



# Effect of partial drying intensity, frozen storage and repeated freeze-thaw cycles on some quality attributes of dehydrofrozen quince fruit

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Received: 18 April 2019 / Accepted: 3 October 2019 / Published online: 23 October 2019  
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## Abstract

The present study investigated the effect of multi-freeze-thaw cycles on thawed water exudate, final water content, color features, and polyphenolic contents of frozen and dehydrofrozen quince fruit. Quince pieces were predried at 40 °C and 3 m/s, until specific final water contents: 2, 1, and 0.3 g H<sub>2</sub>O/g db, then, frozen at – 18 °C and stored during 6 months. Monthly, quinces were thawed at 20 °C to perform quality analyses: treated quinces had remarkable water retention, and no significant difference between values over storage time has been recorded ( $p > 0.05$ ). Convective pre-drying step remarkably reduces the negative impact of freezing/thawing processes and freeze-thaw cycles on quince color and guarantees its stability during frozen storage: a significant decrease of thawing impact on total color difference has been noticed for dehydrofrozen samples (3.32) compared to (12.53) for conventionally frozen ones. Finally, dehydrofreezing allows a better retention of polyphenols content, during frozen storage. Fruits quality, with high water content, such as quinces may be compromised by freezing and frozen storage. Tissue damage occurs as ice accrues and concentrates soluble solids. Convective pre-drying can remove some of the available water, which reduces ice formation during freezing and subsequently storage. This piece of work has proved the potential use of convective air drying before freezing to reduce the negative impact of freezing/thawing processes and freeze-thaw cycles on quince quality and guarantees its stability during storage. These fruits marketability is highly correlated with their textural quality in addition to their color properties and bioactive components. Dehydrofreezing is recommended for better quince fruit quality preservation during storage. Thus, it may be a commercial method to reduce shipping costs and fruits storage.

**Keywords** Dehydrofreezing process · Frozen storage · Freeze-thaw cycles · Quality parameters · Quince fruit

## Abbreviations

TWE	Thawed water exudate
FWC	Final water content
TCD	Total color difference
BI	Browning index
TPC	Total polyphenols content

## Introduction

Quince fruit, a member of the *Rosaceae* family, is known for its nutritional attributes, pleasant odor, and distinctive taste. It is, especially, recognized as an important dietary source of health-promoting compounds, due to its antioxidant and antimicrobial characteristics.

Recent research has shown the beneficial effect of quince fruits on human health, due to the presence of different functional and phytochemical compounds [1]. Nevertheless, this fruit is perishable, as a consequence of its high-water content and susceptibility to quality deterioration.

Freezing is one of the most important long-term storage and preservation process. More than a preservation operation, freezing makes available seasonal fruits throughout the year and thus, responds to an increasing industrial demand. However, the development of ice crystals during freezing process and inevitably during long-term frozen storage,

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causes substantial degradation after thawing, through water exudation, color loss [2] and organoleptic degradation [3]. Therefore, the size and shape of these ice crystals have a crucial and critical impact on the final quality of the stored frozen product [4]. In addition, quality deterioration is usually emphasized by temperature variations that frozen product undergoes during the cold chain: storage, transportation, and consumer handling. These temperature fluctuations, possibly leading to freeze-thaw cycles, are at the origin of three phenomena that are often closely related: mechanical damage, nutrients denaturation, and loss of water-holding capacity. These freeze-thaw cycles may occur several times during storage, transportation and until consumer use and it is very important to determine the quality changes that arise during multiple freezing–thawing problems. Hence, quality loss of frozen fruits should be minimized not only during the freezing step but also over the frozen storage, the distribution steps and during consumer handling during which unavoidable freeze thaw cycles occur.

Partial dehydration prior to freezing process, assigned as dehydrofreezing, has recently been proposed to prevent freezing damage of perishable fruits and vegetables [5]. In dehydrofreezing process, food is dehydrated to desired moisture content and then frozen. This is well established as a commercial method to reduce shipping costs, handling and storage of fruits and vegetables. It also offers convenience of use compared to conventional freezing. Literature provides many researches of the positive impact of osmo-dehydrofreezing on frozen stored fruit quality in term of texture, color, drip loss and polyphenolic compounds [6–8].

Nevertheless, osmotic-drying applied prior to freezing process has certain limitations. Indeed, dehydration time to reach the desired water content is very long. In addition, osmotic dehydration (OD) causes soluble nutrients leaching and water content levels reached after OD are limited.

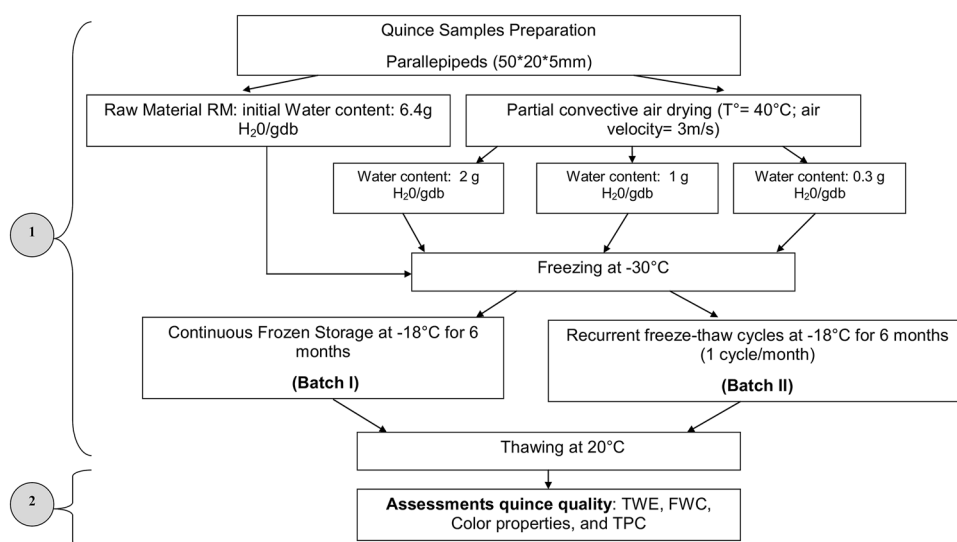
Moreover, sugar or salt concentration in fruit and vegetables, may change final product taste and thus its consumer acceptability. Not to mention added salt and sugars have many harmful effects on health. For example, they increase blood pressure and obesity, both of which increase the risk of cardiovascular disease [9].

Interestingly, despite the fact that it requires more energy than OD, pre-air drying operation can be particularly suitable for fruits and vegetables. Indeed, it allows to reach much lower moisture content, in short time and it was claimed that dehydrofrozen fruits and vegetables have a better quality over conventionally frozen products [10, 11]. However, there are sparsely cited references about the impact of combined air drying and freezing processes on global fruit and especially on bioactive composition of dehydrofrozen/thawed fruits, during long-period frozen storage. In addition, no references were found regarding long-period frozen storage effects on bioactive molecules composition of dehydrofrozen/thawed fruits. Moreover, no study has been conducted previously on the effect of repeated freeze-thaw cycles on the quality changes of stored dehydrofrozen fruits. Thus, this study is focused on the evaluation of (i) the effect of combined air drying and freezing processes on thawed water exudate (TWE), final water content (FWC), color, and total polyphenols content (TPC) of thawed quince fruits, and (ii) the impacts of conventional frozen storage and storage with repeated freeze-thaw cycles, at  $-18^{\circ}\text{C}$  during 6 months, on TWE, FWC, color properties and TPC of dehydrofrozen thawed quince samples.

## Material and methods

The general treatment procedure is presented in Fig. 1. All operations are described subsequently in details.

