Thin layer convective air drying of wild edible plant (*Allium roseum*) leaves: experimental kinetics, modeling and quality

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Abstract The present study deals with the valorization of an edible spontaneous plant of the Tunisian arid areas: *Allium roseum*. This plant is traditionally used for therapeutic and culinary uses. Thin-layer drying behavior of *Allium roseum* leaves was investigated at 40, 50 and 60 °C drying air temperatures and 1 and 1.5 m/s air velocity, in a convective dryer. The increase in air temperature significantly affected the moisture loss and reduced the drying time while air velocity was an insignificant factor during drying of *Allium roseum* leaves. Five models selected from the literature were found to satisfactorily describe drying kinetics of *Allium roseum* leaves for all tested drying conditions. Drying data were analyzed to obtain moisture diffusivity values. During the falling rate-drying period, moisture transfer from *Allium roseum* leaves was described by applying the Fick's diffusion model. Moisture diffusivity varied from 2.55×10^{-12} to 8.83×10^{-12} m²/s and increased with air temperature. Activation energy during convective drying was calculated using an exponential expression based on Arrhenius equation and ranged between 46.80 and 52.68 kJ/mol. All sulfur compounds detected in the fresh leaves were detected in the dried leaves. Convective air drying preserved the sulfur compounds potential formation.

Keywords *Allium roseum* leaves · Drying kinetics · Modeling · Moisture diffusivity · Activation energy · Sulfur compounds

Nomenclature

a, c, n	dimensionless models constants
k, k ₁	models drying rate constants, h ⁻¹
E _a	activation energy, kJ/mol
De	moisture effective diffusivity, m ² /s
D ₀	constant equivalent to the diffusivity at an infinitely high temperature, m ² /s
L	half <i>Allium roseum</i> leaf thickness, mm
MR	moisture ratio
R	universal gas constant, kJ/mol K
r	correlation coefficient
S	standard error
T	temperature, K
t	drying time, s
v	air velocity, m/s
X	water content, g water/g d.b.

Subscripts

0	initial
cal	calculated
eq	equilibrium
exp	experimental
t	at any time

Introduction

Allium roseum is a wild edible plant, used by local population in the south of Tunisia as a vegetable, a condiment and a preservative in food or as an herbal remedy because of its medicinal and sensorial properties. *Allium roseum* leaves are consumed in salad and used as a spice to prepare traditional

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recipes. Besides their culinary uses, leaves are also used in traditional medicine for headaches, stomachaches, and rheumatism treatments (Najjaa et al. 2011). This species belongs to the *Allium* genus which represents the largest and most representative genus of the *Alliaceae* family. *Allium* genus includes approximately 700 species (Lanzotti 2006), the most widely used are onions (*Allium cepa*), garlic (*Allium sativum*), leeks (*Allium porrum*), chives (*Allium schoenoprasum*) and shallots (*Allium ascalonicum*). *Allium* species have diverse biological activities such as antibacterial (Ankri and Mirelman 1999; Najjaa et al. 2011), antifungal (Ankri and Mirelman 1999; Pyun and Shin 2006), antioxidant (Bozin et al. 2008; Najjaa et al. 2011) and therapeutic (Corzo-Martinez et al. 2007; Powolny and Singh 2008) activities. They are proposed to be used for the treatment or the prevention of numerous diseases, including cancer, coronary heart disease, obesity, hypercholesterolemia, diabetes type 2, hypertension, cataract and disturbances of the gastrointestinal tract (Corzo-Martinez et al. 2007; Powolny and Singh 2008; Boivin et al. 2009). These various biological effects are related to their important content of volatile sulfur compounds, typical of the *Allium* plants, which are also responsible of their characteristic pungent aroma and taste (Mondy et al. 2002; Jones et al. 2004; Li et al. 2007). These molecules are the products of the enzymatic reaction of alliinase, which is a C-S-lyase present in the vacuoles with S-alk(en)yl-L-cysteine-S-oxide precursors, located in the cytoplasm. This enzymatic reaction takes place after a tissue disruption in presence of water (Lanzotti 2006) and occurs when cells of fresh *Allium* are broken or when dried product is moistened with water (Méndez-Lagunas and Castaigne 2008). According to Najjaa et al. (2007), the qualitative and the quantitative analyses of essential oil showed the presence of 19 compounds in the whole essential oil of *Allium roseum*. The number of sulfur compounds was higher than that of the non-sulfur compounds.

