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Tannin impregnation pre-treatment of potatoes as a valuable strategy for acrylamide, monochloropropanediol and glycidol mitigation in chips and frying oil

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ABSTRACT

This study focused on evaluating the mitigating effect of five different natural extracts of commercial tannins on the concentration of food contaminants such as acrylamide (AA), glycidols (GD), and monochloropropanediols (MCPDs) in potato chips and frying oils after the impregnation of potatoes with tannins. The impregnated samples were used to perform 4 consecutive fryings to simulate the effect produced in restaurants. AA mitigation was achieved in all pre-treated chips throughout the four frying cycles (except for the chestnut extract). The highest AA mitigation (86.6%) was achieved using quebracho extract. This correlated positively with the progress of Maillard reaction measured at 284 nm. In potato chips, 3-MCPD and GD were decreased by most tannins tested, whereas 2-MCPD was only mitigated using hydrolyzable tannins. However, in frying oils, 3-MCPD showed a decrease using chestnut, grape seed and quebracho extracts, 2-MCPD decreased using all tannins, and no effect was observed on GD. To our knowledge, this is the first study using tannins as a mitigation strategy to decrease MCPDs and GD; and it seems a good approach to keep low concentrations of these compounds. Indeed, hydrolyzable tannins seem the best option to mitigate MCPD and GD and condensed tannins the best one to mitigate AA.

1. Introduction

The mitigation of food processing contaminants has gained attention from food industries and consumers in recent years. One of these food contaminants is acrylamide (AA), an organic molecule whose toxic effects were initially associated mainly with occupational exposure (Hagmar et al., 2001). In 1994, AA was classified as a probable carcinogen, group 2A, by the IARC (International Agency for Research on Cancer, 1994) and in 2002, Swedish researchers raised the alarm about the presence of AA in food, revealing that food could be considered the main source of exposure to AA for the entire population (Löfstedt, 2003). Through its metabolite glycidamide, AA is associated with genotoxicity, carcinogenesis, and embryotoxicity (European Food Safety Agency (EFSA), 2015) because AA can interact with macromolecules, proteins, and nitrogenous bases. Besides, AA is also a potential endocrine disruptor (Matoso et al., 2019). Establishing a tolerable daily intake (TDI) has been impossible to date; however, AA benchmark levels have been established for the main food categories (EU Regulation, N. 2158/2017, 2017).

The AA formation occurs at high temperatures (over 120 °C) in foods with low water content in the presence of reducing sugars and the amino acid asparagine that are contained in cereals, potatoes, cocoa, and coffee (Becalski et al., 2011). It is mainly produced during the Maillard reaction but may also be formed through other pathways during food processing, particularly in French fries (EFSA Panel on Contaminants in the Food Chain, 2015). The presence of AA in food affects industrial production, catering services, and home cooking (Gökmen, 2016).

Other food contaminants are glycidols (GD) and

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monochloropropanediols (MCPDs). Recently, the EFSA (EFSA Panel on Contaminants in the Food Chain, 2016; 2018) has classified GD and MCPDs as "probable human carcinogens", and the IARC has declared them as "possible human carcinogens" (International Agency for Research on Cancer, 2000; 2013). To date, MCPDs and GD are known to be process contaminants found in vegetable and animal oils and fats, formed at temperatures above 160 °C (Craft et al., 2013; C. Li et al., 2016). These contaminants usually form during the deodorization processing, and their toxic action could be due to substances formed inside the gastrointestinal tract, where the esters are hydrolyzed and the free forms are absorbed (Abraham et al., 2013). The precursors, involved in the formation of MCPDs, are mono-, di- or triacylglycerols (Cichelli et al., 2020), and a source of chlorine, which could be chlorine ions (Y. Zhao et al., 2016) or organochlorine present in edible oils (Tiong et al., 2018). In contrast, GD can also be formed in the absence of chlorine (Stadler, 2015). The European Commission has recommended the maximum levels of 3-MCPD, 3-MCPD fatty acid esters, and GD only in certain foods (European Commission, 2020).

The growing interest in these two classes of contaminants has led the EFSA to increase the level of attention to assess better health risks, dietary exposure, and mitigation techniques (EFSA Panel on Contaminants in the Food Chain, 2015; 2016). In Commission Regulation 2158/2017, the EFSA reported on the AA limits to be respected for some high-risk contaminated foods and, in addition, mentioned some useful mitigation techniques that can be adopted by industries (European Commission, 2017). Similarly, Commission Regulation 2023/915 established limits for GD and 3-MCPD in vegetable oils, fats, and children's products (European Commission, 2023).

In recent years, studies focusing on the mitigation of these contaminants have proliferated, and different mitigation strategies have been evaluated. Several studies on the mitigation of AA in food using inorganic salts (Kukurová et al., 2009), metals such as vanadium (Kalita & Jayanty, 2013), amino acids (Bose & Bhattacharjee, 2023), antioxidants (Pantalone et al., 2021), enzymes such as asparaginase (Sajed et al., 2022) and ultrasounds and additives (Bruno et al., 2024) have been conducted.

Regarding the formation of GD and MCPDs, oil refining systems have been studied and optimized (Ramli et al., 2011; Sim et al., 2020; Syed Putra et al., 2023). However, one of the main mitigation strategies for both classes of contaminants has focused on using natural antioxidant substances, such as polyphenols, present in a wide variety of plants.