**Fig. 1** Schematic diagram of global treatment (1/process treatment; 2/quality assessment)



## Treatment processes

### Raw material and sample preparation

Fresh quince samples, with initial water content of  $6.40 \pm 0.85$  g/g db (db: dry basis), were selected randomly from a local market from Tunis (Tunisia). Fruits were peeled, cored and the hard pieces around the core were removed. Quince samples were manually cut with stainless steel knives into parallelepipeds with a length of  $5.12 \pm 0.35$  cm, a width of  $2.27 \pm 0.21$  cm, and a thickness of  $0.5 \pm 0.48$  cm. The initial water content was determined according to AOAC official method 934.06 at 105 °C for 24 h [12].

### Partial air drying

Quince slices were pre-dried in a laboratory thermal convective air dryer unit at 40 °C and 3 m/s as airflow velocity. Previous studies on apples were performed to optimize the water content levels to reach before the freezing step. Experimental results concerning the impact of initial moisture content on dehydrofrozen apples firmness [13] helped establish the range of water content to be considered in this current research as 23, 50, and 66 g/100 g wb (wb: Wet Basis) which corresponds to 0.3; 1; 2 g/g db, respectively.

### Experimental freezing process

Fresh and partially air-dried quince samples were frozen in a freezer (Whirlpool Model AFG 363/G, Italy) with temperature of -30 °C.

### Frozen storage conditions

Frozen and dehydrofrozen quince samples were immediately packed into polyethylene bags and sealed for storage. Representative samples of conventional freezing and dehydrofreezing processes (prior to frozen storage:  $t=0$ ) samples were analyzed. Treated quince slices were divided into two batches depending on the type of storage and placed in a laboratory scale chest freezer (SABA model CV253, France). Freezer's temperature was -18 °C as steady state.

After freezing, two frozen storage types (I and II) were considered:

- Continuous frozen storage (I): frozen and dehydrofrozen quince samples of batch I were kept in the freezer during storage period (6 months). Only representative samples for quality assessments were retrieved each month.
- Frozen storage with freeze-thaw cycles (II): Each month, and during 6 months, all the frozen and dehydrofrozen quince slices of batch II were removed from the storage freezer and thawed. Experimental Thawing Process

Frozen and dehydrofrozen quince pieces of both batch I and II were removed from the storage freezer thawed by leaving them at room temperature until the temperature of quince sample center reached 20 °C.

### Temperature monitoring

K-type thermocouples (NEDA16046F22006P, diameter 1 mm, scope -200 to 200 °C, accuracy  $\pm 1$  °C) linked to an automatic recorder (Dostmann electronic 5020-0309, Germany) were inserted into the center of quince samples for temperature measurements during freezing process. The frozen samples, containing probes already positioned at their centers were removed from the chest freezer. They were then thawed at room temperature until the final temperature reached the room temperature (20 °C), Temperature was recorded every 10 s using the thermocouples and a data logger.

## Quality assessments

### Determination of thawed water exudate (TWE)

Since quince samples have different initial water contents depending on the level reached during the pre-drying process, TWE also known as exudate loss was calculated to better represent the amount of lost water in thawed dehydrofrozen samples. TWE is expressed in grams of water /100 g water in the frozen product before the thawing phase [5, 13]. The measurements were done in triplicate for each treatment (freezing, dehydrofreezing and during storage period). The results were calculated as Eq. (1):

$$TWE = \frac{(m_i - m_f)}{\left(m_i \left(\frac{w}{1+w}\right)\right)} \times 100 \quad (1)$$

where W is the water content of the frozen sample in dry basis,  $m_i$  and  $m_f$  are, the masses of frozen and thawed quince sample, respectively.

### Determination of final water content (FWC)

Water content of thawed quince samples (FWC) was measured by the gravimetric method at 105 °C up to constant weight (24 h) according to AOAC official method 934.06 [12]. FWC measurements were performed in triplicate.

### Color examination

For each treated quince sample, "L", "a" and "b" parameters were measured directly on the surface of the product using a colorimeter (Konica Minolta CR-410, Tokyo, Japan).

The instrument was standardized against a white tile before each session and checked for recalibration between measurements. Color was measured in Hunter L, a, b units, as Total color difference (TCD) and as Browning index (BI), presented by Maskan [14] and Wang, Mu, Fang, Mujumdar, Yang, Xue, Xie, Xiao, Gao and Zhang [15], as following (Eqs. 2 and 3):

$$\text{TCD} = \Delta E^*ab = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \quad (2)$$

where L indicates (whiteness or brightness/darkness), a (redness/greenness) and b (yellowness/blueness).  $L_0$ ,  $a_0$ , and  $b_0$  are fresh or dried quince sample color parameters (before freezing process) and L, a, and b are frozen or dehydrofrozen quince sample color parameters during freeze storage period.

$$\text{BI} = \frac{(100(x - 0.31))}{0.17} \quad (3)$$

where

$$x = \frac{(a + 1.75L)}{(5.645L + a - 3.012b)} \quad (4)$$

Each result value was the mean of six measurements.

### Total polyphenols content (TPC)

**Sample extract preparation** Quince fruit extract was prepared, using triplicate measures systematically issued from two or three distinct fruit samples, by magnetic stirring for 30 min of 2.5 g of frozen or dehydrofrozen/thawed quince fruit with 25 ml of absolute methanol. The mixture was kept in the dark at 4 °C for 24 h and then filtered. The methanolic extract was stored at 4 °C until analysis. Determination of Total phenolic content.

The phenolic content in the extracts was determined by the Folin-Ciocalteu reagent using Gallic acid as the reference compound: 125 µl of the prepared extract was mixed with 500 µl of distilled water in a test tube followed by the addition of 125 µl of Folin-Ciocalteu reagent. The samples were well mixed and then allowed to stand for 6 min before adding 125 µl of a 7% aqueous sodium carbonate solution. Water was added to adjust the final volume to 3000 µl. The resulting mixtures were vortexed and allowed to stand for 90 min in the dark at room temperature before measuring the absorbance at 760 nm with JENWAY 6715UV/V spectrophotometer. Finally, absorbance values were compared with those of standards prepared similarly with known Gallic acid concentrations. Total polyphenols content of frozen and dehydrofrozen quince samples were expressed as grams of Gallic acid equivalents per 100 g dry basis (g GAE/100 g db) ± SD for three replications, through the calibration curve with Gallic acid in the range of 0–500 µg/ml [16].

### Statistical evaluation

Data were reported as mean values ± standard deviation (SD). Multifactor analysis of variance was applied with source of variance being the initial water content W (g H<sub>2</sub>O/gdb), the freeze storage time FST (month) for both storage types (continuous and with repeated CCB cycles), in order to estimate the least significant differences (LSD) among the media of the thawed water exudate (TWE), the final water content (FWC), the total color difference (TCD), the browning index (BI), and the total polyphenol content (TPC), at a confidence level of 95% ( $p < 0.05$ ). Statistical treatment of results was executed using the analysis design procedure of Statgraphics Plus software for Windows (1994, version 4.1, Levallois-Perret, France).

## Results and discussion

### Thawed water exudate TWE

The impact of frozen storage time (FST expressed in months) and recurrent freeze-thaw cycle during storage (1 cycle/month) on the TWE versus the initial water content of quince slices W (g H<sub>2</sub>O/g db) are investigated and data is shown in Table 1.

TWE was expressed as gram of water exudate/100 g water initial W, taking into account the values of water content W of the quince samples prior to freezing step (RM; 2; 1; and 0.3 gH<sub>2</sub>O/gdb).

