Release Kinetic in Yogurt from Gallic Acid Microparticles with Chemically Modified Inulin

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Abstract: Gallic acid (GA) was encapsulated with native (NIn), cross-linked (CIn) and acetylated (AIn) inulin by spray-drying. Inulin microparticles were characterized by encapsulation efficiency (EE) and their release profile in yogurt. The EE was significantly higher for GA-CIn (98%) compared with GA-NIn (81%) and GA-AIn (77%) microparticles, showing the effect of the modification of inulin on interaction of GA-polymer. GA release profile data in yogurt for GA-CIn, GA-NIn and GA-AIn were fitted to Peppas and Higuchi models in order to obtain the GA release rate constant. Although the GA release rate constants were significantly different among systems, these differences were slight and the GA release was fast (80% < 2 h) in the three systems, showing that inulin-systems did not control GA release in yogurt. The mechanism of GA release followed a Fickian diffusion and relaxation of chains for all microparticles. According to the release profile, these microparticles would be best suited for use in instant foods.

Keywords: gallic acid, microencapsulation, release profile, spray-drying, yogurt

Introduction

Polyphenols intake is related to the prevention of diseases associated with oxidative stress, such as cardiovascular diseases and cancer (Manach and others 2004). Currently, there is a growing interest in the development of functional and/or healthy foods that contain these natural bioactive compounds (Munin and Edwards-Lévy 2011). Dairy foods (milk and fermented milk products) as well as probiotic and prebiotic foods, among others, are gaining healthy food market share worldwide (Shiby and Mishra 2013). In this study, the yogurt was selected as a food model because its consumption has been associated with better diet quality, leading to high demand for this dairy product (Petrotos and others 2012).

To design polyphenol-rich dairy-products, such as yogurt, polyphenols are usually added as their free forms pre or post-fermentation. However, they can be degraded (pH, enzymes) and/or associated with macromolecules. Thus, interactions, such as polyphenol–protein (Rawel and others 2002; Papadopoulou and Frazier 2004) and polyphenol–polysaccharide (Le Bourvellec and Renard 2012), have been reported. In addition, some polyphenols have limited water solubility (Wu and others 2008) and unpleasant tastes, such as astringency (Kosaraju and others 2008), making it difficult to incorporate them into foods (Fang and Bhandari 2010). Encapsulation technology allows these drawbacks to be overcome (Shahidi and Han 1993).

The encapsulation of polyphenols has been successful using different encapsulation techniques (Fang and Bhandari 2010). However, spray-drying is the most commonly used encapsulation technology. In these studies, encapsulating agents, such as maltodextrins (Ersus and Yurdagel 2007; Zhang and others 2007; Sáenz and others 2009; Robert and others 2010), gum arabic (Zhang and others 2007), chitosan (Kosaraju and others 2006), citrus fruit fiber (Chiou and Langrish 2007), sodium caseinate-soy lecithin (Kosaraju and others 2008), inulin (Sáenz and others 2009; Robert and others 2012), soybean protein isolate (Robert and

others 2010), cellulose acetate phthalate (Sansone and others 2011), natural fiber polymers (Sun-Waterhouse and others 2012), and nopal mucilage (Medina-Torres and others 2013), have been used. Of these polymers, maltodextrin is the most common biopolymer used as an encapsulating agent by spray-drying because of its high solubility in water. When the polyphenols encapsulated with a soluble biopolymer are added to yogurt, they are quickly released and become exposed to the food matrix, losing their bioactive properties (de Vos and others 2010; Robert and others 2012; García and others 2013).

Inulin is an interesting biopolymer as it is a fructo-oligosaccharide (FOS) composed of fructose units β-(1-2) this is mainly linear and only slightly branched (<5%). It is considered a prebiotic, is hydrolyzed in small amounts in the stomach, and is largely fermented by the large intestinal microflora (Roberfroid 2007). Although inulin is a water dispersible polymer, it can be chemically modified by chain cross-linking or by adding functional groups (acetylation and hydroxypropylation, among others) (Stevens and others 2001).