Good results have been obtained in the mitigation of AA formation, the stabilization of oils and the decrease of GD and MCPD concentrations during frying processes by using antioxidant substances from different origins (synthetic/natural extracts) (B. Li et al., 2023; Pantalone et al., 2023; Wong et al., 2019). In the present study, the interest was centered on the use of tannins, biologically active polyhydroxylated macromolecules obtained from plants, known for their effects such as astringent, antiseptic, antioxidant, antimicrobial and anticancer properties (Aron & Kennedy, 2008). A recent study focused on evaluating AA after the immersion of potatoes in gallotannins solution and later frying in soybean oil has proven to be an interesting alternative to mitigate AA (Campos et al., 2024).

At present, more than 1000 tannins with a well-defined structure ranging from 500D to 20kD molecular mass are known (Khanbabaee & van Ree, 2001). Tannins can be divided into two categories: hydrolyzable and condensed tannins. The first class can be hydrolyzed under acidic conditions and at high temperatures, leading to the formation of glucose and gallic or ellagic acid units, while the other group consists of several monomers of flavan-3-ols or flavan-3,4-diols and are not easily cleavable by any soft treatment due to pH or temperature change. The latter group can be divided into proanthocyanidins and profisetinidins (Khanbabaee & van Ree, 2001) based on their monomeric units, flavan-3-ols and flavan-3,4-diols, respectively. Both categories of tannins have been reported in the literature to mitigate AA formation: proanthocyanidins from apples (Cheng et al., 2010) and muscadine grapes (Xu et al., 2015) or proanthocyanidins from sorghum, cranberry and grape seed (Qi et al., 2018), and hydrolyzable tannins from pomegranates (Mekawi et al., 2019) have been used to achieve the proposed objective. However, to date, they have not been assessed to mitigate the formation of GDs and MCPDs.

These tannins could be an interesting option to mitigate AA, MCPDs and GD formation during potato frying. It has been demonstrated that AA inhibition depends on the phenolic compound structure and on its antioxidant activity (Liu et al., 2015), and they are related to the number of hydroxyl groups of phenolic compounds (Haddarah et al., 2021). Indeed, it has been shown that procyanidins B1 and B2 present a better AA inhibitory effect than catechin and epicatechin. This seems to be related to the C6 and C8 positions on the A ring of epicatechin that can form covalent bonds with active carbonyl groups. Because of that, dimers of catechin and epicatechin that have more active positions confirm a stronger effect on AA mitigation. Besides, flavonols with different structures can synergistically affect AA mitigation (having a significantly higher effect than single compounds) (L. Zhao et al., 2019). Regarding MCPDs, molecules with higher hydroxyl groups acting as hydrogen donors can delay or reduce peroxyradical formation during lipid peroxidation, which also delays the MCPDs esters formation (Wong et al., 2019). Therefore, tannins that are commercial extracts, easy to obtain and cheap, and a mixture of catechin, epicatechin, dimers, trimers, tetramers, etc., or polymers based on gallic acid could have a higher AA and MCPDs mitigation effect than the single catechin, epicatechin or gallic acid.

In the present study, five natural commercial tannin extracts (including hydrolyzable or condensed tannins) have been used to impregnate of potatoes using an aqueous solution of tannins as a pretreatment of frying. Afterwards, the potatoes were fried in high oleic sunflower oil along four frying cycles and the effects on the mitigation of AA, 3-MCPD, 2-MCPD and GD formation were evaluated during the consecutive fryings.

2. Materials and methods

2.1. Standards and reagents

Analytical grade standards: 2-monochloropropandiol (2-MCPD) and deuterated acrylamide-d$_3$ (AA-d$_3$) were purchased from Dr. Ehrenstorfer (Augsburg, Germany, EU), 3-monochloropropandiol (3-MCPD), glycidyl oleate, acrylamide (AA), and deuterated glycidyl oleate-d$_5$ and 3-monochloropropandiol-d$_5$ (3-MCPD-d$_5$) were acquired from Sigma-Aldrich (Saint Louis, MO, USA). Other chemicals and reagents: phosphoric acid, *n*-hexane, diethyl ether, ethyl acetate, methanol, toluene, sodium bromide, sodium hydroxide, anhydrous sodium sulfate, phenylboronic acid potassium ferrocyanide (Carrez I), zinc acetate (Carrez II), were also obtained from Sigma-Aldrich (Saint Louis, MO, USA). All solvents used were of analytical grade. Oasis-HLB cartridges were from Waters (Milford, Massachusetts, USA).

2.2. Tannins

The tested tannins were offered by Silvateam S.p.a. (San Michele Mondovì, CN, Italy). The tannins tested were: a) Two belonging to the hydrolyzable tannin family, a gallotannin extract (Welltan FD/T) from *Tara spinose* (T80) with a concentration >97% of gallotannins, and an ellagitannin extract (Welltan FD/C) from chestnuts (C) with a concentration >75% of ellagitannins; and b) three condensed tannin extracts, a profisetinidin tannin extract (Welltan FD/Q) from *Schinopsis balansae* (QBC) with a concentration of >85% profisetinidines and two different grape proanthocyanidin extracts, Welltan FD/U from grape skin (U, concentration >80%), and Welltan FD/UT from grape seeds (UT, concentration >80%). Table 1 summarizes the types of tannins used.

Table 1
Types of tannins used.

