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Some Technologic Proprieties of Common Date (*Phoenix dactylifera* L.) Fruits

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Abstract: Mech-Degla, Degla-Beida and Frezza are the common (or dried) varieties studied in this research. On average, their water and sugar contents are of 15 and 80% dry basis (db), respectively. In this paper we report on their technological abilities. The experimental study consist the following: complementary vacuum (200 mbars) air-drying at 60°C, soaking in citrus juices, double fermentation (alcoholic and acetic) and water-alcohol extract preparation. The three previously quoted varieties show an interesting drying ability since they water content has been reduced to 5-7% (db) without apparent browning, which allows the possibility to produce first fruit powder then tablets. In order to formulate biologic vinegar and to optimize the traditional process as has traditionally applied in Algerian Sahara, the dates have been submitted to the spontaneous double fermentation: alcoholic and acetic. Using oxygenation during 4 h after 14 days of anaerobic fermentation, the acetic acid content reaches a value above 7 g/100 mL (in the Mech-Degla case). The swelling power (more than 50% in relation to the initial fruit's weight) of Mech-Degla dates immerged in citrus juices as well as the brix degree variation in liquid phase (on average 25%) were also analyzed. Results indicate also the possibility to produce the dates in their auto induced syrup. In addition, the water-alcohol extract obtained reveals an antioxidant activity of about 52%.

Key words: Date, drying, antioxidant activity, immersion, vinegar

INTRODUCTION

Algeria, with more than ten millions of date palms (*Phoenix dactylifera* L.) occupies the fifth world-wide row in date fruit production (Messar, 1996). It is, with Tunisia, the traditional Deglet-Nour (soft date variety) supplier for Europe (Belarbi *et al.*, 2000). The common (or dried) varieties as Mech-Degla, Degla-Beida and Frezza which are characterized by a low trade value and more or less availability represent an average tonnage of 60000 tons (Nancib *et al.*, 1997). Despite this interesting potential raw material, there is not any industrial transformation in Algeria outside few empirical transformations. Nevertheless, some formulations from date fruits have been already suggested by many authors: ketchup, biscuit, ice cream, blend of the date meal and milk (Greiner, 1998; Sibouker *et al.*, 1998; Al Nakhal *et al.*, 1987; Mikki *et al.*, 1987).

The valorization possibilities of common dates, grown in Algerian Sahara and the presentation of the first results obtained in our laboratory are the principal purposes of the present study, taking into account the safeguard of the biodiversity since many palmgrove proprietors try to select only the commercial varieties as Deglet-Nour. It is well known that common varieties are used as livestock foods whereas their overall chemical composition is not so different comparatively to soft varieties. In our view, their hard consistence is their principal defect. Precisely, in the present study, some technologic proprieties of these varieties were investigated taking into account their high sugar content

(80% db), low moisture content (15% db) and rehydration power. Also, as opposed to the citrus juice, the common dates are a low acidity material which leads us to try to improve their taste by soaking them in citrus juice. The new food product thus obtained shows a harmonious savour due to its adequate sugar/acid ratio. It must be recalled about the harmful effects of the white sugar as well as the bioavailability of the citrates (present in the citrus juice) as reported in the literature (Steinmetz, 1991). Consequently, the common date transformed products can positively substitute the ordinary refined sugar.

Finally, the possibilities to produce date fruit powders and tablets, biologic vinegar, date fruits in their auto induced syrup and water-alcohol extract were succinctly investigated.

MATERIALS AND METHODS

Date Sample

Three common varieties of dates grown in southern Algeria constitute the vegetable material in this work: Mech-Degla, Degla-Beida and Frezza. The two firsts varieties are more commercialized than the last. They were obtained from a local market during autumn 2005 and then stored at 6°C. The initial moisture content of date pulp was determined in triplicate at 105°C until steady weight was achieved (AOAC, 1997).

Drying Ability

Date drying as well as soaking, fermentation and extract were performed in Laboratory of Food Technology of University of Boumerdès whereas antioxidant activity was carried out in University of Bejaia (250 km eastward from Boumerdès) in 2006.

