**ABSTRACT**

The objective of this study is, on the one hand, the measurement of some organoleptic parameters (water content, pH, brix, titratable acidity) of a large commercial tomato *Rio Grande* variety, widely cultivated in the north of Algeria. On the other hand, the valorisation of the crude oil extracted from the dried seeds of the same variety using a soxhlet extractor. The extracted oil was analysed by standard methods for the following parameters: acid, peroxide, iodine, saponification and refractive indexes and the unsaponifiable. The results obtained indicate that *Rio Grande* fruits present a product of appreciable quality. The oil seems to have physico-chemical properties similar to those of some edible oils, which makes it possible to consider its use in human food, as well as in other fields (pharmaceutical, cosmetic, etc.).

*Keywords:* Tomato, *Rio Grande* variety, Physico-chemical parameters, Vegetable oil.

**Introduction**

The tomato (*Lycopersicon esculentum* L.) is a plant of the warm regions and can be cultivated in all regions of Algeria. The seeds are sown, depending on the region, during three seasons: a sowing in February-March-April, another in May-August and a sowing in October-November-December-January. Planting is done 20-30 days after sowing. Yields are 35-60 t/ha in the field and 80-160 t/ha in the greenhouse.

Nutritionally, tomato fruits are a source of minerals (Ca, K, Mg, Na, Fe.) and vitamins (A, B6, C, E), which contribute to the reduction of micronutrient deficiency. Tomato cultivation generates tomato residues estimated at 1,305,000 tons per year worldwide (FAO, 2008), the waste from the tomato processing industry consists of skin, seeds, etc. (Ventura *et al.*, 2009). The seeds allow the extraction of vegetable oils, which are sought after for their quality compared to animal fats, which are loaded with saturated fatty acids. These oils are used in the preparation of various dishes or other products useful to humans (soap, cosmetics, etc.).

Among the 117 varieties of tomato cultivated in Algeria, our attention was drawn to *Rio Grande* variety, which originates from the USA. It is a determinate growth and open pollination variety. It is registered in the European catalogue of the GNIS. It is a hardy, high-yielding Roma type, which produces many bright red, elongated medium-sized fruits (60-100 g). The tomatoes contain few seeds and are ideal for making concentrates, coulis, soups, juices and salads. It is a VF resistant variety (resistant to *Verticillium* wilt and *Fusarium* wilt).

Our objective is to evaluate some organoleptic parameters (water content, pH, brix, titratable acidity) of the fruits and to value the crude oil extracted from the seeds with respect to the following parameters: acid, peroxide, iodine, saponification and refractive indexes, as well as the unsaponifiable.

**Material and Methods**

**Biological material**

The ripe fruits of *Rio Grande* variety were harvested from El Karma station in El-Hadjar Wilaya of Annaba (Northern Algeria). The fruits were taken at random from several bunches at different heights and orientations. INPV seed distributors (Institut National de Protection des Végétaux, Ben M’hidi Wilaya of El Tarf) provided tomato seeds (Figure 1).

**Physico-chemical parameters related to fruit quality**

(i) **Determination of the water content**

The water content (WC) is the difference between the fresh weight and the dry weight. 10g of tomato slices were placed in an oven set at 105 ±2°C until a constant weight was obtained (AFNOR, 1982). This difference is expressed as a percentage of the fresh material according to the formula determined by the relationship

\[ WC \% = \frac{(FW - DW) \times 100}{FW} \]

FW: fresh weight just after harvesting (in g) DW: dry weight after oven drying (in g).
(ii) **pH of fresh fruit juice**

The pH is determined according to Afnor standards (1982) using an electronic pH meter and taking care that the electrode is completely immersed in a filtrate obtained after grinding fresh fruit, cut up, seeded and mixed with three times its volume of distilled water.

(iii) **Brix of fresh fruit**

The Brix is the soluble dry matter of an aqueous solution with the same refractive index (RI) as the product being analysed (Granges et al., 2006). The test was carried out at a temperature of 20°C and the conversion was made using a refractive index table to soluble dry residue (expressed as sucrose) (Philippe, 2003). The refractometer is adjusted to give a refractive index of 1.330 for distilled water at 20°C (Davies and Hobson, 1981).