Hydrolyzable tannins	Gallotannin extract from *Tara spinose* (T80)	>97% of gallotannins
	Ellagitannis extract from chestnuts (C)	>75% of ellagitannins
Condensed tannins	Profisetinidin tannin extract from *Schinopsis balansae* (QBC)	>85% profisetinidines
	Proanthocyanidin extracts from grape skin (U)	>80% proanthocyanidins
	Proanthocyanidin extracts from grape seed (UT)	>80% proanthocyanidins

2.3. Samples

The experiments were performed with fresh potatoes (*cv.* Desiree) purchased from a local market. High oleic sunflower oil was used for frying due to its demonstrated high performances during prolonged frying cycles (Pantalone et al., 2023; Romano et al., 2013), and its increasing use by companies producing pre-fried frozen French fries and snacks. Fatty acids composition, acidity, peroxide value and DAG content of the oil are reported in Supplementary Table 1.

Sample preparation was based on a previous study (Qi et al., 2018) with slight modifications. Briefly, 50 g of potatoes were cut at a time into slices of 2.0 ± 0.3 mm and 3 cm in diameter. They were then immediately immersed in a 0.1 mg/mL tannin solution (500 mL) for 15 min, dried with absorbent paper and fried in a Taurus 972.923 fryer (Vmax 1.5 L) with 1 L high oleic sunflower oil at 180 °C for 3 min. Five tannin extracts were tested and, four fryings were performed, separated by 2 h, for each type of tannin. The first frying was performed as soon as the oil reached the temperature; the following ones were performed at 2 h, 4 h and 6 h, keeping the oil at a constant temperature during the whole test. Clean oil was used for each frying set. The negative control was obtained by immersing the potato slices in water for 15 min before frying (Fig. 1). According to Ben Hammouda et al. (Ben Hammouda et al., 2017), the concentration of MCPD esters decreases significantly in less than 24h frying. Therefore, a short frying time was chosen for the experimental plan to avoid the decrease in these compounds due to frying instead of due to the effect of tannins.

Before starting frying (t_0) and after each frying step, 2 mL of oil were withdrawn. At the end, 30 samples of oils and 24 samples of potato chips were obtained. The samples of potato chips were stored at −20 °C and the oils at +4 °C until analysis.

2.4. Determination of procyanidin oligomerization in condensed tannins by HPLC-FLD

The methodology used to determine flavan-3-ols was previously reported by López-Cobo et al. (2016). An Agilent 1200 Series (Agilent Technologies, Palo Alto, CA, USA) equipped with a quaternary pump delivery system, a degasser, an autosampler and a FLD was used for the analyses. A Develosil Diol 100 Å column 5 mm, 250 × 4.6 mm ID (Phenomenex, Torrance, CA, USA) was used. Mobile phase A and B consisted of an acidic acetonitrile ((A), CH_3CN:CH_3COOH, 98:2; v/v) and acidic aqueous methanol ((B), CH_3OH/H_2O/CH_3COOH, 95/3/2; v/v/v). The gradient elution was 3% B for 50 min, 38% B for 3 min, 100% B for 13 min and 100% B for 10 min. Then the initial conditions were set, 0% B for 10 min. Fluorescence detection was performed with an excitation wavelength of 230 nm and an emission wavelength of 321 nm. The injection volume was 10 μL. All the analyses were conducted at 35 °C. The identification of flavan-3-ols was performed according to the previously described (López-Cobo et al., 2016), as they are eluted according to their degree of polymerization (DP), firstly eluting the monomers and then the different oligomers.

Fig. 1. Sample after the first frying cycle (t_0). A) untreated potatoes immerged immersed in water, B) Potato chips pre-treated with C, C) potato chips pre-treated with QBC, D) potato chips pre-treated with UT, E) potato chips pre-treated with U, and F) potato chips pre-treated with T80. (Ct = untreated potatoes immersed in water; C = tannins C; QBC = tannins QBC; U = tannins U; UT = tannins UT; T80 = tannins T80).

2.5. Determination of AA by UHPLC-QqQ-MS

AA analyses were performed following a previously validated method (Pantalone et al., 2023). AA was determined using an Acquity I-Class ultra-high performance liquid chromatography (UHPLC) system coupled to a Xevo-TQ-XS triple quadrupole (QqQ) (Waters Corporation, Milford, CT, USA). AA was eluted on a Restek Allure acrylamide column (150 × 3.0 mm, 5 μm particle size) using isocratic elution as reported previously. Data were processed using Waters' MassLynx 4.1 software (Waters Corporation, Milford, CT, USA).

2.6. Evaluation of maillard reactions trend by UV–vis spectrophotometry

The method developed by Ramírez-Jiménez et al. (2001) was used to determine the browning of potato chips. Briefly, 1 g of homogenized potato chips was weighed and placed in a 50 mL Falcon tube, 10 mL of Milli-Q water was added and mixed vigorously. The samples were centrifuged to remove the solid phase, and the supernatants were transferred to clean 15 mL Falcon tubes. The supernatants were then clarified with Carrez solutions, the samples were centrifuged again and the clean supernatants were transferred to plastic cuvettes and analyzed in a Boeco S-22 UV–VIS spectrophotometer (Hamburg, Germany) at 284 nm. Each sample was analyzed in triplicate.

2.7. Determination of 3-MCPD, 2-MCPD and GD by GC-MS

The extraction of 3-MCPD, 2-MCPD and GD was performed using the different oil samples obtained during the frying process, and the fat fraction was recovered from the potato chips after frying as previously described (Pantalone et al., 2023). Sample preparation for the analytical determination of 3-MCPD, 2-MCPD and GD was done using the official analytical method (AOCS, 2017) with some modifications (Pantalone et al., 2023). GC-MS analyses were performed by gas chromatography coupled to a quadrupole mass spectrometer (GC-Q-MS) (Agilent Technologies, Santa Clara, CA, USA) consisting of a gas chromatograph (7820A Agilent Technologies), a mass spectrometer (5977B Agilent Technologies) and an autosampler (7693 Agilent Technologies). The column used was an Agilent Technologies HP5-MS (30 m × 0.25 mm inner diameter, 0.25 μm film thickness). The GC-MS working conditions were as previously described (Pantalone et al., 2023).

