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Abstract

The aim of this study was to identify optimal storage conditions able to preserving date palm quality and minimising their loss in the supply chain. Hence, the effect of storage at -18, 0, 2 and 4 °C for 3, 6 and 9 months during two harvest seasons (2017 and 2018) on sugars, organic acids, polyphenols and cell wall yields and composition of 'Deglet Nour' Tunisian dates, were studied. Mid Infrared Spectroscopy (MIR) as a non-targeted method allowed to highlight a year effect on chemical composition and to discriminate samples stored at 4 and 2 °C regarding to major components (moisture, sugars, organic acids..). Cell wall yields were stable during the time. However, galactose from pectin side chains decreased with time, causing an increase of lignin, cellulosic glucose, fucose and rhamnose. Procyanidins, accounting for 98% of total polyphenols, were not affected by storage. Regarding quality parameters stability, stored fruits at -18 °C could be the solution for a long term storage but due to its high energetic costs, 2 °C must be the optimal temperature with a lower time.

Keywords: *Phoenix dactylifera* L.; cold storage; cell wall structure; polyphenol

1. Introduction

The date palm tree (*Phoenix dactylifera* L.) is cultivated as a food and cover approximately 3% of cultivated areas in the world (Dowson, 1982). Native to the Middle East region, date palm tree is grown extensively in arid and semiarid regions of the world (Ahmed, Al-Gharibi, Daar, & Kabir, 1995). Date (*Phoenix dactylifera* L.) is a fruit of high economic and nutritional relevance and date palm constitutes the basis of economy for the people living in Tunisian Sahara.

Moreover, in human nutrition, date palm fruits are considered as an important part of the Mediterranean diet regardless to their high nutritional value (protein, dietary fibers,

sugars, organic acids, antioxidants, vitamins, fatty acids, and minerals) (Awad et al., 2011 ; Al-Farsi et al., 2005; Elleuch et al., 2008). Date palm fruits are also used in traditional medicine, and studied for their role against hypertension, cancer, infections, heart diseases, etc. (Vayalil, 2012).

In Tunisia 'Deglet Nour' date palm is the most produced cultivar, it is also the most appreciated cultivar both locally and internationally. Its production is increasing and reaches 241 321 tons from a total date palm production of 305 251 tons in 2018 harvest season (GIFuits, 2018). Moreover, 'Deglet Nour' date palm represent 16% of total agriculture product exportations. However, date palm production is accompanied by a loss in the supply chain due to reducing fruit quality that is a fundamental aspect for the consumer.

Storage at low temperature is an efficient approach to maintain quality and increase postharvest life by reducing fruit metabolic activity (Siddiq & Greiby, 2013). Optimal storage conditions for dates at *Tamr stage* are 0 °C for 6 to 12 months, depending on cultivar: semi-soft dates, like 'Deglet Nour' and 'Halawy', have longer storage-life than soft dates, like 'Medjhool' and 'Barhee'. For extended storage, the use of temperatures below the highest freezing temperature of -15.7 °C is recommended (Kader & Hussein 2009; Jemni et al., 2019; Ismail et al., 2008). Dates fruits with 20% or lower moisture can be kept at -18 °C for more than one year, at 0 °C for one year, at 4 °C for 8 months, or at 20 °C for one month, relative humidity should be kept at 65-75% for all cases (Kader & Hussein 2009). However, in Tunisia, the storage process is not well mastered and date palm fruits are stored arbitrary between 2 and 5 °C. During storage, the ripening-related loss of firmness or softening is due to the cell wall degradation resulting in a lower quality. Fruit softening is a result of changes of the cell wall components, its involve hydrolysis of neutral sugars from pectin side chains, and depolymerisation, which are associated with cell wall degrading enzymes activities, such as polygalacturonase (PG), pectin methylesterase (PME), cellulase, β-galactosidase (β-GAL),

and α-arabinofuranosidase (α-ARF) (Deng et al., 2005; Wei et al., 2010; Wang et al., 2018; Gwanpua et al., 2016; Chen et al., 2017a; Chen et al., 2017b; Awad et al., 2011; Murayama et al., 2002; Hasegawa & Smolensky, 1971). In date palm fruits, the most commonly reported modifications indicate a loss of galactose and uronic acid (Gribaa et al., 2013; Awad et al., 2011). Nutritional compositions of fruits are also modified during storage, and depend on storage conditions such as time and temperature. Total polyphenol amounts in 'Deglet Nour' date palm decrease slightly with storage time (Jemni et al., (2019) but increase with freezing temperatures (A. A. Allaith, Ahmed, & Jafer, 2012; Biglari et al., 2009; Hazbavi, Khoshtaghaza, Mostaan, & Banakar, 2015), it is probably due to a better extractability of phenolic compounds. Since quality parameters are affected by storage, it is very important to understand the effect of such storage conditions on the different characteristics and on consumers' acceptability of the date palm fruit. Many studies are dedicated to the effect of storage on different fruit and vegetable attributes (Ismail et al., 2008; Harker et al., 2003).

Unfortunately, few studies are focused on date palm quality parameters. The ideal storage temperature and time for fresh date palm fruit consumption should be evaluated and identified in order to avoid qualitative and quantitative losses. Therefore, the aim of this work was to assess the effect of cold storage conditions, temperature and time on date palm fruit 'Deglet Nour' organoleptic and nutritional composition in order to define the optimum storage conditions.

2. Material and methods

2.1 Chemical

Polyphenol standards ((+)-catechin, (-)-epicatechin, 4-cafeoylshikimic acid, 5-cafeoylshikimic acid, rutine, isorhamnetin and chrysoeriol) were purchased from Extrasynthese (Lyon, France). Acetonitrile of HPLC grade and methanol were from Carlo

89 Erba Reagents S.A.S (Val de Reuil, France), formic acid, was from Sigma-Aldrich
90 (Deisenhofen, Germany). Ethanol, acetone and sulfuric acid were from Fisher Scientific (Fair
91 Lawn, NJ, USA). Neutral sugar standards (rhamnose, fucose, arabinose, xylose, mannose,
92 galactose, and glucose) were from Fluka (Buchs, Switzerland). N-methylimidazole and acid
93 anhydride were from Acros Organics (Geel, Belgium). Ammonium hydroxide solution
94 (NH_4OH) (33%), Sodium borohydride ($NaBH_4$) and acetic acid were from Merck Chimie
95 SAS, an affliate of Merck KGaA, Darmstadt, Germany

96 **2.2 Plant material**

97 'Deglet Nour' date (*Phoenix dactylifera* L.) were hand harvested and collected from
98 Kebeli oasis in the South of Tunisia (33° 42' 7" North and 8° 58' 25" East) at the end of
99 October during two harvest seasons (2017 and 2018). Fruits were collected at the fully
100 maturity stage, i.e. *Tamr* stage, which corresponds to the last physiological stage as described
101 by Hussain et El-Zeid, (1975) and Al-Shahib et Marshall (2003) when date palm fruit colour
102 darken with soft and semi-soft texture. Date palm spikelets (about 25 kg) were transported in
103 plastic boxes at ambient temperature to postharvest laboratory in the Higher Agronomic
104 Institute of Chott Mariem, Tunisia. Date palm fruits were manually detached from the
105 spikelets and sorted to discard infested, immature and damaged fruits in the order to have a
106 homogenous and uniform sample. Date palm fruits were stored in small PET containers (190x
107 115x 58 mm) at -18 °C, 0 °C, 2 °C and 4 °C during 3, 6 and 9 months.