If the determination is carried out at a temperature of 20°C ± 0.5°C, the following corrections will be necessary:

\[
N = np + 0.0013(t - 20)
\]

np the measurement found at a temperature of 20°C ± 0.5°C

(iv) **Titratable acidity**

The principle of the method is based on the titration of the acidity of an aqueous solution (prepared from 25g of fresh tomato) with a sodium hydroxide solution in the presence of phenolphthalein as a color indicator (AFNOR, 1982). The titratable acidity is expressed in g of citric acid per 100g of product or 100 ml of product.

\[
A\% = \frac{(100 \times V_1 \times 100)}{(V_0 \times M \times 10)} \times 0.07 = 175 \times \frac{V_1}{(V_0 \times M)}
\]

M: mass in grams taken; V₀: volume in millilitres of the test sample; V₁: volume in millilitres of 0.1N NaOH solution 0.07: conversion factor of the titratable acidity into citric acid equivalent.

**Physico-chemical analysis of the seeds**

(i) **Number of seeds per gram**

The calculation was carried out on three samples of 1 gram of seeds each. The average number of seeds per gram was deduced from the average number of seeds in the three samples.

(ii) **Determination of water content**

The method used was the same as the one recommended for the determination of water content in tomato fruits.
(iii) Extraction and oil yield

The oil was extracted from a quantity of tomato seed powder using a Soxhlet device using hexane as solvent. The extraction took 4 hours at a temperature of about 60°C. The solvent was then evaporated in a rotary evaporator. The oil was collected in a smoked labelled glass bottle and then stored in a refrigerator (4°C). The oil extraction yield (Oy) was calculated using the following formula:

\[ \text{Oy} \% = \left( \frac{M0}{M1} \right) * 100 \]

M0: Mass of oil extracted M1: Mass of seed powder used to make the extraction

Physico-chemical analysis of tomato seed crude oil

(i) Acidity index

The acidity is the percentage of free fatty acids conventionally expressed according to the nature of the fattyacid body as oleic, palmitic, lauric acids (AFNOR, 1984). After homogenising the sample to be analysed with neutralised 96° KOH; N: normality of the potash N/10 p: mass of the test sample

The calculation is done according to the following formula: After homogenising the sample to be analysed with neutralised 96° ethanol, the colour change of the potassium hydroxide solution is done with phenolphthalein. The calculation is done according to the following formula:

\[ \text{IA} = V* M * N/P \]

V: volume of potash poured (ml); M: molar mass of KOH; N: normality of the potash N/10 p: mass of the test sample

(ii) Refraction index

The principle of the method used was the same as that recommended for the determination of the brix content in tomato fruit, however the refractive index for the oil was carried out at a temperature of 40°C ± 0.5°C, and the following corrections were necessary

\[ n_p = n_p + 0.00036(t - 40) \]

np the measurement found at a temperature of 40°C ± 0.5°C

(iii) Saponification Index

The saponification number (SI) is defined as the degree of milligrams of potassium hydroxide (KOH) required to saponify one gram of fat, using phenolphthalein as a colour indicator. Excess KOH is titrated in HCL soap solution by a specific extraction solvent (petroleum ether). The unsaponifiable solvent is then evaporated in a rotary evaporator and weighed to constant weight (AFNOR, 1984).

\[ \text{IS} = (V2 - V1) * N * M/P \]

P: Test sample (g) ; M: Molar mass of KOH; N: Normality of HCL ; V1: Volume poured for the test sample (ml) ; V2: Volume poured for the control (ml).

(iv) Iodine Index

The iodine index is defined as the number of grams of iodine fixed per 100 g of fat, it was determined according to the method of Wijs (Wolff, 1968). According to the experimental protocol used, an excess of iodine chloride, called Wijs reagent, is added to the fat in solution in chloroform. After a few minutes of reaction, potassium iodide and distilled water are added. The liberated iodine is titrated with a standard solution of 0.1 N sodium thiosulphate solution (NASO3 0.01N) until complete decoloration.

\[ \text{II} = \left( V_B - V_A \right) * 1.27/p \]

\[ V_B: \text{Volume of Na}_2\text{SO}_3 \text{ solution used for the assay (ml)}; V_A: \text{Volume of Na}_2\text{SO}_3 \text{ solution used for the blank test (ml)}; P : \text{is the mass of the test sample (g) ; 1.27: molar mass of iodine in 100g of the fat.} \]

(v) Peroxide Index

The chemical alteration of unsaturated bodies by oxygen in the air gives rise to a peroxide. The protocol is based on the measurement of the peroxide value by iodometry. According to the standard Afnor (1984), the test sample is solubilised in a mixture (acetate acid/chloroform) to which a quantity of potassium iodide (KI) is added, and starch is used as a colored indicator. The titration of released iodine is done by sodium thiosulphate solution (NASO3 0.01N) until complete decoloration.

