Assessment of Antioxidant Ability of Potato (*Solanum tuberosum*) Peel Extracts to Inhibit Soybean Oil Oxidation at Low Levels with a Minimum Dose

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ABSTRACT

Potato peels are an agro industrial waste of one of the major crops worldwide. However, the potential of potato peels as source of antioxidants in the food industry is not yet sufficiently known. In this work, the antioxidant effect of potato peel extract (PPE) on oxidative stability of soybean oil was evaluated. We found that the addition of low PPE concentrations to soybean oil at four different levels, expressed as chlorogenic acid concentrations (15, 20, 27 and 33 ppm), affected lipid oxidation indices (peroxide, anisidine and conjugated dienes values), fatty acid composition and volatile compounds. Antioxidant effect increased with increasing dose extract. Inhibition percentages of hexanal production increased with the PPE concentration. In addition, low concentrations of PPE showed higher oxidation stability than control untreated samples. Overall, our study shows that low concentrations of PPE exhibited promising antioxidant activity to be applied over a wider range of products in the food industry.

Keywords: *Solanum tuberosum*, potato peel extract, chlorogenic acid, antioxidant activity, dose extract, fatty acid, volatile compounds

1. INTRODUCTION

Oxidation is one of the most important processes occurring in food systems (Wąsowicz et al., 2004). Lipids are very susceptible to oxidation processes and consequently oxidation reactions are one of the major sources of quality deterioration (Shahidi & Zhong, 2005; Suja, Abraham, Thamizh, Jayalekshmy, & Arumughan, 2004). The changes occurring in foods as a result of these oxidation processes include the generation of off-flavors, loss of nutrient value, and the accumulation of toxic compounds, which may be detrimental to the health of consumers (Arabshahi-D, Devi, & Urooj, 2007; Grün, Ahn, Clarke, & Lorenzen, 2006).

The addition of antioxidants is used to delay lipid oxidation. Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tert-butylhydroquinone (THBQ) are the most commonly used synthetic antioxidants to control this process. However, the use of these synthetic compounds has been linked to health risks (carcinogenic potential) and current research is focused in their replacement by natural antioxidants (Prior, 2004). The use of compounds with antioxidant activity has increased dramatically (Moure et al., 2001) due to an emerging methodology for controlling and limiting degradation consequences (Frankel, 1998).

Potatoes (*Solanum tuberosum*) are one of the most commonly consumed vegetables throughout the world, ranking fifth in global agricultural production behind crops such as wheat and maize (FAOSTAT, 2012). This information highlights the economic relevance of this crop and gives an idea of the high quantities of by-products and wastes generated; being potato starch and potato peel wastes the most abundant of the potato industry. Although there are many alternatives for the revalorisation of these by-products, the use of potato peels

extract (PPE) as a source of “natural” antioxidants could be one of the most efficient uses. PPE contains phenolic acids, being chlorogenic acid the largest main component (Habeebullah, Nielsen, & Jacobsen, 2010). Other phenolics such as ferulic, gallic, caffeic and protocatechuic acid, are present in low amounts in potato peel (Ramamurthy, Maiti, Thomas, & Nair, 1992). The PEE could be used as a substitute for synthetic antioxidants due to its high content of phenolic acids strong antioxidant capacity close to that of BHT and BHA (Mohdaly, Sarhan, Mahmoud, Ramadan, & Smetanska, 2010; Rehman, Habib, & Shah, 2004).

Natural antioxidants are readily accepted by the consumer (Nassu, Gonçalves, da Silva, & Beserra, 2003) but they are normally more expensive to extract (Pokorny, 1991). This has led to the search for antioxidant compounds with high activity at low concentrations. In addition, the use of higher concentrations does not ensure an increased activity since pro-oxidant effects can appear (Przybylsky, Lee, & Eskin, 1998).

Several methods are used to measure the oxidative stability such as peroxide and ρ-anisidine value, conjugated dienes or fatty acid composition, but volatile profile analysis is one of the most important techniques (Gordon, 1991; Issaoui et al., 2009). To our knowledge, not many studies regarding the effect of PPE on the oxidation stability can be found in the related literature (Kanatt, Chander, Radhakrishna, & Sharma, 2005; Mohdaly, Sarhan, Mahmoud, Ramadan, & Smetanska, 2010; Rehman, Habib, & Shah, 2004; Samarin, Poorazarang, Hematyar, & Elhamirad, 2012) and even less if we focus on volatile compounds determination (Farvin, Grejsen, & Jacobsen, 2012). The aim of this study was to evaluate the effect of the addition of PPE on oxidative stability of soybean oil in comparison with a synthetic antioxidant (BHT). Peroxide, p-anisidine, totox and

conjugated dienes values, fatty acid composition and volatile compounds were used to assess antioxidant effectiveness.

2. MATHERIALS AND METHODS

2.1. Plant material and substrate preparation

Agria variety potatoes, commonly used for crisp production, were utilized in the present work. Potato peels were obtained by abrasion in a mechanical peeler to obtain uniform peel thickness. Waste materials were then lyophilised and milled to obtain powder peels (PP). The PPE were obtained using different ethanol concentrations, temperatures and extraction times, as previously reported (Rodríguez-Amado, Franco, Sanchez, Zapata, & Vázquez, 2014). PPE hydroalcoholic solutions were then freeze-dried and each PPE powder redisolved in 4 mL of ethanol and further analysed by HPLC and applied to soybean oil samples to determine their oxidation stability, as described below.

2.2. Chlorogenic and ferulic quantification by HPLC

Cinnamic and benzoic acids were determined by reversed phase HPLC using an equipment composed of a Jasco LG-1580-04 gradient mixer, a PU-980 main pump and a UV variable wavelength detector UV-1575. The chromatography column was a 2.4x10 mm Kinetex 2.6 μm particle size C18 (Phenomenex, Torrance (CA), USA). Gradient elution was performed mixing water acidified with 0.5% acetic acid (solvent A) and methanol (solvent B) as follows: 0-3 min, 95%A; 3-18.3 min up to 50%B; 18.3-24.4 min, up to 70% B; 24.4-27.4 95%A and 27.4-35 min, 95% A. Flow rate was 0.4 mL/min. The UV detection profile was performed at 280 nm to detect gallic acid until minute 7 and then 324 nm to detect the other phenolic acids. Limit of quantification was 0.7 mg/L. Calibration

curves were performed for gallic, chlorogenic, ferulic, caffeic and p-coumaric acids ranging from 0.7 to 40 mg/L.