Allium species are extensively used in their dried form as ingredients and flavor additives in precooked foods, meat sausage (Fista et al. 2004; Magra et al. 2006), sauces, soups and pizzas. They are produced in several forms: powdered, granulated, flaked, minced and chopped. Dried products of *Allium* plants are also used as supplements and medicinal preparations (Li et al. 2007). Hence, a sharp increase in the demand of dried *Allium* plants products has been noticed.

Several works have been focused on convective drying of various *Allium* genus plants such as garlic (Madamba et al. 1996; Krokida et al. 2003; Sacilik and Unal 2005; Méndez-Lagunas and Castaigne 2008), onion (Elustondo et al. 1996; Pezzutti and Crapiste

1997; Sarsavadia et al. 1999; Krokida et al. 2003; Kaymak-Ertekin and Gedik 2004; Sarsavadia 2007; Mota et al. 2010) and leek (Doymaz 2008). In these works, the main interest was to study the effects of drying air parameters (air temperature and velocity) on moisture migration inside the product in order to optimize drying operating conditions. Several empirical models have been proposed to describe the drying kinetics of food products (Zhang and Litchfield 1991; Diamante and Munro 1993; Elustondo et al. 1996; Midilli et al. 2002; Togrul and Pehlivan 2002; Midilli and Kucuk 2003; Jain and Pathare 2004; Kavak Akpinar et al. 2006; Vega et al. 2007a, b; Ah-Hen et al. 2011). Nevertheless, no model is found to be universal enough to predict the moisture content throughout the whole range of drying time under different conditions, and for all types of food products. Hence, experimental and modeling investigations are necessary in the design and the simulation of the drying process.

Allium roseum is a seasonal plant, with high water content and available only during the wet season. Hence, it is essential to find an appropriate preservation technique that makes *Allium roseum* leaves available during all the year and at the meantime allows the preservation of most of the organoleptic properties of the plant. Therefore, drying may be an alternative process which ends up with long life product and thus facilitates the use of this plant in food and pharmaceutical industries. However, no work has been reported in the literature on the drying of *Allium roseum*. Thus, the main objectives of this study were to (i) analyze the effects of drying operating conditions on drying kinetics, (ii) evaluate *Allium roseum* moisture diffusivity and activation energy, (iii) test models describing the drying behavior of *Allium roseum* and (iv) reveal the drying effect on volatile sulfur compounds.

Material and methods

Plant material

Allium roseum used in this investigation, was collected at its vegetative stage in January 2011 from the south-east of Tunisia. Botanical identification was carried out in the Range Ecology Laboratory of the Institute of Arid Areas, Tunisia. Plants were stored in a cold chamber maintained at 4 ± 1 °C until use (at most a week). *Allium roseum* leaves had initial moisture content ranging from 3.58 to 4.18 g water/g d.b.

Moisture content was measured by the gravimetric method where samples were maintained at 105 °C up to constant weight (24 h) (AOAC 1984).

Experimental drying procedure

In the drying chamber of a pilot air-dryer, *Allium roseum* leaves were uniformly spread, forming a single thin layer, on a perforated tray placed over an analytical balance (Explorer Ohaus item n°EOB120, Switzerland) with a precision of ± 0.01 g. A digital weighing apparatus allowed continuous mass loss measurements throughout drying tests. Experiments were conducted at three air temperatures (40, 50 and 60 °C) and two air velocities (1 and 1.5 m/s). All drying essays (for each drying operating condition) were carried out in triplicates.

Experimental drying kinetics determination

Drying kinetics curves represent the variation of moisture ratio (MR) versus drying time. Dimensionless moisture ratio may be calculated as follows (Mujumdar 1995):

$$MR = \frac{X_t - X_{eq}}{X_0 - X_{eq}} \quad (1)$$

Where MR is the moisture ratio, X_0 , X_t and X_{eq} are respectively initial water content, water content at any time t and equilibrium water content.

Drying kinetics modeling

Experimental drying data were described by using different models (Table 1) chosen from the most used equations in the literature describing thin layer drying kinetics of agricultural products.