108 Thirty date palm fruits were considered for each biological replicate and for each
109 condition (temperature/time pair), leading to 4 temperatures x 3 times x 3 replicates, i.e. 36
110 samples for each year (2017 and 2018).

111 **2.3 Sample preparations**

After each storage time, date palm fruits were pitted, cut into small pieces, dropped in liquid nitrogen and stored at -20 °C until delivery to INRAE PACA, (Avignon, France). Samples were then ground in liquid nitrogen using an IKA®A11 basic analytical mill (Ika Labortechnik, Staufen, Germany) in order to obtain a fine homogeneous powder. Fresh powders using for the determination of soluble sugars and organic acids were conserved at -80 °C until analysis whereas samples used for polyphenols, cell wall isolation as Alcohol Insoluble Solids (AIS) and Mid Infrared Spectroscopy determination (MIR) were freeze-dried and finally stored at -20 °C until analysis.

2.4 Mid Infrared Spectroscopy

Mid Infrared Spectra were acquired at room temperature using ATR Tensor 27 FT-IR spectrometer (Brucker Optics, Wissembourg, France) equipped with a single-reflectance horizontal diamond crystal (Golden Gate, Bruker Optics). All date palm fruit samples were analyzed using the dried powder of whole fruit to compare their spectral quality according to the storage conditions. Freeze-dried powder was placed on the ATR (Attenuated Total Reflection) crystal and was pressed with a system press tip flap. The spectra were acquired from 4000 to 600 cm^{-1} and corrected against the background spectrum of air. Each spectrum was obtained by taking the average of 16 scans. Nine spectra were acquired on different aliquots for each sample to evaluate its heterogeneity. The crystal was cleaned between measurements with deionized water and well dried. Instrument control and spectra collection were performed using OPUS software (version 4.0, Bruker, France) supplied by the equipment manufacturer. The absorption ranged between 2400 and 2200 cm^{-1}, due to carbon dioxide, was discarded prior to the calculation. Spectral pre-processing and multivariate data analysis were performed with Matlab 7.5 (Mathworks Inc. Natick, MA) software using the SAISIR package (Bertrand & Cordella, 2008). Principal Component Analysis (PCA) was

applied in order to get an overview of the sample discrimination characterized by their infrared spectral data according to storage conditions and was performed using Matlab 7.5.

2.5 Cell walls or Alcohol Insoluble Solids (A.I.S) preparation

Alcohol Insoluble Solids (AIS) were prepared according to previous papers with some modifications (Renard, Voragen, Thibault, & Pilnik, 1990; Renard 2005). Approximately 2 g of freeze-dried date palm powder were dropped in 15 mL of 96% boiling ethanol and let for 30 min. Suspension was then transferred to a 50 mL empty Sep-pack column (Interchim, Montlucon, France) equipped with a sinter of porosity 20 µm. The suspension was washed with ethanol 70% at room temperature until the filtrate was sugar-free as shown by the negative reaction of the phenol sulphuric test (Dubois et al., 1956). Sample was then dried by solvent exchange with acetone: water (v/v 60:40, three times), acetone: water (v/v 80:20, two times) and then with acetone 100% until discolouration of the supernatant. The residue was then dried at 37 °C during 48 h and weighted. AIS yields were expressed in mg/g of Fresh Weight (FW).

2.6 Analysis methods

Sugars and organic acids

Sugars (glucose, fructose and sucrose) and organic acids (malic acid and citric acid) were quantified using colorimetric-enzymatic methods (Boehringer Mannheim Co., Mannhein, Germany) and expressed in mg/g FW. Absorbance was measured at 340 nm with a SAFAS flx-Xenius XM spectrofluorimeter (SAFAS, Monaco).

Neutral sugar analysis

Neutral sugars from AIS samples were analysed as alditol acetates after acid prehydrolysis and hydrolysis. For the quantification of cellulosic glucose and galacturonic

159 acid, 10 mg of AIS samples were submitted to prehydrolysis by adding 250 µL of 72%
160 sulphuric (1 hour at room temperature) (Saeman, Moore, Mitchell, & Millett, 1954). The
161 solution was then diluted by addition of 1 mL of water and 1 mL of inositol (internal
162 standard). For only neutral sugar quantification no prehydrolysis was carried out, and directly
163 1 mL of 1M sulphuric acid and 1 mL of inositol (internal standard) were added to 10 mg of
164 AIS samples. All Samples were hydrolysed for 3 hours in a heater block at 100 °C. After
165 hydrolysis they were derivatised to volatile alditol acetates (Englyst, Wiggins, & Cummings,
166 1982). Extracts were injected on a GC-FID Clarus 500 (PerkinElmer, Waltham, USA) with a
167 capillary column Optima of 30 m × 0.25 mm, coated with 0.25 µm film thickness
168 (Marcherey-Nagel, Duren,Germany). The conditions were as follows: temperature of
169 injection 250 °C in split mode (1:8 ratio) with injection volume of 1.5 µL, column flow 35
170 cm/s, oven temperature 230 °C, FID detector (250°C, H2 flow 45 mL/min/pressurized air).
171 Results were expressed in mg/g AIS.

172 **Uronic acids assay**

173 After acid prehydrolysis (Seaman procedure), samples were used to measure their
174 uronic acid contents with a spectrophotometric method at 520 nm using a spectrophotometer
175 (V-530 Jasco, Tokyo, Japan), and the m-hydroxydiphenyl (MHDP) assay as described by
176 Blumenkrantz & Asboe-Hansen (1973) with galacturonic acid as external standard, expressed
177 as anhydrouronic acids (AUA). Results were expressed in mg/g AIS.

178 **Methanol assay**

179 Methanol in AIS samples was determined by Headspace-GC-MS (HS-GC–MS) after
180 saponification using CD_3OH as internal standard as described by Renard & Ginies, (2009).
181 The degree of methylation (DM) was calculated as molar ratio of methanol to uronic acid.

182 **Lignin content**

Lignin was analyzed in AIS samples as described by Brahem, Renard, Gouble & Le Bourvellec (2017). The amount of lignin was calculated from a linear calibration curve created with commercial alkali lignin.