\[ \text{IP} = \left( V_1 - V_2 \right) * 10/p \]

\[ V_1: \text{Volume of Na}_2\text{SO}_3 \text{ solution used for the test sample (ml)}; V_2: \text{Volume of Na}_2\text{SO}_3 \text{ solution used for the blank test (ml)}; 10: \text{the number of meq of O}_2 / \text{Kg lipid} ; p : \text{is the mass of the test sample (g)} \]

(vi) Percentage of unsaponification

It is based on the saponification of fats by boiling the test sample with an alcoholic KOH solution. The unsaponifiable fraction is extracted several times from the soap solution by a specific extraction solvent (petroleum ether). The unsaponifiable solvent is then evaporated in a rotary evaporator and weighted to constant weight (AFNOR, 1984).

\[ I \% = \frac{P_1* 100}{P} \]

P1: weight difference ; P: test sample weight

Results

Analysis of fruits of the variety Rio Grande

The analysis of the fruits of the variety of tomato studied concerns the parameters relating to the water content, the pH of the fruits, the Brix and the titratable acidity. The results are summarized in Table 1.

Table 1: Some organoleptic parameters of tomato fruits

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content</td>
<td>77.29 ± 0.011</td>
</tr>
<tr>
<td>Fruit pH</td>
<td>4.40 ± 0.155</td>
</tr>
<tr>
<td>Brix</td>
<td>6.78 ± 0.00</td>
</tr>
<tr>
<td>Titratable acidity</td>
<td>3.30 ± 0.20</td>
</tr>
</tbody>
</table>

(vii) Seed analysis of Rio Grande variety

The analysis of the seeds of the tomato variety studied concerns the parameters relating to the number of seeds per gram, the water content, the dry matter content and the oil yield. The results obtained are recorded in Table 2.

Table 2: Some parameters carried out on the seeds of the variety Rio Grande

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of seeds per gram</td>
<td>330 seeds/g ± 3.00</td>
</tr>
<tr>
<td>Water content</td>
<td>8.20 ± 0.16</td>
</tr>
<tr>
<td>Dry matter content</td>
<td>91.08 ± 0.275</td>
</tr>
<tr>
<td>Oil yield</td>
<td>21.67% ± 0.725</td>
</tr>
</tbody>
</table>
Physico-chemical analysis of crude oil from seeds of the *Rio Grande* variety

The physico-chemical analysis of the crude oil from the seeds of the tomato variety studied concerns the parameters relating to the acidity index, the peroxide index, the refractive index, the iodine index, the saponification index and the percentage of unsaponification. The results obtained are recorded in Table 3.

**Table 3**: Physico-chemical characterization of the crude oil of tomato seeds

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid index (mg KOH g⁻¹ lipid)</td>
<td>1.5±0.095</td>
</tr>
<tr>
<td>Peroxide index (meq Kg⁻¹lipide)</td>
<td>15.70±0.95</td>
</tr>
<tr>
<td>Refractive index (40°C)</td>
<td>1.478±0.00</td>
</tr>
<tr>
<td>Iodine index (g I₂ 100 g⁻¹ lipid)</td>
<td>177.66±1.235</td>
</tr>
<tr>
<td>Saponification index (mg KOH g⁻¹)</td>
<td>193.81±2.047</td>
</tr>
<tr>
<td>Unsaponifiable (%)</td>
<td>1.77±0.028</td>
</tr>
</tbody>
</table>

**Discussion**

The study on the organoleptic value and quality of crude oil extracted from tomato seeds *Solanum lycopersicum* var. *Rio Grande* grown in El Karma, region of El-Hadjar wilaya of Annaba (northeast of Algeria) was very interesting.

**Analysis of fruits of the variety *Rio Grande***

(i) **Water content**

This amount of recovered water is still appreciable for the marketing of fresh fruits as the higher the water stock the more vulnerable the fruits become to post-harvest losses (Shankara *et al.*, 2005).

In general, tomatoes are composed of 80% to 85% up to 95% water reserve (Larid, 2012).

