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Changes in physical and biochemical properties of spray dried camel and bovine milk powders.

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ABSTRACT

This study aimed at investigating the changes in skim camel milk (SCMP) and skim bovine milk (SBMP) powders produced by spray-drying. The physical (sorption isotherms at 25 °C and the glass transition temperature T_g at 0.13, 0.23 and 0.33 of water activities (a_w)) and the biochemical (LC-MS, before and after drying) properties were assessed. Compared to SBMP, the results for SCMP indicated lower protein denaturation extent, lower critical a_w for lactose crystallization (a_w = 0.60 instead of 0.70), and lower T_g at 0.13 of a_w (54.6 ± 1.4 °C instead of 57.8 ± 0.4 °C). Fitted to Guggenheim, Anderson and De Boer (GAB) model, the water sorption isotherms showed that both powders exhibited the same monolayer moisture content (X_m = 2.0 g 100 g^{-1}, $p > 0.05$). These findings were linked to the absence of β-lactoglobulin, the high surface lactose content, the high initial lactose crystallization and the low size distribution (d_{50} < 10 μm) of SCMP.

1. Introduction

During this last century, there has been considerable interest in converting milk and milk derivatives into dairy powders as means of extending their shelf-life. In general, dairy powders are manufactured using spray-drying technology. In this process, water is evaporated in a short heat-time contact with dried-hot air. Before drying, milk could be subjected to different pretreatments which could change the structure and the functionalities of the milk powder (Mercan, Sert, & Akın, 2018). In fact, skimmed dairy powders are mainly composed of protein, amorphous lactose and minerals. The amorphous lactose is trapped in a matrix of proteins and exhibits a low molecular mobility. In this amorphous state, lactose is thermodynamically unstable (Jouppila, Kansikas, & Roos, 1997). When exposed to high temperature and/or humidity, dairy powders may undergo several deteriorative reactions (i.e. stickiness, caking, loss of solubility …) (Le Meste, Champion, Roudaut, Blond, & Simato, 2002). Most of these reactions are related to lactose structure modification during and above the glass transition. Consequently, the knowledge of both sorption isotherm and glass transition temperature is mandatory to control dairy powders physical stability during storage.

Several previous researchers investigated the effect of heat treatment on the stability of bovine milk proteins. The thermal denaturation of both caseins and whey proteins showed that certain protein aggregates are formed through intermolecular disulfide bonds depending on time, temperature and heat treatment intensity (Manzo, Nicolai, & Pizzano, 2015; Nabhan, Girardet, Campagna, Gaillard, & Le Roux, 2004). The thermal denaturation of bovine milk proteins and their subsequent aggregation may result in the loss of some functionalities, in particular the solubility (Sharma, Jana, & Chavan, 2012).

Actually, bovine milk is the world's most consumed and processed milk. However, other types of milk such as camel milk constitute the principal dairy resource in many arid and semi-arid regions (Al Haj and Al Kanhal, 2010). As the consumption spectrum of camel milk is widening, some stabilization technologies could be applied to extend its shelf-life, such as drying. The production of camel milk powder could be challenging. In fact, several researchers have acknowledged that camel milk presented some physicochemical differences when compared to bovine milk. The proteins of camel milk are composed of higher β-casein (47%) and lower κ-casein (3.5%) content (Omar, Harbourne, & Oruna-Concha, 2016). The particularity of camel milk whey is the lack of β-Lactoglobulin and the overexpression of α-lactalbumin (Felfoul, Jardin, Gaucheron, Attia, & Ayadi, 2017).

As presented above, camel and bovine milks showed different

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physicochemical characteristics, especially the proteins composition. Such differences are likely to affect the physical and biochemical stability of camel milk powder during storage and processing. Some studies have reported the sensory and rehydration characteristics of camel milk powder (Habtegebriel, Edward, Wawire, Sila, & Seifu, 2018; Ho et al., 2019). However, few of these studies have assessed its physical and biochemical characteristics. Hence, the aim of this work was to investigate the effects of the spray-drying on the physicochemical characteristics of skim camel milk powder (SCMP) in comparison to the skim bovine milk powder (SBMP) and to evaluate their physical stability. Firstly, the thermal denaturation of camel milk proteins before and after drying were appraised using Whey Protein Nitrogen Index (WPNI) and HPLC-Quadrupole Orbitrap/MS (LC-MS). Furthermore, the physical stability during storage by means of the water sorption isotherm (at 25 °C), the glass transition temperatures, and the evolution of the microstructure was evaluated. The stability of skim bovine milk powder (SBMP, produced under the same drying conditions) was also assesed following the same evaluation techniques.

2. Materials and methods

2.1. Milks samples

Camel (*Camelus dromedarius*) and bovine (*Bos taurus*) milks were collected from two separated farms in southern Tunisia (Gabes and Sfax governorates, respectively) and were transported to the laboratory within 2 h at 4 °C, after milking. Milk samples were immediately stabilized against microbiological development with the addition of 0.02% (w/w) of sodium azide. Then, bovine and camel milks were skimmed following 1 or 3 successive centrifugations (2000 g, 15 min, 5 °C), respectively. Thereafter, skim camel and bovine milks (< 1 g L^{-1}) were spray-dried.

2.2. Spray drying conditions

Skimmed camel and bovine milk powders were produced using a laboratory spray dryer (Bücchi B-290, Büchi Labortechnik AG, Flawil, Switzerland). During all experiments, the absolute humidity of air was equal to 5 g of water per kg of dry air. Using the Mollier diagram and targeting a powder's water activity of 0.20, the inlet and outlet drying temperatures were set up to 200 ± 2 °C and 80 ± 2 °C. The average residence time of milk droplets in the drying chamber was equal to 1 s. To guarantee a stable drying kinetics, the drying airflow rate and the pressurized airflow at the sprayer nozzle were held unchanged. All produced powders were immediately stored at 4 °C in sterilized glass vials.