### Samples without pre-drying treatment (untreated)

Data in Table 1 shows that fresh quince samples, without previous partial air drying, have a much higher TWE than all pre-dried samples. Table 1 also shows that fresh quince TWE (RM: Raw Material) was major and increased gradually during the 6 months frozen storage at – 18 °C, with a significant effect of FST on TWE ( $p < 0.05$ ). Indeed according to Reno, Prado and Resende [4], the loss of cellular fluid is an important quality parameter of the freezing process that can be related to the degree of rupture of the cell structure. In fact, this severe structural damage is due to the growth of ice crystals with the separation of the cells and the substantial loss of fluid material across the cellular wall. Thus, the higher the initial water content W, the larger the crystal size. Similar results were observed in several research works on fresh fruits and vegetables: tomatoes, broccoli and strawberries. Indeed, Reno, Prado and Resende [4] reported that TWE intimately correlated with the cellular structure and significantly increased

**Table 1** Thawed water exudate (TWE) of frozen and dehydrofrozen quince fruit samples *versus* Frozen Storage time and repeated freeze-thaw cycles after thawing process

FST (months)	TWE							
	Continuous storage				Recurrent freeze-thaw cycle during storage (1 cycle/month)			
	W (g H <sub>2</sub> O/g db)							
	RM	2	1	0.3	RM	2	1	0.3
0	7.88 ± 0.68 <sup>Aa</sup>	5.16 ± 0.08 <sup>Ab</sup>	3.09 ± 0.47 <sup>Ac</sup>	2.07 ± 0.04 <sup>Ac</sup>	7.63 ± 1.06 <sup>Aa</sup>	5.04 ± 0.49 <sup>Ab</sup>	2.93 ± 0.76 <sup>Ac</sup>	2.04 ± 0.46 <sup>Ac</sup>
1	8.46 ± 0.79 <sup>ABa</sup>	5.35 ± 0.50 <sup>Ab</sup>	3.55 ± 0.63 <sup>Ac</sup>	2.11 ± 0.13 <sup>Ad</sup>	14.32 ± 4.42 <sup>Ba</sup>	9.21 ± 0.15 <sup>Bb</sup>	4.53 ± 1.04 <sup>ABc</sup>	2.20 ± 0.27 <sup>Ad</sup>
2	10.76 ± 0.94 <sup>Ba</sup>	5.57 ± 1.09 <sup>Ab</sup>	3.16 ± 0.66 <sup>Ac</sup>	2.20 ± 0.08 <sup>Ac</sup>	19.21 ± 2.16 <sup>Ca</sup>	12.39 ± 0.36 <sup>Cb</sup>	6.38 ± 0.60 <sup>Bc</sup>	2.58 ± 0.59 <sup>ABd</sup>
3	12.49 ± 1.66 <sup>Ca</sup>	5.72 ± 1.02 <sup>Ab</sup>	3.02 ± 0.62 <sup>Ac</sup>	2.21 ± 0.17 <sup>Ac</sup>	23.19 ± 0.78 <sup>Da</sup>	14.11 ± 0.84 <sup>CDb</sup>	7.07 ± 0.39 <sup>Bc</sup>	3.25 ± 0.76 <sup>ABd</sup>
4	15.38 ± 1.79 <sup>Da</sup>	5.90 ± 0.53 <sup>Ab</sup>	2.63 ± 0.34 <sup>Ac</sup>	2.35 ± 0.12 <sup>Ac</sup>	25.91 ± 1.74 <sup>Ea</sup>	15.91 ± 0.55 <sup>Db</sup>	7.39 ± 0.94 <sup>Bc</sup>	3.56 ± 0.60 <sup>ABd</sup>
5	16.65 ± 2.06 <sup>DEa</sup>	5.61 ± 0.45 <sup>Ab</sup>	2.75 ± 0.28 <sup>Ac</sup>	2.40 ± 0.09 <sup>Ac</sup>	29.12 ± 4.05 <sup>Fa</sup>	17.34 ± 0.29 <sup>Db</sup>	7.46 ± 0.58 <sup>Bc</sup>	4.09 ± 0.91 <sup>ABd</sup>
6	16.90 ± 1.83 <sup>Ea</sup>	5.98 ± 0.64 <sup>Ab</sup>	2.89 ± 0.13 <sup>Ac</sup>	2.40 ± 0.04 <sup>Ac</sup>	33.69 ± 1.59 <sup>Ga</sup>	17.88 ± 1.44 <sup>Db</sup>	7.77 ± 0.84 <sup>Bc</sup>	3.57 ± 0.11 <sup>ABd</sup>

Data are recorded as the mean ± standard deviation. For each type of frozen storage: Values for the same column having different uppercase letter (A, B, C, D, E, F, and G) for TWE are significantly different at a confidence level of 95% ( $p < 0.05$ ). Values for the same row followed by the different lowercase letter (a, b, c, and d) for TWE are significantly different at a confidence level of 95% ( $p < 0.05$ ), with TWE thawed water exudate: (g/100 g water), FST freeze storage time (months), W initial water content (g H<sub>2</sub>O/ g dry basis), RM frozen/thawed raw material

during the freezing process itself and during subsequent frozen storage.

During frozen storage with freeze-thaw cycles, fresh quince samples subjected to the first freeze thaw cycle had an important TWE value (14.32 g/100 g db) much higher than with the continuous storage (8.46 g/100 g db). With the increase of the number of freeze-thaw cycles, TWE of quince fruit, with high initial water content, has significantly increased ( $p < 0.05$ ) during storage time (almost 5 times of the initial value). Since freeze-thaw cycle during freeze storage results in melting followed by restoration of ice crystals, these cycles (1 to 6) lead to more membrane and cell wall damage, thus increasing both cells' collapse and TWE after thawing process. Hence, repeated melting/recrystallization phenomenon was detrimental to fresh food quality, causing higher mechanical damage to cell membrane and loss of food water-holding capacity. Indeed, with repeated freeze-thaw cycles, the cellular membranes remarkably lose their osmotic power and their semi permeability and the fruit cell severely loses its turgor. Moreover, repeated melting and refreezing of the ice crystals caused a loss of tissue integrity which resulted in a loosening and softening of thawed quince tissue. Therefore, physical changes occurred during freeze-thaw cycles lead to an irreversible loss of frozen fruit quality [17].

### Dehydrofrozen samples

Oppositely, a remarkable and significant improvement of water retention was noticed for dehydrofrozen fruits. Indeed, as presented in Table 1, in continuous frozen storage, TWE gradually decreased with the drying intensity and thus, with water content level prior to freezing. TWE exhibited an

initial value of 5.16%, 3.09% and 2.07% for 2; 1; and 0.3 g H<sub>2</sub>O/g db water content, respectively. These results are in general agreement with that reported by Abd-Elhady [18].

In fact, partial dehydration reduced the exudate loss and enhanced the retention of water. This reduction of TWE revealed a great improvement of textural and structural quality due to better cell wall preservation [19]. Furthermore, freezing pre-dried quince samples results in small and more stable ice crystals. In addition, the decrease in TWE was presumably predictable since the amount of residual water in the sample tissue was smaller after partial air drying.

A pair wise comparison between the results obtained prior to frozen storage ( $t = 0$  month) and those obtained after 6 months of storage showed that for all dehydrofrozen samples, TWE remained constant and there were no significant differences between values over time, for the whole continuous storage period. Apparently, the storage time of previously dehydrated quince fruit did not significantly affect the amount of TWE during thawing process. This means that dehydrofreezing process was able to maintain the structural and textural properties of frozen/thawed fruits and improve its stability during storage. Several research works on this positive impact of partial water removal prior to freezing process, were highlighted for frozen rambutan [20] and mango [21].

However, an extensive review of the literature showed that there has been no research found on the effect of multiple freeze-thaw cycles on the quality changes of dehydrofrozen fruits and vegetables. As it was mentioned above, TWE for fresh quince samples increased progressively during storage period. This rise was sharply pronounced with freeze-thaw cycle number increasing. Indeed, over time, and due to different problems that may



occur during cold chain, frozen fruit may undergo several thawing and refreezing cycles before further industrial processing or consumer consumption. This may extremely damage the textural, structural and cellular fruit quality. However, repeated melting and recrystallization phenomena have a less significant impact on TWE for lower water content samples (<1 g H<sub>2</sub>O/g (g/g db)).