The literature pertaining to the addition of encapsulated polyphenols to dairy products is scarce. Enrichment of yogurt with microencapsulated polyphenols from olive mill wastewater with modified starch (Petrotos and others 2012) and from *Rubus ulmifolius* Schott hydroalcoholic extract with sodium alginate (Martins and others 2014) have been reported. In both studies, its shelf life was increased and its nutritional properties were improved without affecting its sensory qualities.

In this research, inulin was chemically modified in order to obtain polymers with the same backbone but with different physical and chemical properties in order to evaluate their effect on gallic acid release in yogurt. Thus, the aim of this research was to study the influence of chemical modifications of inulin (cross-linking or acetylation) on gallic acid release kinetics in yogurt.

Material and Methods

Materials. Gallic acid (GA), 100% was obtained from Sigma-Aldrich (St. Louis, Mo., U.S.A.); Native inulin RaftilinaHP (DP>23) (NIn), was obtained from Alfa Chilena S.A (Santiago, Chile) All other chemicals were purchased from Merck

(Darm- stadt, Germany). Commercial low-fat yogurt was pur-chased in a local market in Santiago, Chile.

Proximate analysis of yogurt. The pH, moisture, proteins, lipids, and ash were determined according to AOAC (1996) methods. Carbohydrate content was determined by the Antrona method (Osborne and Voogt 1986) in a Unicam UV3 UV/Vis spectrometer (U.S.A.).

Chemical modification of inulin. Preparation and charac-terization of cross-linked inulin

Cross-linked inulin (CIn) was synthesized by a reaction with phosphoryl chloride, according to the method described by García and others (2013). Native inulin (100 g) was dispersed in water (400 mL) with constant stirring for 1 h at 25 °C and then sodium sulfate was added followed by the addition of NaOH (1 M) until reached pH 11. POCl$_3$ was added drop-wise at 0.3% (based on weight inulin) maintaining the pH between 10.5 and 11.5. After 1 h the pH was adjusted to 5.5 with HCl (1.0 M). The crosslinked inulin was precipitated with acetone, and dried at 40 °C by 24 h.

The cross-linked inulin was characterized by FT-IR on KBr disks Bruker, vector 22 (Bruker Optics, Billerica, Mass., U.S.A.) ^{31}P-NMR Bruker Avance 400 Spectrometer (Bruker BioSpin Corp., Billerica, Mass., U.S.A.) in deuterated dimethylsulfoxide (DMSO-d6), and the phosphorus (P) content by inductively cou-pled plasma atomic emission spectroscopy (ICP-AES). The degree of cross-linking (CD) was obtained by considering the relationship between the moles phosphorus incorporated into the polymer and the total moles of inulin (Van Hung and Morita 2005).

Preparation and characterization of acetylated inulin. Acetylated inulin (AIn) was synthesized through the reaction with acetic anhydride in N,N-dimethylformamide (DMF), as described by Robert and others (2012). Native inulin (10 g) with acetic an-hydride (35 mL) in DMF (100 mL) at 40 °C by 24 h using sodium acetate (0.05 % w/w) as catalyst. Native and acetylated inulin were characterized by FT-IR (Bruker, vector 22) on a KBr disk and ^{1}H-NMR at 400 MHz (Bruker, Avance 400 Spectrometer) in deuterated dimethylsulfoxide (DMSO-d6). The quantification of the substitution degree (DS) for inulin acetate was determined by ^{1}H-NMR spectroscopy (Poulain and others 2003).