2.3. Oxidation stability of soybean oil under accelerated conditions

This test was conducted to evaluate the effectiveness of PP ethanolic extracts against lipid oxidation. The PPE was used at chlorogenic acid levels of 15, 20, 27.5 and 33 ppm. Also a synthetic antioxidant (BHT) at 200 ppm and a control without PPE were assayed. PPE and BHT samples were added to refined soybean oil (SO) provided by Aceites Abril (San Cibrao das Viñas, Ourense, Spain). Composition of oil according to CODEX Stan 210 normative was: acidity (0.04%), peroxide index (<1.2 meq O_2/kg), moisture (<0.01%) and impurities (<0.01%). The fatty acid profile in percentage was myristic (0.09), palmitic (10.8), palmitoleic (0.1), stearic (5.1), oleic (19.5), linoleic (48.2), linolenic (4.6), arachidic (0.4), eicosenoic (0.2) behenic (0.6) and lignoceric (0.3). Samples of 20 mL soybean oil ($\approx$ 16 g; ρ=0.8 g/L) were mixed with 250 μL of PP ethanolic extracts. Oil samples were stored in glass containers at 60ºC during 14 days followed by determination of peroxide value, p-anisidine value, conjugated dienes, Totox index, fatty acid and volatile compounds.

2.4. Determination of peroxide value (PV)

The *PV* was determined following the AOAC procedure 965.33 (AOAC, 2007). Oil samples (0.5 g) were dissolved with 10 mL of trichloromethane. Then, 15 mL of acetic acid and 1 mL of saturated aqueous solution of potassium iodide were added. The sample was slightly agitated 1 min and kept 5 min in the dark. Once incubation was finished, 75 mL of distilled water was added and the sample was vigorously shaken. Finally, liberated iodine was titrated with sodium thiosulfate

147 0.01 N in an automatic titrator. The *PV*, expressed as milliequivalents O_2 kg^{-1},
148 was calculated according to the formula:

149 $$PV = \frac{V \times N \times 1000}{W} \quad (1)$$

150 where, *V* is the volume (mL) of sodium thiosulfate consumed in the titration, *N* is
151 the normality of the sodium thiosulfate solution and *W* is the sample weight of
152 the sample (g).

153

154 *2.5. Determination of p-anisidine value (AV)*

155 Determination of *AV* of the oil samples was determined following an IUPAC
156 method (IUPAC. 1987). Oil samples (0.5-2 g) were dissolved in isooctane in a
157 25 mL volumetric flask. The sample was then reacted with p-anisidine solution
158 in acetic acid (0.25% w/v) for 10 minutes to produce a coloured complex.
159 Absorbances of the samples with and without p-anisidine solution were
160 measured at 350 nm and the parameter *AV* was calculated as:

161 $$AV = \frac{25 \times \left[1.2 \times \left(E_b - E_a\right)\right]}{W} \quad (2)$$

162 where, E_b is the net absorbance of the oil-solution, E_a is the net absorbance of
163 the oil-anisidine-solution and *W* is the weight of the sample (g).

164 *Determination of Totox value (TV)*

165 The overall oxidation state of oil given by the *TV* was calculated according to
166 the formula:

167 $$TV = AV + 2PV \quad (3)$$

168

169 *2.6.Determination of conjugated dienes values (CDV)*

170 The *CDV* were quantified using an UV spectrophotometer (UV-1800, Shimadzu
171 Corporation, Kyoto, Japan) at 233 and 268 nm. Before analysis, 20 μL of

soybean oils were diluted with hexane in a volumetric flask of 25 mL. The *CDV*, expressed as percentage of conjugated dienoic acid (White, 1995) were calculated as follows:

$$CDV = 0.84 \times \frac{A_s}{bc - K_o} \quad (4)$$

where, A_s is the absorbance observed at 233nm, *b* is the cell length in cm, *c* is the concentration of the diluted sample (g L^{-1}) and K_0 is the absorptivity by acid or ester groups. In this case, c was considered as 0.5 g L^{-1}, the final concentration for most edible oils; and K_0 was considered for acids (value of 0.03).

2.7. Determination of fatty acid profile

Samples of oil were transesterified with a solution of boron trifluoride (14%) in methanol. Separation and quantification of the fatty acid methyl esters (FAMEs) were carried out using a gas chromatograph (Agilent 6890N, Agilent Technologies Spain, S.L., Madrid) equipped with a flame ionization detector and an automatic sample injector HP 7683, and using a Supelco SPTM–2560 fused silica capillary column (100 m, 0.25 mm i.d., 0.2 μm film thickness, Supelco Inc, Bellefonte, PA, USA). The chromatographic conditions were as follows: initial column temperature was 120°C during 5 min, programmed to increase up to 200°C at a rate of 5°C min^{-1} and maintained for 2 min, then up to 240°C at 1°C min^{-1} for 5 min. The injector and detector were maintained at 260°C and 280°C respectively. Helium was used as carrier gas at a constant flow-rate of 1.1 mL min^{-1}, with the column head pressure set at 35.56 psi. The split ratio was 1:50, and 1 μL of solution was injected. Nonanoic acid methyl ester (C9:0 ME) at 0.3 mg mL^{-1} was used as internal standard. Individual FAMEs, were identified by

comparing their retention times with those of authenticated standards (Supelco 37 Component FAME Mix).

2.8. Analysis of volatile compounds (VC)

Extraction of *VC* was performed using solid-phase microextraction (SPME). An SPME device (Supelco, Bellefonte, PA, USA) containing a fused-silica fibre coated with a 50/30 μm of divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) was used. For headspace SPME (HS-SPME) extraction, 0.36 g of each sample was used. The fibre, previously conditioned by heating in a gas chromatograph injection port at 270°C for 60 min, was inserted into the sample vial and then exposed to headspace. Extractions were carried out in an oven at 60ºC for 45 min, after sample equilibration for 15 min at the extraction temperature, ensuring a homogeneous temperature for sample and headspace. Once sampling was finished, the fibre was withdrawn into the needle and transferred to the injection port of the gas chromatograph–mass spectrometer (GC–MS) system. A gas chromatograph 6890N (Agilent Technologies, Santa Clara, CA, USA) equipped with a mass selective detector 5973N (Agilent Technologies) was used with a DB-624 capillary column of 30 m× 0.25 mm id, 1.4 μm film thickness (J&W Scientific, Folsom, CA, USA). The SPME fibre was desorbed and maintained in the injection port at 260°C during 8 min. The sample was injected in splitless mode. Helium was used as a carrier gas with a linear velocity of 40 cm/s. The temperature program was isothermal for 10 min at 40ºC, raised to 200ºC at a rate of 5ºC/min, and then raised to 250ºC at a rate of 20ºC/min, and held for 5 min: total run time 49.5 min. Injector and detector temperatures were both set at 260ºC. The mass spectra were obtained using a mass selective detector working in electronic impact at 70 eV, with a multiplier

voltage of 1953 V and collecting data at a rate of 6.34 scans/s over the range *m*/*z* 40–300. Compounds were identified comparing their mass spectra with those contained in the NIST05 (National Institute of Standards and Technology, Gaithersburg, MD, USA) library (>80% of coincidence) and/or by calculation of retention index relative to a series of standard alkanes (C5–C14) for calculating Kovats indices (Supelco) and matching them with data reported in literature.