2.8. Statistical analyses

The effects of the type of tannin used and the number of frying cycles on AA, 3-MCPD, 2-MCPD and GD concentrations were evaluated by univariate ANOVA factor analyses. Statistica 8.0 software (StatSoft, Tulsa, OK, USA) was used. *P*-Values <0.05 were considered statistically significant. Pearson's linear correlations were also calculated at a level of $p < 0.05$. All chemical analyses were performed in triplicate, and the analytical data were used for statistical comparisons.

3. Results and discussion

3.1. Effect of tannins on formation of AA

The tannin concentration used for the pre-treatment of the potato chips was chosen following a study reported in the literature, where the concentration of 0.1 mg/mL was found to be optimal to obtain the maximum inhibition (Qi et al., 2018). The mean AA content in the 24 frying cycles ranged from 384 to 3070 μg/kg in the second frying with QBC and the first frying with tannin C, respectively (Fig. 2).

Only 8% of the samples, corresponding to the first two frying cycles with QBC tannin, presented an AA content below the maximum limit of AA recommended by the EFSA. It is important to remark that the potato cultivar used in the present study generates high amounts of AA (Elmore et al., 2015), so it was used as a real model to evaluate the mitigation effects on AA formation. Impregnation of the potatoes with tannin solutions before frying mitigated the formation of AA in all samples throughout the four frying cycles, apart from the first frying of the tannin C-treated potatoes.

The results obtained showed an AA content decrease of up to 75.3% in potatoes treated with purified proanthocyanidins isolated from grape skin and seeds (U and UT, respectively) (Fig. 2). However, the greatest inhibition of AA formation was obtained using a potato pre-treatment with profisetinidin tannins (QBC), another type of condensed tannins based in flavan-3,4-diols. In this case, the maximum decrease of AA was 86.6%. To our knowledge, this type of tannin has never been tested before for AA mitigation, but it has proven to be very effective. Briefly, among the condensed tannins, the QBC sample showed the best performances, probably due to the higher number of -OH groups contained in the molecules compared to U and UT samples (Qi et al., 2018; Zhang et al., 2016).

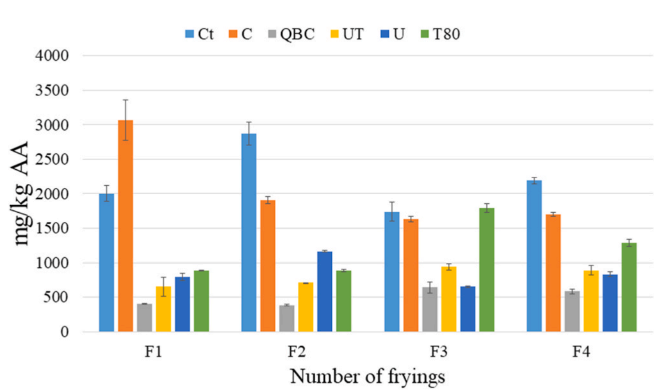

Fig. 2. Effect of tannins pre-treatment on the formation of AA in potato chips. The values are reported with their standard deviations. (Ct = untreated potatoes immersed in water; C = tannins C; QBC = tannins QBC; U = tannins U; UT = tannins UT; T80 = tannins T80).

Table 2 shows the DP of the different condensed tannins: the QBC extract had a composition of 58.1% monomer, 27.9% dimer, 9.4% trimer and 4.5% polymer; the U extract had a composition of 52.6% monomer, 26.9% dimer, 11.6% trimer, 3.3% tetramer, 0.8% pentamer, 0.1% hexamer and 4.7% polymer; and the UT extract had a composition of 45.9% monomer, 26.3% dimer, 11.1% trimer, 4.6% tetramer, 2.0% pentamer, 0.6% hexamer and 0.3% heptamer and 9.1% polymer. The trend of AA decrease could be related to the different compositions of the extracts; it seems that a higher monomer concentration results in higher AA mitigation. Indeed, Qi et al. (2018) suggested that, at equal mass, procyanidins with higher DP contained fewer active sites than procyanidins with lower DP. This hypothesis was also confirmed by Li et al. (2023), who reported how procyanidins can inhibit AA synthesis (B-type much more than A-type), underlining also how procyanidin B2 and flavan-3-ols monomeric catechins showed a synergistic action against AA formation.

Finally, the use of gallotannins (T80)- and ellagitannins (C)-based extracts also showed the ability to reduce AA formation in potato chips by up to 69% for T80 and up to 33.4% for tannin C. However, this effect was much lower than that obtained with condensed tannins. Xu et al. (2015) also identified the same trend. This behavior can be explained due to the trapping capacity of the Maillard reaction intermediates of flavan-3-ols; in fact, Totlani and Peterson (Totlani & Peterson, 2005) reported that epicatechin (EC) can act as a carbonyl trapping agent for C2, C3 and C4 sugar fragments and Maillard reaction precursor such as glyoxal, methylglyoxal, acetol, erythrose, etc. Therefore, EC can inhibit the formation of Maillard products, including AA.