Polyphenol quantification

Polyphenol were identified by HPLC-ESI-MS^2 and their composition was determined by HPLC-DAD with or whitout thioacidolysis as described by Guyot, Marnet, Sanoner & Drilleau (2001). Their identification was performed using an Acquity Ultra performance LC (UPLC) apparatus from Waters (Milford, MA, USA) and their characterization and quantification were performed using an Ultra Fast Liquid Chromatography Prominence system (Shimadzu, Kyoto, Japan) controlled by the LabSolutions software (Version 5.57, Shimadzu, Kyoto, Japan).

Polyphenol identification by HPLC-ESI-MS^2

HPLC/ESI-MS^2 analysis was performed on an Acquity Ultra performance LC (UPLC) apparatus from Waters (Milford, MA, USA), equipped with a photodiode array detector (detection at 280, 320, 350 and 520 nm) coupled with a Bruker Daltonics (Bremen, Germany) HCT ultra ion trap mass spectrometer with an electrospray ionization source. Separations were achieved using a Kinetex 2.6 µm C18 100A LC column 100x4.6 mm (Phenomenex, Torrence, CA, USA) protected by a guard column of the same material (C18 100A LC column 100x4.6 mm (Phenomenex, Torrence, CA, USA) operated at 30 °C. The mobile phase consisted of water/formic acid (99:1, mL/mL) (eluent A) and acetonitrile (eluent B). The flow rate was 1 mL/min. The elution program was follows: 3-9% B (0-5 min); 9-16% B (5-15 min); 16-50% B (15-45 min); 50-90% B (45-48 min); 90-90% B (48-52 min); 90-3% B (52-55 min); 3-3% B (55–60 min). Samples (crude extracts) were injected at a level of 10 µL. For polyphenol characterization, a capillary voltage of 2 kV was used in the negative ion mode. Nitrogen was used as drying and nebulizing gas with a flow rate of 12 L/min. The desolvation

temperature was set at 365 °C and the nebulization pressure at 0.4 MPa. The ion trap was operated in the Ultrascan mode from m/z 100 to 1000.

Polyphenol quantification by HPLC-DAD

Separations were achieved using a Kinetex 2.6 µm C18 100A LC column 100x4.6 mm (Phenomenex, Torrence, CA, USA) operated at 30 °C. The mobile phase consisted in water:formic acid (99:1, v/v) (eluent A) and acetonitrile (eluent B). The flow rate was 1 ml/min. The elution program was as follows: 3-9% B (0-5 min); 9-16% B (5-15 min); 16-50% B (15-45 min); 50-90% B (45-48 min); 90-90% B (48-52 min); 90-3% B (52-55 min); 3-3% B (55–60 min). 20 µl of samples were injected. Quantification was achieved by comparaison with standard solutions of known concentrations at 280 nm for (+)-catechin, (-)-epicatechin and (-)-epicatechin benzyl thioether (quantified as (-)-epicatechin); at 320 nm for cafeoylshikimic hexoside-1, cafeoylshikimic hexoside-2, 4-cafeoylshikimic acid, 5-cafeoylshikimic acid, cafeoylsinapoyl hexoside; at 350 nm for flavonols (quercetin quantified as quercetin-3-rutinoside and isorhamnetin quantified as isorhamnetin rutinoside and isorhamnetin hexoside) and for flavones (quantified as chrysoeriol rhamnosyl hexoside and chrysoeriol hexoside sulfate).The average degree of polymerisation was calculated with the molar ratio of all flavan-3-ol units (thioether adducts plus terminal units) to (-)-epicatechin and (+)-catechin corresponding to terminal units. Results were expressed in mg/g of Fresh Weight and total polyphenol content quantified as the sum of the individual compounds.

Statistical analysis

Results are presented as mean values of biological triplicates for each storage temperature and time. Data are reported as pooled standard deviation (Pooled SD). Pooled SDs were calculated for each series of replicates using the sum of individual variances weighted by individual degrees of freedom (Box, Hunter, & Hunter, 1978). Statistical analysis

were established using XLSTAT package of Microsoft Excel. Significant differences ($p<0.05$) between means and interactions between variables were evaluated by two-way ANOVA and Tukey's multiple range test.

3. Results

3.1 Mid-infrared spectroscopy

A Principal Component Analysis (PCA) was carried out using the spectral data in the range between 1500 and 900 cm^{-1} in order to evaluate the possibility of using these data to discriminate date palm samples according to their storage conditions (Fig. 1). The eigenvectors associated with this PCA were represented in Fig. 2. The first two components (PC1 and PC2) explained more than 85% of the total variance with 66.7 % for the PC1 and 18.7% for the PC2 respectively. As regards to the years, the 2017 samples were more gathered than the 2018 ones probably in relation with a highest variability in 2018 than in 2017. The storage conditions did not involve change of date palm characteristics in 2017 whereas in 2018, samples were separated in two clusters; one of which was overlapped with 2017 samples. In 2018, the storage conditions impacted the date palm quality by separating on the left samples stored during 3 and 6 months (T3 and T6) at 2°C and 4°C from the others. This spectral region considered as the fingerprint region (1500 and 900 cm^{-1}) corresponds to the absorption of fruit major components, such as sugars, and bands are assigned to C-O, C-C, O-C-H, C-O-H stretching or bending vibrational modes (Talari, Martinez, Movasaghi, Rehman, & Rehman, 2017). This spectral range contains qualitative and quantitative information about sugars, organic acids, cell walls and phenolic compounds, as demonstrated in Bureau et al. (2012) and Canteri et al., (2019). In our work, the main absorptions were observed at 983 cm^{-1} characterizing the samples localized on the left of the map in opposition with a cluster of peaks around 1028 cm^{-1} characterizing the samples on the right (Fig. 3). This

area incorporates bands typical of soluble sugars (glucose, fructose, sucrose) such as bands assigned to the C-O and C-OH stretch (1025, 1055 cm^{-1}) and of polyphenols (1200 cm^{-1}) which are the abundant chemicals in date palm fruit, bands typical of polysaccharides (cellulose and pectins) assigned to O-C-H stretch (972, 982 cm^{-1}).

3.2 Cell wall yields and compositions

The AIS content of 'Deglet Nour' date palm were 104.4 mg/g and 74.3 mg/g Fresh Weight (FW) for 2017 and 2018 respectively (Table 1). They were in the range of those found by Gribba et al., (2013) and Mrabet et al., (2012) but much lower than those reported by Benchabane et al., (2000) which are 346 mg/g and 310.4 mg/g FW of AIS content respectively in 'Deglet Nour' and 'Ghars' cultivars at *Tamr stage*. The difference could be due to factors affecting fruit quality such as year with specific pedoclimatic conditions or agricultural practices or the used of different analytical methods that introduce some variations in the content of extracted components (Myhara et al., 2000; Gribba et al., 2013; Shafiei et al., 2010; Mustafa et al., 1986) Date palm fruits were richer in AIS content than other fruits like apple, i.e. 17 mg/g to 25 mg/g FW (Le Bourvellec et al., 2011), pear, i.e. 28 mg/g FW (Le Bourvellec et al., 2013) and apricot, i.e. 30.5 mg/g FW (Femenia et al., 1998a), but contained less than fig flesh cell, i.e. 110 to 160 mg/g FW (Trad et al., 2014).

