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The emulsification properties of octenyl- and dodecenyl- succinylated inulins

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ABSTRACT

The emulsification properties of a series of inulin samples modified using varying amounts of octenyl- and dodecenyl-succinic anhydride have been studied by determining the droplet size as a function of time, temperature and in the presence of electrolyte using laser diffraction. It was found that ~2% modified inulin was required to stabilise 15% w/v medium chain triglyceride emulsions and that the minimum droplet size was achieved when the % hydrophobe content was >8 mol%. The dodecenyl derivatives produced emulsions with a smaller droplet size than the octenyl derivatives. Apart from OSA-inulin with a low degree of modification, stability was maintained when stored for a period of up to 21 days at room temperature and at 50 °C. The zeta potential of the emulsion droplets was determined by Laser Doppler Velocimetry and was found to increase from ~5 mv to ~60 mv as the pH increased from 2 to 7 due to the presence of carboxylate ions present in the linkage between the inulin and alkenyl chains. The droplet size was found to increase on the addition of electrolyte indicating that the adsorbed polymer layer was insufficient to provide a steric repulsive barrier and that stabilisation was mainly due to electrostatic repulsive forces.

1. Introduction

Inulin is a storage polysaccharide and is found in a range of fruits, vegetables and cereals including chicory, leek, garlic, Jerusalem artichoke, banana, rye and barley (Franck, 2006; van Loo, Coussement, de Leenheer, Hoebregs, & Smith, 1995). It is produced commercially from chicory, which contains about 15–20% inulin (Franck, 2002; Meyer, 2009; van Loo et al., 1995). Inulin is a polyfructan and consists of linear chains of β-(2,1) fructose units which terminate with a glucose unit at the reducing end (Franck, 2006; Meyer, 2009; Verraest, Peters, Batelaan, & van Bekkum, 1995). It is a polydisperse material and the degree of polymerisation (DP) varies with the source. Inulin from chicory has a DP between 2 and 60 (Franck, 2006; Meyer, 2009). It is classified as dietary fibre since it is not digested in the human digestive tract and is fermented by colonic microflora to give short chain fatty acids which have a beneficial effect on overall health (Franck, 2006; Gibson & Roberfroid, 1995; Meyer, 2009). The solubility of inulin is dependent on the DP and it will form very low viscosity solutions even at concentrations of ~20% (Franck, 2006; Meyer, 2009). On standing inulin will form gels at concentrations above 15% as a result of precipitation and crystallisation of the inulin molecules (Alvarez-Sabatel, de Maranon, & Arboleya, 2015; Meyer, 2009). This behaviour has led to the use of inulin in a variety of food systems including dairy and low fat food products (Franck, 2002; Meyer, Bayarri, Tarrega, & Costell, 2011; Solowiej et al., 2015; Teeuwen, Thone, & Vandorpe, 1992).

There has been considerable interest recently in the chemical and enzymatic modification of inulin to produce fatty acid ester derivatives which have potential application as surfactants to stabilise foams and emulsions (Kokubun, Ratcliffe, & Williams, 2013; van Kempen, Schols, van der Linden, & Sagis, 2014). It has been shown that modification can be readily achieved by the interaction of inulin with alkenyl succinic anhydride (ASA) in aqueous solution at room temperature and that the products are surface active and form micellar aggregates in solution (Kokubun et al., 2013). Alkenylated starch and gum Arabic are used in the Food Industry as emulsifiers and a particular application is in the stabilisation of concentrated flavour oil emulsions used in beverages etc. (Bhandari & Singhal, 2002; Ward, 2002; Wurzburg, 2006). Most of the studies reported have involved the octenyl succinylated derivative and the degree of substitution (DS) has been very low to comply with food

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regulations. Very few studies have been reported at higher DS and using longer alkenyl chains (Wang, Williams & Senan, 2014). The aim of the present work, therefore, is to investigate the emulsification properties of inulin modified using octenyl- and dodecenyl-succininic anhydrides.

2. Materials and methods

2.1. Materials

The alkenyl succinylated inulin samples used in this study were produced by chemical modification of Fibruline® DS2 and Inutec N10 using 2-octen-1-yl-succinic anhydride (OSA) and 2-dodecen-1-yl-succinic anhydride (DDSA) as reported previously (Kokubun et al., 2013). Fibruline® DS2 and Inutec N10 were obtained from Cosucra and Beneo Biobased Chemicals respectively and previous work using Gel permeation Chromatography coupled to multiangle light scattering has indicated that they are polydisperse. The Inutec N10 was found to have a weight average and number average molar mass of ~3120 and ~2160 g/mol respectively (Evans, Gallagher, Ratcliffe, & Williams, 2014, 2015) while the Fibruline DS2 was found to have values of 3760 and 3000 g/mol respectively (Kokubun et al., 2013). Details of the various samples used in this study are listed in Table 1. Medium chain triglyceride (MCT) gold oil was obtained from Trec Nutrition UK and was used as supplied.