The laboratory hot air oven dryer (Model HERAEUS), connected to the vacuum pump was used. The date pulps were cut into 3 mm cubes, spread uniformly in a monolayer on the tray of the drier and vacuum-dried (200 mbar) at 60°C. The drying was stopped when the constant weight was reached and/or the color of outside part of date pulp changes from pale yellow-beige (initial aspect) to caramelized aspect.

Fick's second law of diffusion is used to model the drying behaviour of date pieces:

$$dW/dt = D d^2W/dx^2$$

where,

W = Moisture content at time t.

x = Date piece thickness (m).

D = Effective water diffusivity (m² sec⁻¹).

For a thin layer, taking into account certain assumptions for simplification and knowing that diffusion process for any geometry could be reduced to the analytical solution corresponding to a sphere (Hebbar and Rastogi, 2001), the solution of the above equation is as follows (Falade and Abbo, 2007; Senadeera *et al.*, 2003; Pala *et al.*, 1996; Crank, 1975):

$$MR = \frac{W - We}{Wo - We} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp \left(-n^2 \pi^2 \frac{Dt}{\Psi R^2} \right)$$

$$\begin{split} \Psi &= \mathrm{Ss/Sp} = \pi/6 \\ R &= (3V)/(\Psi \mathrm{Sp}) = \mathrm{Rs} \ / \Psi = 3x/\pi \end{split}$$

where,

MR = Moisture ratio. Wo, We,

W = The initial, equilibrium and at time t moisture content (% dry basis), respectively.

 $D = \text{Water diffusivity } (m^2 \text{ sec}^{-1}).$

 Ψ = Shape factor.

Ss = Surface area of the sphere (with radius Rs) having volume equal to that of the cubic date piece (V).

Sp = Surface area of date piece.

R = Equivalent radius of date piece.

For long drying time the following straight-line equation is deducted:

$$ln(MR) = C - Kt$$

where,

C = Constant.

 $K = Drying constant (min^{-1}) = 2\pi^3D/3x^2$.

The plot ln(MR) versus drying time using Microsoft Office Excel 2003, the diffusion coefficient D could be determined from the slope of the above straight line:

Slope =
$$-K = -(2\pi^3D)/(3x^2)$$

To evaluate the goodness of the model fit, two criteria were used: the coefficient of determination (R²) and the Mean Relative Error (MRE) calculated as:

$$MRE = \frac{100}{N} \sum_{i=1}^{N} \frac{\left| MRei - MRpi \right|}{MRei}$$

where,

Mrei = MR experimental value.

Mrpi = Predicted value from the model

N = No. of experimental data points. The model is acceptable if MRE< 10%.

We consider the studied date varieties are able for drying if their moisture content could be reduced without browning to approximately 5%(db), value which is required for fruit powders (Espiard, 2000).

Soaking in Citrus Juices

The citrus fruits were purchased from local market. Fruits were washed, halved and squeezed (by lemon-press) in laboratory. The obtained orange (brix degree = 9.5; pH = 3.9) and lemon juices (brix degree = 9% and pH = 2.5) were centrifuged and then used without storage as soaking liquids. The soaking consists habitually of hydration (or dehydration) of the product in water (or solution) until they reach their maximum (or minimum) weight with or without discarding of soaking medium (Prodanov *et al.*, 2004). At the same time, a suitable texture for consumption is reached while some metabolic reactions take place, affecting the composition of seeds (Frias *et al.*, 2000). In our case, the most undesirable effect consisting of fermentation can not take place because of the low pH of the medium. On the other hand, the mass transfer between the phases is the most important physical

Table 1: Matrix of experiences

Test	Kid jus	Dilution	Time	Inter.	Inter.	Inter.	Inter.			
N°	(Fact 1)	(Fact 2)	(Fact 3)	12	13	23	123	°Brix	pН	ΔΡ/Ρο
1	-	-	-	+	+	+	-	17.3	2.4	0.38
2	+	-	-	-	-	+	+	16.0	3.9	0.38
3	-	+	-	-	+	-	+	11.0	3.0	0.54
4	+	+	-	+	-	-	-	10.0	4.5	0.43
5	-	-	+	+	-	-	+	22.0	2.2	0.49
6	+	-	+	-	+	-	-	23.0	3.8	0.53
7	-	+	+	-	-	+	-	17.0	3.3	0.56
8	+	+	+	+	+	+	+	16.0	4.6	0.50

Level -: Lemon 1 4 h; Level+: Orange 1024 h

phenomena which implies: an increase of the sugar content in the liquid medium, an increase of the volume of the dates (swelling) and texture changes (Chenoll *et al.*, 2007; Fito and Chiralt, 2003).