The AIS compositions of whole fruit date palm were characterized by a high amount of lignin (up to 268 mg/g CWM for 2018), cellulosic glucose (up to 137 mg/g CWM for 2018) and galacturonic acid (up to 175 mg/g CWM for 2018) (Table 1). Xylose was the main non-cellulosic neutral sugar in the AIS (between 63 and 101 mg/g CWM in 2017 or 2018), followed by arabinose (22-28 mg/g CWM in 2017 and 2018) and galactose (17-22 mg/g CWM for 2017 and 2018). Non-cellulosic glucose, mannose, rhamnose and fucose were only minor components (< 10 mg /g CWM). Mrabet et al., (2012) reported also that in some date

281 palm fruit cultivars such as the 'Deglet Nour' cultivar, lignin was the major component
282 followed by cellulose and uronic acid which is in agreement with our observations. Gribaa et
283 al., (2013) have shown that in date palm cell walls the major non-cellulosic polymers are
284 pectins and not hemicelluloses. Mrabet et al., (2012) found that xylose, arabinose and
285 galactose were the major neutral sugars present in date palm fruit. The composition of date
286 palm cell walls indicated a prevalence of lignin, cellulose, pectins and associated material, the
287 degree of methylation of pectins was >50%, reaching 86% in 2017. Xylose might originates
288 from xylogalacturonans as the other diagnostic sugars for hemicelluloses i.e. non-cellulosic
289 glucose, fucose, and mannose were present in low amounts. These sugar patterns are
290 comparable to those reported by Mrabet et al., (2015) and Elleuch et al., (2008). In our
291 experiment, AIS contents varied with the year and were statistically lower in 2018 than in
292 2017 (Table 1). However, storage time had no effect on AIS yield content meaning that cell
293 wall contents were stable over time whatever the temperature (Table 1), in contrast to other
294 fruits where cell walls contents change considerably during storage (Chen et al., 2015;
295 Femenia, Sánchez, Simal, & Rosselló, 1998b; Murayama, Katsumata, Horiuchi, &
296 Fukushima, 2002; Kim et al., 1999).

297 The year effect was significant for all components, except methanol contents, this
298 could be due to the pedoclimatic conditions. As function of storage time, a significant
299 increase was observed in lignin, cellulosic glucose, fucose, rhamnose, whereas a decrease in
300 galactose content was observed. This tendency may be related to galactose degradation by
301 galactosidase as this enzyme was identified as active enzyme during ripening (Serrano et al.,
302 2001), which resulted to an apparent increase on lignin and other neutral sugars. Gribaa et al.,
303 (2013) also observed a loss of galactose during ripening. In the same way, in our experiments
304 no change was observed for galacturonic acid, xylose and non-cellulosic glucose. A

significant slightly increase in mannose and arabinose contents was also observed. This trend in increasing arabinose levels is contrary to other studies showing its decrease (Ahmed & Labavitch, 1980 ; Brahem et al., 2017) or its stability (Gribaa et al., (2013) in different fruit species during ripening. This difference could be due to lower arabinose contents in other date palm fruits (Elleuch et al., 2008), and to specific enzymatic activities of date palm fruit as function of time, like galactosidase which increased with ripening (Serrano et al., 2001) and low degrading arabinofuranosidase and/or arabinanase during the fruit maturation in specific conditions (Gribaa et al., (2013).

The storage temperatures also impact the cell wall composition (Table 1) especially pectic polysaccharides. With the temperature increase, galacturonic acid, galactose and arabinose contents decreased whereas an increase in cellulosic glucose content was observed. The other neutral sugar contents were not affected by storage temperatures. Galacturonic acid and neutral sugars changes with increasing temperature could be explained by the pectin depolymerisation and hydrolysis of neutral sugars from pectin side chains (Brummell, 2004; Zhang et al., 2010) due to an increase in both polygalacturonase and β-galactosidase activities during storage (Serrano et al., 2001).

3.3 Sugars and organic acids

Sucrose was the main sugar in 'Deglet Nour' date palm fruit, followed by both, glucose and fructose, almost in the same concentration. Sucrose contents were 268 mg/g in 2017 and 353 mg/g FW in 2018) (Table 2) followed by glucose up to 161 mg/g FW in 2017 and fructose up to 137 mg/g FW in 2017. Sucrose concentrations were in accordance with other results such as 238 mg/g FW in 'Deglet Nour' date palm (Al-Farsi & Lee, 2008) and 239.8 to 350.9 mg/g FW (Ben-Amor et al., 2016). According to Jemni et al., (2019), glucose

328 and fructose concentrations range from 142.8 to 235.8 mg/g FW and from 96.3 to 130.5 mg/g
329 FW respectively, in agreement with the present data.

330 Malic acid was the main organic acid in 'Deglet Nour' date palm fruit, followed by
331 citric acid. Their concentrations were 4.40 mg/g FW in 2017, 2.39 mg/g FW in 2018 for malic
332 acid whereas for citric acid its content did not exceed 1.57 mg/g FW in 2018. This was in
333 agreement with Ghnimi et al., (2018), who found that malic acid is predominant in some
334 Emirati dates ranging from 0.86 to 3.43 mg/g FW, and citric acid ranging from 0.11 to 1 mg/g
335 FW.

336 Characterizing date palm fruit using infrared spectral data showed that the most
337 discriminating region was between 1500 and 900 cm^{-1}. This region is well described to
338 contain the bans of absorption of sugars, the main components of date palm fruits (Bureau et
339 al., 2019). The observed data obtained with MIRS (Figure 1) were in accordance with the
340 PCA performed on the sugar and organic acid contents (results not shown), which clearly
341 separated samples according to the year but not to the storage temperature. The sugar and
342 organic acid contents of date palm fruits varied depending on the considered year. Le
343 Bourvellec et al., (2015) also found that year significantly affects primary metabolite contents
344 in tree apple cultivars. This was mainly due to different pedoclimatic conditions as function of
345 year.