2.3. Physicochemical characterization

The free and linked water, the total solids, the ash, and the total fats of skim camel (SDM) and bovine milks (SCM) as well as their corresponding powders (Table 1) were investigated as described by Schuck, Jeantet, & Dolivet, 2012. The lactose quantification was performed using HPLC Aminex A-6 ion exchange column (Bio-Rad, Hercules, CA, USA) operating at 60 °C and an eluent (0.005M of H_2SO_4) flow rate of 0.4 mL min^{-1}. The detection of lactose was performed using refractometry (RI2031 plus, Jasco, Germany) as described by Aburjaile et al. (2016).

The initial lactose crystallization was determined as follows (Schuck et al., 2012):

$$C° = \frac{LH \times 19}{L} \times 100$$

with, C°: powder crystallinity; L: Lactose content; LH: linked humidity. Factor 19 corresponds to the ratio between the molecular weight of lactose (342 g mol^{-1}) and water (18 g mol^{-1}).

Table 1
Biochemical and physical characteristics of skim camel and bovine milk powders.

	Skim bovine milk powder (SBMP)	Skim camel milk powder (SCMP)
Water activity (a_w)	0.252 ± 0.01[a]	0.251 ± 0.01[b]
Powder composition (%)		
Total solids	96.5 ± 0.1 [a]	96.1 ± 0.5 [a]
Total protein	33.1 ± 0.3 [a]	33.3 ± 0.2 [a]
Caseins	27.5 ± 0.1 [a]	26.1 ± 0.1 [b]
Whey	5.6 ± 0.5 [a]	7.2 ± 0.1 [b]
Fats	1.0 ± 0.1 [a]	1.1 ± 0.1 [a]
Lactose	54.5 ± 0.5 [a]	53.3 ± 0.7 [a]
Ash	7.9 ± 0.1 [a]	8.4 ± 0.2 [b]
Whey Protein Nitrogen Index (WPNI in g of N_2 kg^{-1})	8.9 ± 0.2 [a]	11.5 ± 0.2 [b]
Granulometry d_{50} (µm):	9.2 ± 0.1 [a]	8.8 ± 0.2 [a]
Densities (kg.m^{-3})		
Loose Bulk density (L.B.D)	233.4 ± 0.7 [a]	287.2 ± 1.2 [b]
Packed Bulk Density (P.D.B)	378.1 ± 0.5 [a]	638.2 ± 0.8 [b]
Particle Density (P.D)	1487.2 ± 3.2 [a]	1478.4 ± 1.0 [b]
Initial lactose crystallization (% of total lactose content)	10.4 ± 0.2 [a]	15.0 ± 0.2 [b]

Powders composition are expressed in %: g 100 g^{-1} dry basis; d_{50}: diameter of 50% of the particles; Values are presented as mean ± standard deviation (SD); Same letter in the same row represent the statistical data significance ($p > 0.05$).

The analysis of water activity was conducted using an a_w-meter (Novasina RTD 200/0 and RTD 33, Pfäffikon, Switzerland) at 25 °C. The loose bulk density (L.B.D), packed bulk density (P.B.D), particles density (P.D) were estimated as recommended by Mitra et al. (2017). The size distribution of skim camel and bovine milk powder particles was checked using a light laser scattering Mastersizer 2000 (Malvern Instruments Ltd., Malvern, UK), equipped with a dry powder feeder (Scirocco 2000, Malvern Instruments, Worchestershire, UK). The feeder was operating at a vibration rate of 40% and a dispersive air pressure of 4 bars. The d_{50} (diameter of 50% of the particles) was chosen as a size distribution indicator as recommended by Nikolova et al. (2014).

2.4. The whey protein nitrogen index

The non-casein nitrogen (NCN, at pH = 4.3 or 4.6 for skim camel and bovine milk, respectively) and the non-protein nitrogen (NPN, after acidification with 12% of TCA) were determined as described by Schuck et al. (2012). The whey protein nitrogen index (WPNI, Table 1) was calculated as follows:

$$WPNI\ (g\ N2\ kg-1) = \left(\frac{NCN}{6.25} - \frac{NPN}{6.19}\right) * 10$$

2.5. Powder reconstitution

Reconstituted skim camel milk powder (RSCMP) and reconstituted skim bovine milk powder (RSBMP) were obtained by rehydration of respective powders with MiliQ water. The mixtures were stirred (580 rpm) for 30 min at 25 °C. The reconstituted milks were stored at 4 °C overnight and then warmed up to the room temperature (25 °C).

2.6. LC-MS analysis

The LC-MS analyses (Fig. 1 and Fig. 2) were performed using an Agilent-1100 Rp-HPLC system (Agilent Technologies, Waldbronn, Germany) coupled with a Q-Exactive™ Hybrid Quadrupole-Orbitrap™ (Thermo-Fisher scientific, Waltham, MA, USA) mass spectrometer. The HPLC system was equipped with a column C4 (VYDAC, reference 214TP5215, length 150 mm, inner diameter 2.1 mm, pore size 300 Å,

Table 2
Protein characterization from LC-MS peak integration for skim bovine and camel milk before and after powders reconstitution.