2.9. Mathematical modelling and statistical analysis

2.9.1.Modelling of soybean oil oxidation

The kinetics of oxidation product formation was described by the Weibull equation reformulated to manage the time as independent variable (Murado & Vázquez, 2010):

$$Y = Y_m\left[1-\exp\left(-\ln 2\left(\frac{t}{\tau}\right)^a\right)\right] \quad (5)$$

where, Y is the oxidation process (peroxides, anisidine, etc.), Y_m is the maximum oxidation process, τ is the time required to achieve the semi-maximum oxidation process, a is a form parameter. Other interesting parameters used to characterize kinetics and compare antioxidant efficiency between extracts can be defined as follows (Vázquez, Lorenzo, Fuciños, & Franco, 2012):

$$v_m = \frac{Y_m a}{\tau}(\ln 2)^{1/a}\,\alpha^\alpha \exp(-\alpha) \quad \text{with} \quad \alpha = \frac{a-1}{a} \quad (6)$$

$$\lambda = \frac{\tau}{(\ln 2)^{1/a}}\left[\alpha^{1/a} + \frac{\exp(-\alpha)-1}{a\alpha^\alpha \exp(-\alpha)}\right] \quad (7)$$

where, v_m is the maximum rate of oxidation process obtained at the inflection point of equation (5), and λ is the lag phase of oxidation process (days).

247 *2.9.2. Numerical methods and statistical analysis*

248 Fitting procedures and parametric estimations were carried out by minimisation
249 of the sum of quadratic differences between observed and model-predicted
250 values, using the non linear least-squares (quasi-Newton) method provided by
251 the macro '*Solver*' of the Microsoft Excel 2007 spreadsheet. Then, confidence
252 intervals from the parametric estimates (Student's *t* test), consistence of
253 mathematical models (Fisher's *F* test) and residual analysis (Durbin-Watson
254 test) were evaluated using the "*SolverAid*" macro, which is freely available from
255 the Levie's Excellaneous website:
256 http://www.bowdoin.edu/~rdelevie/excellaneous/. For *AV* and *CD* kinetics, net
257 oxidation products formation was normalized by subtracting the corresponding
258 initial value of oxidation products to all experimental data.
259

260 **3. RESULTS AND DISCUSSION**

261 *3.1. Composition of the potato peels extract (Total and individual phenolics)*

262 The PPEs used in this work were prepared from peels of Agria variety potatoes
263 using different ethanol concentrations and temperatures of extraction
264 (Rodríguez-Amado, Franco, Sanchez, Zapata, & Vázquez, 2014). Four PPEs
265 recovered using different processing conditions and corresponding to different
266 yields of antioxidant compounds and *in vitro* antioxidant activities were selected
267 for their study in soy oil stability (Table 1). According to HPLC analysis, the two
268 major phenolic compounds identified and quantified in the ethanolic extracts
269 were chlorogenic (Cl) and ferulic (Fer) acids (Table 1). Chlorogenic and caffeic
270 acids are the major phenolic compounds of potato peel reported in the literature
271 (Deuber, Guignard, Hoffmann, & Evers, 2012; Wijngaard, Ballay, & Brunton,
272 2012), although other phenolic acids such as gallic, ferulic, p-hydroxybenzoic,

p-coumaric and trans-o-hydroxycinnamic can also be found (Mohdaly, Hassanien, Mahmoud, Sarhan, & Smetanska, 2013).

The observed differences in the concentration of both hydroxycinnamic acids among the four studied extracts (Table 1) were due to a selective extraction as a result of the different extraction conditions utilised. According to our previous study, the recovery of phenolic compounds increased with increasing temperature at medium to high ethanol concentrations. For this reason, the extract recovered using the highest temperature and a medium-high ethanol concentration (PPE_{33}) produced the highest chlorogenic and ferulic concentrations. Conversely, the mildest extraction conditions led to the production of an extract (PPE_{15}) with the lowest concentrations of phenolic compounds.

The selective extraction based on the process conditions has been previously reported. For instance, other authors found that higher amounts of gallic acid were extracted using subcritical water compared to methanol or ethanol (Farvin, Grejsen, & Jacobsen, 2012; Singh & Saldaña, 2011). According to the aforementioned authors, conventional aqueous extracts also contained significantly ($P<0.001$) higher levels of gallic acid when compared to ethanol extracts. Singh et al. (2011) also found that ethanol concentration affected chlorogenic acid content in microwave-assisted extraction of phenolic antioxidants from potato peels.

3.2. Effect of addition of PPE on the oxidation stability of soybean oil

Oil stability was determined under accelerated oxidation conditions (at 60 ºC, 15 days) because ambient conditions would need a longer period (months) of storage time (Mohdaly, Smetanska, Ramadan, Sarhan, & Mahmoud, 2011).