2.2. Methods

2.2.1. Preparation of emulsions

Oil-in-water (O/W) emulsions were prepared by mixing 1.5 g MCT oil with 8.5 g of ASA-inulin solution at varying concentrations for 3 min at 24 000 rpm, using an IKA T25 digital Ultra-Turrax mixer. This time was chosen since it was found to give the minimum droplet size for the emulsions.

2.2.2. Emulsion droplet size

The droplet size was determined immediately after emulsion preparation and further measurements were made periodically for up to 21 days using a Malvern Mastersizer 2000 at room temperature (25 °C). Before measurement, background readings were made and subtracted from the total scattering received from the samples. Two or three drops of the sample were introduced into the dispersion unit containing distilled water. The dispersion unit pump speed was 2000 rpm. The obscuration was between 10% and 30%. The refractive index of the dispersing medium and the dispersed particles were 1.33 and 1.45 respectively. Measurements were performed in duplicate and the average value reported. Accelerated aging experiments were performed by storing samples in an oven at 50 °C and droplet size measurements were performed as described above. The influence of adding electrolyte (0.5 M NaCl) after emulsification on the droplet size was also investigated.

Table 1
DS of modified inulin samples.

Inulin	Reagents	DS[a]/mol%
N10	OSA	5.2
DS2	OSA	5.6
DS2	OSA	7.9
DS2	OSA	7.1
DS2	DDSA	4.3
DS2	DDSA	5.8
DS2	DDSA	7.9
DS2	DDSA	11.4

[a] Determined by NMR spectroscopy (Kokubun et al., 2013).

2.2.3. Droplet zeta potential

The zeta potential of inulin-coated emulsion droplets was determined by Laser Doppler Velocimetry using a Zetasizer Nano ZS (Malvem Instrument Lab, Malvern, UK) equipped with a 5 mw He–Ne laser (λ_0 633 nm) and a digital correlator. Measurements were carried out using a folded capillary cell DTS1060 (Malvern Instrument Lab, Malvern, UK). The cell was washed with ethanol and deionised water several times and dried before measurements. Two drops of the emulsion prepared as above were added into 10 mL 0.01 M NaCl in deionised water and mixed for 30 s and the pH was adjusted to between 2 and 10 using 0.1 M NaOH or 0.1 M HCl. Ten runs were performed for each sample. Zetasizer Software 6.20 © 2002–2010 Malvern Instruments Ltd was used for data analysis and the zeta potential was determined from the electrophoretic mobility using the Smoluchowski equation.

3. Results and discussion

3.1. Effect of ASA-inulin concentration

The droplet sizes for emulsions prepared using OSA- and DDSA-inulin at varying concentration are presented in Figs. 1 and 2 respectively. Although the surface weighted mean diameter ($d_{3,2}$) was found to remain relatively constant as the concentration increased, the volume weighted mean ($d_{4,3}$) diameter, which is more sensitive to the presence of larger droplets, was found to decrease significantly with increasing concentration for both OSA- and DDSA-inulin. The minimum droplet size was found to occur at a concentration of 2.0–2.5% indicating that this concentration was necessary to fully coat all of the droplets produced during the homogenisation process. The droplet size was generally smaller for the DDSA-inulins compared to the OSA-inulins over the concentration range studied indicating their increased affinity for the droplet surface. We have previously shown that DDSA-inulins are more effective at reducing the surface tension compared to OSA-inulins. For example, a 1% solution of DDSA-inulin with DS 12 mol% gave a surface tension of 30 mN/m, while a 1% solution of OSA-inulin with DS 12 mol% gave a surface tension of 35 mN/m (Kokubun et al., 2013). It is assumed that the molecules adsorb onto the surface of the oil droplets through the alkenyl chains and that the carbohydrate moieties extend away from the surface into the aqueous phase. The extent to which the molecules extend away from the surface will depend on the DS and the position of the hydrophobic groups along the inulin chain. van Kempen et al. (2014) determined the area per molecule for oligofructose fatty acid esters adsorbed at the air–water interface from surface tension measurements and found that they had a greater cross sectional