Gallic acid encapsulation

Elaboration of microparticles with cross-linked inulin and experimental design. The gallic acid (GA) microparticle system with cross-linked inulin (GA-CIn) was prepared according to a face centered central composite design, using spray-drying as the encapsulation method. Ten experiments (4 experimental points, 4 axial points, and 2 central points) were performed. The GA/CIn ratio (1:10–1:30) and the air inlet temperature (140–200 °C) were evaluated as independent variables. The de-pendent variable was the GA encapsulation efficiency. The re-sponse surface methodology was applied to determine the optimal conditions for each system studied, thus maximizing the GA en-capsulation efficiency. The following quadratic model was used (Eq. (1)):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \epsilon \quad (1)$$

where y is the dependent variable predicted by the model (GA encapsulation efficiency); β_0 the constant coefficient of the in-tercept; β_1 d β_2 e the linear effects, β_{11} d β_{22} e the quadratic effects, β_{12} the cross-product and ϵ s the error term. The GA/CIn ratio and air inlet temperature are represented by x_1 d x_2, respectively.

The microparticles were elaborated as follows: CIn (5–15 g) were dissolved in distilled water (94.5–84.5 g), heated at 55 °C and then cooled until 30 °C. Gallic acid (0.5 g) was added with con-stant stirring to the encapsulating agent solution. Each dispersion was homogenized at 19000 rpm for 3 min with a Polytron PT 2100 (Kinematica AG, Luzern, Switzerland) and fed to a mini spray-dryer B-290 (Büchi, Flawil, Switzerland). The spray-dryer was op-erated at an air inlet temperature ranging from 140 to 200 °C. The air flow, rate of feeding and atomization pressure were: 600 L/h, 2 mL/min and 5 bar, respectively. The powders obtained were stored to exclude light and were kept at −20 °C until analysis.

Elaboration of microparticles with acetylated or native inulin. Gallic acid (GA) microparticle systems with native inulin (GA-NIn) or acetylated inulin (GA-AIn) were elaborated under optimal conditions (air inlet temperature of 168 and 101 °C for GA-NIn and GA-AIn, respectively; GA/encapsulating agent ratio of 1:25 and 1:30 for GA-NIn and GA-AIn, respectively), as de-scribed previously by Robert and others (2012). Briefly, the native inulin was dissolved in water and heated at 70 °C and then cooled to room temperature, and the modified inulin was dissolved in an ethanol:water (80:20 % v/v). Gallic acid was then added, with constant stirring, to native and modified inulin.

Microparticles powder analysis

Total gallic acid: Native or cross-linked inulin microparticle sys-tems (GA-NIn and GA-CIn) (50 mg) were dispersed in 2 mL ethanol:acetic-acid:water (50:8:42 v/v/v), whereas acetylated in-ulin microparticle systems (GA-AIn) (50 mg) were dispersed in 2 mL of methanol. Each dispersion was agitated using a vortex (1 min) and then ultrasonicated twice for 20 min, filled up to 250 mL with 0.005% aqueous phosphoric acid, filtered (0.22 μm Millipore filter), and injected to HPLC (Cui and others 1999) as described in section chromatographic procedure.

Surface gallic acid: Native or cross-linked inulin microparticle systems (GA-NIn, GA-CIn) (50 mg) were dispersed in 2 mL of ethanol:methanol (1:1 v/v), whereas acetylated inulin mi-croparticle systems (GA-AIn) (50 mg) were dispersed in 2 mL of water:ethanol (80:20 v/v). The dispersions were agitated by vor-texing for 1 min and then filled up to 100 mL with 0.005% aque-ous phosphoric acid. Then, the dispersions were filtered (0.22 μm Millipore filter) and injected to HPLC (Cui and others 1999) as described in section chromatographic procedure.

Chromatographic procedure: The gallic acid analysis was per-formed by HPLC, using a Merck Hitachi L-6200 pump (Merck), a Waters 996 photodiode-array detector and a C18 column (3 μm, 4.6 i.d. × 150 mm, Atlantis^{TM}, Waters, Dublin, Ireland). An isocratic mobile phase of methanol:water (1:1 v/v) containing 0.005% phosphoric acid was used at a flow rate of 0.8 mL/min. Gallic acid detection was at 270 nm and was quantified using a calibration curve (0.1–20 μg/mL, $R^2 = 0.999$).