346 Sucrose contents were significantly affected by storage time and temperature.
347 Generally, sucrose contents decreased with time for the different temperatures from 268 to
348 134 mg/g FW in 2017 and from 354 to 211 mg/g FW in 2018, except a slight increase or no
349 changes at -18 °C in the two years. These results are in agreement with the study of Jemni et
350 al., (2019) who found the same sucrose decrease in freezing 'Deglet Nour' date palm (0 °C, -
351 40 °C and -80 °C) stored during 10 months. Alhamdan, A. M., & Al-Helal, I. M. (2008)

352 showed also a significant decrease in sucrose content in 'Barhi' freezing date palm for 3, 6
353 and 9 months independently to the storing method. Glucose contents were significantly
354 affected by temperature but not by storage time (Table2). Glucose contents increased
355 generally, with increasing temperature (Table 2). On the contrary, fructose contents were
356 significantly affected by storage time but not by temperature (Table 2). Fructose contents
357 increased with time for the different freezing temperatures and whatever the year. According
358 to Ismail et al., (2008) and Jemni et al., (2019) respiration which could occur during storage,
359 combined with a slowly hydrolysis of sucrose could explain the changes and variation
360 between different sugars (glucose and fructose). An increase of total soluble sugars occurs
361 also in strawberry fruits stored at 6 °C indicating that a new biosynthesis had taken place
362 during storage (Cordenunsi et al., 2005).

363 Citric acid contents presented an opposite trend according to the year. In 2017, citric
364 acid contents increased with storage time whereas in 2018 they decreased. Moreover, this
365 effect was also function of the temperature, especially in 2017. While citric acid contents
366 increased with the storage time at -18 °C, 0 °C and 2 °C, its contents were quite stable at 4 °C.
367 These results are in agreement with those of Jemni et al., (2019) who found that the titratable
368 acidity of 'Deglet Nour' date palm increases after storage at 0 °C from 0.18 to 2.02 g/100 g
369 FW. Malic acid contents were highly affected by storage time. In 2017, they decreased
370 significantly with storage time at the lowest temperatures (-18 °C and 0 °C), and were quite
371 stable at 2 °C and 4 °C. However, in 2018 no change was observed in malic acid contents
372 except a slight decrease at 2 °C and 4 °C after only 6 and 9 months. Other authors also shown
373 opposite trend according to storage as function of fruit botanical origin: Remberg et al.,
374 (2010) found that titratable acidity in 'Summered' apple fruit increases after four months at
375 low temperature (1 °C) while Dziedzic & Blaszczyk, (2019) reported that organic acids in

sweet cherry cultivar 'Regina' decrease after a storage at 2°C for two weeks. The results observed could be due to difference in metabolic pathway.

So, according to malic and citric acid behaviour, we could estimate that 2 °C and 4 °C were the best temperatures for storing date palm fruits.

3.4 Polyphenols

Four major polyphenol groups were identified in 'Deglet Nour' date palm fruit including flavan-3-ols, flavonols, flavones and hydroxycinnamic acids (Table 3). A total of 11 individual compounds were identified and quantified (Table 3). These groups coincide with those found previously in Deglet Nour date palm cultivar (Hammouda, Chérif, Trabelsi-Ayadi, Baron, & Guyot, (2013)). The content of polyphenols ranged between 13.9 (2017) and 12.1 (2018) mg/g of FW, in accordance with Hammouda, Chérif, Trabelsi-Ayadi, Baron, & Guyot, (2013). Among the four major groups, procyanidins were the predominant class accounting for 98% of total polyphenols, i.e. 13.5 (2017) and 11.9 (2018) mg/g of FW, close to the 12.44 mg/g FW found by Hammouda, Chérif, Trabelsi-Ayadi, Baron, & Guyot, (2013). (−)-Epicatechin was always the predominant constitutive unit, accounting between 97% and 98% of total constitutive units in 'Deglet Nour fruit whereas (+)-catechin was only present as terminal unit and accounted from 0.1% to 0.5% of the total constitutive units. The average degree of polymerization (DPn) of procyanidins ranged between 32 (2017) and 38 (2018). This DPn varies depending on the fruit type, variety, maturation stage and fruit tissue (Hammouda, Chérif, Trabelsi-Ayadi, Baron, & Guyot, 2013) and is highly linked to astringency perception (Lea & Arnold, 1978). However date palm fruit at *Tamr stage* (full ripe) and especially 'Deglet Nour' are not perceived as astringent (Myhara et al., 2000) even if their DPn is high (Haslam and Lilley, 1988).

399 This discrepancy between analytical characterization and perception can be explained
400 by the complexity of the date palm fruit matrix, its high sugar contents, and interactions
401 occurring between procyanidins and cell wall polysaccharides after cellular rupture during
402 mastication (Renard, Baron, Guyot, & Drilleau, 2001) which compete with formation of
403 adducts with proteins and so with sensory perception. Concerning flavan-3-ols, any
404 monomers were detected, specifically in the Deglet Nour fruit.

405 In our study, the DPn of procyanidins were affected by year, storage time and
406 temperature. A significant increase was found after 6 and 9 months of storage at 0, 2 and 4 °C
407 (From 32 in fresh date palm before storage to 45 after 9 months at 0 °C) (Table 3). This could
408 be due to a preferential degradation of low molecular weight procyanidins. Compared to
409 procyanidins, the other polyphenol classes (i.e., hydroxycinnamic acids, flavonols and
410 flavones) were present in very low concentrations (Table 3). Hydroxycinnamic acids
411 accounted for less than 2% of total polyphenols in the fruits. Hammouda, Chérif, Trabelsi-
412 Ayadi, Baron, & Guyot, (2013) have shown that hydroxycinnamic acids account for 0.7 % of
413 total polyphenols in date palm fruit ('Deglet Nour' and 'Ftimi' cultivar). The main component
414 of this class was 5-cafeoylshikimic acid followed by 4-cafeoylshikimic acid as previously
415 reported in 'Deglet Nour' date palm (Hammouda, Chérif, Trabelsi-Ayadi, Baron, & Guyot,
416 2013). The other hydroxycinnamic acid compounds, i.e. the two cafeoylshikimic hexoside
417 and cafeoylsinapoyl hexoside were present in lower amount.
418 Flavonols in Deglet Nour date palm fruit were mainly quercetin and isorhamnetin
419 glycosides. Only one quercetin glycoside and two isorhamnetin glycosides were found, i.e.
420 isorhamnetin hexoside which was in higher concentration than isorhamnetin rutinoside.

421 Flavones were mainly chrysoeriol (luteolin 3′-methylether) glycosides. Two
422 chrysoeriol glycosides were found, i.e. chrysoeriol rhamnosyl hexoside and chrysoeriol
423 hexoside sulfate present in the same contents.
424 All these concentrations and relative composition of each class are consistent with
425 previous works (Hammouda, Chérif, Trabelsi-Ayadi, Baron, & Guyot, 2013; Mansouri et al.
426 2005 and Hong et al., 2006).
427 Polyphenol contents were significantly affected by year but not by storage time and
428 temperature. The storage did not provide a significant loss of total polyphenol compounds.
429 This was mainly due to the fact that procyanidins were stable during storage (Table 3).
430 However, the other minor phenolic compounds tended to decrease with storage time and
431 temperature probably because of their susceptibility to browning or due to their low content,
432 their slightest variation may induce an effect. Le Bourvellec et al., (2018) also found that
433 apricot phenolic contents were not affected by storage. Total phenolics and flavonols were
434 also stable at low temperature (6 °C) in strawberry fruits (Cordenunsi et al., 2005).
435 Storing date palm at low temperatures did not affect polyphenol amounts. In contrast
436 to many fruits that tend to lose stability over storage (Kevers et al., 2007), dates are relatively
437 stable. Thus, based on this experiment, date palm fruits could be stored at the highest
438 temperatures (2 or 4°C) in the aim to guarantee the maximal shelf life with minimal costs.