Peaks			Concentration (μg μL^{-1})		**Denaturation Extent (%)**
Number	Identification	Molecular Weight (Da)	**Before drying (skim milk)**	After drying (reconstituted skim milk)	
Bovine milk					
2	K-casein (Variant A)	19 034	0.704 ± 0.01 [a]	0.48 ± 0.01[b]	31.8
5	n.id	n.d	0.846 ± 0.01 [a]	abs	100
6	α_{s1}-casein (Variant A)	23 614	9.76 ± 0.1 [a]	9.54 ± 0.1[a]	2.2
	α_{s1}-casein (1 Phosphorus)	23 693			
	α-Lactalbumin (Variant B)	14 176			
8	β-casein (Variant A)	24 023	5.76 ± 0.06 [a]	7.17 ± 0.1[b]	0
9	Mixture of β-Lactoglobulin	n.d	0.672 ± 0.01 [a]	0.45 ± 0.01[b]	33
10	β-Lactoglobulin (Variant B)	18 276	0.544 ± 0.01 [a]	abs	100
11	β- Lactoglobulin (Variant A)	18 363	0.8 ± 0.01 [a]	0.63 ± 0.01[b]	21.2
Camel milk					
1	Fragment of α-Lactalbumin	6059	1.17 ± 0.01 [a]	0.621 ± 0.01[b]	46.9
2	α-lactalbumin	14 421	7.65 ± 0.1 [a]	7.398 ± 0.1[b]	3.3
	α_{s1}- casein (6 Phosphorus)	24 768			
4	PGRP	19 137	1.1 ± 0.01 [a]	1.1 ± 0.01[b]	0
	α_{s2}- casein	22 000			
6	Camel Serum Albumin	66 600	0.66 ± 0.01 [a]	0.567 ± 0.01[a]	14.1
8	n.id	11 781	0.66 ± 0.01 [a]	abs	100
9	β-casein (4 Phosphorus)	24 970	8.82 ± 0.1 [a]	9.88 ± 0.1[b]	0
	β-casein	24 651			
10	n.id	17 823	2.25 ± 0.02 [a]	abs	100
11	ϒ-casein	13 901	0.93 ± 0.1 [a]	1.0 ± 0.1[b]	0

n.id: non-identified; n.d: non-determined; abs: absence; PGRP: Peptido-Glycan Recognition Protein. Values are presented as mean and standard deviation (SD).

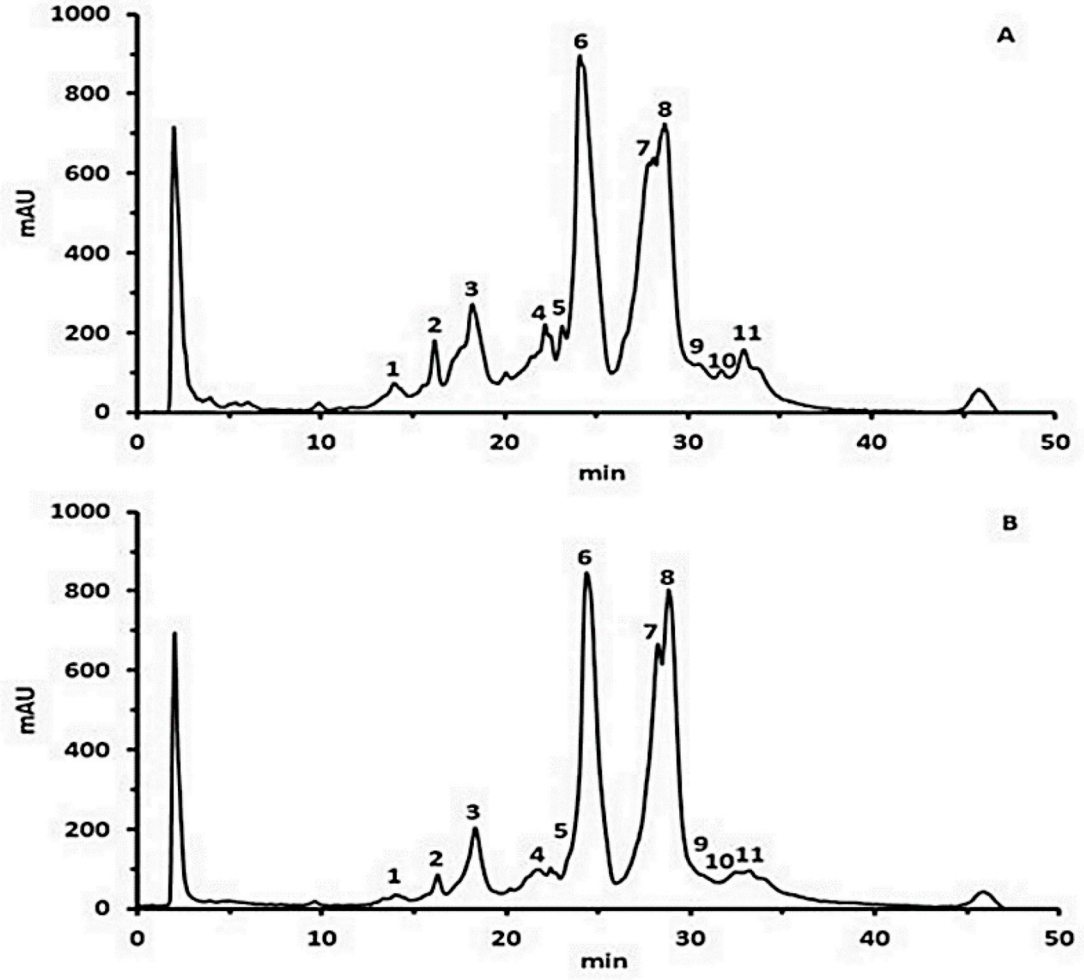

Fig. 1. HPLC-UV chromatograms recorded at 214 nm for bovine milk (A) and reconstituted bovine milk (B). The pics identification was presented in Table 2.

