Quantification of Acrylamide and Hydroxymethylfurfural in the Consumption of Algarrobin in the City of Piura-Peru

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Keywords
Acrylamide, Hydroxymethylfurfural, Algarrobin, Soluble solids.

Summary
The study found 280 ug/kg of acrylamide (carcinogenic with genotoxic potential) in experimental carob syrup samples that were cooked at a constant temperature of 110ºC; less than the 303 ug/kg of the commercial samples. Correlatively, these results indicated that the more time of exposure of solids soluble and water evaporation during a constant temperature cooking, is related to a higher content of acrylamide in carob syrup. The different levels of acrylamide contains in the carob syrup marks depends on the productive method, having a variety range from 0 ug/kg of acrylamide to 303 ug/kg. Additionally, the more concentration of solids caused by the temperature, major is the soluble solids that increase other components different than sugars which contribute to a bitterness flavor in carob syrup.

The low per capita consumption and the low frequency of carob syrup consume in the range delimited from 0.7 g/person/day contribute to not to pass the values limits of acrylamide intake. The combined presence of acrylamide and HMF (hydroxymethylfurfural) do not overcome the maximum limit consumption of acrylamide; in other words it is not dangerous (real) for the human health considering the low rate of peruvian intake.

There are some commercial samples that indicate an acrylamide result of 0 ug/kg which are probably related to an optimal technical process or the metabolization to another element that are not studied yet. On the other hand, a young person with a lower weight of 63.7 kg, do not should eat more than 25 daily portions of 42 g of carob syrup with an acrylamide content of 0.303 mg/kg (ppm); instead an adult with a 71.3 kg weight can intake 28 daily portions of carob syrup without any associated health risk to acrylamide consumption. Finally, the less contain of acrylamide in carob syrup is associated to a major daily portions of carob syrup consumption.

CAA = Amount of acrylamide in algarrobin (ug / kg) * Kg consumption of algarrobin / kg person-day

CHMFA = Amount of HMF in algarrobin (ug / kg) * Kg consumption of algarrobin / kg person-day

Objectives
Quantify the presence of acrylamide and hydroxymethylfurfural (HMF) in the consumption of algarrobina in Piura City-Peru.

Methods
The carob pod is harvested in a yellow state. The sugars of carob pod are extracted by a leaching process from the carob tree. Correlatively, it is chopped in boiling temperature in natural environmental conditions. Then, the extract is filtered and concentrated to more than 70º Brix in order to obtain soluble solids. Four samples of carob syrup (with different soluble solids) were analyzed by using ion chromatography, mass spectrophotometry and liquid chromatography to quantify the content of acrylamide and HMF. To determine the amount of acrylamide and HMF consumption in carob syrup, it was used the per capita consumption of the surveyed people, specifically the intake for an average person with 72 kg weight.

Results
For one kilogram of carob, 171.4 ml of algarrobin was obtained, with a density of 1.4 g/ml, a pH: 4.796, 4.26, 5.02 and 5.27 respectively, with a content of soluble solids of 77.07, 81.3, 74.98 and 82.6% and a per-capita consumption of algarrobin of 0.17 lt.
The content of acrylamide in the algarrobin was different in each sample: 303, 250, 83, 25 ug / kg and the content of HMF in the same samples was: 593, 431, 25.0 ug / kg.

Conclusion
The different samples of carob syrups were obtained at different concentrations of soluble solids, indicating different contents of acrylamide and HMF, being important the different thermic treatments and the degree of standardization of productive processes.

Results and Discussion

<table>
<thead>
<tr>
<th>Components</th>
<th>Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity (%)</td>
<td>12.76 (b.h)</td>
</tr>
<tr>
<td>Ashes (%)</td>
<td>3.45 (b.h)</td>
</tr>
<tr>
<td>Solids soluble (*Brix)</td>
<td>59</td>
</tr>
<tr>
<td>pH</td>
<td>5.29</td>
</tr>
<tr>
<td>Dry matter (%)</td>
<td>87.24</td>
</tr>
</tbody>
</table>

Table 1: Analysis of carob pulp.