Condensed tannins showed a higher AA mitigating effect than the hydrolyzable tannins (ranging from 6.3 to 53.2% depending on the extract used). This effect could be attributed to a possible dual effect; on the one hand, the structure of hydrolyzable tannins favors the reaction with asparagine more than proanthocyanidins (condensed tannins) and, on the other hand, the ability of condensed tannins to precipitate amino acids by complexation (Jin et al., 2013). Besides, it has been described that the capacity of decreasing AA formation is linked to the antioxidant capacity of the extract used (Haddarah et al., 2021). In this sense, it has been demonstrated that ellagitannins are great oxygen consumers, so they are pro-oxidant substances, whereas gallotannins have a low capacity to consume oxygen but show high antiradical power and condensed tannins act as excellent oxygen consumers, showing even higher antioxidant activity (Barbehenn et al., 2006; Motta et al., 2021). This fact could explain that the treatment of potatoes with C tannin showed AA contents even higher than the AA concentration found in the untreated potato chips (53% increase in AA in the first frying). It is also important to underline that chestnut tannin extracts showed a low degree of purity and is also hypothesized that other components of the

Table 2
Degree of polymerization of the different condensed tannins expressed as percentage (%).

Degree of polymerization	QBC	U	UT
Monomer	58.1	52.6	45.9
Dimer	27.9	26.9	26.3
Trimer	9.5	11.6	11.2
Tetramer	–	3.3	4.6
Pentamer	–	0.8	2.0
Hexamer	–	0.1	0.6
Heptamer	–	–	0.3
Polymer	4.5	4.7	9.1

QBC = tannins from quebracho, U = tannins from grape skin, UT = tannins from grape seed.

extract could be pro-oxidant agents.

These results are consistent with those obtained by Xu et al. (2015), who found an AA decrease of up to 60.3% using polyphenols extracted from muscadine grape skin and seeds (condensed tannins). Furthermore, the suitability of gallotannins of Tara pods as AA mitigation agents was recently demonstrated by Campos et al. (Campos et al., 2024). In fact, these authors showed that the impregnation of potato chips with Tara gallotannins is a valuable alternative to mitigate AA formation and to enhance the antioxidant power of potato chips.

3.2. Effect of tannins on maillard reaction progress

It has long been known that AA is a product of the Maillard reaction. However, there are also other compounds produced during this reaction, such as the brown-colored melanoidins, which are responsible for the surface color of potato chips during frying. It has been reported that changes in food color during the Maillard reaction are strongly correlated with the AA concentration (Serpen & Gökmen, 2009), and that the Maillard reaction is associated with the development of UV-absorbing intermediate compounds (measured at 284 nm) prior to the generation of brown pigments (Chawla et al., 2009).

Thus, the present study focuses on the evaluation of the effect of tannins with different structures and characteristics on AA formation by observing the progression of the Maillard reaction. Fig. 3 shows that the Maillard reaction progression, measured at 284 nm, was lower in potatoes impregnated with condensed tannins.

The results shown in Fig. 3 suggest that the trend of AA formation is consistent with the Maillard reaction progression. Maillard reaction compounds improve when carbonyl compounds from lipid oxidation increase. Thus, from the third frying, we noticed an increase in absorbance due to the progression of lipid oxidation. Moreover, in this case, the chestnut extract showed the worst results, confirming our hypothesis on the possible presence of prooxidant compounds. It is also confirmed that at the end of the fryings, the condensed tannins showed the best performance. In fact, a very high correlation was found between the analysis at 284 nm and the AA content ($r > 0.89$, $p < 0.05$) for QBC and UT tannins. In contrast, it was lower for the U sample. As observed for AA, the progression of the Maillard reaction measured at 284 nm was lower in potato chips impregnated with condensed tannins. This could be due to other compounds present in the extract that interfere with the Maillard reaction. In this regard, Kotsiou et al. (2010) reported opposite results in fried potatoes when they used olive oil extracts and the single phenols present in it; briefly, they obtained high amounts of AA using the extract, and an attenuating effect using the single phenols. Recently, some authors (Zhang & Jin, 2024) noticed about the reaction of condensed tannins with asparagine precipitating them avoiding its reaction with reducing sugars and consequently the AA formation.

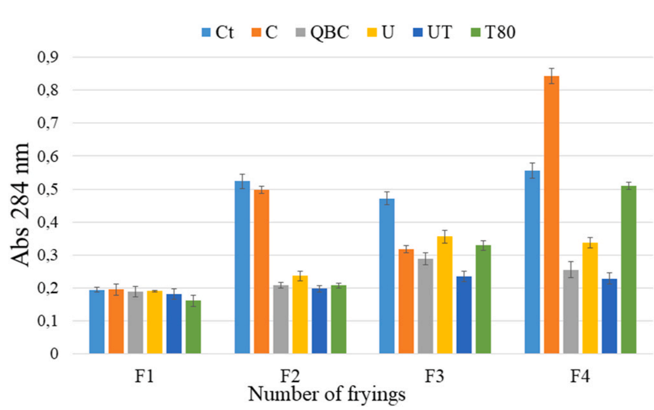

Fig. 3. Trend of Maillard reaction of potato chips pre-treated with different tannin extracts. The values are reported with their standard deviations. (Ct = untreated potatoes immersed in water; C = tannins C; QBC = tannins QBC; U = tannins U; UT = tannins UT; T80 = tannins T80).

3.3. Influence of tannins in the content of 3-MCPD, 2-MCPD and GD of oils and potato chips

MCPDs and GDs (declared as possible human carcinogens) were determined in oils and chips because, although these compounds are initially formed in the oils at high temperatures during the deodorization process, it is interesting to monitor how they change after being submitted to different frying cycles in the presence of tannins and how they are transferred to chips during frying.