299 The assay was performed at 60 ºC due to rapid hydroperoxide decomposition at
300 elevated temperatures (Frankel, 1998), which would correspond to 4 months
301 time at ambient temperature (Warner, Frankel, & Mounts, 1989). To evaluate
302 antioxidant effectiveness of PPE in soybean oil, peroxide value (*PV*), p-
303 anisidine value (*AV*), conjugated dienes (*CDV*) and Totox value (*TV*) were
304 determined as lipid oxidation indices.
305 The PPE was used at levels of chlorogenic acid of 15, 20, 27.5 and 33 ppm.
306 Additional treatment included a synthetic antioxidant (BHT) at a level of 200
307 ppm and a control without any antioxidant. The addition of PPE at different
308 levels to soybean oil affected all lipid oxidation indices (Figure 1). In general, a
309 continuous increase in *PV* with storage time was observed ($P<0.001$) for all oil
310 samples (Figure 1A). These experimental data were well-described by the
311 kinetic equation (5) obtaining high values of correlation among predicted and
312 experimental data: the determination coefficients (R^2) were superior to 0.990 in
313 all cases and the robustness of numerical fittings was validated by Fisher´s F-
314 test. The values of the most interesting parameters, in terms of the oxidation
315 description, from equations (5-7) are summarised in Table 2.
316 Initially rate in *PV* formation was almost null starting to increase after 6-8 days
317 of oil storage time (value of the delay phase parameter, λ). In whole period and
318 for all samples *PV* was in the range of 14.47 to 180.78 meq/kg oil (Figure 1A).
319 Initially a slow rate in *PV* formation was observed, increasing after 5 days of oil
320 storage time. During the whole 14-day period and for all samples, *PV*-values
321 over samples ranged from 14.47 to 180.78 meq/kg oil. Control oil samples
322 reached a maximum *PV* of 180.78 meq/kg oil after 14 days of storage whereas
323 the *PV* of the sample containing 33 ppm of chlorogenic acid was found to be
324 141.5 meq/kg oil after this period of time. These data indicate a higher stability

of the oil treated with PPE than the control, suggesting the ability of this extract to control oil oxidation. It was also confirmed by the values of maximum rate of oxidation (v_m) in which chlorogenic concentrations of 27 and 33 ppm were lower than those of the control without PPE but higher than control with BHT. Nevertheless, the time required to achieve the semi-maximum oxidation process (τ) was similar with and without PPE. In general, the increase of PPE reduced the oxidation process but for the parameter v_m those differences were not significant. It might be due to the small differences among the concentrations used in the present work.

In general, the antioxidant effect of PPE increased with increasing extract concentration. However, even the highest PPE concentration was less effective than BHT, which achieved the lowest *PV* value (102.3 meq/kg oil) at the end of the storage and a rate of 16.6 meq kg^{-1} oil day^{-1}.The inhibitory rates of oxidation were 22, 21, 17, 11 and 43% after 14 days for 15, 20, 27.5, 33 ppm of PPE and 200 ppm of BHT, respectively.

According to our results, the PPE concentrations tested in this study (50 ppm, equivalent to 33 ppm of chlorogenic acid) might have been insufficient to match the BHT results. But, probably, increasing PPE concentration would have improved the control of oil oxidation. In fact, some authors argue the need of using concentrations 8-12 times higher than those of synthetic antioxidants to control oil oxidation during storage (Rehman, Habib, & Shah, 2004). Recently, Mohdaly et al. (2010) found lower *PV* values in soybean oil treated with 100 and 200 ppm PPE than in control samples with 200 ppm of added BHT or BHA.

PV results give a clear indication of lipid oxidation (Suja, Abraham, Thamizh, Jayalekshmy, & Arumughan, 2004). These studies also reveal higher rate of formation of primary oxidation products in soy oils than in other seed oils (Kim,

Yeo, Kim, Kim, & Lee, 2013; Suja, Abraham, Thamizh, Jayalekshmy, & Arumughan, 2004). Significant negative correlations were found between PUFA and *PV* (r=-0.863, P<0.01; Table 3).

For further confirmation of these results *AV* was also determined in soy oil samples. This index relates to secondary oxidation products (carbonyls), reflecting the magnitude of aldehydic formation in oils (McGinley, 1991; Khan & Shahidi, 2001). The *AV* is highly influenced by the type of lipid and oxidation time (Kim, Yeo, Kim, Kim, & Lee, 2013) and in fact, significant differences (P<0.001) were found during storage.

In control sample, the net formation of carbonyls was higher than in samples with PPE reaching a maximum of 14.5 (Figure 1B). Values for PPE at 50 ppm and BHT samples were 11.3 and 6.9, respectively. Again these results showed that PPE had a slightly higher antioxidant activity than control samples due to certain effectiveness in retarding the formation of carbonyl compounds (λ) but lower than BHT at 200 ppm. Nevertheless, the differences among λ-values were not statistically significant (P>0.05). Percentages of inhibition showed values of 6.9, 7.0, 9.0 and 19.0% for PPE and 46.0% for BHT. A significant increase in *AV* (P<0.001) was noted after 7-10 days of storage, corresponding to high peroxide values in this period of storage. This result is in agreement with those of Suja et al.(2004) who found a similar trend concerning the production of secondary lipid oxidation products when evaluating the antioxidant activity of methanolic extract of sesame cake in soybean, sunflower and safflower oils.

The measurement of conjugated dienes is also good variable for the assessment of oil oxidation (McGinley, 1991; Shahidi & Wanasundara, 1997) and several authors had employed it to evaluate the antioxidant activity of different extracts, such as garlic (Chatha, Anwar, Manzoor, & Bajwa, 2006) or

377 *Moringa oleifera* (Siddiq, Anwar, Manzoor, & Fatima, 2005). As pointed out by
378 Kim et al. (2013) *AV* and *CDV* are highly influenced by the type of lipids and
379 oxidation time. Initially, rate of formation of *CDV* was slow and went on
380 increasing after 5.5-9.6 days of storage (Figure 1C) but not significant
381 differences between maximum oxidation rates were found ($P>0.05$).
382 The formation of conjugated dienes has been related to the oxidation of PUFA
383 (Kim et al., 2013; Roman, Heyd, Broyart, Castillo, & Maillard, 2013). In this work,
384 we observed indeed a negative Pearson correlation between *CDV* and PUFA
385 ($r= -0.81$; $P< 0.01$, $n=20$). In addition, a highly positive correlation between *CDV*
386 and PV was observed ($r= 0.93$; $P< 0.01$, $n=20$) which is in agreement with
387 previous results reported by other authors in soybean oil (Kim et al., 2013).
388 However, unlike the above reported parameters, a lower final *CDV* value was
389 obtained for the 33 ppm PPE extract (1.93) than for the BHT treated sample
390 (2.37), showing inhibition percentages of 52 and 41%, respectively. Therefore,
391 the highest assayed level of PPE showed higher ability to inhibit double bound
392 conjugation and to reduce the loss of PUFA than BHT and so, demonstrated a
393 high antioxidant potential. Moreover, *CDV* values of samples treated with all
394 PPE concentrations was lower than in the control sample.
395 Figure 1D depicts the changes in the total oxidation values (Totox index, *TV*) of
396 the soybean oil subjected to experimental storage conditions. *TV* represents a
397 deterioration oxidative index, because it accounts for both peroxides and
398 aldehydes (Shahidi & Wanasundara, 2002). In general, the kinetic trends were
399 similar to those obtained in *PV* production. There was also a marked increase in
400 *TV* after 6.2-7.8 d. After this period, *TV* increased faster in control samples than
401 in samples treated with PPE. The best inhibition percentage (17.37%) was

achieved by the extract containing 33 ppm chlorogenic acid while BHT samples raised to a 40.48% inhibition.