Non-linear optimization method, using the computer program (Curve Expert 1.3), was used to estimate equations parameters.

The parameters of each model were determined by minimizing the difference between calculated and experimental data. Models fitting adequacy was evaluated by using two statistical parameters: the standard error (S), the correlation coefficient (r). These parameters are defined as follows:

Table 1 Mathematical models applied to fitting *Allium roseum* leaves drying curves

Model name	Model expression
Newton (Mujumdar 1995)	$MR = \exp(-k_N t)$
Page (Diamante and Munro 1993)	$MR = \exp(-k_P t^n)$
Henderson and Pabis (Zhang and Litchfield 1991)	$MR = a \exp(-k_H t)$
Logarithmic (Togrul and Pehlivan 2002)	$MR = a \exp(-k_L t) + c$
Two term (Midilli et al. 2002)	$MR = a \exp(-k_1 t) + c \exp(-k_2 t)$

$$S = \sqrt{\frac{\sum_{i=1}^{n_{\text{exp}}} (MR_{\text{exp}i} - MR_{\text{cal}i})^2}{n_{\text{exp}} - n_{\text{param}}}} \quad (2)$$

$$r = \sqrt{1 - \frac{\sum_{i=1}^{n_{\text{exp}}} (MR_{\text{exp}i} - MR_{\text{cal}i})^2}{\sum_{i=1}^{n_{\text{exp}}} (MR - MR)^2}} \quad (3)$$

Where MR_{Cal} is the value of the moisture ratio calculated by using the tested model, MR_{exp} is the experimental value of the moisture ratio, n_{param} is the parameters number of the particular model and n_{exp} is the number of experimental points.

Moisture diffusivity and activation energy

Experimental drying data were used to determine water diffusivity by using Fick's second diffusion equation:

$$\frac{\partial MR}{\partial t} = D_e \nabla^2 MR \quad (4)$$

Analytical solution of Fick's equation for an infinite slab (Eq. (5)) was used in order to estimate moisture diffusivity (Crank 1975) of *Allium roseum* leaves.

$$MR = \frac{X_t - X_{eq}}{X_0 - X_{eq}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-(2n+1)^2 \frac{\pi^2 D_e t}{4 L^2} \right] \quad (5)$$

In Eq. (5) MR is the moisture ratio, D_e is the moisture diffusivity (m^2/s), t is the drying time (s) and L is the half *Allium roseum* leaf thickness ($L = 0.45 \times 10^{-3}$ m).

This equation was applied assuming one-dimensional moisture diffusion without volume change with a constant diffusivity, a uniform moisture distribution and negligible external resistance. When time is sufficiently large, all the terms of the series are negligible compared to the first (Crank 1975):

$$\ln MR = -\frac{\pi^2 D_e t}{4 L^2} + \frac{8}{\pi^2} \quad (6)$$

The moisture diffusivity could be related to temperature by a simple Arrhenius equation as given below:

$$D_e = D_0 \exp \left(-\frac{E_a}{RT} \right) \quad (7)$$

Where D_e is the moisture diffusivity (m^2/s), D_0 is the constant equivalent to the diffusivity at infinitely high temperature (m^2/s), E_a is the activation energy (kJ/mol), R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ/mol K}$) and T is the absolute temperature (K).

Eq. (7) was linearized as following:

$$\ln(D_e) = \ln(D_0) - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (8)$$

Separation and characterization of volatile sulfur compounds

Fresh and dried leaves were crushed. 1 g of *Allium roseum* powder was mixed with 1 ml of distilled water. Compounds emitted in a closed 4-ml vial at room temperature were trapped at 60°C for 30 min and transferred to the GC–MS injector by headspace SPME (Teyssier et al. 2001). GC–MS analysis was

carried out with an “Agilent technologies 6890 N Net work GC system” gas chromatography type. The injector port temperature was 150°C , the detector (FID) temperature was 200°C . The column used is a capillary tube HP-5MS (30 m length,

Fig. 1 Effect of air temperature on moisture ratio of *Allium roseum* leaves during drying at air velocity of 1 m/s (a) and 1.5 m/s (b)

Fig. 2 Effect of air velocity on moisture ratio of *Allium roseum* leaves during drying at temperature of 40°C (a); 50°C (b) and 60°C (c)