The surface gallic acid (SGA) was calculated as the surface GA and experimental total GA ratio, expressed as percentage. The encapsulation efficiency (EE) corresponded to difference between 100 and SGA (%).

Particle size: Particle size was determined by laser light scattering using a Mastersizer X (Malvern Instruments, Worcestershire, UK) with a 300 mm lens. Microparticles were dispersed in isopropanol or ethylene glycol prior to analysis.

Gallic acid release in yogurt

GA release profiles in the yogurt were obtained from GA-NIn, GA-CIn, and GA-AIn microparticles. Microparticles (500 mg)

of each system were placed in a cellulose filter bag and into a vessel (polyethylene) containing yogurt (100 g), and then capped and stored in refrigeration at 4 °C with stirring. The experiments were performed in triplicate. Aliquots (1 mL) of each system were removed at specific time intervals and the initial weight of the yogurt was maintained by the addition of yogurt. Each sample was filled up to 10 mL with 0.005% aqueous phosphoric acid, centrifuged, and the supernatant was injected to HPLC (Cui and others 1999). The quantification of GA released was monitored by HPLC as described above (section chromatographic procedure).

Kinetic release analysis

The data were fit to Higuchi (Higuchi 1963) and Peppas (Peppas and Sahlin 1986) kinetic models (Pothakamury and Barbosa-Cánovas 1995) according to Eq. (2) and (3), respectively.

$$M_t/M_\infty = kt^{1/2} \quad (2)$$

$$M_t/M_\infty = kt^n \quad (3)$$

where M_t is defined as a quantity of GA released at any time t and M_∞ s the initial GA loading of the polymer. The release rate constants (k) were obtained from the slope of a plot of M_t/M_∞ s. (time)$^{1/2}$ for Higuchi and from the intercept of a plot of natural log M_t/M_∞ s. natural log time for Peppas.

Statistical analyses

A one-way analysis of variance for GA encapsulation efficiency, recovery and release rate constants between microparticle systems was performed. All the statistical analyses were calculated using Statgraphics software version 7.0 (Manugistics Inc, Statistical Graphics Corporation, 1993, Rockville, Mass., U.S.A.).

Results and discussion

Characterization of chemically modified inulin

The chemical modification of native inulin was performed in order to obtain encapsulating agents with the same backbone but with different physical and chemical properties. Table S1 shows the characterization of native, cross-linked and acetylated inulin. The chemical modifications were confirmed by the presence of new functional groups, which are absent in native inulin.

Cross-linking of inulin by a reaction with multifunctional reagents, such as phosphoryl chloride (POCl$_3$), generates di-ester monophosphate linkages (Stevens and others 2001; Singh and others 2007). The modification of cross-linked inulin was confirmed by ^{31}P-NMR and FT-IR (both spectra in supplementary material) as shown in Table S1. The phosphorus level was determined by atomic emission spectroscopy (ICP-AES), obtaining a cross-linking degree (CD) value of 0.052, which was obtained from the relationship between moles of phosphorus incorporated into the native inulin and the total moles of native inulin (García and others 2013).