439 **4. Conclusion**

440 The use of a non-destructive and non-targeted method as infrared spectroscopy and
441 specific chemical characterizations such as sugars, organic acids, polyphenols and cell walls
442 allowed to evaluate the behavior of ‘Deglet Nour’ date palm fruits during storage at different
443 temperatures during two years. The principal results concerned a good stability of the date
444 palm fruits during storage. However, significant differences were highlighted between the

two-harvest years for all studied parameters and spectra, which can be attributed to the effect of agronomic and climatic conditions. The main polyphenols, i.e. procyanidins, were stable with time and temperature, some losses were observed only for minor compounds. The changes of cell wall during storage were linked to the depolymerisation of pectins and the loss of their side chains, whereas the total content of cell wall was stable.

Then, in order to prolong the shelf-life of dates for a long-term period and minimize global costs, 2 °C must be considered as the optimal temperature.

Table 1. AIS yields (mg/g fresh weight), neutral sugars and lignin content (mg/g AIS) of 'Deglet Nour' date fruit during storage at different temperatures in the two harvest seasons (2017 and 2018).

433

	Yields	Rha	Fuc	Ara	Xyl	Man	Gal	NC Glc	C Glc	MeOH	AUA	DM (%)	Lig
Year: 2017													
Before storage	104.4	4	3	22	63	9	19	9	115	16	102	86%	118
After 3 months													
-18°C	91.2	4	2	23	81	9	17	8	117	15	101	85%	126
0°C	90.2	4	2	22	63	10	18	7	131	16	116	74%	179
2°C	86.5	4	2	22	68	9	17	9	111	16	107	83%	99
4°C	91.2	4	2	22	75	8	16	7	104	17	99	94%	134
After 6 months													
-18°C	89.3	5	3	24	74	9	17	11	110	14	92	85%	177
0°C	91.2	4	3	24	72	9	18	4	112	14	74	103%	110
2°C	94.9	5	3	23	67	8	18	7	112	14	81	97%	113
4°C	91.5	4	3	23	67	8	17	8	108	15	87	95%	199
After 9 months													
-18°C	83.6	6	3	23	67	9	18	7	118	14	92	83%	135
0°C	84.8	5	5	25	77	10	19	7	119	15	114	71%	131
2°C	91.3	6	5	26	68	9	22	6	126	15	124	68%	99
4°C	92.4	6	5	23	69	9	19	7	114	15	108	78%	138
Year: 2018													
Before storage	74.3	6	8	25	74	10	21	7	134	17	175	53%	170
After 3 months													
-18°C	72.7	6	6	24	74	10	21	6	135	18	160	62%	204
0°C	80.3	6	5	24	87	9	20	6	125	17	158	60%	172

	2°C	83.6	5	5	23	67	9	20	6	127	16	137	64%	137
	4°C	81.8	5	6	23	71	9	19	6	124	16	125	88%	148
After 6 months														
	-18°C	78.3	5	3	25	101	9	19	5	127	17	171	53%	154
	0°C	83.6	5	3	23	76	9	19	6	116	14	153	51%	132
	2°C	79.5	6	3	22	84	8	17	5	117	13	147	47%	186
	4°C	83.9	5	3	23	91	8	17	7	116	13	162	44%	122
After 9 months														
	-18°C	76.7	6	4	28	89	10	22	6	137	14	161	48%	262
	0°C	87.2	7	4	24	81	9	19	10	121	13	156	45%	175
	2°C	90.8	7	5	25	86	10	20	8	135	12	131	50%	151
	4°C	88.8	7	3	23	76	9	18	7	119	13	141	50%	257
SD Pooled		3.4	0.4	0.4	0.9	5.3	0.5	0.6	0.9	5.4	0.6	6.6	0.1	13.4
Year F-value		64.6**	33.4**	97.6**	4.2*	24.5**	5.5*	21.4**	6.1*	24.7**	0.8	381.8**	199.2**	52.3**
S.Time F-value		1.0	24.5**	22.5**	8.6*	2.5	7.5*	20.8**	1.5	5.9*	42.1**	2.6	18.2**	5.5*
S.Temperature *F*-value		4.2*	1.0	0.3	3.8*	2.4	2.3	5.8*	0.3	3.7*	2.6	3.3*	2.8	13.2**
Year*S.Time *F*-value		3.7*	1.8	42.5**	2.1	4.3*	0.6	12.4**	5.9*	0.3	10.4*	20.2**	18.8**	21.7**
Year*S.Temperature *F*-value		1.2	0.3	2.1	1.7	0.2	2.7	6.7*	5.0*	2,7	12.5**	7,6*	0,0	4.1*
S.Time*S.Temperature *F*-value		0.7	0.9	1.8	0.8	1.1	0.4	2.2	3.9*	1.3	0.6	3.4*	3.8*	6.5**
Year*S.Time*S.Temperature *F*-value		0.9	0.5	2.0	1.7	3.2*	0.9	1.7	1.9	0.6	0.5	1.6	1.9	8.1**

Rha: rhamnose, Fuc: fucose, Ara: arabinose, Xyl: xylose, Man: mannose, Gal: galactose, NC Glc: Non-Cellulosic glucose determinated without Seaman hydrolysis, C Glc: Cellulosic glucose deteriminated with Saeman hydrolysis AUA: anhydrous uronic acids, MeOH: methanol, DM: degree of methylation, Lig: lignin, S.Time: Storage time, S.Temperature: Storage temperature.

Pooled SD: pooled standard deviation, F-value: Fisher's value

* Significant at p <0.0001; ** Significant at p <0.05

Table 2. Sugars and organic acids (mg/g FW) variation of 'Deglet Nour' date fruit during storage at different temperatures in the two harvest seasons (2017 and 2018). Statistical results (Pooled SD, two-way ANOVA) and interaction effects between variables.