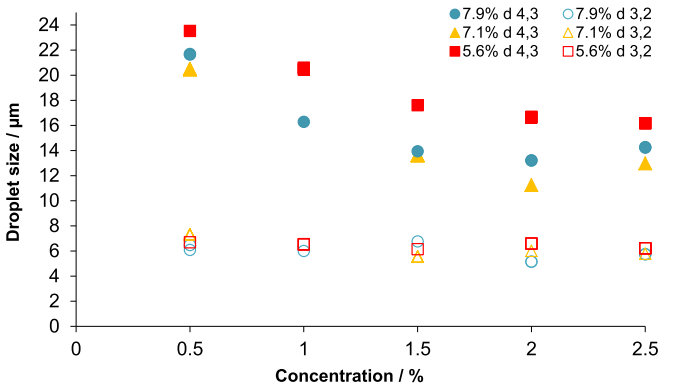

Fig. 1. Droplet size for emulsions prepared using various OSA-inulins in the presence of different OSA-inulin concentrations.

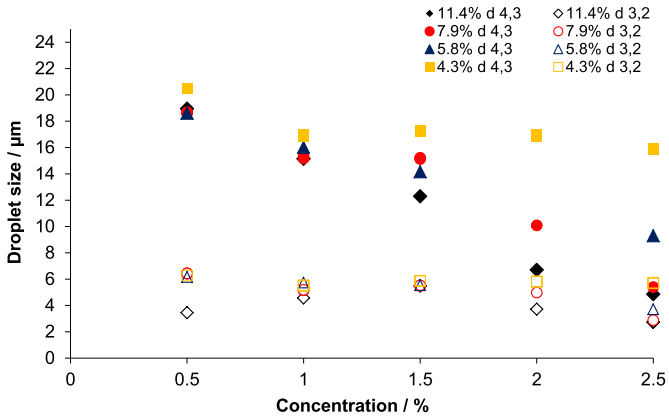

Fig. 2. Droplet size for emulsions prepared using various DDSA-inulins in the presence of different DDSA-inulin concentrations.

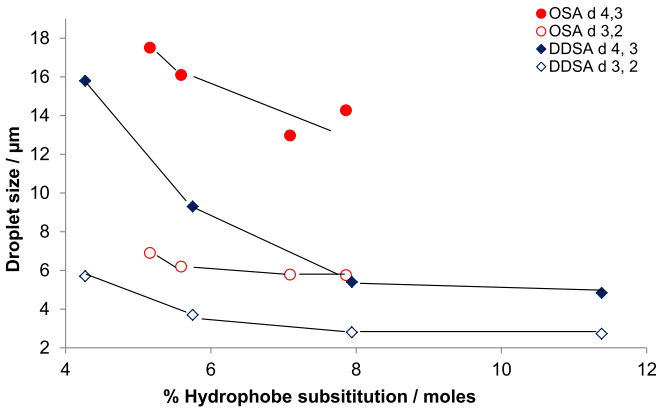

Fig. 4. Droplet size for emulsions prepared using ASA-inulins as a function of hydrophobe content.

area than surfactants with one or two sugar units in the head group. They concluded, therefore, that the oligofructose residues do not extend vertically away from the surface but adopt a more tilted orientation.

The succinylation reaction used in the synthesis of the ASA-inulins gives rise to the formation of a half ester and hence there will be a carboxylate group present in the linkage between the alkenyl chain and the inulin molecule. The zeta potential for emulsion droplets with the DS values 7.9% OSA and 11.4% DDSA were determined as a function of pH and the results are shown in Fig. 3. It was noted that the zeta potential increased as the pH increased and had a value of ~−5 mv and ~−60 mv at pH 2 and pH 7 respectively. The increase is due to the ionisation of the carboxylate group as the pH increased (Wurzburg, 2006).

3.2. Effect of DS

The droplet size for emulsions prepared using 2.5% OSA- and DDSA-inulin are plotted as a function of the DS in Fig. 4. The surface weighted mean ($d_{3,2}$) and the volume weighted mean ($d_{4,3}$) diameters of both OSA- and DDSA-inulin were found to decrease as the DS increased up to a value of ~8 mol% and then remained constant. It is estimated that this level of substitution corresponds approximately to 1.5 OSA-/DDSA-residues per inulin chain. Wang, Williams and Senan (2014) determined the droplet size of MCT emulsions using DDSA-modified gum Arabic and found the droplet size to be smaller for emulsions prepared with gum containing 10% hydrophobe compared to 5% hydrophobe. The droplet size was found to be smaller for emulsions prepared with DDSA-inulin compared to OSA-inulin at equivalent DS values indicating that the increased alkenyl chain length for the former facilitates more effective adsorption onto the oil droplets during the homogenization process as discussed above.