Convective airflow drying applied prior to freezing allows reaching lower water contents than osmotic dehydration and thus can be a good solution to improve fruit's stability and preserve cell's integrity during storage period. Indeed, some studies have shown quality advantages of air dehydration over osmotic dehydration. According to Ramallo and Mascheroni [22], hot air dehydration, as a freezing pretreatment, markedly decreased exudate volume during product thawing. Afterwards, exudate decreased with the progress of drying process. In contrast, osmo-dehydrofreezing treatment results in a higher exudate volume during fruit thawing.

### Final water content FWC

The mean final moisture contents (g H<sub>2</sub>O/g db) of frozen and dehydrofrozen quince samples during storage at -18 °C for 6 months and after thawing process are gathered in Table 2.

Table 2 illustrates a general decrease of water content after thawing operation for all frozen and dehydrofrozen quince pieces. This reduction is mainly due to water exudation occurred during thawing process. These findings are strongly correlated with TWE results, previously obtained ( $p < 0.05$ ).

### During continuous storage

As it is presented in Table 2, final water content (FWC) decreased significantly ( $p < 0.05$ ) after freezing/thawing processes for high initial water content sample. According to Yadav and Singh [23], this is due to aggressive structural damage occurred from ice crystals formation. Indeed, this ice crystals growth can weaken the cell wall and possibly reduces the retention of moisture. On the other hand, during frozen storage, crystals undergo metamorphic changes: recrystallization occurs because systems tend to move toward an equilibrium state. This phenomenon may increase ice crystal size and apply additional cellular membrane stresses, thus causing the movement of water toward the product surface [24].

However, during continuous storage, FST had insignificant impact on final moisture content of dehydrofrozen/thawed quince samples. Several studies described the same effect on different food products such as tomatoes stored at -12 and -20 °C for 12 months [25], rambutan fruits stored at -18 °C for 120 days, and mangoes stored at -18 °C during 20 weeks. The combined process of partial removal of water and freezing appears to be a good solution to mitigate the negative impact of the possible freeze-thaw process on cell integrity and thus moisture retention.

### During freeze-thaw cycles

Results presented in Table 2 show that an increase in the number of freeze-thaw cycles (1 to 6) resulted in a significant amount of loss in moisture content of conventionally frozen (for RM) and dehydrofrozen quince fruit with 2 g H<sub>2</sub>O/g db initial water content, subjected to freezing/thawing

**Table 2** Effect of dehydrofreezing process and frozen storage conditions on final water content (FWC) of frozen and dehydrofrozen quince after thawing process

FST(months)	Continuous storage				Recurrent freeze-thaw cycles during storage (1 cycle/month)			
	W (g/g db)							
	RM	2	1	0.3	RM	2	1	0.3
0	6.11 ± 0.34 <sup>Aa</sup>	2.03 ± 0.17 <sup>Ab</sup>	1.04 ± 0.04 <sup>Ac</sup>	0.32 ± ± 0.04 <sup>Ad</sup>	6.18 ± 0.4 <sup>Aa</sup>	2.05 ± 0.77 <sup>Ab</sup>	1.07 ± 0.03 <sup>Ac</sup>	0.32 ± 0.01 <sup>Ad</sup>
1	5.98 ± 0.33 <sup>ABa</sup>	1.92 ± 0.13 <sup>Ab</sup>	1.00 ± 0.01 <sup>Ac</sup>	0.32 ± 0.01 <sup>Ad</sup>	5.66 ± 0.19 <sup>Ba</sup>	1.73 ± 0.14 <sup>Bb</sup>	0.94 ± 0.06 <sup>ABc</sup>	0.31 ± 0.03 <sup>Ad</sup>
2	5.76 ± 0.24 <sup>BCa</sup>	1.90 ± 0.09 <sup>Ab</sup>	0.97 ± 0.52 <sup>Ac</sup>	0.32 ± 0.04 <sup>Ad</sup>	5.27 ± 0.13 <sup>Ca</sup>	1.49 ± 0.19 <sup>Bb</sup>	0.84 ± 0.45 <sup>ABc</sup>	0.31 ± 0.00 <sup>Ad</sup>
3	5.52 ± 0.08 <sup>CDa</sup>	1.87 ± 0.04 <sup>Ab</sup>	0.96 ± 0.02 <sup>Ac</sup>	0.33 ± 0.01 <sup>Ad</sup>	4.48 ± 0.29 <sup>Da</sup>	1.37 ± 0.34 <sup>Cb</sup>	0.75 ± 0.07 <sup>Bc</sup>	0.31 ± 0.03 <sup>Ad</sup>
4	5.47 ± 0.39 <sup>Da</sup>	1.82 ± 0.05 <sup>Ab</sup>	0.97 ± 0.02 <sup>Ac</sup>	0.31 ± 0.02 <sup>Ad</sup>	3.92 ± 0.12 <sup>Ea</sup>	1.11 ± 0.04 <sup>Cb</sup>	0.74 ± 0.09 <sup>Bc</sup>	0.30 ± 0.02 <sup>Ad</sup>
5	5.61 ± 0.50 <sup>Da</sup>	1.84 ± 0.07 <sup>Ab</sup>	1.01 ± 0.06 <sup>Ac</sup>	0.33 ± 0.01 <sup>Ad</sup>	3.62 ± 0.47 <sup>Fa</sup>	1.03 ± 0.12 <sup>Cb</sup>	0.74 ± 0.07 <sup>Bc</sup>	0.30 ± 0.05 <sup>Ad</sup>
6	5.35 ± 0.17 <sup>Da</sup>	1.86 ± 0.03 <sup>Ab</sup>	0.97 ± 0.17 <sup>Ac</sup>	0.32 ± 0.05 <sup>Ad</sup>	3.21 ± 0.31 <sup>Ga</sup>	1.02 ± 0.04 <sup>Cb</sup>	0.74 ± 0.54 <sup>Bc</sup>	0.30 ± 0.03 <sup>Ad</sup>

Data are recorded as the mean ± standard deviation. For each type of frozen storage: Values for the same column having different uppercase letter (A, B, C, D, E, F, and G) for FWC are significantly different at a confidence level of 95% ( $p < 0.05$ ). Values for the same row followed by the different lowercase letter (a, b, c and d) for FWC are significantly different at a confidence level of 95% ( $p < 0.05$ ). With: FWC final water content (g H<sub>2</sub>O/ g dry basis), FST freeze storage time (months), W initial water content (g H<sub>2</sub>O/ g db), RM frozen/thawed raw material

process. Indeed, after 6 months of storage, final water content was reduced to almost half of its initial value. Similar observations of the effect of freeze-thaw cycles on moisture content were also reported in papaya [17], and in some Nigerian soups [26]. Moisture content has a downward tendency with the increase of water exudation after thawing step and, which is typically assigned to three main factors: ice crystals formation, high internal pressure, and irreversibility of water removal from cell. Repeated operations of melting and ice crystal reformation, during storage period, strongly amplify the effects of these factors and dramatically decrease moisture content retention, which in turn leads to a reduction of final water content) [26].