(ii) **Fruit pH**

The pH value is an advantage from the point of view of food stability. This result is consistent with those reported by Lamb (1977) who reported pH values ranging from 4.2 to 4.6, as well as those indicated by Amoussou (1998) ranging from 4.0 to 4.4. According to Evoda (1988) the ideal value should be between 4.0 and 4.5. Indeed, this pH level considerably reduces the rate and range of microorganisms that can grow on the product. Based on this criterion, the *Rio Grande* variety could present an appreciable pulp quality.

(iii) **Brix**

The measurement of the refractive index expressed in Brix is a good indicator of the soluble dry matter content in tomatoes (Granges and Déprez, 2002), which is an important parameter for the industrial processing of these fruits, and is between 5 and 7% (Fagbouhou and Kiki, 1999), with values around 4 to 9% being acceptable. This values higher than those found by Granges and Gillioz (2006), Dossou *et al.* (2007), with 4.3 % and 6.2 % respectively. Nevertheless, it is similar to that reported by Hounoundj (1985). We can consider that *Rio Grande* variety has the required dry matter value for industrial processing.

(iv) **Titratable acidity**

During the ripening of tomatoes, the acid content decreases in favor of the increase in sugar content, so the ripe tomatoes harvested have a low acid content (Larid, 2012; Louati, 2009), which explains the value of 3.30% titratable acidity recorded in *Rio Grande* variety. This value is significantly lower than the 8.43% and 5.72% obtained by Dandjouma *et al.* (2005), but is consistent with the results reported in the studies of Granges and Gillioz (2006), Granges and Déprez (2002), which recorded titratable acidities between 2.7% and 3.7. These authors consider that an acidity of 3 to 3.5% indicates a good quality of the tomato. *Rio Grande* variety, with 3.30 % is perfectly within the norms (below 8%) of Afnor (1982).

**Seed analysis of *Rio Grande* variety**

(i) **Number of seeds per gram**

In general, 1g of tomato seeds represents an average number of seeds between 250 and 350 (Marques and Moreau, 2005). *Rio Grande* variety presented 333 seeds per gram. This parameter is closely, related to the normal realization of ovule fertilisation, which is under the influence of soil and climatic conditions (Hountondj, 1985). In the same work, the same author reported that there is a relationship between the number of seeds per fruit and the average fruit weight. Moreover, Evoda (1988) found that the larger the fruit, the more seeds it contains. This was clearly, seen in the harvesting of fruits of *Rio Grande* variety.

(ii) **Determination of moisture content**

The moisture content of the seeds is important for obtaining a good oil yield. Our sample showed a moisture content of 8.20%. This value is lower than the 10% required for oil extraction (Ahishakiye and Ait Ammour, 2010). Therefore, no further drying was required before oil extraction.

(iii) **Determination of dry matter content**

The dry matter content of tomato seeds of the variety *Rio Grande* was 91.08%, this rate is favorable to the direct extraction of oil without recourse to prior drying of seeds. This result agrees with the result reported by Cotte (2000) which was 92% and is higher than the 88% reported by Knoblich *et al.* (2005).

(iv) **Oil yield**

The oil content without counting the traces left in the cake is 21.67%. This result is very close to the yield (21.8%) recorded by Lazos *et al.* (1998). This rate is very high compared to the results obtained by Al-Wandawi *et al.* (1985), Roy *et al.* (1996), with respectively 14.5% and 19.22%. On the other hand, this content is quite low considering the results obtained by Giannelos *et al.* (2005) who found yields ranging from 31% to 39% and Minani and Fonseca (1985) with 27.1%. In general, tomato seeds appear to be richer in oil than some conventional oilseeds, such as grape seed (12-13%) and soybean (19.00-23%). There is variability in the analytical data. This variation is largely due to the varieties studied, the origins of the samples, the extraction processes and the analytical methods used.

**Physico-chemical analysis of crude oil from seeds of the *Rio Grande* variety**

(i) **Acidity index**

A low acidity value expresses the sensitivity, purity and stability of an oil at room temperature (Tchiégang-Meguéné, 2003). Our oil generated an acid value equal to 1.5 mg KOH g⁻¹ lipid, a relatively high value compared to 1 mg KOH/g lipid, reported by Kobori and Jorge (2004), Lazos *et al.*
(1998) but it is comparable to 1.4 mg KOH g⁻¹ lipid, reported by Apria (1969). These differences may be attributed to the fact that the seeds after crushing were not immediately used for oil extraction, as well as to the storage conditions of the oil before analysis. However, this result is within the norms as it does not exceed the 3% required for edible vegetable oils (APRIA, 1969).