3.3. Effect of addition of PPE on the fatty acid profile of soybean oil

Fatty acid profile was determined as an estimation of oil lipolysis (Farvin, Grejsen, & Jacobsen, 2012). The predominant FAs in the soy oil were the polyunsaturated FAs (PUFA), with a mean value of 55.77 g/100g, followed by monounsaturated FAs (MUFA) with a content of 26.62 g/100g, and a 16.90 g/100g concentration of saturated FAs (SFA). The predominant PUFA was linoleic (50.01 g/100g) and within MUFA, oleic acid was the most abundant (25.79 g/100g) whereas palmitic and stearic were the predominant SFA with contents of 10.59 and 4.99 g/100g, respectively.

Fatty acid content was significantly ($P<0.01$) affected by thermal oxidation time. Profiles of soy oil oxidation showed a two-phase behaviour with an increase in the fatty acid content followed by a decrease (below 10%) until the end of the storage period. These findings are in agreement with previously published results where the values of UFA decrease significantly ($P<0.001$) during oxidation of *Pinus halepensis* seed oil (Dhibi, Flamini, Issaoui, & Hammami, 2012). Among all these fatty acids, PUFAs can be used as indicators of oxidative deterioration, since double bonds in the hydrocarbon chain are the preferred substrates in oxidative reactions (Kim et al., 2013). The oxidative degradation of PUFA mainly occurred after day 10 of oxidation, with decreases in all cases higher than 5% (data not shown). Linoleic and linolenic acids were the most affected by heating, reducing its content from 50.37 to 48.20% and from 4.27 to 3.92% of oil total fatty acids, respectively.

The decline in unsaturated fatty acid content is in agreement with data reported by other authors (Choe & Min, 2006; Frankel, 1998; Kim et al., 2013). However, according to some studies, following the changes in fatty acid content would not be appropriate to assess lipid oxidation since they are reduced along oil oxidation (Roman, Heyd, Broyart, Castillo, & Maillard, 2013).This variability in fatty acid concentrations makes necessary the use of other alternatives to evaluate the oxidation stability of oils. One parameter that could be useful to determine the degree of oxidation is the use of fatty acid ratios (Kim et al., 2013).

As expected, control samples suffered a higher oxidation while the addition of PPE resulted in less oil oxidation, showing higher fatty acid contents. As in other studies, the samples containing potato extracts showed higher fatty acid contents compared to control samples with no antioxidants (Farvin, Grejsen, & Jacobsen, 2012). With regard to PPE extracts, the antioxidant capacity maintained the relationship $CL_{27.5} > CL_{20} > CL_{33}$. In contrast to lipid oxidation indices, the use of higher concentrations did not showed increased activity, what might be related to the occurrence of pro-oxidant effects (Przybylsky, Lee, & Eskin, 1998).

Other fatty acid ratios to be consider would be oleic (O/L), palmitic (P/L) and stearic over linoleic acid (S/L), palmitic (P/O) and stearic over oleic acid (S/O), and the ratios between SFA/UFA and MUFA/PUFA (Issaoui et al., 2009; Kim et al., 2013). Significant differences ($P<0.001$) were found for these ratios during thermal oxidation time, reaching the highest and lowest values in control and BHT samples, respectively. Correlations between fatty acid ratios and the main oxidation parameters were determined using the Pearson's linear correlation coefficient (Table 3). Significant results were found between these ratios and ρ-

anisidine and *CDVs*. The higher correlations (P<0.01) were found with the ratios O/L, P/L and S/L to AV (r=0.75, r=0.84 and r=0.96, respectively) and to *CDV* (r=0.65, r=0.78 and r=0.92, respectively). Therefore, these parameters would be useful indicators of the degree of lipid oxidation, being O/L (Issaoui et al., 2009; Kim et al., 2013) and P/L (Kim et al., 2013) among the major parameters used to study oil oxidative stability.

3.4. Effect of addition of PPE on the VC profile of soybean oil

The study of different natural extracts on the oxidative stability of different oils has been widely studied (Rehman, Habib, & Shah, 2004; Rodríguez-Amado, Franco, Sanchez, Zapata, & Vázquez, 2014; Samarin, Poorazarang, Hematyar, & Elhamirad, 2012; Yassari & Yasari, 2013). However, fewer studies have focused on quantitative changes in VC regarding oil treated with these antioxidant compounds during storage. Also, to the best of our knowledge, no studies about the effect of natural extracts on VC profiles can be found in the literature, with the only exception of a study carried out in horse mackerel (Farvin, Grejsen, & Jacobsen, 2012). During soybean oil oxidation several VC responsible for off-odours and flavours are produced during storage. These compounds, such as alcohols, aldehydes, ketones and esters, represent characteristic groups of fatty acid, secondary oxidation products resulting from auto-oxidation of oleic, linoleic and linolenic acid (Frankel, Hu, & Tappel, 1989; Warner, 1999). This decrease in palatability and loss in nutritional value are not well accepted by consumers and have large economic consequences for oil manufacturers.

In total 16 VC were identified on the basis of mass spectra analysis. These VC could be classified into thirteen aldehydes (pentanal, hexanal, 2-hexenal, 2,4-

heptadienal, 2-octenal, nonanal, 2-nonenal, benzaldehyde, decanal, 3-ethyl-2,4-nonadienal, 4-oxononanal, 2,4-decadienal and 2-dodecenal), two ketones (3-octen-2-one, 3,5-octadien-2-one) and one alcohol (1-octen-3-ol). Total aldehydes and ketones are depicted in Figure 2A and 2B.

Aldehydes were the major group of identified compounds, being hexanal, pentanal and nonanal the predominant VC, followed by 2,4-heptadienal and 3,5-octadien-2-one. Aldehydes are probably the most interesting lipid-derived VC because they can produce a wide range of flavours and odours (Shahidi, Rubin, & D'Souza, 1986). Hexanal, nonanal and hexanal/nonanal ratio (Figures 2C, 2D and 2E) are usually associated to oxidation in vegetable oils (Issaoui et al., 2009; Steenson, Lee, & Min, 2002), although other compounds are also closely related to the overall rancidity of soybean oil.