One fruit was halved, pitted, weighed and blanched (steam blanching) during 5 min at 70° C and then immerged in citrus juice (w/v ratio = 1/3). Quadruplicate samples were used.

Experimental data were analysed using a 2³ factorial design as described by Goupy (1996). The factor levels (low and high) are shown in Table 1. Three responses are considered: juice brix degree, juice pH and date swelling power. This last is quantified using the swelling degree:

Swelling degree =
$$\Delta P/Po = (P-Po)/Po$$
,

where Po and P are the weights of each halved date before and after soaking, respectively.

A discontinuous but regulate agitation of the citrus juices was applied with moderation in order to avoid the delitescence of the pulp as well as an excessive oxygenation of the liquid phase.

Date Vinegar

Vinegar was known by most ancient civilizations (Tesfaye *et al.*, 2002). Moreover, it can be prepared from various fruits juices (Casale *et al.*, 2006). The vinegar is habitually produced by a two stage fermentation process; being the first one, the conversion of fermentable sugars to ethanol by yeasts and the second the oxidation of ethanol by bacteria (Adams, 1998). In our case, Mech-Degla and Degla-Beida have been submitted to the spontaneous (without artificial inoculation) and simultaneous fermentation in unique cycle according to the overall traditional procedure used currently in certain regions of southern Algeria. In this experiment, we have used seven plastic jars provided with holed cover (one perforation of 0.5 mm) and containing whole dates immerged in water (w:v ratio = 1:2) at 30°C. To observe the temperature effect, one fermentation test was performed at 25°C with Mech-Degla variety. Concerning the traditional procedure of vinegar production in southern Algeria, the temperature is not controlled. One metallic nail (No. 12, with a weight of about 15 g) and 1 g of red pepper were added to the mixture. Different physicochemical parameters were analysed every 5 days during 45 days as that is pre-established by popular beliefs. The formation kinetic of the ethylic alcohol and acetic acid is investigated with the aim to understand and optimize the process.

Water-Alcohol Extract

Among all tested water/alcohol ratios, the 1/1 fraction was chosen. In any case, for the food applications, the ethanol presents many advantages compared to other organic solvents (Escribano-Bailon and Santos-Buelga, 2003). For the extract preparation, 100 g of grinded *Mech-Degla* pulp were macerated during 4 days in 150 mL of solvent at 23°C, sheltered from the light and then filtered through Whattman filter paper. This operation was repeated 5 times according to the principle of multiple washings. The extract thus obtained was submitted to the vacuum concentration. Determination of phenolic and favonoids in the concentrated extract was carried out according to the method of Juntochote *et al.* (2006) and Bahorun *et al.* (1996), respectively whereas its antioxidant

activity (inhibition% of the linoleic acid oxidation) was determined according to the method described by Hashimoto et al. (2003) and was computed as:

Inhibition% =
$$100-A_1(t = 96 \text{ h})/A_0(t = 96 \text{ h})100$$
,

where Ao and A₁ are the absorbance of the control and extract sample, respectively.

RESULTS AND DISCUSSION

Drying Ability

The initial water contents of Mech-Degla, Degla-Beida and Frezza dates are of (14.77±1.29)% (db), (14.15±1.56)% (db) and (14.89±1.88)% (d.b), respectively.