Thus, the effect of immersing potato chips in a solution containing tannins with different structures and, then frying the potatoes in high oleic sunflower oil was evaluated. It was observed that most of the extracts produced a decrease in 3-MCPD, 2-MCPD and GD in the frying oils and/or potato chips, suggesting that this category of polyphenols may perform a comparative mitigating action on these contaminants. Fig. 4 shows the concentrations of 3-MCPD, 2-MCPD and GD obtained just before and after potato frying in the frying oils and in the fried potato chips.

Concerning frying oils, QBC was able to significantly decrease the concentration of 3-MCPD compared to the initial content in sunflower oil ($p < 0.05$). A good mitigation of 3-MCPD concentration was also found when using C or UT extracts. In contrast, the use of U or T80 extracts led to higher amounts of 3-MCPD (Fig. 4A). Regarding 2-MCPD in frying oil (Fig. 4B), this contaminant decreased significantly compared to the control after the use of all tannin extracts. Finally, the GD did not show significant differences compared to the oil before frying, except in the case of the pre-treatment with QBC extract, which presented higher values of GD than the initial oil (Fig. 4C).

Regarding potatoes, all tannin extracts showed a significant decrease in the content of 3-MCPD. These data are consistent with the information reported where tocols, phenolic compounds, natural extracts, and synthetic antioxidants have shown to be able to avoid the formation of cyclic acyloxonium intermediates at high temperatures and inhibit the formation of 3-MCPD (Mou et al., 2023).

The best results were obtained using the QBC extract, followed by T80 and U, UT and C extracts (Fig. 5A). Again, QBC was the extract allowing the highest mitigation of 3-MCPD formation, similar to the results observed in frying oils. QBC is a condensed tannin extract containing profisetinidins (flavan-3,4-diol polymers) that possess more hydroxyl groups than condensed proanthocyanidin tannins (U and UT extracts). The higher number of hydrogens donated by the antioxidant could delay the peroxyl radical formation during lipid peroxidation and, therefore, the formation of 3-MCPD esters would start later (Wong et al., 2019).

Initial 2-MCPD content in potato chips was 3 times lower than in the frying oil, and a significant decrease of this compound was only observed in the first two frying cycles after the use of C and T80 extracts, the two extracts containing hydrolyzable tannins. The proanthocyanidin extracts showed no significant effect on this contaminant (Fig. 5B). Finally, GD presented a decrease throughout the frying cycles after the use of C, U and T80 extracts (Fig. 5C). It is known that water from the foodstuff is released during frying and it can react with the triacylglycerols ester linkages, producing di- and monoglycerides, glycerol, and free fatty acids (Choe & Min, 2007). These molecules, in addition to being more susceptible to oxidation and thermal degradation, are also the precursors of GD. Therefore, it can be assumed that the addition of tannins could slow down the formation of DAGs and MAGs from TAGs and interfere with the formation of GD (Budilarto & Kamal-Eldin, 2015).

Moreover, an indirect effect of tannins could be occurring because they could decrease the oil absorption during frying and consequently decrease the impregnation of potatoes with GD and MCPD. This hypothesized mechanism is based on the information reported by Dana and Sam Saguy (Dana & Saguy, 2006), who noticed that a foaming tendency