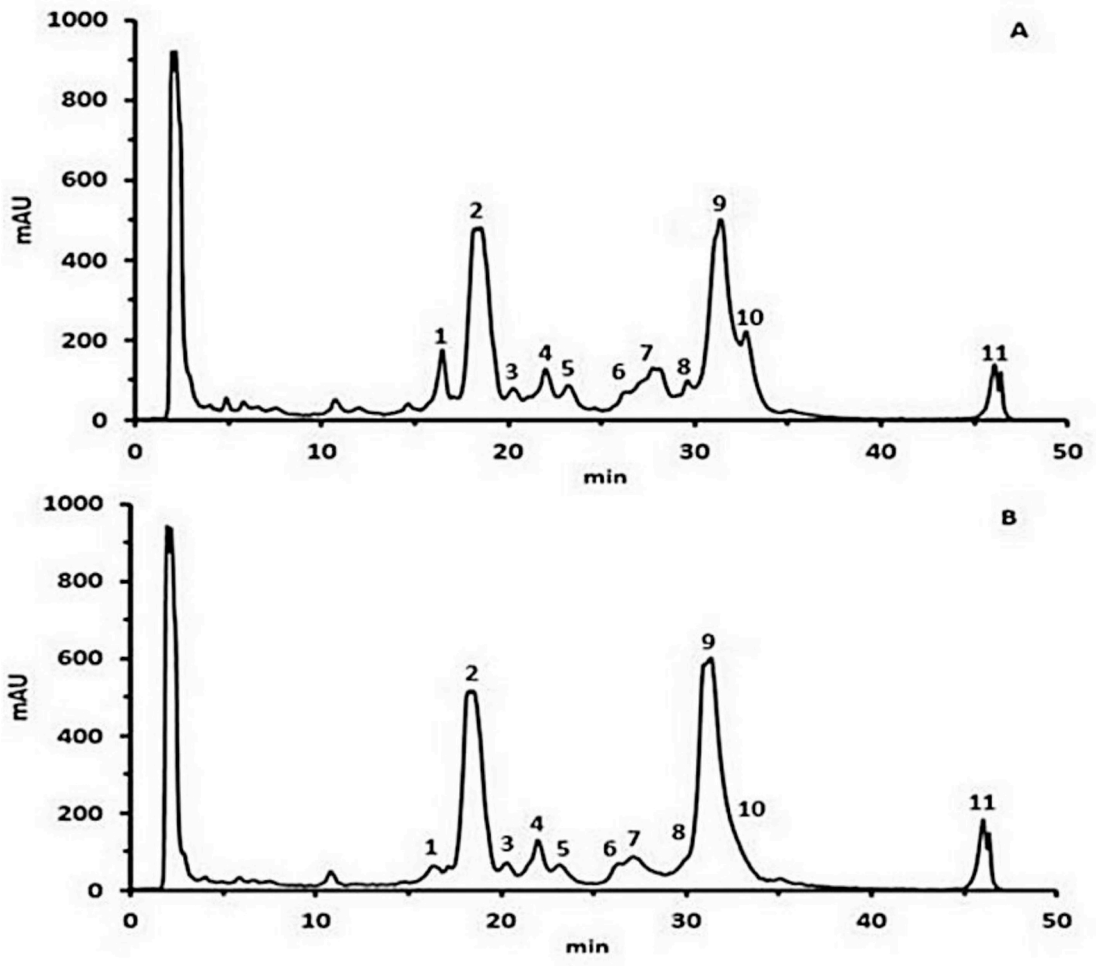

Fig. 2. HPLC-UV chromatograms recorded at 214 nm for camel milk (A) and reconstituted camel milk (B). The pics identification was presented in Table 2.

Grace™, Fisher-scientific, USA). Camel and bovine milks before (skim milks) and after drying (reconstituted milks) samples were prepared as described by Felfoul et al. (2017).

A gradient from 37% to 90% of a solvent (acetonitrile: 80% (v/v) and TFA: 0.1% (v/v) in deionized water) was applied during 50 min with an elution flow rate of 0.25 mL min^{-1}. Eluted proteins were then, electro-sprayed in a mass spectrometer Q-Exactive. Samples were firstly ionized using a HESI-II source operating at a voltage of 4.2 kV. The mass spectra acquisition speed was set up to a resolving power of 140000 and an m/z ranging from 800 to 3000. Mass spectra were then analyzed using BioPharma Finder™ software (version 2.0.66.12, Thermo-Fisher scientific, Waltham, MA, USA). The Uniprot database (http://www.uniprot.org/) was used to identify camel and bovine milk proteins (*Camelus dromdarus*, Taxon identifier: 9838 and *Bos taurus*, Taxon identifier 9913). The quantification of protein fractions in camel and bovine milks (Table 3) was estimated based on the integrated peak areas of HPLC chromatographs and protein content of skimmed and reconstituted milks. The denaturation extent was evaluated as follow:

$$Denaturation\ extent = \frac{Concentration\ before\ drying - Concentration\ after\ drying}{Concentration\ before\ drying} \times 100$$

2.7. Dynamic vapor sorption (DVS)

The water adsorption isotherms of SCMP and SBMP (Fig. 3) were assessed using the dynamic vapor sorption methodology at 25 °C. Twenty milligrams of SCMP or SBMP were loaded into a clean and dry aluminum pan. A surface measurement DVS advantage (Surface Measurement Systems Ltd., London, UK) equipped with a Cahn microbalance, was used to generate a water adsorption cycle from 0 to 0.90% of a_w (Carpin et al., 2017).

The experimental data, up to 0.40 of a_w, were fitted to the Guggenheim, Anderson and De Boer (GAB) model using the OriginPro 8 software (OriginLab Corporation, Northampton, USA). The GAB model equation is:

Table 3
Glass transition temperatures and water sorption isotherm properties of skim bovine and camel milk powders.

	Skim bovine milk powder (SBMP)	Skim camel milk powder (SCMP)
Glass transition temperature T_g (°C)		
a_w = 0.13	57.8 ± 0.4 [a]	54.6 ± 1.4 [b]
a_w = 0.23	46.6 ± 1.0 [a]	48.2 ± 1.0 [a]
a_w = 0.33	31.9 ± 2.4 [a]	32.6 ± 1.7 [a]
Lactose crystallization conditions		
a_w	0.70 ± 0.0 [a]	0.60 ± 0.0 [b]
X_c (g 100g^{-1})	19.3 ± 0.2 [a]	14.1 ± 0.1 [b]
GAB model constants		
X_m (g 100g^{-1})	2.0 ± 0.2 [a]	2.2 ± 0.2 [a]
C	12.6 ± 2.9 [a]	20.0 ± 1.9 [b]

a_w: water activity; X_c: necessary water for total crystallization of amorphous lactose; GAB: Guggenheim, Anderson and De Boer; X_m: monolayer moisture content; C: water binding energy by the monolayer; Values are presented as mean ± standard deviation (SD); Same letter in the same row represent the statistical data significance ($p < 0.05$).

