Animal Feeding Stuffs—Determination of Water-Soluble Chlorides Content", Part 1(6495): Titrimetric Method (2015).

[17]ISO., "International Organization for Standardization, -Water Quality — Determination of Sodium and Potassium", Part1(9964): Determination of Sodium by Atomic Absorption Spectrometry (1993).

[18] AOAC., "Official Methods of Analysis of the Association of Official Analytical Chemists", 15th ed., Association of Official Analytical Chemists, Arlington VA, pp. 1058-1059 (1990)

[19] Rodriguez-Amaya D.B., Kimura M., "HarvestPlus Handbook for Carotenoid Analysis, Copyright HarvestPlus". USA. pp. 1-57 (2004). (AOAC.,Official Methods of Analysis of the Association of Official Analytical Chemists, Washington, 16th ed. DC, USA, (1997).

[20] Meyers K. J., Watkins C. B., Pritts M. P., Liu R. H., Antioxydant and Antiproliferative Activities of Strawberries, *J. Agric. Food Chem.*, **51(23)**: 6887–6892 (2003)

[21] Ba K., Tine E., Destain J., Cisse N., Onart P., Etude Comparative Des Composés Phénoliques, du Pouvoir Anti-Oxydant De Diff érentes Variétés de Sorgho Sénégalais Et Des Enzymes Amylolytiques De Leur Malt. *Biotechnol. Agron. Soc. J.*, **14**: 131–139 (2010).

[22] Mole S., Waterman P.G., A Critical Analysis of Techniques for Measuring Tanins in Ecological Studies. II. Techniques for Biochemically Defining Tanins. *Oecologia.*, **72**: 148-156 (1987)

[23] Kumaran A., Karunakaran R. J., Activity-Guided Isolation and Identification of Free Radical-Scavenging Components from an Aqueous Extract of Coleus Aromaticus. *Food Chem.*,**100 (1)**: 356–361 (2007).

[24] Bahorun T., Gressier B., Trotin F., Brunet C., Dine T., Luyckx M., Vasseur J., Cazin M., Cazin J.C., Pinkas M., Oxygen Species Scavenging Activity of Phenolic Extracts from Hawthorn Fresh Plant Organs and Pharmaceutical Preparations, *Arzneim Forsch.*, **46**: 1086–1108 (1996).

[25] Oyaizu M., Studies on Product of Browning Reaction Prepared from Glucose Amine, *JPN. J. Nutr.*, **44(6)**: 307–315 (1986).

[26] Brand-Williams W., Cuvelier M. E., Berset C., Use of Free Radical Method to Evaluate Antioxidant Activity, *LWT – Food Sci.Technol.*, **28(1)**: 25–30 (1995).

[27] Watts B. M., Ylimaki G. L., Jeffery L., Elias L.G.," Méthodes de Base Pour l'Evaluation Sensorielle des Aliments", CRDI, Ottawa, ON, Canada(1991).

[28] Oakenfull D., Gelling Agents, *Crit. Rev.Food Sci. Nutr.*, **26 (1)**: 1–25 (1987).

[29] Fellows P.J., "Food Processing Technology: Principles and Practice, Wood Head Publishing", Cambridge, UK(2000).

[30] European Food Safety Authority (EFSA). Opinion of the Scientific Panel on Dietetic Products, Nutrition And Allergies [NDA] Related to the Tolerable Upper Intake Level of Sodium. *EFSA J.*,**3(6)**: 209 (2005).

[31] Anonyme., Forum futura-sciences: "les Forums De La Science, Biologie; Précipitation Des Protéines"(2010). (http://forums.futurasciences.com/biologie/428724-precipitation proteines.htmL) (Consulted May 2018).

[32] Pavlova V., Karakashova LA., Stamatovska V., Delchev N., Necinova L., Nakov G., Menkinoska M., Blazevska T., Storage Impact on the Quality of Raspberry and Peach Jams, *Hyg. Eng. Des.*, **664**: 25-27(2013).

[33] Perrin R., Scharff J.P., "Chimie Industrielle", Ed. Masson; Paris (1979).

[34] Danijela B., Branka L., Verica D., Free Radical Scavenging Activity and Phenolic Content in Strawberry Fruit and Jam, *Agric. Conspec. Sci.*, **74(3)**: 155–159 (2009).

[35] Rababah T., Al-Mahasneh M., Aludatt M.H., Kilani I., Effect of Jam Processing and Storage on Total Phenolics, Antioxidant Activity, and Anthocyanins of Different Fruits, *J. Sci. Food Agric.*, **91(6)**: 1096–1102 (2011)

[36] REMIK N.E.,"Reponses Photoadaptatives de la Chlorophycee Haematococcus Pluvialis Flotow et Production d'astaxanthine », Thèse de Doctorat en Environnements et Écosystèmes Marins et Continentaux, Lille 1, France(1999).

[37] Lagha-Benamrouche S., "Les Composés Bio-Actifs Des Sous Produits D'orangers : Les Antioxydants Des Ecorces et Des Feuilles D'oranges", Universitaires Européennes, pp. 97 (8-613 (2019) (ISBN 978-613-9-52324-5).