In Table 1, the analysis performed on the carob pulp is shown, indicating a content of 59% soluble solids, showing the content of sugars and other compounds, within their content of soluble solids and a content of 87.24% of matter dry, according to Clua [1], mentions that carob is an energy food, with a high content of sugars, which contributes 10% of protein to the diet, as well as the minerals: calcium, iron and phosphorus. These minerals are better absorbed when combined with foods that contain ascorbic acid (vitamin C) and citric acid, as is the case with orange and grapefruit juices. Also the carob is a legume with a high content of sugars (20-50%), fiber and tannins and low in protein and fat, its main components are: the pulp that represents 90% of the fruit, highlighting its high content in sugars such as sucrose, glucose and fructose and in tannins and the seed that represents the remaining 10%.

On the other hand, Eizaguirre [2], mentions that carob contains less fat: 2%, 10% protein, 40% natural sugars and does not contain gluten so it is suitable for celiac. Also noteworthy in its composition is 13% soluble fibers (pectin and lignin) that help to carry out digestion and the benefits for the intestinal flora increase the amount of lactobacilli. Contains tannins included in the group of polyphenols, with antioxidant, anti-inflammatory and anti-inflammatory properties and beneficial for the heart and kidneys. It also contains zinc, manganese, iron, copper, sodium, magnesium, phosphorus, calcium and potassium in important quantities.

The yield of algarrobin in relation to the carob pod: The Yield (ml in carob / kg of carob) is 17.14% This means that 1 kilogram of carob represents approximately 171.4 ml of carob syrup, this data is very important to obtain costs and projected profits To obtain a bottle of algarrobin (760 ml), 4.3 kg of carob raw material is needed.

In Table 2, it is observed that the samples have different contents of soluble solids (SS), different pH and different contents of acrylamide and HMF; this can be due according to different thermic and technology treatment which must be constant in order to avoid sugars burning, each time the concentration increases. According to Mogues [3], it indicates that the caramelization or pyrolysis of monosaccharide sugars occurs when they are heated above their melting temperature, resulting in the appearance of enolization, dehydration and fragmentation reactions, which cause the formation of furanic derivatives which, by polymerization, form dark macromolecular pigments. If it is a disaccharide there must be a previous hydrolysis. According to the refractometer results, the concentration of the ashes, the soluble tannins and the cyclites are related to an increase of the soluble solids, on the other hand, the rain of sugars are replaced by ashes. In this stage, the operator must move the palette carefully, lowering the fire combustion for the purpose of avoiding an excessive sugar burning.

Table 2: Acrylamide content in algarrobin.

<table>
<thead>
<tr>
<th>Samples of algarrobin</th>
<th>Acrilamide (AA) ug/Kg</th>
<th>HMF ug/Kg</th>
<th>pH</th>
<th>SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>303</td>
<td>593</td>
<td>4.79</td>
<td>77.07</td>
</tr>
<tr>
<td>M2</td>
<td>250</td>
<td>431</td>
<td>4.26</td>
<td>81.3</td>
</tr>
<tr>
<td>M3</td>
<td>83</td>
<td>25</td>
<td>5.02</td>
<td>74.98</td>
</tr>
<tr>
<td>M4</td>
<td>25</td>
<td>0</td>
<td>5.27</td>
<td>82.6</td>
</tr>
</tbody>
</table>

The contact of the algarrobina with the content of the deposit (the part that gives to the direct fire), accelerate the unfolding of the sugars and generate to a greater presence of acrylamide. From the same table 2 we can observe a correlation between the content of acrylamide and the content of hydroxymethyl furfural, possibly due to the splitting of the sugars. The low content of acrylamide and HMF is probably associated to the unfolding to other unverified genotoxic components.

Population surveyed
The population of Piura district is 279 927 people (according to 2010 projections of INEl-Peru). To determine the amount of population surveyed, the researcher used the following formula

\[ n = \frac{N^2 \times Z^2 \times p \times q}{a^2 \times (N-1) + Z^2 \times p \times q} \]

Replacing

\[ n = 400. \]

From the total population of Piura, 400 piuran pedestrians were surveyed aleatory. The respondents were classified in different ages and sexes (male and female).

Consumption per capita of algarrobina
The table 3 shows the per capita consumption of carob syrup consumers. The average surveyed people (18-62 years) consume 0.01 to 0.340 liters per year.

There is a group of people who do not consume algarrobina inside their home or outside it, another group of people consume algarrobina in meetings (cocktails) and less frequently, algarrobina in juices (as a flavoring and / or sweetener) and another group of people who buy algarrobina and consume it inside their home.
especially in mixed juices, in breakfasts as a complement additive in cakes, desserts, etc.