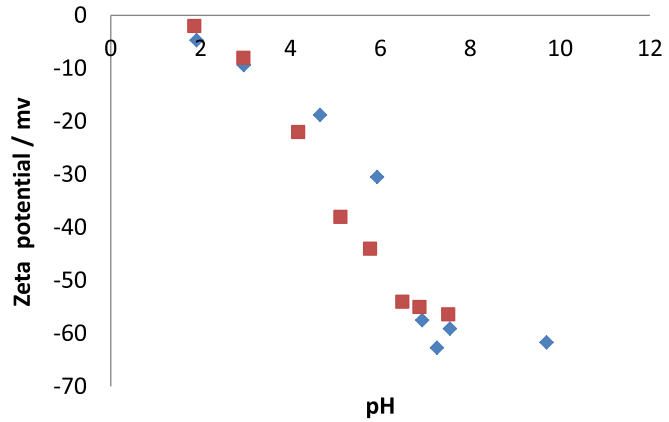

Fig. 3. Zeta potential of emulsion droplets stabilised by OSA- (diamonds) and DDSA-inulin (squares) as a function of pH.

3.3. Emulsion stability on aging

The droplet sizes for emulsions prepared using 2.5% OSA- and DDSA-inulin were monitored over time at room temperature (25 °C) to assess their effectiveness on aging and the results are presented in Figs. 5 and 6. With the exception of OSA-inulins with

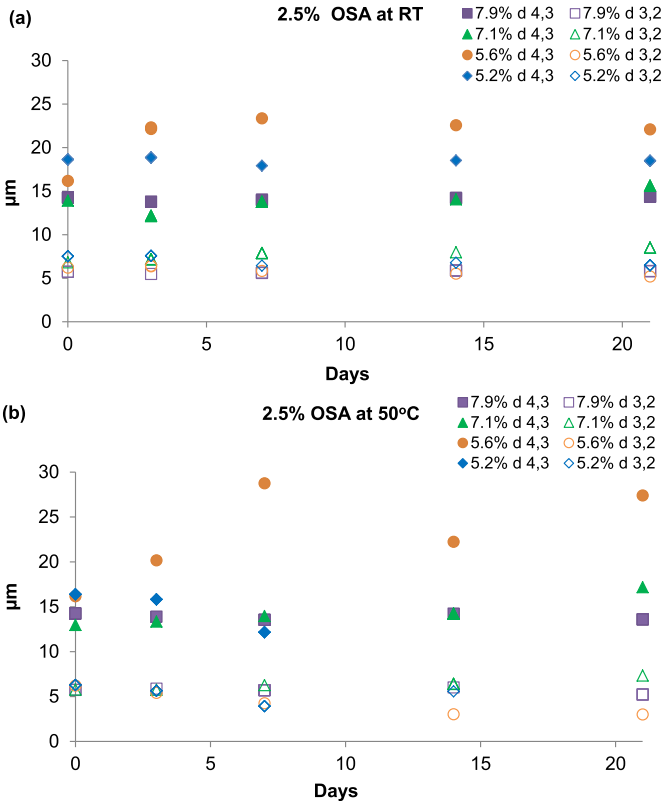

Fig. 5. Droplet size for emulsions prepared using 2.5% OSA-inulin as a function of time at (a) room temperature and (b) 50 °C.