A plot of moisture content versus time during vacuum-air drying of date pieces is shown in the Fig. 1. As it can be seen, the water content objective (5%) has been reached easily for all studied varieties. Moreover, the drying curve of Degla-Deida seems more abrupt than for Mech-Degla and Frezza for which the curves are superposed. The different drying behaviour of tissues could be explained by their more or less fibrous texture as well as their composition in hydrophilic components as sugars and pectin. On the other hand, the desired final water content has been obtained before equilibrium state without any visual browning. To verify the fitting of the suggested model, the variation of ln(MR) as function of the drying time (for the first 150 min) is shown in Fig. 2. The R² (>0.98 for both dates) and MRE (= 3 and 6% for Frezza and Degla-Bieda, respectively) values indicate that the model correctly fit the set of data, for water content ranking from Wo to W ≈ 5%(db) for Degla-Beida and 7% (db) for Frezza. From the straight-line equations (Fig. 2), the effective diffusivity values D are deduced: $5.73\ 10^{-11}$ and $3.61\ 10^{-11}$ m² sec⁻¹ for Degla-Beida and Frezza, respectively, i.e., Degla-Beida releases water more easily than Frezza since $D_{\text{Mech-Degla}} \sim 1.6\ D_{\text{Frezza}}$. D values thus obtained are in agreement with those reported $(10^{-12}-10^{-8}\ \text{m}^2\ \text{sec}^{-1})$ for other food materials

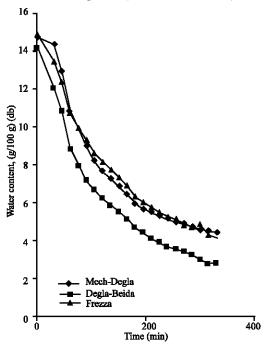


Fig. 1: Vacuum-drying curves of different common date varieties at 60°C

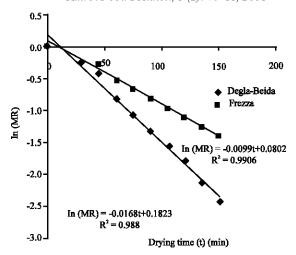


Fig. 2: ln (MR) versus drying time at 60°C for two common date varieties cut in cubes

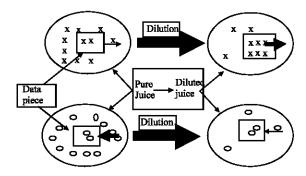


Fig. 3: The influence of juice dilution on molecule diffusion intensity in halved date-citrus juice system: in pure juice which contains more C vitamin, molecules diffuse more intensively from juice to the date (see thickness of flitch). The juice dilution decreases the rate diffusion. The inverse phenomenon is observed in case of sugar molecules. x = sugar molecules; O = C vitamin C molecules

(Nguyen and Price, 2007; Babalis and Belessiotis, 2004). Further, the D value for both Degla Beida and Frezza is lower than those obtained (7.48 10⁻¹⁰-1.11 10⁻⁸) for the Nigerian date varieties dried at 60°C as such without cutting (Falade and Abbo, 2007). We believe that the initial water content, physicochemical characteristics of date tissues and cutting operation (which involves a big contact surface between fruits and dried air) may explain this difference in drying behaviour of date varieties.

After drying, the date pieces have been submitted to the grinding and thus sieving in order to obtain a powder with uniform granules. During storage, the powders loose more or less quickly their flow ability. This inconvenient for powders becomes an advantage for the tablet formulation (Bimbenet *et al.*, 2002). The preliminary laboratory tests have given satisfactory results.

Date Immersion in Citrus Juices

Complex phenomena of mass transfers take place in the dates-citrus juice system. As far as we know, there is no published study on the date immersion in liquid. Figure 3 shows the influence of the dilution on the displacement of sugar and C vitamin molecules. To quantify the processes, the matrix of experiments is plotted in Table 1.

The highest brix degree is obtained with two variants (tests 1 and 2): in pure lemon juice (without any dilution) after 24 h of soaking and in pure orange juice with the same treatment length. Concerning the swelling power, five variants (tests 6-8) permit to obtain a swelling degree above 0.5. The test 6 is the optimal variant since it permits to reach a highest brix degree (23%), so highest swelling degree (0.53) and adequate pH (3.9 \approx pure orange pH). In any case, the other variants should be chosen having in mind the consumer wishes. For example, we have already formulated an improved date powders with four different sugar/acid ratios (acidified by the citron juice); the tasting test (evaluated by 25 panel members) shows consumers preference towards the final product with the sugar/acidity ratio = 120.

Date Vinegar

The ability to the fermentation of both varieties is the principal information given by the Table 2.