By contrast, experimental results show clearly that repeated freeze-thaw cycles during storage had insignificant effect on final water content of dehydrofrozen/thawed quince samples once their initial moisture content level was low ( $\leq 1$  g H<sub>2</sub>O/g db). Indeed, air dehydration applied before freezing step decreased the amount of freezable water in fruit tissues, implying lower extent of structural damage, due to a smaller quantity of formed ice crystals and then less exudate loss and better water retention. On the one hand, these results could be due to the fact that air-dried fruit has a lower amount of liquid phase in cell tissues than fresh ones. On the other hand, Ramallo and Mascheroni [22] reported that compared to conventionally freezing or to osmo-dehydrofreezing methods, there is a greater dehydration degree in cells located more externally in the solid when drying by hot air which explain the exudate loss reduction and thus the greater water retention. So, pre-drying before fruit freezing should be a relevant way to maintain the structural and textural properties of frozen/thawed fruits and improve its moisture retention during storage period. These results should

also apply under temperature fluctuations that may occur during cold chain and which lead to freeze-thaw cycles.

## Color evaluation

























### Total color difference TCD

Color is an important factor in the perception of quince fruit quality. In order to better study the dehydrofreezing process, continuous storage and temperature fluctuation during storage (at 0, 3 and 6 months) effects, some images of treated quince pieces were presented in table n 3.

In addition, Table 4 shows the total color differences TCD of frozen and dehydrofrozen quince slices after thawing process, during storage at  $-18$  °C for 6 months, for continuous storage and with recurrent freeze-thaw cycles.

**Continuous frozen storage** The mean values of the basic color parameters “L<sub>0</sub>”, “a<sub>0</sub>”, and “b<sub>0</sub>” of the fresh quince fruits were  $83.7 \pm 0.55$ ,  $-1.32 \pm 0.27$ , and  $26.87 \pm 1.10$ , respectively. As it is shown in Tables 3 and 4, partial convective air drying, as well as continuous frozen storage, led to significant changes in fresh quince color ( $p < 0.05$ ). Indeed, it has been noticed that drying induced color change towards the most intense zone of the yellow and red colors. Similar results, concerning the effect of drying conditions on quince color have been raised by Hajji et al. [5] and Krokida et al. [27]. These color changes, which occurred during drying process, may be due to the presence of heat sensitive reactions. This involves degradation of sensitive pigments, browning of ascorbic acid and non-enzymatic Maillard reactions [28]. In addition, quince sample became darker after dehydrofreezing/thawing pro-

**Table 3** Photos of frozen and dehydrofrozen quince samples, during Continuous Storage *versus* freeze-thaw cycles, after 0, 3, and 6 months

Quince samples photos during the whole experiment								
FST (months)	Continuous Storage				Recurrent freeze-thaw cycle during storage (1 cycle/month)			
	RM	2	1	0.3	RM	2	1	0.3
0								
3								
6								

**Table 4** Effect of dehydrofreezing and frozen storage conditions on color parameter: Total Color Difference (TCD) of frozen and dehydrofrozen/thawed quince fruit

TCD								
FST (months)	Continuous storage				Recurrent CCB during storage (1 cycle/month)			
	W (g/g db)							
	RM	2	1	0.3	RM	2	1	0.3
0	12.53 ± 1.09 <sup>Aa</sup>	10.84 ± 0.15 <sup>Ab</sup>	3.57 ± 1.07 <sup>Ac</sup>	3.32 ± 0.49 <sup>Ac</sup>	13.43 ± 0.94 <sup>Aa</sup>	10.92 ± 0.15 <sup>ABb</sup>	2.74 ± 0.53 <sup>Ac</sup>	3.63 ± 0.64 <sup>Ad</sup>
1	13.92 ± 0.08 <sup>Aa</sup>	13.11 ± 1.53 <sup>Bb</sup>	2.26 ± 0.33 <sup>ABc</sup>	3.60 ± 0.37 <sup>Ad</sup>	28.60 ± 0.69 <sup>Ba</sup>	14.83 ± 0.49 <sup>Ab</sup>	2.570.65 <sup>Ac</sup>	4.03 ± 0.09 <sup>Ad</sup>
2	16.53 ± 1.44 <sup>Ba</sup>	14.74 ± 0.23 <sup>Bb</sup>	2.33 ± 0.24 <sup>Ac</sup>	4.33 ± 0.14 <sup>Ad</sup>	39.46 ± 0.95 <sup>Ca</sup>	17.90 ± 1.38 <sup>Bb</sup>	3.67 ± 0.46 <sup>Bc</sup>	4.76 ± 0.16 <sup>ABc</sup>
3	19.07 ± 0.33 <sup>Ba</sup>	16.50 ± 1.61 <sup>Cb</sup>	3.45 ± 1.25 <sup>ABc</sup>	5.28 ± 0.20 <sup>Ad</sup>	41.92 ± 0.41 <sup>Ca</sup>	22.86 ± 1.09 <sup>Cb</sup>	4.69 ± 1.96 <sup>Cc</sup>	6.21 ± 0.63 <sup>BCd</sup>
4	21.63 ± 0.44 <sup>Ca</sup>	17.66 ± 0.84 <sup>Cb</sup>	4.01 ± 0.50 <sup>Bc</sup>	6.06 ± 1.38 <sup>Bd</sup>	45.37 ± 0.45 <sup>Da</sup>	29.27 ± 0.41 <sup>Db</sup>	7.11 ± 0.89 <sup>Dc</sup>	6.64 ± 0.60 <sup>Cd</sup>
5	22.23 ± 0.36 <sup>Ca</sup>	18.53 ± 1.04 <sup>Cb</sup>	5.25 ± 0.33 <sup>Bc</sup>	6.03 ± 0.50 <sup>Bc</sup>	45.55 ± 0.20 <sup>Da</sup>	32.59 ± 0.35 <sup>Eb</sup>	8.75 ± 1.10 <sup>Dc</sup>	6.89 ± 0.27 <sup>Cd</sup>
6	23.26 ± 0.79 <sup>Ca</sup>	19.76 ± 0.26 <sup>Cb</sup>	5.80 ± 0.11 <sup>Bc</sup>	6.06 ± 0.17 <sup>Bc</sup>	46.08 ± 0.24 <sup>Da</sup>	33.18 ± 0.18 <sup>Eb</sup>	8.69 ± 0.51 <sup>Dc</sup>	7.41 ± 0.29 <sup>Cd</sup>

Data are recorded as the mean ± standard deviation. For each type of frozen storage: Values for the same column having different uppercase letter (A, B, C, D and E) for TCD are significantly different at a confidence level of 95% ( $p < 0.05$ ). Values for the same row followed by the different lowercase letter (a, b, c and d) for TCD are significantly different at a confidence level of 95% ( $p < 0.05$ ). With: TCD total color difference, FST freeze storage time (months), W initial water content (g H<sub>2</sub>O/g db), RM frozen/thawed raw material

cess (Table 3). It can be seen in Table 4, that there were significant differences ( $p < 0.05$ ) during the whole experiment storage period (6 months), in total color difference for quince sample with high water content ( $\geq 2$  g/g db). On the adverse effect of freezing/frozen storage on color of quince with high water content, it seems that convective air-drying applied prior to freezing process induced less color changes (Table 3). These color losses are almost stable during the whole continuous frozen storage period for quince samples with lower water content levels. Indeed, according to Forni et al. [29], the partial dehydration step reduces the phenolase activity and thus increases color stability of dehydrofrozen/thawed apricot during storage.

In agreement with the results of the TWE analysis (Table 1), considering the relationship between color properties and thawed water exudate, the effect of freezing and frozen storage on color changes in quince fruit could be correlated. Indeed, during freezing process, changes occurred due to ice formation, play an important role in enzymatic and non-enzymatic reactions rates. Ice crystals may release and leach the enclosed contents of fruit tissues, such as enzymes and chemical substances, affecting negatively the product quality during freezing and frozen storage. These changes are related to enzymatic browning, and degradation of pigments [17, 30]. Indeed, pigments degradation was considered as one of the main chemical changes to frozen foods during storage, and closely correlated with concentration of solutes surrounding the ice crystal, thus related to the exudate loss during thawing process [31]. These results are in line with previous findings on different food products such as strawberries [32], mango [21], beef meat [33] and Barhi dates [34].