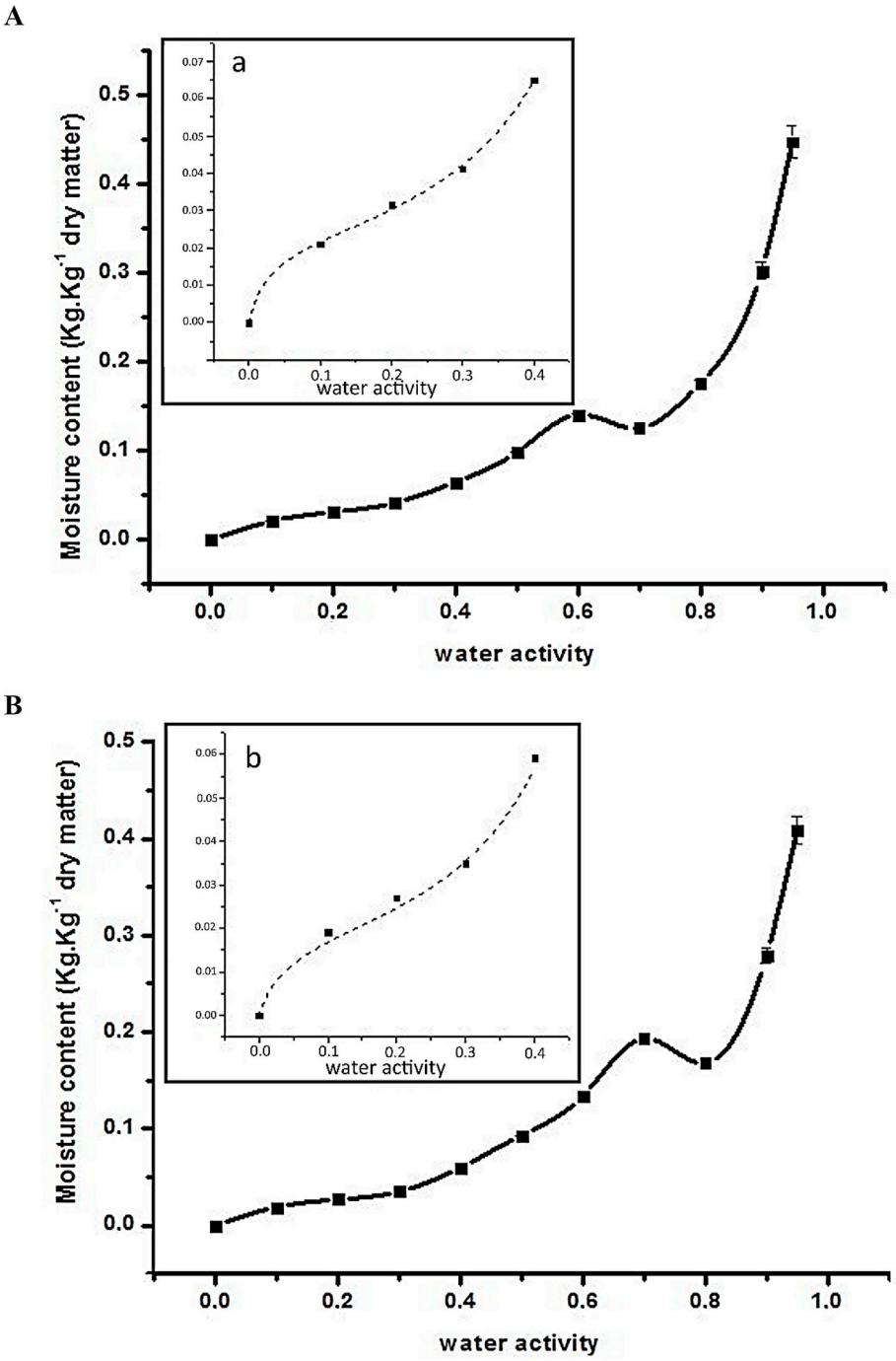

Fig. 3. Representative sorption isotherms of SCMP (A) and SBMP (B) determined at 25 °C. The experimental data of SCMP (a) and SBMP (b) from 0 to 0.40 of a_w, were fitted to GAB model ($R^2 > 0.98$). X_m: monolayer moisture capacity. C: monolayer water energy binding constant.

$$X = \frac{Xm.\ C.\ k.\ aw}{(1 - k.\ aw).\ (1 - k.\ aw + C.\ k.\ aw)}$$

where, X_m represents the monolayer moisture capacity (g 100 g^{-1}); the C constant is the water binding energy by the first layer; K constant describes the multilayer sorption ability and a_w is the studied water activity. Up to 0.40 of a_w, the K constant for SCMP and SBMP was greater than 1. This constant couldn't be interpreted since it described the multilayer sorption binding energy, up to 0.90 of a_w (Chirife, Timmermann, Iglesias, & Boquet, 1992).

2.8. Modulated dynamic scanning calorimetry (MDSC)

The MDSC was used to evaluate the glass transition temperature (T_g) of skim camel and bovine milk powders. Initially, the glass transition temperature of both SCMP and SBMP was studied at water activities of 0.13, 0.23, 0.33. Before analysis, each milk powder was equilibrated for 30 days at 20 ± 2 °C with saturated salt to reach the desired a_w (the a_w of LiCl, CH_3COOK, and $MgCl_2$ were equal to 0.13, 0.23, and 0.33, respectively). Six mg of each samples were sealed in a hermitic aluminum pan. A differential scanning calorimetry Q1000 (TA Instruments, Eschborn, Germany), operating in heat mode only (−30 to +200 °C), was used to assess the MDSC analysis against an empty aluminum pan