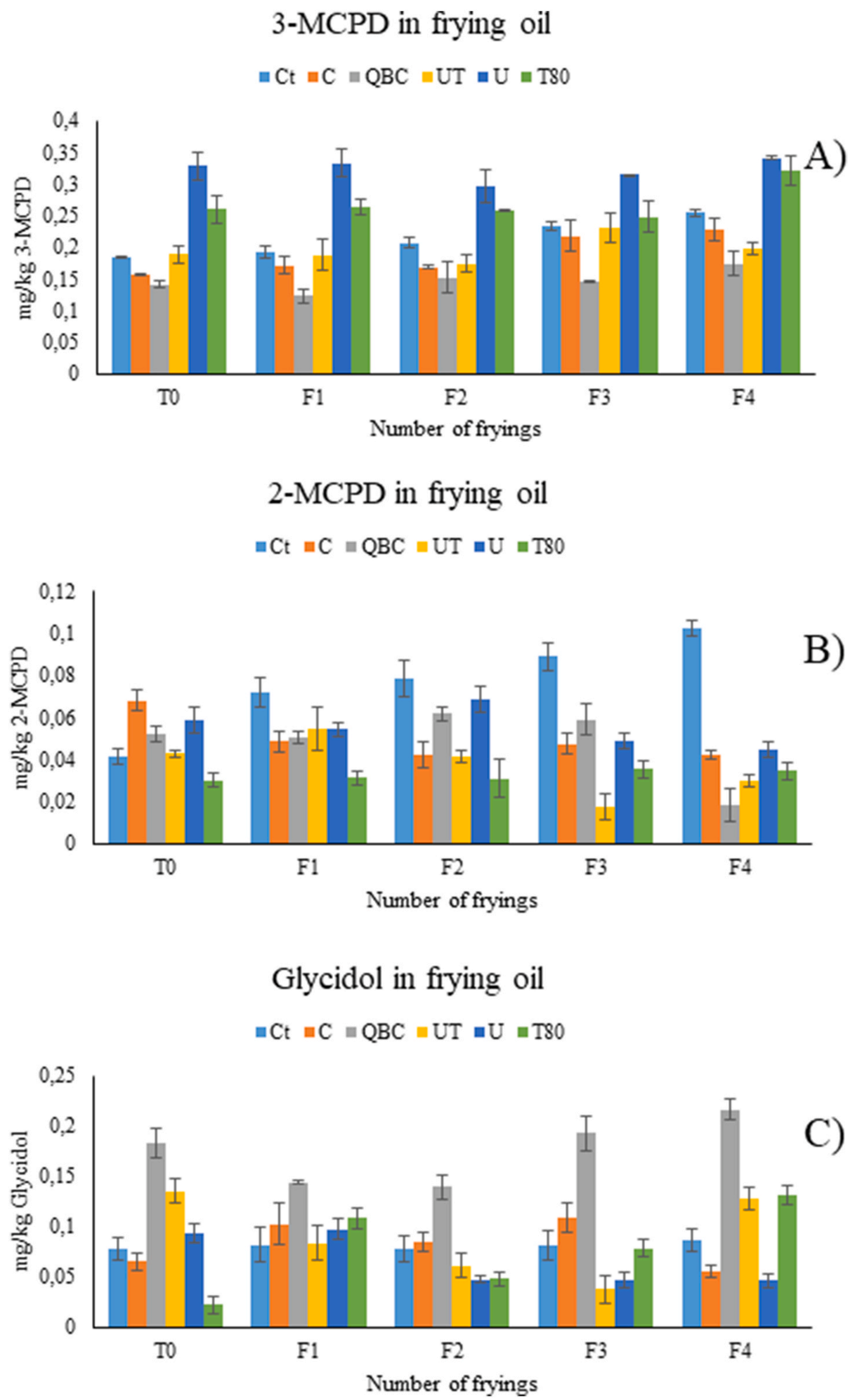

Fig. 4. Average content (μg/kg) of 3-MCPDs, 2-MCPDs and GDs in frying oils after the 4 frying cycles of potatoes treated with each tannin extract (A, B and C, respectively). (Ct = untreated potatoes immerged in water; C = tannins C; QBC = tannins QBC; U = tannins U; UT = tannins UT; T80 = tannins T80). Different letters in the same graph indicate statistically significant differences ($p < 0.05$).

of oil is increased by mono and diglycerides formed during the hydrolysis of triglycerides at high temperatures while frying. Thus, steam bubbles released from foods are entrapped by foaming for longer periods, accelerating the hydrolytic processes and increasing the formation of degradation compounds. The degradation compounds are considered surface-active agents, and they can decrease the interfacial tension between the food and oil, causing an excessive absorption of oil. Based on this hypothesis, it could be assumed that if tannins are able to decrease the hydrolytic phenomena, a low quantity of surface-active agents are produced and lower amounts of frying oil (that contains GD and MCPDs) are absorbed.