Acetylation is an esterification reaction between acetyl groups of acetic anhydride and hydroxyl groups of native inulin. The acetylation of inulin was confirmed by ^{1}H-NMR and FT-IR (both spectra in supplementary material, Table S1). The substitution degree (SD) value was 1.6 and was determined from ^{1}H-NMR spectroscopy, considering the relationship between areas of the methyl proton of the acetyl groups and those of the native inulin (Poulain and others 2003). Similar results were reported by Damian and others (1999), Wu and Lee (2000), Poulain and others (2003), and Robert and others (2012).
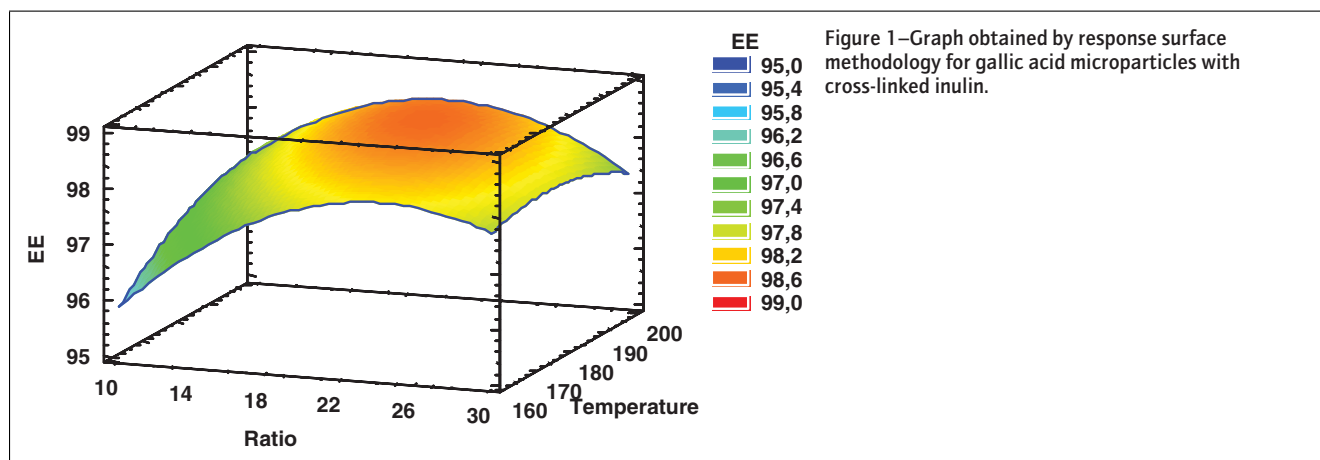
Gallic acid encapsulation with cross-linked inulin by spray drying

A face centered central composite design for the GA-CIn microparticle system was applied to evaluate the effect of the process (air inlet temperature) and formulation (GA/CIn ratio) variables on gallic acid encapsulation efficiency (EE).

The EE ranged between 95.9% and 98.6% and the response surface methodology (RSM) was applied to optimise the EE, which considered the linear, quadratic, and cross-product forms for independent variables studied at $P \leq 0.05$ significance levels. The ANOVA results showed that the linear ($P = 0.0107$) and quadratic ($P = 0.0028$) forms of the GA/CIn ratio (x_1) were significant on EE, whereas the linear ($P = 0.0573$) and quadratic ($P = 0.1347$) forms of the air inlet temperature (x_2) were not significant. In addition, the cross-product (x_1x_2) between air inlet temperature and the GA/CIn ratio was significant ($P = 0.0317$), therefore the linear form of the air inlet temperature (x_2) was considered in the quadratic model (Eq. (4)).

$$EE = 56.7976 + 0.8794 x_1 \ 0.3459 \ x_2 0.0112 \ x^2_1 0.0021 x_1 x_2 \quad (4)$$

Based on Eq. (4), all factors showed an influence on the EE. The model fitted with a high value coefficient of determination (R^2 adj: 90.4%) adjusted by degree of freedom and low residual values (below 0.4).

Figure 1–Graph obtained by response surface methodology for gallic acid microparticles with cross-linked inulin.

Table 1–Characterization of gallic acid microparticles with cross-linked, acetylated native inulin obtained under optimal conditions.

System	GA/GE ratio	Inlet air temperature (°C)	EE (%)	Recovery (%)	Particle size $D_{(3,2)}$ (μm)
GA-CIn	1:22	186	98 ± 0.1[a]	99.0 ± 0.5	3.5
GA-AIn∗	1:30	101	77 ± 1.5[c]	87.5 ± 0.2	10
GA-NIn∗	1:25	168	81 ± 0.5[b]	93.0 ± 2.1	4.4

GA, gallic acid; CIn, cross-linked inulin; AIn, acetylated inulin; NIn, native inulin; EA, encapsulating agent. EE, encapsulation efficiency. Different letters show significantly differences among systems ($P \leq 0.05$); ∗ Microparticles prepared in this study, under optimal condition described by Robert and others (2012).