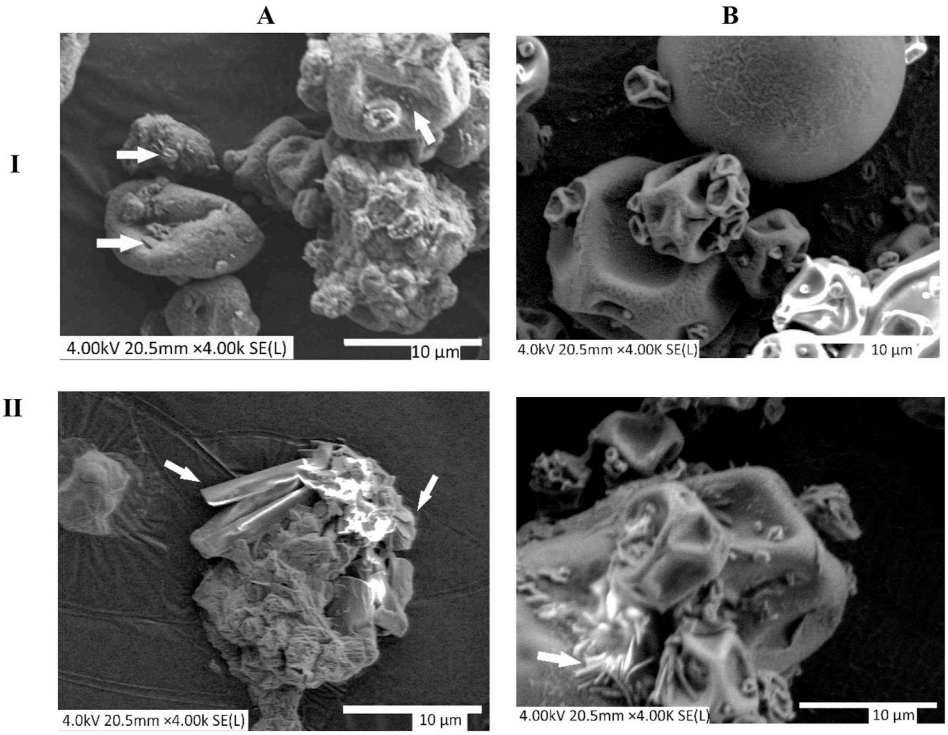

Fig. 4. SEM micrographs of the powder particles of SCMP (A), and SBMP (B) observed at 0.13 (I) and 0.53 (II) of water activity, respectively. The white arrows represent the lactose crystals.

as presented by Syll et al. (2012). The T_g was identified as the midpoint temperature when changes in heat capacity are observed in the reversed MDSC profile.

2.9. Powders microstructure

The microstructure of the produced powders was obtained using the scanning electron microscopy (SEM). To avoid undesirable water adsorption, the powders were rapidly seeded onto a double-sided adhesive tape (fixed on aluminum discs). The samples were, then, covered with carbon using a BAL-TEC-SCD-005 sputter coater (Bal-Tec Co., Balzers, Liechtenstein). Micrographs were finally observed at a magnification 1.00k and 4.00k, using a Hitachi S-4700 (Hitachi, Tokyo, Japan), operating at 4.0 kV of accelerating voltage. SEM observations were realized after equilibrating the studied powders at a water activity of 0.13 and 0.53 (Fig. 4).

2.10. Statistical analysis

All analyses and measurements in this work were carried out in triplicate. The statistical differences were examined using SPSS 19 software (IBM SPSS statistics, Version 19, USA) following the student's *t*-test with a confidence level of 95%.

3. Results and discussions

3.1. Physicochemical characterization

3.1.1. Powders composition

The composition of the produced powders is shown in Table 1. Skim camel (SCMP) and skim bovine (SBMP) milk powders presented a water activity of 0.25 ($p > 0.05$, Table 1). The amounts of total protein, lactose and fats in SCMP and SBMP were statistically similar ($p > 0.05$, Table 1). Unlike the caseins fraction, SCMP contained higher whey proteins quantity than that of SBMP ($p < 0.05$, Table 1). Nevertheless, higher ash content was found in skim camel milk powder ($p < 0.05$, Table 1). In this current study, the composition of camel milk powder was in agreement with the values reported by Zouari et al. (2020). The latter acknowledged that the lactose, proteins, fat and ash contents were equal to 52.7 ± 0.2 g 100 g^{-1}, 33.3 ± 0.2 g 100 g^{-1}, 1.0 ± 0.1 g 100 g^{-1} and 8.8 ± 0.1 g 100 g^{-1}, respectively.

3.1.2. Powders densities and crystallinity

The densities of the produced powders are presented in Table 1. Compared to SBMP, higher loose and packed bulk densities were recorded for SCMP ($p < 0.05$, Table 1). On the contrary, lower particle density for SCMP was found as compared to that of SBMP ($p < 0.05$, Table 1).

Results of this study highlighted that the initial lactose crystallization percentage of SCMP was significantly higher than that of SBMP (15.0 ± 0.2% and 10.4 ± 0.2% for SCMP and SBMP, respectively, $p < 0.05$, Table 1). This observation could be related to the difference in the surface lactose content of the powders. Indeed, Zouari et al. (2020) studied the surface composition of camel and bovine milk powders. This author reported that camel milk powder showed a higher surface lactose content which could be exposed to residual humidity during processing. This could promote lactose crystallization during the first step of processing and could explains the higher initial lactose crystals content of camel milk powder.

Furthermore, the analysis of powder size distribution indicated that SBMP had significantly higher d_{50} than that of SCMP (9.2 ± 0.1 µm against 8.8 ± 0.2 µm, $p < 0.05$, Table 1). Several studies have reported that the d_{50} ranged from 12 to 128.76 µm, depending on feed characteristics (e.g. composition and concentration) and the spray-dryer properties (Fitzpatrick et al., 2007; Nijdam & Langrish, 2006). Interestingly, camel milk powders showed smallest d_{50} than that of bovine milk powders. This could be related to the differences in the physicochemical characteristics of both milks.

3.2. Powders biochemical stability

3.2.1. Whey protein nitrogen index

The Whey Protein Nitrogen Index (WPNI) of SCMP and SBMP is presented in Table 1. In fact, the whey proteins were highly unstable under heat treatments (Nabhan et al., 2004). In this study, skim camel and bovine milks were sprayed into fine milk droplets. Under this condition, a rapid evaporation rate was supposed to occur during drying. Therefore, the temperature of milk droplets quickly reaches the outlet drying temperature (Woo, 2013).