**Freeze thaw cycles** Changes in optical properties of frozen quince with high water content levels ( $\geq 2$  g/g db) were more pronounced with the breaking of cold chain during storage (Table 3).

For multiple freeze-thaw cycles, as it is presented in Table 4, TCD increased gradually ( $p < 0.05$ ) with the increase of cycle number. This occurred because repetitive freezing/thawing steps lead to larger ice crystals formation exclusively in the extracellular areas causing increased amounts of cell damage. In fact, these findings brace the research works of Talens et al. [35] and Rincon and Kerr [21] who assumed that a postulated mechanism for color change during freezing and frozen storage is that the release of cellular liquid into intracellular spaces and the decrease in cell compartmentalization, produce more transparent tissue and cause darker samples with less vivid fruit color.

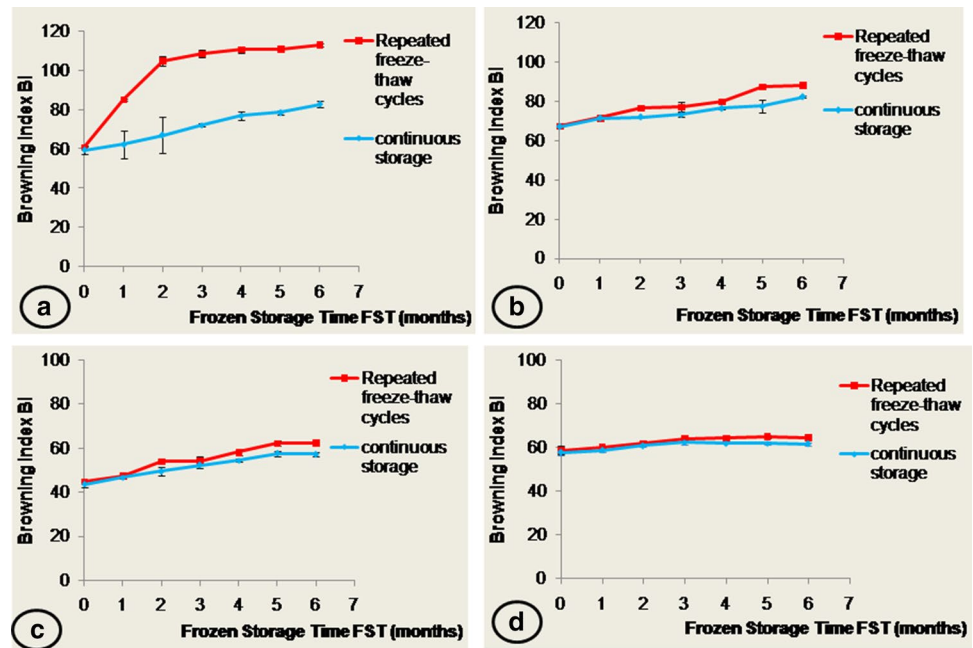
It is worth noticing that, after the third freeze-thaw cycle, the total color difference TCD of dehydrofrozen quince ( $\leq 1$  g H<sub>2</sub>O/g db) remains stable for the rest of storage period. Therefore, it is interesting to consider this result closely linked with both the damage level of sample tissues and the final moisture content of quince samples. Indeed, the reduced availability of water molecules in cellular tissues after pre-drying helps to better maintain the textural quality of plant cells and to minimize the phenomenon of nutrients leaching especially pigments responsible for fruits color of the fruit.

### Browning index "BI"

Data on the color derivative parameter i.e. browning index (BI) of stored frozen and dehydrofrozen quince fruits are plotted and depicted in Fig. 2a, b, c and d.



**Fig. 2** Changes of Browning Index “BI” during both types of frozen storage, of quince fruit: at different water content level. **a** untreated quince samples, **b** predried at 2 g/g db **c** predried at 1 g/g db and **d** predried at 0.3 g/g db



Results presented in Fig. 2 strongly correlate with results presented in Table 3 and with total color difference cited above. Indeed, the browning index of untreated frozen quince samples (Fig. 2a) increased significantly ( $p < 0.05$ ), from  $59.44 \pm 1.08$  to  $82.88 \pm 0.08$ , during storage time, in line with the increase of total color difference (Tables 3 and 4). It could be inferred that the surface of quince slab becomes transparent, pale and fade due to water exudation after thawing process (Table 3). This noticeable shift of quince color could be explained by the loss of membrane integrity and pigment diffusion from the center of the fruit to the outmost cell layers which occurs after freezing/thawing process, and during storage as previously cited.

Moreover, Tagubase et al. [36] reported that phytochemical, such as polyphenols, carotenoids and anthocyanins, provide to fruits and vegetables their color. Polyphenols are well known to be more sensitive to enzymatic browning reactions. After freezing process and eventually during frozen storage, the cells became de-compartmentalized, facilitating reactions between enzyme and their substrates. With this assumption, considerable pigment losses were reported during frozen storage.

Furthermore, during freeze-thaw storage, BI increased extremely ( $p < 0.05$ ) with freeze-thaw cycle number all along the storage period. Therefore, it can be postulated that this rise is due to aggressive cell breakdown and more enzymatic activity of sensitive fruit components such as phenolase, polyphenol oxidase, affected by repeated melting and recrystallization phenomena during multiple freeze-thaw cycles.

Previous analysis of quince photos (Table 3) total color difference TCD of stored dehydrofrozen quince fruit at different water content levels (Table 4) provided compelling

evidence that convective airflow drying prior to freezing attenuates color changes during frozen storage, even under freeze-thaw conditions. These facts are well consolidated in browning index analysis of dehydrofrozen quince samples. Indeed, as it is shown in Fig. 2c and d, BI values decreased compared to those of conventionally frozen fruit and remained almost stable during the whole frozen storage period: they ranged between  $43.57 \pm 0.85$  and  $57.31 \pm 1.21$  for dehydrofrozen fruit at 1 g H<sub>2</sub>O/g db water content and between  $57.8 \pm 11.38$  and  $61.69 \pm 0.76$  for dehydrofrozen quince slabs at 0.3 gH<sub>2</sub>O/g db water content. In fact, it has been stated in several previous studies on color stability of frozen products that ice-crystal formation increases during the storage period, resulting in the breakdown of cellular tissues and pigment losses. On the other hand, the pre-dried products were sufficiently dehydrated, preventing the formation of large ice crystals; therefore, ice-crystals formation in these samples did not proceed to the breaking point, even after long-term storage. This allows a better pigment retention and thus ensures a preservation of frozen product color.

It is also important to note that the effect of multiple freeze-thaw cycles is increasingly lower with drying intensity and storage period. As it is shown in Fig. 2b, c and d, BI curves for continuous storage and under repeated thaw/freeze cycles are almost confused. After the third freeze thaw cycle, the BI rate increases lower gradually over storage time and each month caused less effect than the previous, as compared to standard freezing in Fig. 2a.

Overall, these results lead to the conclusion that dehydro-freezing process preserves better the optical quality of frozen quinces during storage even under temperatures changes (freeze-thaw cycles) that may occur during cold chain.

## Total polyphenols content TPC

Quince fruit is an important source of beneficial effective bioactive compounds, especially polyphenolic compounds [37]. In view of their nutritional importance, a quantitative analysis of the total polyphenols in different treated quince samples was carried out and presented in Table 5, in order to study the effect of dehydrofreezing process and storage conditions on their initial contents.