Figure 1 shows the graphs of surface response for the GA–CIn microparticle system, where the response variable was maximized at medium values of the GA/CIn ratio and inlet air temperature within the range studied. The optimal conditions of the GA/CIn ratio and inlet air temperature were 1:22 and 186 °C, respectively.

Optimisation of gallic acid microencapsulation with native inulin (GA-NIn) and acetylated inulin (GA-AIn), was previously reported by our group (Robert and others 2013). In this study, we used the same independent variables but different experimental design. Thus, GA-NIn, GA-AIn and GA-CIn were elaborated under optimal spray drying conditions to obtain high encapsulation efficiency and then characterized in order to compare their release kinetics in yogurt.

Characterization of the gallic acid microparticles with native and modified inulin

Table 1 shows encapsulation efficiency, recovery, and particle size for gallic acid microparticles with cross-linked, acetylated and native inulin obtained under optimal condition (GA-CIn GA-AIn and GA-NIn). As seen, the optimal conditions (inlet air temperature and GA/EA ratio) in the spray-drying process are specific for each system microparticles (Gharsallaoui and others 2007).

The recovery of gallic acid after spray drying (Table 1) was over 87% for GA-CIn, GA-AIn and GA-NIn. Although the degradation of the phenolic compounds has been associated with degradation reactions by heat (Bravo 1998), the recovery of gallic acid was high, which could be attributed to the short drying times (5–30 s) and/or the rapid formation of a dry crust (Gharsallaoui and others 2007).

The GA encapsulation efficiency was significantly higher for GA-CIn microparticles (98%) than GA-NIn (81%) and GA-AIn (77%) showing the effect of the type of inulin modification. The

EE of GA-NIn and GA-AIn reached similar values regard with those previously reported by our group (Robert and others 2012). A wide range of polyphenol EE (8–83%) by spray-drying has been reported using encapsulating agents of different natures (maltodextrin, inulin, soybean protein isolate, methyl β-cyclodextrin, hydroxypropylmethyl cellulose, gum arabic, modified starch, chitosan and alginate) (Kosaraju and others 2006; Ersus and Yurdagel 2007; Zhang and others 2007; Sáenz and others 2009; Robert and others 2010; Robert and others 2012; Sun–Waterhouse and others 2012).

The highest GA EE for GA-CIn could be explained by the formation of a fine and dense network structure that increased GA retention during the drying process and/or by the hydrogen bond formation between the phosphoryl group in CIn and the hydroxyl group in GA. On the other hand, the acetylation of inulin decreases its solubility in water (Damian and others 1999) whereby ethanol was used to GA-AIn elaboration, which could explain the lowest GA encapsulation efficiency (77%) for GA-AIn microparticles. The hydroxyl group of the ethanol could compete with the hydroxyl group of the GA for the carbonyl group in AIn, thus diminishing the GA-AIn interaction. In the same way, ethanol could change the surrounding and/or conformation of the AIn.