For SCMP and SBMP, the measured WPNI was close to 11.5 ± 0.2 g of N_2 Kg^{-1} and 8.9 ± 0.2 g of N_2 Kg^{-1}, respectively. Despite its higher whey content, SCMP showed significantly higher WPNI than that of SBMP ($p < 0.05$, Table 1). This could related to the composition of SCMP and SBMP whey proteins as well as their thermal denaturation sensitivity (i.e. presence of initial free thiol group). Similar observations were reported by Farah (1986), who analyzed the heat denaturation of camel whey proteins by means of WPNI. This author also concluded that camel milk whey proteins have a significantly lower heat sensitivity (up to 90 °C for 30 min) than that in bovine milk samples. Therefore, higher WPNI was recorded to SCMP as compared to SBMP.

3.2.2. LC/MS of camel and bovine proteins composition before and after drying

Figs. 1 and 2 show the proteins composition of bovine and camel milks (skim 'A' and reconstituted 'B'), respectively. Indeed, SCMP and SBMP were used to produce reconstituted camel and bovine milks (RSCMP and RSBMP set up to the same total solids as in skim milks (Table 1)). The powders were reconstituted using demineralized water without heating. The total protein content of the RSCMP and RSBMP was equal to 2.5 ± 0.1 g 100 g^{-1} and 3.0 ± 0.1 g 100 g^{-1}, respectively. The statistical analysis showed that the protein content was significantly higher in untreated skim camel and bovine milk than in reconstituted milk ($p < 0.05$). The protein identification in either unprocessed or reconstituted camel and bovine milks were assessed using a HPLC-Quadrupole-Orbitrap/MS.

The concentration and the denaturation extent of the identified proteins for both milks are presented in Table 2. The results showed that the α-casein and the β-casein in both RSDM and RSCM remained stable (Table 2). A loss of 31.8% of κ-casein variant-A (peak 2, Table 2) was only observed in RSCM. The κ-casein was not detected in both SDM and RSDM. The UV profiles, however, highlighted the presence of ϒ-casein in only skimmed and reconstituted camel milks (peak 11, Fig. 2). This casein was not denaturized during drying step ($p > 0.05$, peak 11, Table 2).

The analysis of RSCM revealed the disappearance of an unidentified protein after drying (peak 5, Fig. 1). Furthermore, results of this work underlined the disappearance of β-Lactoglobuline variant-B (peak 10, Table 2) and the loss of β-Lactoglobuline variant-A (21.2%, peak 11, Table 2) in RSCM. The other whey proteins, especially the α-Lactalbumin, remained intact (peak 6, Table 2). In this study, the β-Lactoglobuline was the most sensitive bovine milk whey protein during drying step. Actually, it was reported that in a co-current drying system the particle temperature will be raised until reaching the outlet drying temperature (Woo, 2013, pp. 29–56). When approaching 80 °C (the outlet drying temperature), a thermal degradation of β-Lactoglobulin in whatever the variant 'A or B' (Petit, Six, Moreau, Ronse, & Delaplace, 2013). The thermal degradation of β-Lactoglobulin could be responsible of the low WPNI value for SBMP as compared to that of SCMP (Table 1).

The analysis of the UV-profiles of SDM and RSDM underlined the total absence of β-Lactoglobulin. Furthermore, two unidentified proteins had disappeared in RSDM (peaks 8 and 10, Fig. 2). These proteins had a molecular weight of 11781 and 17823 Da, respectively. The results highlighted the presence of a specific whey protein identified as the peptidoglycan recognition protein (PGRP) in SDM and RSDM (Fig. 2). This protein remained stable after drying (peak 4, Table 3). Moreover, the analysis of RSDM profile indicated a denaturation percentage of 14% for the camel serum albumin protein (CSA, peak 6, Table 2). The denaturation of CSA was in contradiction with the reported result by Elagamy, 2000. This author reported that the CSA was not affected when the camel milk was heated at 75 °C for 30 min. The findings highlighted that the α-Lactalbumin (the major whey protein) in RSDM was not denaturized. Similar trends were reported by Zhang et al. (2016). These authors proved that the α-Lactalbumin was relatively heat stable during spray drying. In this study, a loss of a fragment of α-Lactalbumin (46%, peak 1, Fig. 3, Table 2) was noticed in RSDM. This fragment corresponded to the sequence from 27 to 78 (with no disulfide bound) in native α-Lactalbumin of camel milk (Uniprot database, A0A2H4WWA5).

3.3. Powders physical stability

3.3.1. Water sorption isotherm

The water sorption isotherms of SCMP and SBMP are presented in Fig. 3. The water sorption isotherms describe the relationship between the equilibrium water content and the water activity. The obtained isotherms for SCMP and SBMP showed sigmoid curves exhibiting a break-point (Fig. 3). At this point, the total quantity of amorphous lactose content crystallizes. Similar sorption isotherms were reported for bovine milk powders (Berlin, Anderson, & Pallansch, 1968). The total amorphous lactose quantity had crystallized at a water activity of 0.60 for SCMP (Fig. 3A). This was significantly lower than that of SBMP (0.70 of a_w, Fig. 3B). The required amount of water to induce the total lactose crystallization was equal to 14.1 ± 0.1 g 100 g^{-1} and 19.3 ± 0.2 g 100 g^{-1} ($p < 0.05$, Table 3). It was reported that in dairy powders the amorphous lactose, being very hygroscopic, and adsorbed water from ambient air moisture (Roos, 2002). In this study, the measured water activity and water amount to induce the total crystallization of lactose in SCMP were significantly lower than those of SBMP ($p < 0.05$, Table 3). This could be related to the higher initial lactose crystallization percentage in SCMP (Table 1).