0.25 mm external diameter), with a non-polar stationary phase (5 % phenyl methyl silicone and 95 % dimethyl polysiloxane). The column temperature was programmed from 75 °C to 100 °C at a rate of 2 °C/min then at a rate of 5 °C/min up to 180 °C. Total time of analysis was 28.5 min. The carrier gas was helium (99.999 %) and the column temperature was programmed from 70 to 250 °C at a rate of 5 °C/min. The injection port temperature was 200 °C. The mass spectrometer is an “Agilent technologies 5975B inert MSD” type (quadrupole). Total ion chromatograms and mass spectra were recorded in the electron impact ionization mode at 70 eV. The transfer line and the source temperature were maintained at 250 °C and the mode of data acquisition is the scan mode which ranged m/z from 50 to 550 u.m.a. The identification of sulfur compounds was accomplished by comparing the

retention time and the mass spectra data with those of standards sulfur compounds.

Results and discussion

Experimental drying kinetics

Air temperature effect on drying kinetics

Allium roseum leaves were dried to a final moisture content ranging from 0.076 to 0.130 g water/g d.b. for the different operating conditions. The moisture removed from *Allium roseum* leaves during convective air drying was very

Table 2 Parameter values for models used to describe the thin layer drying kinetics of *Allium roseum* leaves

Model name	Drying conditions		Model parameters					Statistical parameters	
	v (m/s)	T (°C)	k (h ⁻¹)	k ₁ (h ⁻¹)	n (-)	a (-)	c (-)	r	S
Newton	1	40	0.134	-	-	-	-	0.983	0.055
		50	0.191	-	-	-	-	0.993	0.037
		60	0.345	-	-	-	-	0.990	0.045
	1.5	40	0.148	-	-	-	-	0.982	0.058
		50	0.183	-	-	-	-	0.993	0.037
		60	0.355	-	-	-	-	0.986	0.053
Page	1	40	0.213	-	0.775	-	-	0.996	0.028
		50	0.247	-	0.840	-	-	0.999	0.017
		60	0.273	-	1.258	-	-	0.998	0.018
	1.5	40	0.233	-	0.766	-	-	0.995	0.030
		50	0.223	-	0.878	-	-	0.997	0.027
		60	0.272	-	1.295	-	-	0.996	0.028
Henderson and Pabis	1	40	0.111	-	-	0.887	-	0.997	0.024
		50	0.170	-	-	0.929	-	0.998	0.021
		60	0.369	-	-	1.051	-	0.993	0.040
	1.5	40	0.122	-	-	0.884	-	0.996	0.026
		50	0.169	-	-	0.955	-	0.995	0.031
		60	0.379	-	-	1.050	-	0.989	0.050
Logarithmic	1	40	0.108	-	-	0.894	-0.009	0.997	0.025
		50	0.170	-	-	0.928	0.001	0.998	0.021
		60	0.261	-	-	1.220	-0.193	0.998	0.021
	1.5	40	0.115	-	-	0.897	-0.018	0.997	0.026
		50	0.165	-	-	0.960	-0.009	0.995	0.031
		60	0.212	-	-	1.379	-0.377	0.999	0.014
Two terms	1	40	0.106	3.027	-	0.857	0.144	0.999	0.013
		50	0.158	2.314	-	0.883	0.119	0.999	0.010
		60	0.369	0.369	-	0.525	0.525	0.993	0.041
	1.5	40	0.116	3.922	-	0.852	0.146	0.999	0.015
		50	0.147	1.274	-	0.874	0.153	0.997	0.023
		60	0.380	0.379	-	0.525	0.525	0.989	0.053