As seen in Table 1, the size of the microparticles obtained under optimal conditions is presented according to the value $d_{3,2}$. These values are within the ranges reported in the literature for microparticles obtained by the spray-drying process (Gharsallaoui and others 2007). The system with acetylated inulin (AG-AIn) had higher particle sizes compared with the native and cross-linked inulin. The size distribution for each system was unimodal, with most of the particles ranging from 1 to 10 μm for GA-NIn and GA-CIn and 5–40 μm for GA-AIn.
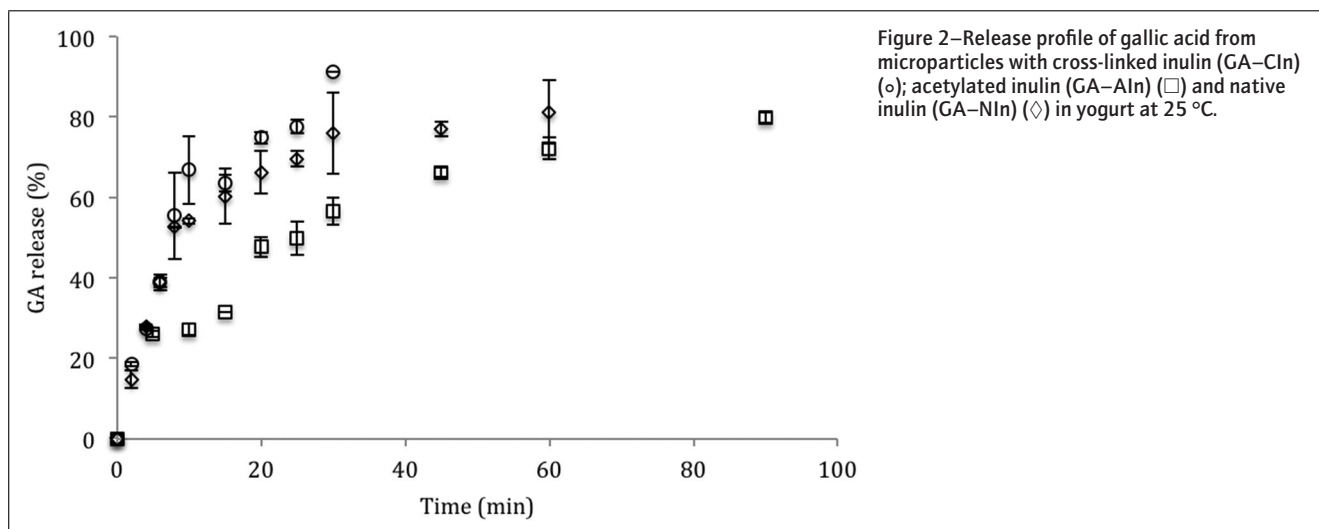

Figure 2–Release profile of gallic acid from microparticles with cross-linked inulin (GA–CIn) (○); acetylated inulin (GA–AIn) (□) and native inulin (GA–NIn) (◇) in yogurt at 25 °C.

Table 2–Kinetic parameters for gallic acid release from microparticles with native, cross-linked or acetylated inulin in yogurt.

System	n	Peppas $10^2 k_{obs} \pm 10^2$ SD (min^{-n})	R^2	Higuchi $10^2 k_{obs} \pm 10^2$ SD (min$^{-0.5}$)	R^2
GA–NIn	0.58	12.4 ± 0.02[b]	0.906	13.7 ± 2.5[b]	0.967
GA–CIn	0.62	15.3 ± 0.2[a]	0.924	17.2 ± 0.6[a]	0.951
GA–AIn	0.53	10.6 ± 0.05[c]	0.934	9.1 ± 0.5[c]	0.963

NIn, native inulin; CIn, cross-linked inulin; AIn, acetylated inulin.
Different letters show significantly differences among systems ($P \leq 0.05$).

Gallic acid release in yogurt

The initial proximate composition of the yogurt was: pH 4.0, moisture 90.0 ± 1.0 g/100 g, proteins 3.5 ± 0.2 g/100 g, lipids 0.1 ± 0.01 g/100 g, carbohydrates 5.7 ± 1.0 g/100 g and ash 0.7 ± 0.0 g/100 g.

The release profile of GA from native (GA–NIn), cross-linked (GA–CIn), and acetylated (GA–AIn) inulin microparticles in yogurt at 4 °C are shown in Figure 2.

In general, the GA was released quickly from microparticles (<2 h). As seen in the release profile graph (Fig 2), GA–AIn and GA–NIn systems studied showed a biphasic behaviour as was previously reported (Poulain and others 2003; Robert and others 2012; García and others 2013; Palma and others 2014). The first zone was attributed to a release of the nonencapsulated GA (superficial GA) on the surface of the microparticles. The second zone was assigned to the encapsulated GA release. In contrast, the GA release profile from GA–CIn corresponded to encapsulated GA because the uncovered GA was only 2%. The 80% GA release from microparticles studied was reached at 25 min for GA–CIn, at 60 min for GA–NIn and at 90 min for GA–AIn, indicating that inulin-systems did not control GA release.