The obtained sorption isotherms were fitted to GAB model up to 0.40 of water activity. Results of this study indicated that SCMP (Fig. 3a) and SBMP (Fig. 3b) presented the same monolayer water (X_m = 2.0 ± 0.2 and 2.2 ± 0.2 g 100 g^{-1}, $p > 0.05$, Table 3). Gaiani et al. (2009), suggested that X_m was related to the surface hydrophobicity of milk powder. This indicated that both SCMP and SBMP had the same surface hydrophobicity. Interestingly, the constant '*C*' for SCMP was significantly higher than that of SBMP (20.0 ± 1.9, 12.6 ± 2.9, $p < 0.05$, Table 3). The '*C*' constant describes water energy binding by the monolayer (i.e. surface hygroscopicity). This indicated that although SCMP and SBMP had the same surface hydrophobicity, it was possible to observe higher amounts of hygroscopic compounds at the surface of SCMP (i.e. amorphous lactose and minerals). Indeed, recently Zouari et al. (2020) demonstrated that skim camel milk powder contained twice the surface lactose content compared to skim bovine milk powder. This will lead to higher lactose mobility and explains the lower stability of lactose against crystallization as well as the highest water binding energy by skim camel milk powder.

3.3.2. Glass transition temperature

The glass transition temperatures (T_g) of SCMP and SBMP are summarized in Table 3. The glass transition temperature is an important indicator of the physical stability of dairy powder (Bhandari & Howes, 1999). It was extensively demonstrated that the glass transition temperature is strongly related to the water activity of powders (Schmitz-Schug, Gianfrancesco, Kulozik, & Foerst, 2013). The analysis of the glass transition temperatures indicated that increasing the water activity by 10% resulted in a decrease of about 10 °C in the T_g (Table 3). The depression of T_g was directly associated with the effect of water plasticization on the amorphous compounds (Jouppila & Roos, 1994).

Interestingly, only at 0.13 of a_w, the T_g of SCMP was slightly but significantly lower than that of SBMP (54.6 ± 1.4 °C and 57.8 ± 0.4 °C, respectively, $p < 0.05$, Table 3).

It has been reported that the mobility of lactose increased while increasing water activity (Haque and Suzuki, 2006). At low water activity, amorphous lactose displayed rotational mobility. It was acknowledged that higher amorphous lactose content at the surface enhanced the rotational mobility (Fennema, 1996). As advanced for the analysis of water sorption isotherms, higher amorphous lactose content could be observed on the surface of SCMP compared to the surface of SBMP. This will lead to the decrease of T_g at low water activity (a_w = 0.13). At 0.23 and 0.33 of a_w, the plasticizing effect of water is more remarkable. The rotational mobility of lactose decreases and is accompanied by the appearance of translational mobility (Le Meste et al., 2002). Thus, the lactose at the surface of both milk powders exhibited the same glass transition temperature at water activities of 0.23 and 0.33.

3.3.3. Evolution of the microstructure

In order to visually assess the lactose crystallization, the surface of camel and bovine milk powders were investigated at two a_w (0.13 and 0.53), using scanning electron microscopy (Fig. 4). The microstructure of SCMP and SBMP at 0.13 of water activity was presented in Fig. 4I. The SEM observations showed different particle's sizes and similar shapes with a collapsed and shrinked structure. The obtained camel and bovine milk powders presented a distinguished tendency to aggregation and clustering (Fig. 4I). Several studies have reported the same general aspect of bovine milk powder, especially produced at low feed concentration (≈10%) (Fyfe, Kravchuk, Nguyen, Deeth, & Bhandari, 2011; Kelly et al., 2016). At 0.13 of a_w, small lactose crystals were apparent at the surface of SCMP (Fig. 4IA, white arrows) as compared to SBMP (Fig. 4IB). The existence of these crystals was linked to the higher initial crystallization of skim camel milk powder (15.0 ± 0.2%, Table 1). Actually, it was demonstrated that at low a_w (0.11–0.33), lactose was in an unstable amorphous state with no apparent lactose crystals (Kim, Chen, & Pearce, 2002). At 0.53 of a_w, all tested samples showed lactose crystals with different sizes and shapes [SCMP (Fig. 4IIA) and SBMP (Fig. 4IIB), white arrows]. In fact, by increasing the water content, structural relaxations of lactose are induced leading to the increases of its mobility, i.e. translational mobility (Fan & Roos, 2016). As a consequence, the residual β-lactose crystallized as α-lactose monohydrate in shape of prisms and tomahawks (Warburton & Pixton, 1978). These crystals were recognizable at the outer of the particle surface of camel and bovine milk powder (Fig. 4II).

4. Conclusions

In this work, skim camel and bovine milk powders were produced using spray drying. Results of this study indicated that camel milk powder presented higher bulk and tapped bulk density as compared to bovine milk powder. The whey protein nitrogen index (WPNI) and HPLC-Quadrupole-Orbitrap/MS analyses showed that the essential of caseins and whey proteins of camel and bovine milks were preserved after drying. By the same token, these analyses indicated that the denaturation extent of spray-drying on camel milk proteins was very limited compared to that of bovine milk. The LC/MS indicated the absence of β-Lactoglobuline and the overexpression of α-Lactalbumin in both skim and reconstituted camel milk. This protein remained stable after drying. The most denaturized protein was the CSA (Camel serum albumin) with a percentage of 14%. The analysis of the water sorption isotherms indicated that lactose in skimmed camel milk powder presented lower water activity to induce total crystallization than that of skim bovine milk powder. Besides, analysis of the glass transition temperature indicated that at only 0.13 of a_w, camel milk powder presented significantly lower T_g than that of SBMP. Nevertheless, for both milk powder the T_g decreased while increasing the water content due to water plasticization effect. This work confirmed the interesting ability of camel milk to be processed into spray-dried powder.

Findings

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CRediT authorship contribution statement

Ahmed Zouari: Conceptualization, Methodology, Software, Visualization, Investigation, Writing - original draft, Writing - review & editing. **Valerie Briard-Bion:** Conceptualization, Visualization, Investigation, Software. **Pierre Schuck:** Conceptualization, Visualization, Investigation. **Fréderic Gaucheron:** Conceptualization, Visualization, Investigation. **Guillaume Delaplace:** Conceptualization, Visualization, Investigation. **Hamadi Attia:** Supervision. **Mohamed Ali Ayadi:** Conceptualization, Supervision, Writing - review & editing.

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