Acetic acid and alcohol formation kinetics (case of Mech-Degla date submitted to the simultaneous double fermentation at 25 and 30°C) are shown in Fig. 4 and 5. It must be noticed that both alcohol

Table 2: Microbiologic characteristics of Mech-Degla and Degla-Beida dates

	(Colonies mL ⁻¹)						
Date varieties	Total germs	Yeasts	Moldiness	Acetic bacterium			
Mech-degla	0	220	15.10^3	27.10 ³			
Degla-Beida	0	550	260.10^3	2300.00			

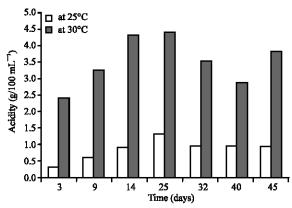


Fig. 4: Formation kinetic of the acetic acid in the reaction medium at 25 and 30°C (case of Mech-Degla date)

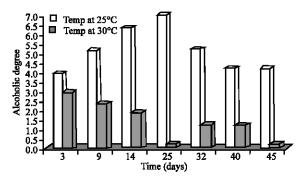


Fig. 5: Formation kinetic of the alcohol in the reaction medium at 25 and 30°C (case of Mech-Degla date)

Table 3: Chemical characteristics of vinegars obtained with application of the oxygenation

Parameters	Vinegar of Mech-Degla	Vinegar of Degla-Beida
pH at 25°C	3.71	3.39
Acidity (g 100 mL ⁻¹).	8.70	4.80
Brix degree at 25°C	20.60	14.08
Alcoholic degree (g 100 mL ⁻¹)	7.40	6.03

Table 4: Physicochemical characteristics of the date hydro alcoholic extract

Parameters	Content
Moisture (%)	20.00
pH	5.78
Total acidity (% in citric acid)	0.68±0.079
°Brix	72.47
Senders (%)	1.13±0.045
Refraction index	1.47067
Density	1.0263
Total phenolics (%)	2.125±0.547
Tannins (%)	0.762±0.438
Flavonoides (µg mL ⁻¹)	643.38 ± 130.844
Antioxidant activity (inhibition %)	52.15±0.047

and acetic acid, are analyzed at the same time, in each sample and at each time interval. The histograms show that the acetic acid synthesis increases dramatically at 30°C, whereas the alcoholic degree remains at the low level. On the opposite, at 25°C, the alcohol synthesized by yeasts is not oxidized completely until acetic acid by acetic bacterium. In fact, the temperature of 30°C is more appropriate for tropical climates (Adams and Twiddy, 1987).

The optimization consisted in applying oxygenation (3 mg O_2 mL⁻¹) at time corresponding to the alcohol maximum (Table 3). Absence of correlation between pH and total acidity may be explain by the high tampon power of the middle due to the simultaneous presence of acetic acid (CH₃COOH) and its conjugated basic (CH₃COO⁻).

Using a membrane recycle bioreactor and extracts of dates as alcoholic fermentation substrate, Mehaia and Cheryan (1991) have lead to an ethanol concentration of 68 g $\rm L^{-1}$ and to an acetic concentration of 45 g $\rm L^{-1}$ that is comparable to our results.

Water-alcohol Extract

It must be recalled that the hydroalcoholic extract is prepared so as to substitute the synthesised antioxidants BHA and BHT usually used as conservators in margarines (Table 4).

The very viscous liquid thus obtained could be used as ingredient in various food assortments: baking, confectionery, jelly and as cane sugar substitute. Results show also that the phenolic content is higher than those found (0.14 and 0.23%) by Khalil *et al.* (2002) for syrups obtained from Egyptian varieties Siwi and Amhat. Among 28 fruits consumed in China, Guo *et al.* (2003), using other analysis method, have demonstrated that the date fruit show a second antioxidant power.

CONCLUSIONS

Mech-Degla, Degla-Beida and Frezza dates can be valorised using some of their technologic proprieties such as drying, swelling and fermentation. Tablets were obtained in laboratory from powders with an average water content of 5% (db). Further, the fruits show an interesting swelling power (50% in relation to the initial weight) which provides the opportunity to formulate the dates in their "auto induced" syrup with brix degree equal to 25% (on average). The possibility to improve the traditional process of vinegar production has been also verified. On the other hand, the date tissue possesses an antioxidant activity which is above 50%, corresponding to the inhibition percents of the linoleic acid oxidation.

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