To study the extent of changes in VC during oil oxidation, PPE was used at three levels of chlorogenic (20, 27.5 and 33 ppm). Additional treatment included BHT at level of 200 ppm and a control without PPE. VC were significantly ($P<0.01$) increased as storage time increased, with the exception of hexanal/nonanal ratio (Figure 2E). Also an increment in total aldehydes concentration was observed, but differences among treatments were smaller ($P>0.05$) until day 10. After this period of time, differences between the control and the other treatments were more pronounced. For ketone VC, differences among samples ($P<0.001$) were observed after 5 days.

Regarding hexanal (Figure 2C), as storage progressed this volatile compound showed a gradual increase after 5 days ($P<0.01$), reaching 515 UA at the end of the storage period. The samples containing antioxidants showed lower hexanal contents than the control sample. Within PPE, inhibition percentages of hexanal production increased with increasing extract concentration, reaching inhibition

505 percentages of 49.6, 54.6 and 58.0% for CL_{20}, $CL_{27.5}$ and CL_{33}, respectively. Oil
506 with BHT exhibited the highest percentage of inhibition with a value of 72.9%.
507 As previously mentioned, aldehydes (hexanal in particular) resulting from auto-
508 oxidation of linoleic acid (Frankel, Hu, & Tappel, 1989). In this study, we found
509 that linoleic acid negatively correlates with hexanal ($r= -0.76$, $P< 0.01$, Table 3).
510 This is in agreement with the results found by other authors in vegetable oils
511 (Roman, Heyd, Broyart, Castillo, & Maillard, 2013).
512 For nonanal (Figure 2D), inhibition percentages of PPE extract were superior to
513 BHT for the three concentrations, with values in the range 44.8-50.2%, while
514 BHT only reached a 19.9% of inhibition respect to control sample. Although this
515 volatile compound results from the auto-oxidation of oleic, in the present work
516 we did not find significant correlations between this fatty acid and nonanal.
517 Concerning oil freshness, hexanal/2-hexenal and hexanal/nonanal ratio can
518 also be used to estimate the degree of oxidation of oils (Issaoui et al., 2009;
519 Morales, Rios, & Aparicio, 1997). This ratio was the lowest in soybean oil
520 treated with BHT followed by 33 ppm of chlorogenic acid sample. Within
521 hexanal/2-hexenal ratio, PPE extracts showed the lowest ratios and therefore
522 the highest inhibition percentages. The values for this ratio were higher than 1
523 which indicates higher hexanal than 2-hexenal contents at the end of storage.
524 This result reveals that oxidation increases hexanal and decrease 2-hexenal
525 levels (Issaoui et al., 2009), resulting in a low oil quality.
526 Finally, as a result of oil oxidation others VC (not detected till moment)
527 appeared at the end of heating, including 2,4-decadienal, a potential toxic
528 compound, useful marker of the oil oxidation degree that contributes to off-
529 flavors in this product. This compound was also found by other authors in seed
530 oils (Dhibi, Flamini, Issaoui, & Hammami, 2012). Results showed inhibition

percentages higher in BHT. Regarding PPE, $CL_{27.5}$ was the sample with the highest percentage. As for hexanal, This VC resulted from linoleic acid auto-oxidation, and so we find a significant correlation (Table 4) between this fatty acid and 2,4-decadienal ($r=-0.82$, $P<0.01$). Other VC that appeared after 14-day of storage is 2,4-heptadienal, originated from the oxidation of linolenic acid (Frankel, Neff, & Selke, 1981) ($r=-0.79$, $P<0.01$). Inhibition results also showed percentages higher in BHT than in samples treated with PPE, however CL_{20} and $CL_{27.5}$ exhibited percentages similar to those obtained for BHT (52.3, 55.8 vs. 60.5%, respectively).

From these results it is clear that the PPE were effective in retarding lipid oxidation, even at low concentrations. The overall order of oxidative stability based on the majoritarian VC isolated (hexanal) was $CL_{33} > CL_{27.5} > CL_{20}$. In nonanal and the total aldehydes identified was $CL_{27.5} > CL_{33} > CL_{20}$ and $CL_{27.5} > CL_{20} > CL_{233}$ in the minority VC 2,4-decadienal and 2,4-heptadienal.

Unlike lipid oxidation indices (*PV*, *AV*, *CDV* and *TV*) where the use of higher PPE concentrations ensured an increase in the antioxidant activity, the use of low concentrations of PPE were sufficient to obtain good oxidation stability results in the volatile profile.

From the results we can conclude that the soybean oil oxidation can be minimized by using potato peels extracts at low level. However, we found that stabilization of oil with potato peels extract was not comparable to that obtained using maximum levels (200 ppm) of BHT. In addition, potato peel extracts had a strong antioxidant activity both in initial and final steps of the oxidation, and thereby so they could be recommended as a potent source for the stabilisation of more complex food systems. Further studies are necessary to evaluate the

antioxidant activity using higher amounts of PPE and over a wider range of food matrix.

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FIGURE CAPTIONS

Figure 1. Effect of antioxidant extracts obtained from potato peel wastes on the evolution of lipid oxidation indexes during storage of soybean oil. Experimental data (points) were fitted to the equation [5] (continuous lines). Concentrations of extracts: 33 ppm (○), 27 ppm (□), 20 ppm (△), 15 ppm (▽). Soy (●) and BHT (◆) are the controls without antioxidant and within 200 ppm of commercial antioxidant, respectively.

Figure 2. Effect of antioxidant extracts obtained from potato peel wastes on the evolution of volatile compounds during storage of soybean oil. Concentrations of extracts: 33 ppm (○), 27 ppm (□), 20 ppm (△), 15 ppm (▽). Soy (●) and BHT (◆) are the controls without antioxidant and within 200 ppm of commercial antioxidant, respectively.

Table 1. Extraction conditions of the PPE obtained using different ethanol concentrations, temperatures and extraction times (Rodríguez-Amado, Franco, Sanchez, Zapata, & Vázquez, 2014)

	Extraction conditions		Chologenic acid (ppm)	Ferulic acid (ppm)
	T (ºC)	Ethanol (%)		
PPE_{33}	76.8	83.8	33	6.41
$PPE_{27.5}$	57.5	100	27.5	3.00
PPE_{20}	57.5	60	20	4.97
PPE_{15}	25	60	15	2.73

Table 2. Numerical estimations and confidence intervals (α=0.05) corresponding to the equations [5-7] applied to predict the most relevant parameters of peroxides, anisidine, Totox and conjugate dienes formation in soybean oil oxidation affected by antioxidant extracts obtained from potato peel wastes.