		Sugars			Organic acids	
		Glucose	**Fructose**	**Sucrose**	**Citric acid**	**Malic acid**
Year: 2017						
Before storage		169	137	268	0.9	4.4
After 3 months						
	-18 °C	126	139	311	0.8	4.4
	0 °C	172	170	208	0.3	3.5
	2 °C	168	153	207	1.0	4.6
	4 °C	167	176	231	1.3	4.1
After 6 months						
	-18 °C	137	154	192	1.2	3.4
	0 °C	194	130	134	0.6	3.6
	2 °C	142	147	171	1.3	4.2
	4 °C	147	149	355	1.0	4.3
After 9 months						
	-18 °C	103	195	384	1.5	3.5
	0 °C	209	150	223	1.8	3.5
	2 °C	163	137	202	0.2	4.3
	4 °C	154	141	324	1.2	4.1
Year: 2018						
Before storage		134	87	354	1.6	2.4
After 3 months						
	-18 °C	138	95	333	1.7	2.5
	0 °C	124	110	350	0.9	2.3
	2 °C	135	132	326	0.3	2.4
	4 °C	151	136	253	0.1	2.0
After 6 months						
	-18 °C	100	107	373	0.0	2.2
	0 °C	148	14	236	0.0	2.1
	2 °C	135	118	252	0.0	1.7
	4 °C	156	78	211	0.0	1.9
After 9 months						
	-18 °C	107	115	340	0.0	2.1
	0 °C	130	128	290	0.0	2.2
	2 °C	142	178	272	0.0	2.1
	4 °C	137	166	256	0.0	1.8
SD Pooled		7.8	7.0	12.7	0.05	0.1
Year F-value		59.0**	114.1**	98.5**	436.1**	1834.4**
S.Time F-value		0.6	21.6**	29.5**	56.3**	45.1**
STemperature *F*-value		35.7**	2.1	57.4**	48.7**	17.0**
Year*S.Time *F*-value		0.6	11.4**	16.1**	192.1**	7.3*
Year*S.Temperature *F*-value		14.0**	14.9**	53.8**	36.6**	54.3**
S.Time*S.Temperature *F*-value		4.8*	7.6**	12.6**	44.0**	5.6*
Year*S.Time*S.Temperature *F*-value		3.8*	14.7**	17.8**	115.1**	5.3*

S.Time: Storage time, S.Temperature: Storage temperature
Pooled SD: pooled standard deviation, F-value: Fisher's value
* Significant at $p < 0.0001$; ** Significant at $p < 0.05$

Table 3. Total polyphenols, procyanidins (mg/g of FW) and minor phenolic compounds (µg/g of FW) variation of 'Deglet Nour' date fruit during storage at different temperatures in two harvest seasons (2017 and 2018). Statistical results (Pooled SD, two-way ANOVA) and interaction effects between variables.

	Procyanidins					Hydroxycinnamates					Flavonols			Flavones		Total PP
	PCA	**DP**	**CAT %**	**EC %**	**EC_{ext} %**	**CSH1**	**CSH2**	**CSA4**	**CSA5**	**CSpH**	**QR**	**IhR**	**IhH**	**ChRh**	**ChhS**	
Year: 2017																
Before storage	13.5	32	0.4	2.7	96.9	13	18	98	116	30	9	12	24	5	5	13.9
After 3 months																
-18 °C	12.6	34	0.4	2.6	97.0	13	16	94	108	29	9	15	27	6	6	13.0
0 °C	11.9	33	0.4	2.7	96.9	12	15	87	108	28	8	12	23	7	5	12.2
2 °C	12.4	30	0.4	2.9	96.7	12	14	97	109	27	10	14	26	7	5	12.7
4 °C	13.2	29	0.4	3.1	96.5	14	17	110	129	31	10	15	29	6	5	13.5
After 6 months																
-18 °C	14.9	38	0.1	2.5	97.4	12	14	81	104	30	6	9	20	5	4	15.1
0 °C	14.7	40	0.1	2.4	97.5	9	9	57	72	17	9	10	21	4	3	15.0
2 °C	14.2	38	0.2	2.5	97.4	11	12	73	93	19	11	10	22	5	3	14.5
4 °C	14.4	37	0.2	2.5	97.3	12	15	82	103	28	11	10	22	5	3	14.7
After 9 months																
-18 °C	13.0	39	0.2	2.4	97.5	12	14	81	104	30	6	9	20	5	4	13.3
0 °C	13.6	45	0.1	2.1	97.8	9	8	43	59	13	6	9	20	4	3	13.8
2 °C	14.4	41	0.1	2.3	97.5	11	12	70	87	21	11	10	25	6	4	14.6
4 °C	14.6	39	0.2	2.4	97.5	13	15	74	93	28	6	10	20	5	3	14.9
Year: 2018																
Before storage	11.9	38	0.4	2.2	97.3	8	9	53	0.082	21	5	12	17	2	4	12.1
After 3 months																
-18 °C	13.8	35	0.5	2.3	97.2	8	12	68	0.110	26	6	12	21	3	5	14.1

0 °C	12.3	45	0.4	1.8	97.8	7	6	30	57	11	6	12	18	3	4	12.4
2 °C	12.4	40	0.4	2.1	97.5	6	6	41	64	14	6	12	20	3	4	12.5
4 °C	13.4	40	0.4	2.1	97.5	8	6	31	57	12	6	12	17	2	4	13.5
After 6 months																
-18 °C	12.6	37	0.5	2.2	97.3	7	8	51	95	18	5	12	20	1	4	12.8
0 °C	11.7	46	0.5	1.7	97.8	10	7	28	49	14	3	13	15	2	3	11.8
2 °C	11.9	47	0.5	1.6	97.9	10	7	24	41	14	4	13	15	3	3	12.0
4 °C	11.0	46	0.5	1.6	97.8	10	7	26	46	14	5	12	16	3	3	11.1
After 9 months																
-18 °C	12.7	37	0.5	2.2	97.3	7	9	58	102	19	10	12	20	2	5	12.9
0 °C	11.9	47	0.5	1.6	97.9	10	7	26	48	15	6	13	16	3	3	12.0
2 °C	12.0	48	0.5	1.6	97.9	10	8	29	46	14	5	13	15	3	3	12.1
4 °C	11.6	48	0.5	1.6	97.9	10	7	23	39	14	4	11	14	2	3	11.7
SD Pooled	0.5	1.3	0.02	0.08	0.08	0.5	0.5	2.2	3.0	1.2	0.7	0.6	1.3	0.4	0.3	0.5
Year *F*-value	56.3**	136.4	1125.8**	391.5**	153.7**	296.6**	798.6**	2098.3**	744.5**	343.2**	150.2**	10.7*	112.6**	314.6**	4.6*	64.7*
S.Time *F*-value	1.7	70.7*	86.9**	67.1**	91.6**	0.8	19.5**	176.5**	109.1**	15.0**	5.4*	29.5**	23.5**	17.4**	54.6**	1.4
S.Temperature *F*-value	1.7	22.9*	5.6*	17.5**	19.1**	11.4**	42.4**	147.2**	183.2**	61.9**	4.3*	0.5	3.9*	4.3*	9.3**	2.1
Year*S.Time *F*-value	25.8**	7.0*	259.4**	3.3*	19.7**	34.5**	26.7**	48.5**	12.0**	11.0*	18.1**	37.1**	2.2	9.1*	2.6	25.0*
Year*S.Temperature *F*-value	3.2*	22.8*	6.2	21.8**	23.8**	20.1**	23.2**	73.3**	103.5**	17.7**	22.9**	3.4*	7.3*	1.7	1.6	3.6*
S.Time*S.Temperature *F*-valu	1.8	2.9*	1.5	4.0*	3.4*	3.6*	4.6	4.4*	6.4**	1.8	7.2**	1.3	1.0	0.5	0.9	1.8
Year*S.Time*S.Temperature	0.7	1.0	1.7	0.3	0.6	3.9*	8.7**	8.3**	6.3**	12.6**	4.6*	0.6	2.0	2.2	1.5	0.7