important and varied from 96 to 98 % (Ben Haj Said et al. 2013). Typical drying curves exhibiting moisture content changes during drying and under different air temperatures are shown in Fig. 1. Moisture ratio follows an exponential decrease. It decreases faster in the beginning of the drying processes and gradually slowed down through the end (Ben Haj Said et al. 2011). Drying curves were characterized by a constant- and a falling-rate drying period (Sanjuán et al. 2003; Da Silva et al. 2013; Rodríguez et al. 2014). *Allium roseum* leaves drying behaviour results of the two mechanisms that involved in the drying process: convection and diffusion (Da Silva et al. 2013). In the process beginning, the limiting process is convection (water transfer from the leaves surface to the air), as the external resistance to the mass flow is higher than the internal one. Thus, the drying rate is constant (the initial linear behavior). Further, after critical moisture content, the internal resistance that limits the drying, due to the water diffusion (Rodríguez et al. 2014). Thus, the drying rate is decreased and the drying curve shows that exponential decay shape. This decrease could be explained by a reduction in the absorbed energy by the product surface while the drying process advances. This reduction, observed at the end of drying, could also be due to the lower water content of the product partially dried as well as to the dried surface which constitutes a barrier against heat penetration and water migration (Sharma and Prasad 2005). Furthermore, drying kinetics obtained at different temperatures show an almost identical slope at the beginning of the process. Same tendencies were also reported by Curcio et al. (2008). Drying behaviour differences due to temperature appears after about 2 h. Hence, an increase in temperature accelerated the drying process and produced a higher dehydration rate. This is due to the increase, at higher temperature, of heat transfer between drying air and *Allium roseum* leaves and to the acceleration of water migration throughout the leaves (Mota et al. 2010). Indeed, when the drying temperature augmented, water vapour pressure inside the leaves also increased increasing the pressure gradient between the surface and the interior of the sample which generated higher drying rate and water transfer (Arslan and Musa Özcan 2010).

Drying curves, presented in Fig. 1, show also a very important reduction in the drying time (more than 70 %) between air drying temperatures of 40 and 60 °C. The same trends are obtained with 1.5 m/s drying air velocity. Total drying duration required to reduce the moisture content of *Allium roseum* leaves to about 8–12 % d.b. at 1 m/s varied from 7, 22 to 28 h for temperatures of 60, 50 and 40 °C, respectively. Drying durations found for *Allium roseum* leaves are lower than those found during convective air drying of garlic (*Allium sativum*) at the same air velocity. Hence, garlic drying durations at 1 m/s are 32, 27.5 and 13 h at 40, 50 and 60 °C, respectively (Sharma and Prasad 2001; Sharma et al. 2009). These differences could be due to the apparatus used for drying, to the

product initial moisture content and to the differences related to the plant variety.

These experimental results showed that temperature is an important factor for *Allium roseum* leaves drying process. Similar results are reported for garlic (Madamba et al. 1996; Pezzutti and Crapiste 1997; Sharma and Prasad 2001) and onion (Sarsavadia et al. 1999; Jain and Pathare 2004; Sharma and Prasad 2005; Arslan and Musa Özcan 2010).

Air velocity effect on drying kinetics

Dehydration characteristics of *Allium roseum* leaves at 1 and 1.5 m/s and at different temperatures (40 °C (a); 50 °C (b) and 60 °C (c)) are presented in Fig. 2. A superposition of the drying kinetics curves at 1 and 1.5 m/s was observed. Statistical analysis (One way ANOVA) indicates that air velocity had no significant effect on the drying kinetics and did not affect the evolution of moisture content during the process. Negligible moisture resistance at the product surface compared to the internal resistance may explain this behaviour

Fig. 3 Experimental and predicted (Page model (a) and Logarithmic model (b)) moisture ratio variation of *Allium roseum* leaves during drying at 1 m/s

during thin layer drying (Madamba et al. 1996). These results indicate that the limiting drying factor is water transfer inside the *Allium roseum* leaves and not water evaporation on the product surface. Same results, concerning the effect of air velocity on drying kinetics, are reported for onion (Pezzutti and Crapiste 1997) and garlic (Madamba et al. 1996). Madamba et al. (1996) explain air velocity negligible effect by a strong retention of water molecules due to the colloidal and hydrophilic nature of food products and of organic materials generally.

Drying kinetics modeling

The model coefficients for the five tested models were estimated by a non-linear regression analyses. The goodness of the models fit is characterized by the highest value of correlation coefficient (r) and lowest value of standard error (S). The estimated values of models coefficients and the corresponding values of the correlation coefficients (r), the standard errors (S) are shown in Table 2. All tested models were found to satisfactorily describe the thin layer air drying kinetics of *Allium roseum* leaves for all the drying conditions applied.