	PEROXIDE INDEX		
Chlorogenic acid (ppm)	τ	v_m	λ
15	10.14±1.09	22.68±6.26	6.33±1.02
20	10.52±0.70	24.19±5.87	6.93±0.68
27	10.03±1.05	20.72±5.99	6.27±1.04
33	10.04±0.98	20.91±5.79	6.37±0.99
Control (Soy)	10.46±1.26	24.59±6.37	6.51±0.96
Control (BHT)	12.11±2.17	16.60±2.47	7.77±0.62
	ANISIDINE VALUE		
15	55.64 (n.s.)	13.24±0.89	7.93±2.00
20	12.38±7.01	2.19±0.55	7.83±1.18
27	11.04±1.05	2.22±0.75	7.59±1.44
33	10.40±0.98	3.22 (n.s.)	8.60±2.43
Control (Soy)	11.47±2.15	2.22±0.32	7.49±0.58
Control (BHT)	67.60±6.99	1.87±0.85	10.15±3.74
	CONJUGATE DIENES		
15	10.44±7.15	1.90±1.81	9.59 (n.s.)
20	62.82 (n.s.)	51.47 (n.s.)	22.39 (n.s.)
27	12.49±10.46	0.39±0.13	7.51±1.65
33	8.55±3.91	0.24 (n.s.)	5.50 (n.s.)
Control (Soy)	10.80±0.57	1.09±0.69	9.37±0.78
Control (BHT)	10.51±0.43	0.77 (n.s.)	9.54±3.47
	TOTOX INDEX		
15	10.99±3.93	43.68±16.53	6.30±1.55
20	10.35±0.91	46.36±10.01	6.57±0.84
27	10.10±1.01	42.99±10.72	6.24±0.92
33	10.06±0.95	43.40±10.47	6.33±0.89
Control (Soy)	10.51±1.25	51.25±12.77	6.54±0.93
Control (BHT)	12.15±0.95	34.33±10.47	7.78±0.89

n.s.: not significant

Table 3. Matrix of correlation between lipid oxidation indexes and the main parameters of oxidative stability

	PV	AV	CD	Linoleic	PUFA	PUFA.SFA	MUFA.PUFA	P.L	S.L	O.L	Hexanal
PV	1										
AV	0.977**	1									
CD	0.930**	0.954**	1								
Linoleic	-0.852**	-0.836**	-0.803**	1							
PUFA	-0.864**	-0.843**	-0.809**	0.997**	1						
PUFA.SFA	-0.908**	-0.873**	-0.815**	0.764**	0.791**	1					
MUFA.PUFA	0.695**	0.679**	0.583**	-0.521**	-0.544**	-0.833**	1				
P.L	0.869**	0.837**	0.777**	-0.716**	-0.731**	-0.958**	0.781**	1			
S.L	0.979**	0.956**	0.924**	-0.808**	-0.819**	-0.936**	0.723**	0.929**	1		
O.L	0.749**	0.745**	0.653**	-0.574**	-0.591**	-0.851**	0.975**	0.820**	0.774**	1	
Hexanal	0.806**	0.826**	0.870**	-0.761**	-0.759**	-0.686**	n.s.	0.664**	0.799**	0.517*	1

** P<0.01; * P<0.05; n.s.: not significant

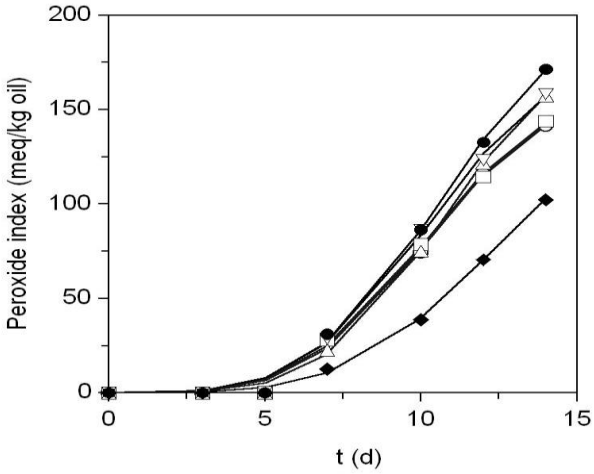
P/L: palmitic/linoleic acid ratio; S/L: stearic/linoleic acid ratio; O/L: oleic/linoleic acid ratio.

Table 4. Matrix of correlation between fatty acids and volatile compounds

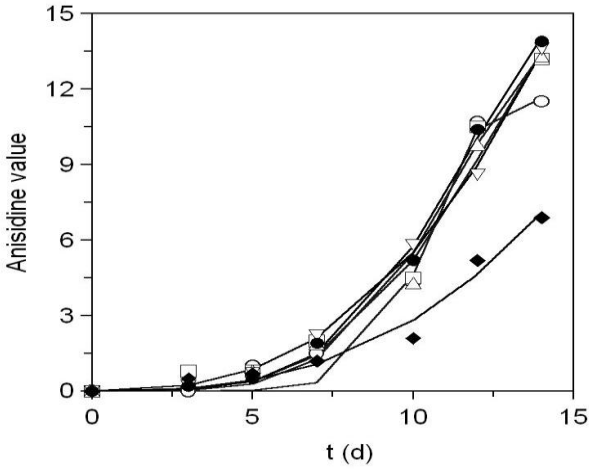
	Oleic	Linoleic	Linolenic	n3	n6	n6/n3	Hexanal	2-hexenal	Nonanal	2,4-heptadienal	2,4-decadienal
Oleic	1										
Linoleic	0.556*	1									
Linolenic	n.s.	0.839**	1								
n3	n.s.	0.853**	0.997**	1							
n6	0.554*	1.000**	0.840**	0.854**	1						
n6/n3	n.s.	n.s.	-0.785**	-0.773**		1					
Hexanal	n.s.	-0.761**	-0.633**	-0.637**	-0.762**	n.s.	1				
2-hexenal	n.s.	-0.735**	-0.730**	-0.713**	-0.737**	n.s.	0.709**	1			
Nonanal	n.s.	-0.774**	-0.682**	-0.666**	-0.774**	n.s.	0.725**	0.673**	1		
2,4-heptadienal	n.s.	-0.873**	-0.794**	-0.789**	-0.874**	n.s.	0.805**	0.877**	0.786**	1	
2,4-decadienal	n.s.	-0.819**	-0.682**	-0.685**	-0.820**	n.s.	0.921**	0.844**	0.755**	0.918**	1