Fresh quince samples present a total polyphenols content of  $3.11 \pm 0.07$  g AGE/100 g db. These values corroborate those reported in the literature. TPC of fresh quince fruit varied between 1.71 and 3.44 g/100 g db [37]. According to De Ancos et al. [38], the amount of total phenolics variations, in fresh fruits, depends on period of harvesting, environmental characteristics, cultivar variability, or fruit maturity.

It was also possible to bring out the significant effect of drying process on total polyphenols content ( $p < 0.05$ ). These changes are in fact due to the partial water removal during partial drying. Indeed, convective airflow drying treatment originated quince samples with visibly lower amounts of phenolic compounds: TPC losses, after drying, as compared with fresh samples, varied from 63 to 85% depending on the drying intensity. According to Djendoubi Mrad et al. [39], a reduction in TPC during drying process, is attributed to the binding of polyphenols with other compounds or to alterations in the chemical structure of polyphenols which cannot be determined by available methods. Moreover, loss of polyphenol content, after drying step, is also ascribed to its heat labile nature and to the impact of heat treatment which may cause irreversible chemical changes to phenol contents. Furthermore, during

dehydration process, some chemical and biochemical reactions may occur, such as enzymatic oxidation, hydrolysis of polymeric compounds, and polymerizations [40]. In view of this fact, it will be interesting to optimize the pre-drying operation and to modulate its conditions in order to reach better quality objectives with the intention of producing high quality foods.

On the other hand, conventional freezing/thawing process showed the lowest retention of TPC compared to dehydrofreezing process. These findings are in agreement with those of other researchers, who claimed that this reduction on polyphenols content during freezing could be related to the polyphenol oxidase (PPO) linked to the cellular wall, released with cellular disruption of fruits [41]. In parallel, degradation of polyphenolic compounds is more important during thawing step and their interaction with oxidative enzyme is more active at high water content fruit samples. Furthermore, the intense textural damage after freezing/thawing process for high water level fruit leads to extremely high water exudation and therefore subsequently to more lixiviation of water soluble nutrient [40].

Several researchers studied the effect of the dehydrofreezing process on polyphenols content, on different fruits and vegetables such as strawberries [42], grapes [43], peppers [44] and mangoes [40]. These authors reported that dehydrofreezing caused a slight depletion of polyphenolic compounds in dehydrofrozen samples compared to frozen ones, which proved a higher polyphenols retention, respect to conventional freezing. This clearly demonstrates that dehydrofreezing is useful for alleviating polyphenolic compounds loss in frozen samples.

**Table 5** Impact of dehydrofreezing and frozen storage conditions on total polyphenols content (TPC) of frozen and dehydrofrozen thawed quince fruit

FST (months)	Continuous storage				Recurrent freeze-thaw cycles during storage (1 cycle/month)			
	W (g/g db)							
	RM	2	1	0.3	RM	2	1	0.3
0	$2.72 \pm 0.01^{Aa}$	$1.15 \pm 0.01^{Ab}$	$0.81 \pm 0.02^{Ac}$	$0.45 \pm 0.01^{Ad}$	$2.72 \pm 0.01^{Aa}$	$1.21 \pm 0.01^{Ab}$	$0.81 \pm 0.02^{Ac}$	$0.45 \pm 0.01^{Ad}$
1	$2.63 \pm 0.00^{Ba}$	$1.14 \pm 0.01^{Ab}$	$0.80 \pm 0.01^{Ac}$	$0.45 \pm 0.01^{Ad}$	$2.49 \pm 0.06^{Ba}$	$1.02 \pm 0.02^{Bb}$	$0.72 \pm 0.01^{Bc}$	$0.45 \pm 0.01^{Ad}$
2	$2.54 \pm 0.02^{Ca}$	$1.09 \pm 0.03^{Bb}$	$0.80 \pm 0.03^{Ac}$	$0.45 \pm 0.01^{Ad}$	$1.90 \pm 0.02^{Ca}$	$0.86 \pm 0.04^{Cb}$	$0.66 \pm 0.02^{Cc}$	$0.43 \pm 0.03^{ABd}$
3	$2.23 \pm 0.03^{Da}$	$0.98 \pm 0.04^{Cb}$	$0.79 \pm 0.01^{ABc}$	$0.44 \pm 0.02^{Ad}$	$1.61 \pm 0.04^{Da}$	$0.72 \pm 0.01^{Db}$	$0.61 \pm 0.01^{Dc}$	$0.41 \pm 0.03^{Bd}$
4	$2.10 \pm 0.01^{Ea}$	$0.95 \pm 0.01^{Db}$	$0.77 \pm 0.01^{Bc}$	$0.44 \pm 0.01^{Ad}$	$1.34 \pm 0.03^{Ea}$	$0.66 \pm 0.01^{Eb}$	$0.60 \pm 0.01^{Dc}$	$0.40 \pm 0.01^{Bd}$
5	$2.03 \pm 0.01^{Fa}$	$0.96 \pm 0.04^{CDB}$	$0.72 \pm 0.02^{Cc}$	$0.44 \pm 0.01^{Ad}$	$1.18 \pm 0.01^{Fa}$	$0.63 \pm 0.01^{Eb}$	$0.59 \pm 0.01^{Db}$	$0.41 \pm 0.01^{Bc}$
6	$2.00 \pm 0.01^{Fa}$	$0.94 \pm 0.01^{Db}$	$0.72 \pm 0.04^{Cc}$	$0.44 \pm 0.02^{Ad}$	$1.04 \pm 0.04^{Ga}$	$0.60 \pm 0.01^{Fb}$	$0.59 \pm 0.02^{Db}$	$0.41 \pm 0.01^{Bc}$

Data are recorded as the mean  $\pm$  standard deviation. For each type of frozen storage: Values for the same column having different uppercase letter (A, B, C, D, E, F and G) for TPC are significantly different at a confidence level of 95% ( $p < 0.05$ ). Values for the same row followed by the different lowercase letter (a, b, c and d) for TPC are significantly different at a confidence level of 95% ( $p < 0.05$ ). With: TPC total polyphenols content (g/100 g water), FST freeze storage time (months), W initial water content (g H<sub>2</sub>O/g db), RM frozen/thawed raw material

### Continuous frozen storage

As it is shown in Table 5, continuous frozen storage time (FST) had a significant effect on TPC ( $p < 0.05$ ) for freshly frozen and dehydrofrozen/thawed quince pieces with high initial water contents (2 g H<sub>2</sub>O/g db). TPC losses occurred after 6 months of storage are about 26% and 18%, for RM and with 2 g H<sub>2</sub>O/g db water content, respectively. Many authors have pointed out that polyphenolic compounds in vegetables and fruits decrease during frozen storage. Hence, significant losses (31%) of TPC were detected in Swedes vegetables stored for 6 months at  $-20\text{ }^{\circ}\text{C}$  [45], a reduction of 19% has been recorded after 1 year of storage at  $-30\text{ }^{\circ}\text{C}$  for frozen kale [46], and a frozen storage at  $-18\text{ }^{\circ}\text{C}$  for 6 months reduced the TPC of haskap berries by 37.08% [47]. Indeed, during the conventional storage of frozen products, the amount of formed ice remained generally constant. While the number of ice crystals decreases due to the increase in average crystals size and induced large ice crystal formation which may destroy cell walls. By thawing, cells' hydrophilic colloids could not return to their state before freezing and cause important losses of cell exudates and thus significant amounts of nutrients loss [48].

However, other previous published data on several fruits showed that some phenolic compounds increased after frozen storage, while others decreased and some phenolic compounds were not significantly affected by the whole freezing process. These changes in polyphenols behavior may be due to the coexistence of different mechanisms of phenolic modification in frozen fruits, under different freezing conditions [40, 49].

Furthermore, these differences in bioactive compounds retention were dependent on polyphenols type [50]. Moreover, Puupponen-Pimiä et al. [45] postulated that these behavior variations were highly plant species-dependent.