The correlation coefficient values (r) varied from 0.982 to 0.999 whereas the standard error (S) values ranged from 0.010 to 0.058 for different drying conditions. Fig. 3 shows the adequacy between calculated (Page model) and experimental drying curves of *Allium roseum* leaves.

Drying rate constant, k , in the different drying models increased with increasing temperatures. For example, the Newton model drying rate constant (k) values were 0.134 h^{-1} , 0.191 h^{-1} and 0.345 h^{-1} at 40, 50 and 60 °C drying air temperatures, respectively. The increase of drying rate constants (k) with temperature was also shown for onion (Sarsavadia et al. 1999), pumpkin (Guiné et al. 2011) and *Aloe vera* thin layer convective air drying (Vega et al. 2007b).

In order to take into account the effect of the drying variables on the studied models parameters, calculated values of k , k_1 , n , a and c were correlated to drying air temperature. Each parameter (Y) has shown a linear dependency with temperature. Hence, drying rate constants (k , k_1) and dimensionless models constants (n , a and c) may be written as:

$$Y = AT + B \quad (9)$$

Table 3 Linear model ($AT+B$) coefficients describing models parameters dependency upon temperature

Model name	Model parameters	v (m/s)	Linear model coefficients		Statistical parameters	
			$A (\times 10^2)$	$B (\times 10^2)$	r	S
Newton	$k (\text{h}^{-1})$	1	1.055	-30.042	0.967	0.040
		1.5	1.035	-28.883	0.934	0.056
Page	$k (\text{h}^{-1})$	1	0.3	9.433	0.997	0.003
		1.5	0.195	14.517	0.753	0.024
	$n (-)$	1	2.415	-24.983	0.921	0.144
		1.5	2.645	-34.283	0.949	0.125
Henderson and Pabis	$k (\text{h}^{-1})$	1	1.29	-42.833	0.954	0.057
		1.5	1.285	-41.917	0.939	0.067
	$a (-)$	1	0.82	54.567	0.963	0.033
		1.5	0.83	54.8	0.997	0.010
Logarithmic	$k (\text{h}^{-1})$	1	0.765	-20.283	0.994	0.012
		1.5	0.485	-7.85	0.999	0.001
	$a (-)$	1	1.63	19.9	0.910	0.105
		1.5	2.41	-12.633	0.920	0.145
	$c (-)$	1	-0.92	39.3	0.842	0.083
		1.5	-1.795	76.283	0.855	0.154
Two terms	$k (\text{h}^{-1})$	1	1.315	-44.65	0.944	0.065
		1.5	1.32	-44.567	0.915	0.082
	$k_1 (\text{h}^{-1})$	1	-13.29	854.833	0.966	0.503
		1.5	-17.715	1071.583	0.962	0.716
	$a (-)$	1	-1.66	158.5	0.832	0.157
		1.5	-1.635	156.8	0.837	0.151
	$c (-)$	1	1.905	-68.983	0.837	0.176
		1.5	1.895	-67.283	0.874	0.149

The calculated coefficients (A, B) (Eq. (9)) describing the temperature dependency of the studied model parameters are recapitulated in Table 3. Correlation coefficient (r) values of the models drying rate constants (k and k_1) were found to be higher than 0.9 whereas the standard error (S) values ranged from 0.001 to 0.716 for the different proposed models and the two air drying velocity levels. Calculated dimensionless models constants (a , c and n) showed correlation coefficient (r) values ranging between 0.832 and 0.997 whereas standard error (S) values ranged from 0.010 to 0.176 for all tested models and the two air drying velocity levels.

These linear relations can be used to predict *Allium roseum* leaves moisture ratio at any time during the convective air drying and at any air temperature in the range of 40–60 °C with a high accuracy. A linear increase of drying constants k (min^{-1}) with temperature was also found when drying onion (Sarsavadia et al. 1999) and red bell pepper (Vega et al. 2007a). According to Vega et al. (2007a), the drying rate constant k (min^{-1}) is related to temperature by the Arrhenius equation and could therefore be considered as a pseudo-diffusivity. Midilli and Kucuk (2003) showed logarithmic relations between models parameters and temperature for thin layer drying of pistachio. Page model parameters dependency upon temperature was also described by a power equation in

Table 4 Moisture diffusivity of *Allium roseum* leaves

Drying conditions		Moisture diffusivity $\times 10^{12}$ (m^2/s)
v (m/s)	T (°C)	
1	40	2.55
	50	3.73
	60	8.63
1.5	40	2.98
	50	4.01
	60	8.83

the case of parsley leaves thin layer convective drying (Kavak Akpinar et al. 2006).