Mathematical models Higuchi (Higuchi 1963) and Peppas (Peppas and Sahlin 1986) were used to fit kinetic data in order to obtain the release rate constant and to understand the GA release mechanism from microparticles in yogurt. Table 2 shows the kinetic parameters obtained from the GA release curves from microparticles in yogurt.

We expected to find differences on the GA release rate constants among systems because the acetylated inulin becomes more apolar when hydroxyl groups are replaced by acetyl groups (Poulain and others 2003), thus decreasing its solubility and GA release. Conversely, the phosphate groups incorporated in the inulin chains in the cross-linked inulin would allow enhanced solubility leading to faster GA release. In some cases the crosslinked polymers are more resistant to water, for example cross-linked starch (Alummoottil and others 2006). However, polymer modification, nature of polymer backbone and modification degree can influence the polymer solubility (Stevens and others 2001; Robert and others 2012; García and others 2013).

The GA release rate constants were the lowest from GA–AIn microparticles, whereas the GA–CIn microparticles showed the highest GA release rate constants for both mathematical models. Although the GA release rate constants were significantly different among systems, these differences were slight and the release was fast in all systems. The results of the kinetic release experiments are important for evaluating the applicability of the microparticles in food, because when the release is very slow the microparticles could be used in functional foods. Contrary, when release is fast, as in this study, the GA would become exposed to the food matrix and would undergo degradation (pH, enzymes) and/or interactions with macromolecules such as proteins and/or

polysaccharides, therefore diminishing its bioaccesibility to human body (Rawel and others 2002; Papadopoulou and Frazier 2004; Le Bourvellec and Renard 2012). In this case, the microparticles would be best suited for use in instant foods.

In this study for GA–CIn, GA–Nin, and GA–AIn microparticles, the data from GA release graph adjusted to both Higuchi and Peppas models (Table 2) with correlation coefficients above 0.90. A good correlation in Higuchi model showed that the release mechanism followed a Fickian model. However, according to "n" parameter in Peppas model, the release mechanism followed an anomalous diffusion ($n > 0.5$) where Fickian diffusion and relaxation of chains occurred simultaneously.

The effect of the medium (type of food model) can be seen when we compared the GA release rate constant in water (Robert and others 2012) and yogurt (this study) for each polymer, a different effect was observed for CIn, AIn, and NIn. The GA release rate constant for GA–CIn (28.3×10^{-2} min^{-n} data not published) and GA–NIn (28.1×10^{-2} min^{-n}) in water were higher than yogurt (12.8×10^{-2} and 12.4×10^{-2} min^{-n}, respectively). In contrast, in the GA–AIn system we observed a lower release rate constant in water (4.5×10^{-2} min^{-n}) than yogurt (10.6×10^{-2} min^{-n}). Depending on the pH, the GA ($pk_a = 3.4$) can exist in a solution in two forms: neutral and/or anionic. At the pH in yogurt (pH = 4.0) and in water (pH = 5.5) the main form of GA would be in ionized form (anionic). However, a change in the food model pH could change the polymer's degree of dissociation and/or its conformation. Thus, the release profile of the active compound from microparticles would depend on the encapsulating agent, and dissolution medium (food model pH).

Conclusion

In this study, cross-linked inulin was the better encapsulating agent than acetylated and native inulin for encapsulation of gallic acid, measured by encapsulation efficiency (higher interaction GA-polymer). However the inulin modification did not control the GA release in yogurt, being fast in the three-microparticle systems. This result suggests that native and modified inulin microparticles would be best suited for use in instant foods.

Acknowledgment

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Supporting Information

Additional Supporting Information may be found in the online version of this article.

Table S1. Characterization of native, cross-linked and acetylated.

C: Food Chemistry