There were relatively few trends about the impact of frozen storage on TPC of dehydrofrozen fruits and no data was recorded about the effect of coupling convective air drying and freezing on the polyphenolic content of fruits during their storage. Khattab et al. [51] have studied the effect of steam blanching as a pre-freezing treatment on TPC of Haskap Berries, throughout the freeze storage period (up to 6 months at  $-18\text{ }^{\circ}\text{C}$ ). They noticed that steam blanching preserved phenolic compounds during frozen storage as compared to the un-blanching samples. This may be attributed to the inhibition of the polyphenol oxidase (PPO) and other oxidative enzymes that catalyze oxidative reactions, which cause a significant decrease of phenolic compounds during storage period.

### Freeze-thaw cycles

In the presence of multiple rupture of cold chain, polyphenols content drastically decreases during frozen storage for quince samples with high initial water content: 62% for RM and 51% for 2 g H<sub>2</sub>O/g db). The considerable amount of polyphenols losses, observed for high water levels quince samples, might be due to the mechanical stress caused by repeated melting during thawing, and ice crystals reformation during freezing which lead to a reduction in moisture content retention and thus nutrients leaching. Baygar and Alparslan [52] stated that repeated freeze-thaw cycles causes instability in tissues structure and important nutrients losses as the cycle number increased. It was emphasized that formed ice crystals are the principle reason for damaged membrane cell. In fact, during each freeze-thaw cycle, water refreezes but does not renucleate. Rather, it is deposited on the surface of larger crystals, so the net result is that total number of crystals diminish and mean crystal size increases, leading to cell deterioration and leaching of frozen fruit phenolics compounds. In addition, refreezing food product, especially with high initial moisture content, after thawing process is to be avoided because any damage caused, whether physical, chemical or even microbiological, in the first freeze-thaw cycle is multiplied in the subsequent cycles.

From an extensive review of the literature, there has been no recorded data about the effect of freeze-thaw cycles on polyphenolic compounds of stored dehydrofrozen fruits. As it is shown in Table 4, it is worth highlighting that dehydro-freezing process is a relevant solution to sustain cold chain problems of frozen foods. TPC losses were in the range of 27% and 9% dehydrofrozen quince samples 1, and 0.3 g/g db, respectively. Indeed, water partial removal prior to freezing reduces the negative effect of freeze-thaw cycles. TPC losses rate started to decrease over the storage period and each consequent month was causing less degradation than the preceding one. It is anticipated from this decrease with frozen storage time that TPC may reach a plateau during long-period of storage. This behavior correlated with observations described previously on the Browning Index (BI) for quince with low initial water content level (Fig. 2c, d).

### Quality evaluation of quince fruit during frozen storage

Coupling air drying, as pretreatment for partial water removal of quince fruit cells, and freezing operation contribute to quince quality stability in terms of thawed water exudate which reflects a better color retention and an improvement of bioactive phenolic compound preservation during long-term frozen storage, even under repetitive freeze-thaw cycles. Linear correlations were

investigated between all pairs of the response variables TWE, TCD, FWC and TPC losses for frozen and dehydrofrozen/thawed quince fruit (Table 6).

Table 6 shows the correlation coefficients between operating parameters: FST and storage type and response variables: TWE, FWC, TCD and TPC of frozen and dehydrofrozen quince samples. It presents Pearson product moment correlations between each pair of variables. These correlation coefficients reveal the statistical significances and measure the strength of the linear relationship between the different pairs of response variables ranged between -1 (blue) and +1 (red). They indicate statistically significant non-zero correlations at the 95% confidence level.

It is worth stating that positive correlations are found between different parameters: initial water content, FST and storage type and all different responses variables (TWE, FWC, TCD and TPC), especially for initial water content that is revealed by correlation coefficients systematically > 0.7. A high positive relationship is shown between TWE and all other variables specifically the TCD, the TFC and the TPC losses. This means the higher the amount of TWE during thawing, the higher the TCD, FWC, and TPC losses. Indeed, high initial moisture content promotes the increase of water volume and ice crystals growth during freezing which result in an important TWE amount during thawing and thus more nutrients leaching and quality loss.

### Conclusion

Conventional freezing process and long-term frozen storage generated quality losses of high water content quince fruits ( $\geq 2$  g H<sub>2</sub>O/g db. These quality reductions were sharply accentuated by freeze-thaw cycles.

Partial air-drying, applied as a pretreatment to freezing process, preserved the quality of stored frozen quince. Effectively, experimental results clearly showed that conventionally frozen quince samples had more important thawed water exudate (TWE), compared with all partially airflow dried-frozen samples, with a significant increase of TWE during continuous storage at -18 °C for 6 months. Furthermore, this augmentation was deeply pronounced with an increase in the number of freeze-thaw cycles. Nevertheless, for dehydrofrozen samples, the amount of TWE remained constant during the whole frozen storage period with an insignificant effect of freeze storage time (FST) and multiple thaw-freeze cycles for low water content dehydrofrozen quince samples ( $\leq 1$  g H<sub>2</sub>O/g db). Accordingly, after freezing/thawing processes, quince samples with high initial water content levels ( $\geq 2$  g H<sub>2</sub>O/g db) reveal a significant amount of loss in final moisture content, during both types of frozen storage. In contrast, dehydrofreezing process seems to be a relevant solution to improve cell moisture retention during storage period. Repeated freeze-thaw process had insignificant effect on final water content of dehydrofrozen/thawed quince samples with low initial moisture content levels ( $\leq 1$  g H<sub>2</sub>O/g db). Conventional freezing and frozen storage time showed a clear effect on color derivative parameters (TCD and BI)

**Table 6** Matrix of correlation coefficients calculated between frozen storage time, frozen storage type, TWE, TCD, FWC, and TPC losses for frozen and dehydrofrozen quinces

**Pearson correlation coefficients**  
X: not significant at 95%

Storage type	1	X	X	0.36	0.29	0.48	0.41
W	X	1	X	0.75	0.72	0.78	0.54
FST	X	X	1	0.31	0.31	0.43	0.43
TWE	0.36	0.75	0.31	1	0.95	0.72	0.9
TCD	0.29	0.72	0.31	0.95	1	0.69	0.81
FWC loss	0.48	0.78	0.43	0.72	0.69	1	0.75
TPC loss	0.41	0.54	0.43	0.9	0.81	0.75	1
	Storage type	W	FST	TWE	TCD	FWC loss	TPC loss

Operating parameters: *W* Initial water content of quince samples (g/g db), *FST* frozen storage time (month), and storage type: Responses variables: *TWE* thawed water exudate, *FWC* final water content of thawed samples (g/g db), *TCD* total color difference (-), *TPC* total polyphenol content (g GAE/100 g db)

of frozen quince fruit. These variations in color properties are more pronounced with the breaking of cold chain during storage. However, drying applied before freezing stage increased color stability of quince sample during storage. Total polyphenols content were greatly affected by freezing process itself, subsequent frozen storage and repeated freeze-thaw cycles. This negative impact decreased gradually, during storage, for dehydrofrozen quince fruit.

To conclude, dehydrofreezing process is a pertinent way to mitigate quality damage that results from freezing and thawing processes and which may also occur during storage period. It is clear here that the pre-drying step has to be optimized in terms of energy consumption and quality losses. In this study, at this stage, it was mainly important to study the effect of different initial water contents during frozen storage and multiple freeze thaw-cycles on relevant parameters.

**Acknowledgements** The authors acknowledge that this project is in the framework of a PhD MOBIDOC program and funded by the EU and administered by PASRI. Also thanks to STIFEN INDUSTRIES (Lebna, Tunisia) for the financial support and for providing raw material for this research.

## Compliance with ethical standards

**Conflict of interest** All authors declare no conflict of interest.

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