Moisture diffusivity

The variation of experimental $\text{Ln}(\text{MR})$ versus drying time for *Allium roseum* leaves at various conditions of temperature and air velocity are shown in Fig. 4. A linear relationship was found between $\text{Ln}(\text{MR})$ and drying time for all drying conditions with a correlation coefficient higher than 0.98. Eq. (6) and the slopes deduced from these linear regressions allowed

Fig. 4 Linear relationship between $\text{Ln}(\text{MR})$ and drying time for *Allium roseum* leaves at various temperature levels at air velocity of 1 m/s (a) and 1.5 m/s (b)

Fig. 5 Influence of drying air temperature on average moisture diffusivity in drying of *Allium roseum* leaves at air velocity of 1 m/s (a) and 1.5 m/s (b)

Table 5 Activation energy of *Allium roseum* leaves

Drying air velocity (m/s)	Activation energy (kJ/mol)
1	52.68
1.5	46.80

the calculation of moisture diffusivity value for each treatment. The values of *Allium roseum* leaves moisture diffusivity (De) are recapitulated in Table 4. Calculated moisture diffusivities of *Allium roseum* leaves varied from 2.55×10^{-12} to 8.83×10^{-12} m²/s. Moisture diffusivity (De) values increased with drying air temperature and velocity. Moisture effective diffusivities found in the present study are almost equal to those found by Barbosa et al. (2007) in the case of lemon-scented verbena leaves which ranged from 2.91×10^{-12} to 11.71×10^{-12} m²/s.

These values were lower than reported diffusivities for garlic dried in a range of temperature of 45–75 °C and air velocity of 2–4 m/s which varied from 3.4×10^{-11} to 5.8×10^{-11} m²/s (Pezzutti and Crapiste 1997). In addition, moisture diffusivity values for onion dried in a range of temperature of 50–70 °C varied from 1.32×10^{-10} to 1.62×10^{-10} m²/s (Mitra et al. 2011). These differences could be explained by the dependence of moisture diffusivity upon the composition, the structure, the plant variety and the operating conditions.

Activation energy

Figure 5 shows the curves expressing the variation of moisture diffusivity with the absolute drying temperature. Activation energy for water diffusion was obtained from Eq. (8) and the slopes calculated of moisture diffusivity versus temperature curves.

The values of activation energy (Ea) of *Allium roseum* leaves are recapitulated in Table 5. The activation energy for water diffusion was found to be 52.68 kJ/mol and 46.80 kJ/mol

for drying air velocity of 1 and 1.5 m/s, respectively. It was lower at an air velocity of 1.5 m/s compared to an air velocity of 1 m/s. The activation energy for *Allium roseum* leaves convective air drying was lower than 61.91 and 69.52 kJ/mol values found for mint drying at air velocity of 0.5 and 1 m/s, respectively and at drying temperatures of 30, 40, and 60 °C (Park et al. 2002). However, the activation energy found for *Allium roseum* leaves convective drying was slightly higher than 27.8 kJ/mol value found for the dehydration of garlic at drying temperatures of 45, 60 and 75 °C (Pezzutti and Crapiste 1997) and 26.376 kJ/mol found for onion drying at 30, 50 and 60 °C (Mota et al. 2010).