To the best of our knowledge, no other studies have studied the

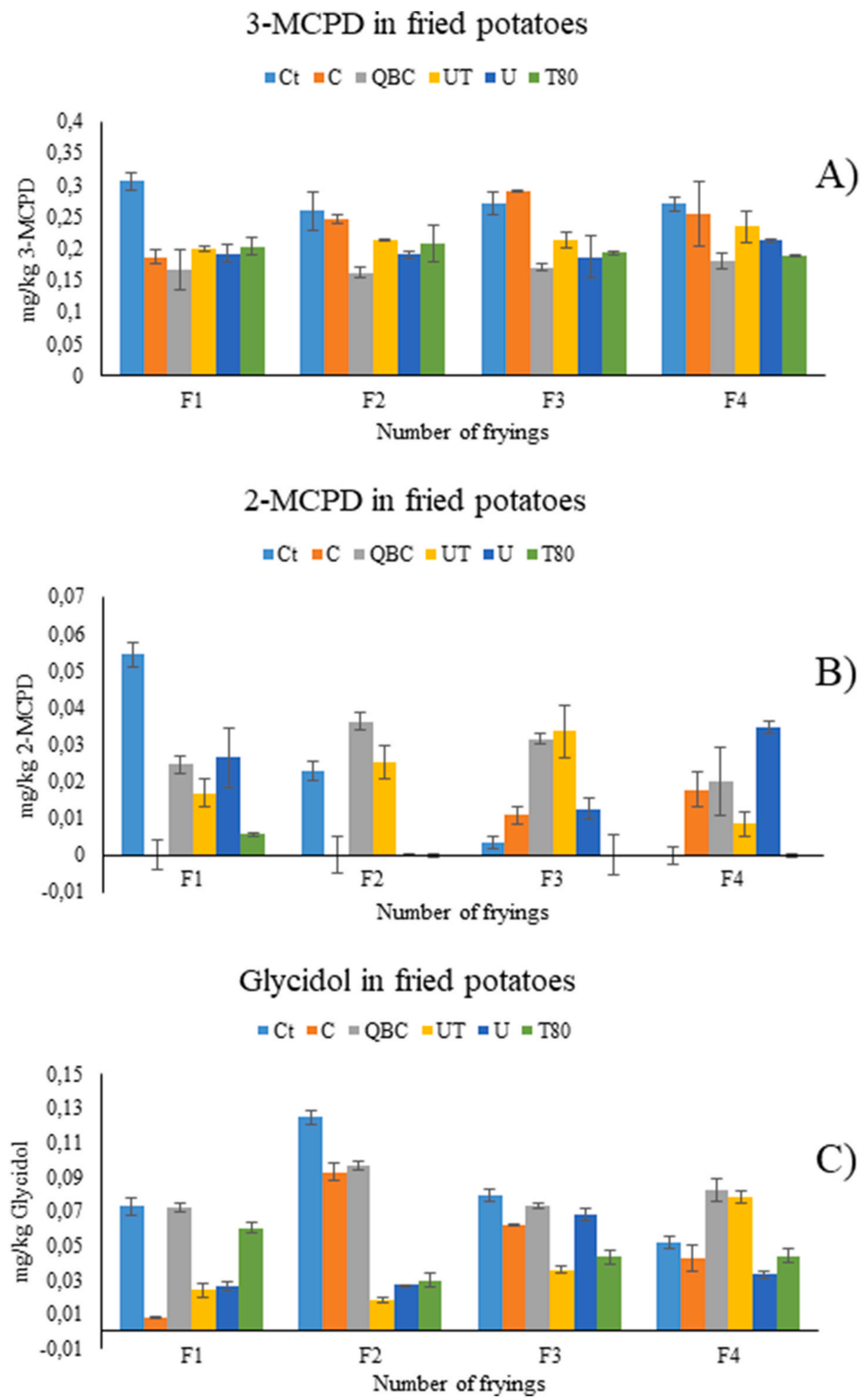

Fig. 5. Average content (μg/kg) of 3-MCPDs, 2-MCPDs and GDs in potato chips after the 4 frying cycles of potatoes treated with each tannin extract (A, B and C, respectively). (Ct = untreated potatoes immerged in water; C = tannins C; QBC = tannins QBC; U = tannins U; UT = tannins UT; T80 = tannins T80). Different letters in the same graph indicate statistically significant differences ($p < 0.05$).

mitigation of 3-MCPD, 2-MCPD and GD in the final product and even in the frying oil by adding antioxidants to the potatoes before frying. Other studies have included antioxidants in the oil before starting the frying process; for example, decreases in the concentration of 3-MCPD in oils have also been found after successive potato frying cycles when oil with rosemary extracts was added (Yıldırım & Yorulmaz, 2018). However, in this study, no significant differences in GD were found after the different frying cycles (Yıldırım & Yorulmaz, 2018). Wong et al. (Wong et al., 2019) found that the addition of synthetic and natural antioxidants to the oil improved the oil stability and decreased the levels of 3-MCPD and GD in both frying oil and potato chips.

Univariate analysis of variance was performed to evaluate the effects of tannin extracts, the number of frying cycles and the combined effect of these variables (Table 3) on the content of MCPDs, GD and acrylamide

Table 3
Factorial ANOVA (univariate results). Columns T indicate the significance level of the effect of the type of tannin extract; column F indicate the significance level of the effect of the number of frying cycles; columns T*F indicate the significance level of the combined effect of the type of tannin extract and the number of frying cycles.

	Frying oil			Potato chips		
Compounds	T	F	T*F	T	F	T*F
3-MCPD	***	0.151	0.157	***	0.673	0.573
2-MCPD	**	0.639	0.882	***	0.364	**
GD	***	*	**	***	0.087	**
AA				***	***	***

*$p < 0.05$, **$p < 0.01$, ***$p < 0.001$.

in the studied samples.

Regarding potatoes, the AA content was significantly influenced by the type of tannin extract used, the number of frying cycles performed, and the combined effects of tannin extract type and the number of frying cycles. The GD and 2-MCPD contents were also affected by the type of tannin extract and the cross-effect of tannin extract type and number of frying cycles, whereas 3-MCPD were only significantly influenced by the type of tannin extract used to impregnate the potatoes.

Regarding the oil used for frying, the content of GD was significantly affected by the type of tannin extract used, the number of frying cycles performed and the combined effects of the type of tannin extract and the number of frying cycles, whereas 2-MCPD and 3-MCPD were only affected by the type of tannin extract used.

4. Conclusion

This study assessed the mitigating effect of five different natural extracts of commercial tannins on the concentration of AA, MCPDs and GD in potato chips and frying oils after the impregnation of potatoes with tannins. The results obtained in the present study highlight that condensed tannins were the most efficient in terms of AA mitigation. Among them, quebracho extract, an extract based on flavan-3,4-diols, reported the highest mitigation activity. Interesting results were also obtained using tannins from a grape seed extract. Regarding the mitigation of GD and MCPDs in potato chips and frying oil, the data obtained for different tannins showed that not all molecules are mitigated by the same type of tannin extract. Briefly, analyzing the contaminant values in potato chips, most tannins decreased 3-MCPD and GD, and only hydrolyzable tannins decreased 2-MCPD. Regarding frying oil, a decrease in 3-MCPD was found when using C, UT and QBC extracts, whereas 2-MCPD decreased when using all tannins, and no effect was found on GD.

It is important to recognize some limitations of the study, including that only one concentration of tannins was assayed, and it lacks a sensory evaluation. However, to our knowledge, this is the first report on the use of tannin impregnation of potatoes as a GD and MCPDs mitigation treatment in frying oil and potato chips. Various mechanisms are proposed to explain the complex process of mitigation; however, none of them, taken alone, could provide a complete description of the mechanisms. Thus, these data encourage further research focused on the study of the minimum amounts of tannins that allow the highest mitigation and on the evaluation of sensory and rheological properties of fried potatoes. In addition, the use of model systems could improve the understanding of the mechanism of tannin inhibition against MCPDs and GD.

CRediT authorship contribution statement

Sara Pantalone: Writing – original draft, Investigation, Data curation. **Vito Verardo:** Writing – review & editing, Software, Methodology, Conceptualization. **Eduardo Guerra-Hernández:** Writing – review & editing, Formal analysis, Conceptualization. **Alberto Zafra-Gómez:** Writing – review & editing, Supervision, Resources. **Nicola D'Alessandro:** Writing – review & editing, Methodology, Conceptualization. **Ana Maria Gómez-Caravaca:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.lwt.2024.116696.

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