** P<0.01; * P<0.05; n.s.: not significant

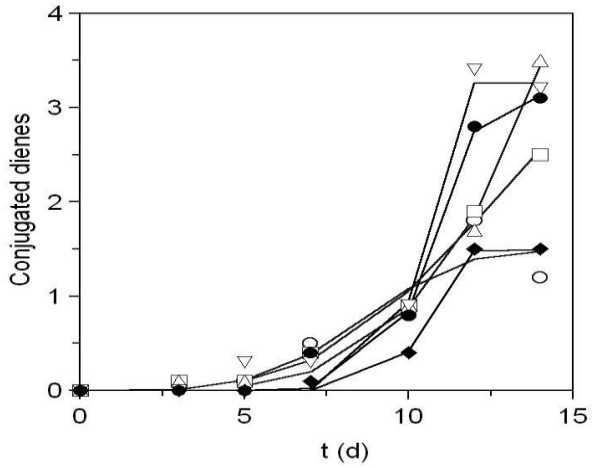
Figure 1.



A



B



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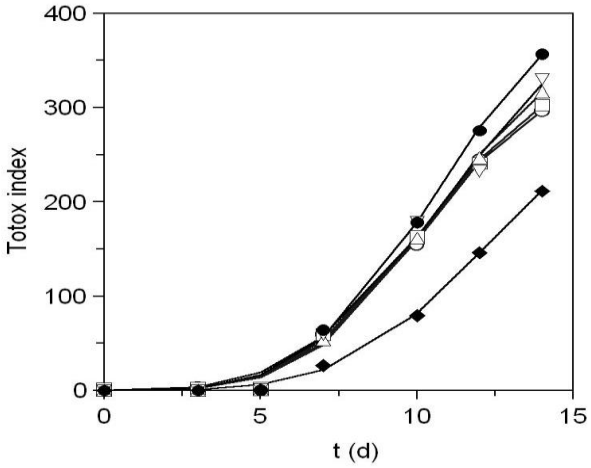
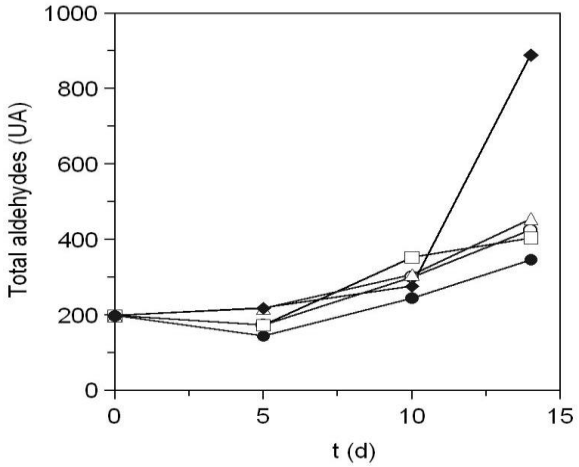


D

Figure 2



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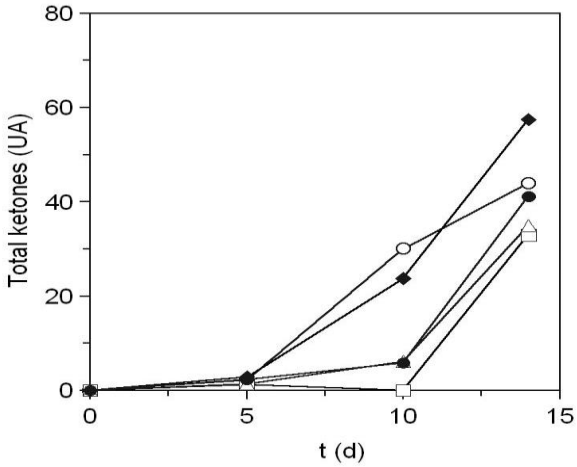

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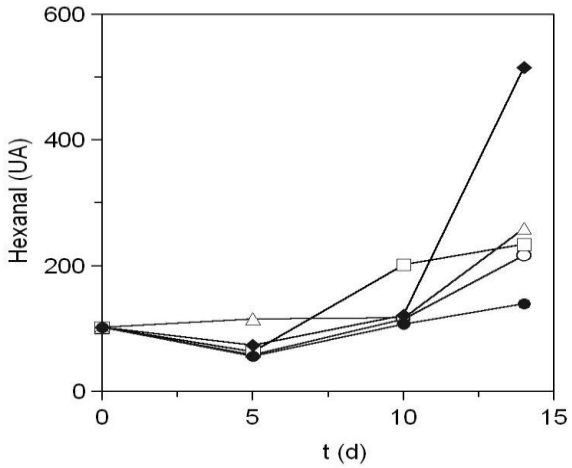

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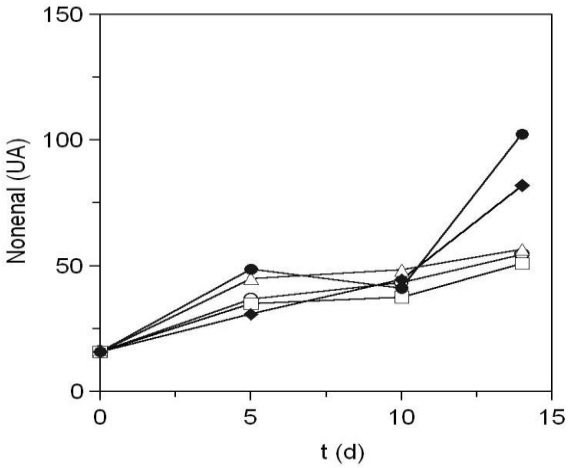

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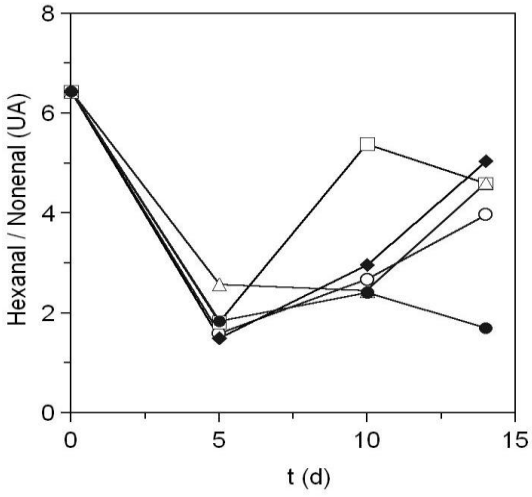

E

GRAPHICAL ABSTRACT