Drying effect on volatile sulfur compounds

Table 6 shows the GC chromatographic separation of *Allium roseum* leaves sulfur compounds. A total of five compounds were identified, by SPME analysis, in fresh *Allium roseum* leaves, four disulfides (dimethyl-disulfide, methyl-2-propenyl-disulfide, cis-propenyl-methyl-disulfide, trans-propenyl-methyl-disulfide) and a trisulfide (dimethyl-trisulfide). For chive leaves (*Allium schoenoprasum*), only disulfides were detected, which are dimethyl-disulfide, dipropyl-disulfide, methyl-propyl-disulfide, methyl-1-propenyl-disulfide and propyl-1-propenyl-disulfide (Mellouki et al. 1994). Dimethyl-disulfide (47.57 %) is the major volatile sulfur compound found in *Allium roseum* leaves. According to Mellouki et al. (1994), chive leaves are also very rich in dimethyl-disulfide. For chives leaves, it is the dipropyl-disulfide which occupies the first place (Mellouki et al. 1994). This compound has not been detected in *Allium roseum* leaves. For garlic (*Allium sativum*), three major volatile sulfur compounds have been detected and are, by order of abundance, the di-2-propenyl-trisulfide, the methyl-2-propenyl-trisulfide and the di-2-propenyl-disulfide. The methyl-2-propenyl-disulfide and the dimethyl-trisulfide, abundant compounds in *Allium roseum* leaves, have also been

Table 6 Relative concentrations of sulfurous components of fresh and dried *Allium roseum* leaves (expressed as weight percentages)

Compound	Retention (min) time	Weight percentage (%)						
		Fresh leaves	Drying air conditions					
			1 m/s			1.5 m/s		
			40 °C	50 °C	60 °C	40 °C	50 °C	60 °C
Dimethyl-disulfide	2.30	47.57	29.25	56.27	62.36	37.76	30.40	62.49
2-propenyl-methyl-disulfide	3.97	15.53	nd*	25.06	11.22	13.31	4.86	6.17
Cis-propenyl-methyl-disulfide	4.21	2.21	nd	2.74	nd	nd	nd	nd
Trans-propenyl-methyl-disulfide	4.36	11.64	nd	6.79	7.79	5.48	nd	6.24
Dimethyl-trisulfide	5.01	8.46	nd	3.18	16.29	nd	nd	20.92

*nd: not detected

detected in garlic but in small quantities (Sowbhagya et al. 2009).

SPME analysis of volatile sulfur compounds of fresh and dried *Allium roseum* leaves revealed some interesting results. All sulfur compounds detected in the fresh leaves were detected in the dried leaves (Table 6). These results showed that convective air drying preserved the sulfur compounds potential formation (Méndez-Lagunas and Castaigne 2008). This indicates a protection of the alliinase activity and a preservation of the reaction precursors (Li et al. 2007). According to Méndez-Lagunas and Castaigne (2008), the decomposition of the sulfur compounds precursors starts at drying temperatures higher than 100 °C. These results are in accordance with those of the present study which proved that high drying temperatures (60 °C) have not affected the potential of volatile sulfur compounds formation. Dimethyl-disulfide, the major compound, was found in dried leaves at 60 °C with a percentage higher than in fresh and dried leaves at lower temperatures. Volatile sulfur compounds preservation in dried *Allium roseum* leaves is corroborated by the results of Teyssier et al. (2001) which showed the presence of dipropyl-disulfide, propyl-1-propenyl-trisulfide and methyl-1-propenyl-trisulfide in onion powder obtained by hot air drying at temperature varying from 45 °C to 85 °C. (Méndez-Lagunas and Castaigne 2008) showed that sulfur compounds-forming potential was 91 % preserved by drying temperature cycling from 40 to 60 °C. They explained the enzyme activity protection at high drying temperatures by its high molecular mass and by the high content of the plant leaves in sugars (Méndez-Lagunas and Castaigne 2008).

Conclusion

Allium roseum leaves drying curves showed only the falling drying rate period. Temperature was shown to have a considerable effect on the variation of moisture ratios during drying time while air velocity seemed to have a negligible effect on the drying process. The thin-layer drying characteristics of the leaves were satisfactorily described by five thin layer drying models. Moisture diffusivity was calculated from the experimental data and varied from 2.55×10^{-12} to 8.83×10^{-12} m²/s with the temperature dependence represented by a simple Arrhenius-type relationship. The activation energy for moisture diffusion was between 46.80 and 52.68 kJ/kg. Convective air drying allowed the preservation of *Allium roseum* leaves organoleptic quality (Jones et al. 2004; Li et al. 2007). It can be used as a valorization method with a good preservation of typical sulfur compounds of the plant and responsible of its characteristic taste. Drying is found to be a good method to block volatile sulfur compounds biosynthesis reaction and to preserve their potential formation during the dried product use.

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