(ii) Refractive index
The refractive index provides information on the degree of light deflection by the oils. The value obtained was 1.4783, very close to those reported by Apria (1969), Demirbas (2010) with respectively 1.4740 and 1.4733 but, slightly higher than 1.4708 mentioned by Kobori and Jorge (2004). In general, this value is outside the range established by Food Codex (2009) for the refractive indices of vegetable oils.

(iii) Saponification number
The saponification index obtained was 193.81 mg KOH/g. It is higher than those obtained by other authors with 172 mg KOH/g and 188 mg KOH/g respectively Kobori and Jorge (2004), Lazos et al. (1998), Amalou et al. (2013). However, this result is close to the values recorded in the work of Demirbas (2010) which were 195 mg KOH/g and 190.2 mg KOH/g respectively. This result is in line with the Codex standard for vegetable oils. This index varies according to the extraction method and the varieties used.

(iv) Iodine index
In seed analysis, the iodine value is very important because it is in relation to the values of this index that vegetable oils are classified as drying, semi-drying and non-drying oils. In fact, the iodine index gives us information on the degree of unsaturation of the fatty acids contained in a given oil. It is directly related to the degree of oxidation, so the more unsaturated an oil is, the higher its iodine value (Wolff, 1968).

The result obtained was 177.66 g iodine/100 MG. This value is extremely higher than those reported in the works of Kobori and Jorge (2004), Amalou et al. (2013) with respectively 128.59 and 117 g iodine/100 MG. It is even higher than the standards for some vegetable oils such as Sunflower (118-141 g iodine/100 MG), Soybean (124-139 g iodine/100 MG) etc. This important difference can be explained by the presence of alloys in the extracted oil due to the type of materials used during the crushing of the seeds, knowing that the latter was carried out using a coffee mill and a copper mortar. All these data show that our oil sample is highly polyunsaturated, which allows it to be classified as a drying oil, since the iodine index is > 150, which could make its conservation very difficult due to auto-oxidation.

(v) Peroxide index
This index measures the level of oxidation of the oil. It varies according to the extraction method (Lovett, 2005). The peroxide value obtained in our tomato oil sample was 15.70 meq/kg MF, which is in line with the value reported by Demirbas (2010). Nevertheless, it is higher than the 10.20 meq/kg MG and 9.30 meq/kg MG reported by Kobori and Jorge (2004) and Lazos et al. (1998).

The peroxide value of most edible vegetable oils does not exceed 10 meq/kg MF, such as soybean, corn, and sunflower. This index is an appreciable criterion of the first stages of oxidative deterioration of an oil. The high value of the peroxide value of our oil can also, be related to storage conditions. However, our oil sample presents a peroxide value that is within the limits set by the standards Food codex (2009) such as olive oil with an index ≤ 20.

(vi) Unsaponifiable
Unsaponifiable constituents are present in minute quantities. The unsaponifiable content of our oil sample was 1.77%; it is lower than the 1.4% obtained by Lazos et al. (1998), very close to the 1.8% mentioned in the study of Amalou et al. (2013) and significantly lower than the 4.33% reported by Demirbas (2010). This very low result is perfectly in line with the standards established by Food codex (1999 and 1981) for the main vegetable oils (≤ 15 for sunflower, soybean, olive oil and ≤ 28 for corn oil).

Conclusion
Rio Grande tomato variety is in great demand on the Algerian market, especially in the food industry. The aim of our work was to evaluate some organoleptic parameters of the fruits (water content, pH, brix, titratable acidity) as well as to value the oil extracted from the dried seeds of the same variety using a soxhlet type extractor. This extracted oil was analyzed by standard methods for the following parameters: acid, peroxide, iodine, saponification, refractive index and unsaponifiable matter.

The results obtained indicate a good quality of the fruits with values that comply with current standards, as for the extracted oil, it seems to present interesting physicochemical properties overall. However, the acidity, the iodine and peroxide index show that precautions must be taken during pre-refining and packaging to limit the degradation of the physico-chemical and functional quality of this oil. The saponification, unsaponifiable, and brix measurements of this oil give it interesting pharmaco-nutritional qualities comparable to those of conventional edible oils. However, it is much more interesting to consider its use in cosmetology, for which it seems perfectly suited.

Acknowledgements
The authors are grateful to Badji Mokhtar University of Annaba, Faculty of Medicine, Department of Pharmacy, Laboratory of Botany for the scientific support especially the instrumental facilities to perform different analyses.

References