Each value in table 3 is an average of 20 respondents of algarrobin consumption liters /year, which are 20 * 20 = 400 surveys. The per capita consumption of algarrobin in Piura is 170 ml / year * 1.4 / 360 = 0.66 gr / day approximately. Correlatively, the population average of Piura consumes 0.7 gr of carob syrup daily.

The results determined that the per capita consumption of carob syrup in Piura city (238g/year/person) is very similar to the world honey consumption (220 grams per inhabitant per year).

Determination of acrylamide and HMF daily consumption in the city of Piura
The per capita consumption results obtained by the 400 surveyed people were used to calculate the highest values of acrylamide and HMF with the following equation:

\[
\text{COAA} = \text{Amount of acrylamide in the algarrobin (ug /kg)* Kg consumption of algarrobin/ kg person-day}
\]

\[
\text{COAA} = 303\text{ug} / \text{Kg} \times 0.0007\text{kg / day} = 0.212\text{ug / person-day.}
\]

\[
\text{COAA} = 0.212\text{ug of acrylamide / day-person: Exposure = 0.003 ug / kg person day.}
\]

This value of 0.003 ug acrylamide / day-kg person, is well below that proposed by the FAO in 2002 (0.3-0.8 ug / kg-person-day), and as proposed by JECFA, the year 2005 (0.3 - 2 ug / kg-person-day), for average consumers and for extreme consumers 0.6 5.1 ug / kg- person-day).

\[
\text{CHMFA} = \text{Amount of HMF in algarrobin (ug / kg) * Kg consumption of algarrobin / kg person-day}
\]

Similarly, in the consumption of HMF in algarrobin (CHMFA)

<table>
<thead>
<tr>
<th>Person consumption</th>
<th>0.01</th>
<th>0.02</th>
<th>0.08</th>
<th>0.08</th>
<th>0.1</th>
<th>0.12</th>
<th>0.15</th>
<th>0.15</th>
<th>0.17</th>
<th>0.18</th>
<th>0.19</th>
<th>0.21</th>
<th>0.22</th>
<th>0.24</th>
<th>0.24</th>
<th>0.25</th>
<th>0.26</th>
<th>0.33</th>
<th>0.34</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surveyed Average</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>16</td>
<td>17</td>
<td>18</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 3: Annual average lt consumption of algarrobin.

Conclusion

- The content of acrylamide in the algarrobin consumption in Piura, does not exceed the values of acceptable daily intake, because the per capita consumption of algarrobin is low and infrequent.
- The low per capita consumption (0.7 gr / day) and the low frequency of consumption of algarrobin, contributes to not overpass the values of intake expressed in acrylamide and HMF.
- The different acrylamide contents in the algarrobin samples indicate different process techniques, without standardization.
- The sum of acrylamide and HMF in algarrobin (0.009 ug / kg person day), do not exceed the limits of intake of acrylamide; so it gives confidence regarding these components, its current consumption.
- There are samples of algarrobin that indicated 0 ug / kg of acrylamide / HMF, it may be due to the actual content of acrylamide (optimal process technique) or because said component disappeared, becoming other components not yet studied.
- A higher content of acrylamide, lower daily servings of algarrobin consumption.

Recommendations

- Research studies should be conducted on the content of acrylamide in potato chips, in the city of Piura.
- Make acrylamide studies for samples that are stored for a long time.
- INDECOPI, should conduct studies on the various processed foods consumed in Peru, on the content of acrylamide and include in NTP 209,600 [6].
- Studies should be carried out on the content of asparagine in the carob tree and see its effects of this amino acid by thermal treatment.
- More information should be provided to the Piurana community, on toxicological substances in food consumption, and on innocuous quantities, contributing to the prevention of chronic non-communicable diseases.
- Establish a monitoring to check the effectiveness of this result (acrylamide and HMF), some high-consumption processed foods (meat grills, hamburgers, reused oils, reheated bee honeys, chiffes, blancmange, nougat, roasted peanuts, etc.), through the frequency of consumption and size of the ration of this type of food [9,10].

References

1. Clua Graciela. The carob was a natural food suitable for celiacs University Buenos Aires. 2011.


10. www.made-in-argentina.com