PCA: procyanidins, , DP: average degree of polymerization of procyanidins, %CAT:percentage of (+)-catechin as terminal unit, % EC: percentage of (-)-epicatechin as terminal unit, $\%EC_{ext}$: percentage of (-)-epicatechin as extension unit, , CSH1: Cafeoylshikimic hexoside_1, CSH2: Cafeoylshikimic hexoside_2, CSA4: 4-cafeoylshikimic acid, CSA5: 5-cafeoylshikimic acid, CSpH: cafeoylsinapoyl hexoside, QR: Quercetin-3-rutinoside, IhR: isorhamnetin rutinoside, IhH: isorhamnetin hexoside ChRh: chrysoeriol rhamnosyl hexoside, , ChhS: chrysoeriol hexoside sulfate, Total PP: total: total polyphenols, S.Time: Storage time, S.Temperature: Storage temperature, F-value: Fisher's value, * Significant at p <0.0001; ** Significant at p <0.05

Fig 1. PCA results on mid-infrared spectral data between 1500 and 900 cm^{-1} based on storage conditions of Deglet Nour'. The code corresponds to the year (17 : 2017 ; 18 : 2018), to storage time (T0 : initial time ; T3 : 3 months storage ; T6 : 6 months storage and T9 : 9 months storage) and to the temperature (18 : -18 °C ; 0 : 0 °C ; 2 : 2 °C ; 4 : 4 °C and te : control). A) as function of the year B) as function of the storage time C) as function of the storage temperature

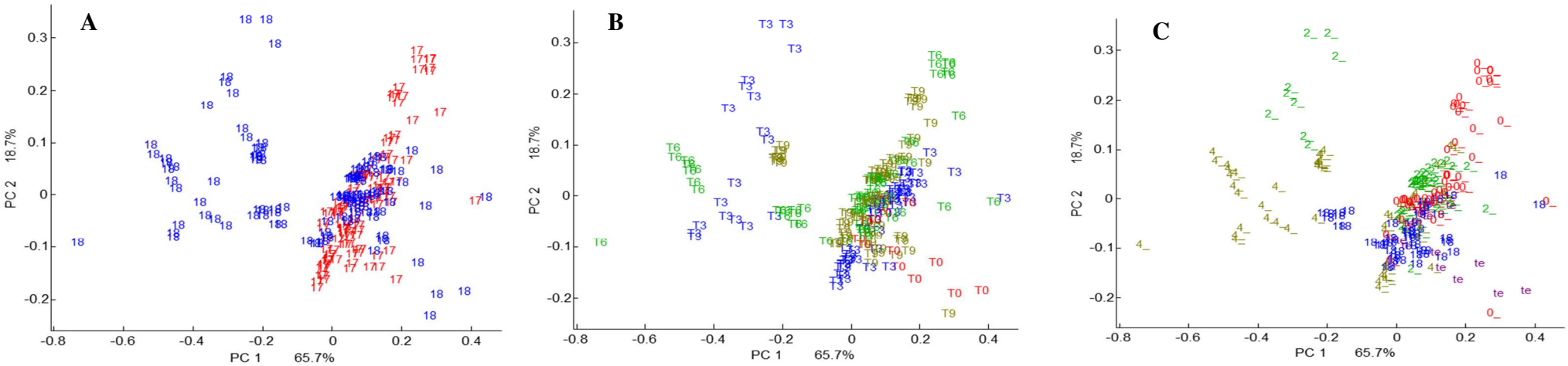
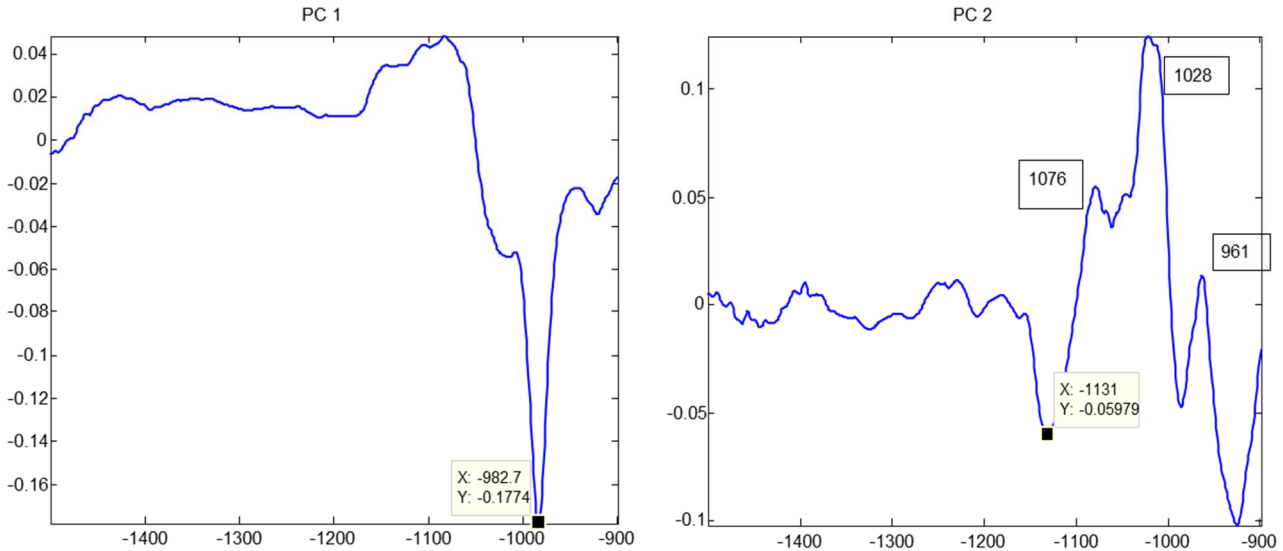


Fig. 2: Eigenvectors associated to PCA results (A), (B) and (C) on FT-IR spectra (1500-900 cm^{1})



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