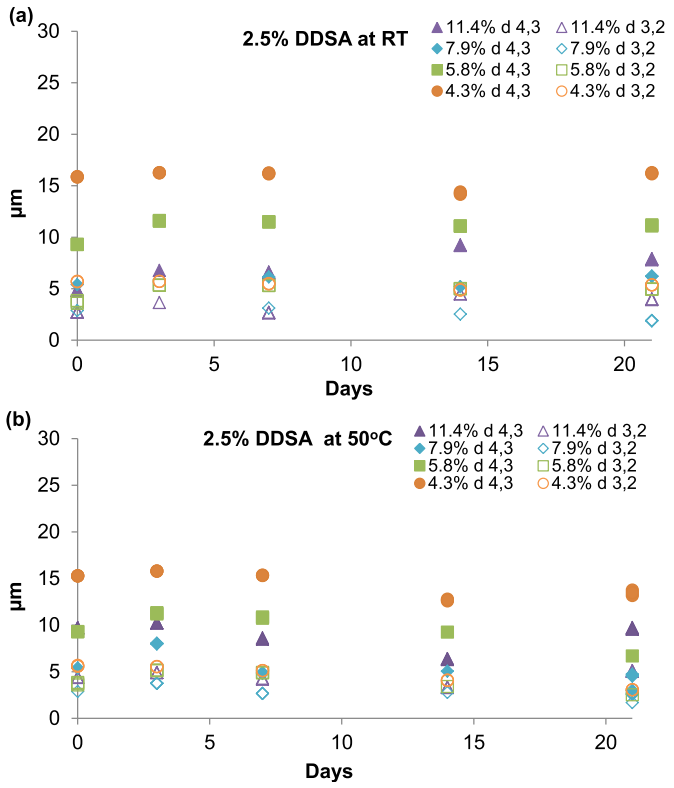

Fig. 6. Droplet size for emulsions prepared using 2.5% DDSA-inulin as a function of time at (a) room temperature and (b) 50 °C.

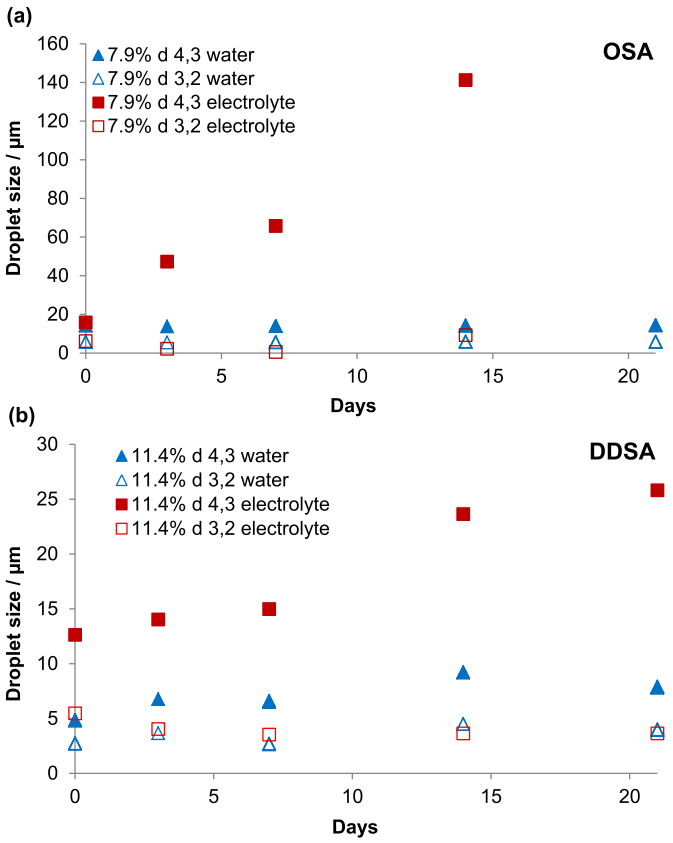

Fig. 7. Droplet size for emulsions prepared using (a) 2.5% OSA-inulin and (b) 2.5% DDSA-inulin after addition of 0.5 NaCl.

DS values of 5.2 and 5.6 mol%, the surface weighted mean ($d_{3,2}$) and the volume weighted mean ($d_{4,3}$) diameters for both the OSA- and DDSA-inulins remained relatively constant over the 21 day period both at room temperature and 50 °C indicating that flocculation and/or coalescence did not occur.

3.4. Emulsion stability in the presence of electrolyte

The droplet sizes for emulsions prepared using 2.5% OSA- and DDSA-inulin after the addition of electrolyte are given in Fig. 7a and b. The surface weighted mean ($d_{3,2}$) and the volume weighted mean ($d_{4,3}$) droplet diameters for emulsions prepared using OSA-inulin increased significantly at room temperature (25 °C) and oil separation was noted after 14 days. For the emulsions prepared using the DDSA-inulin, the surface weighted mean ($d_{3,2}$) diameter remained constant but the volume weighted mean ($d_{4,3}$) diameter increased indicating that some droplet aggregation or coalescence had occurred. This finding indicates that electrostatic repulsive forces, which arise due to the presence of the carboxylate group in the linkage between the alkenyl chain and carbohydrate head group, play a key role in the ability of the modified inulins to stabilise the emulsions. It also suggests that the adsorbed layer thickness is insufficient to provide stability through steric repulsions indicating that the molecules must adopt a fairly flat conformation at the interface.

4. Conclusions

It has been shown that OSA- and DDSA-modified inulins are able to stabilise 15% w/v O/W emulsions at concentrations above ~2%. DDSA-inulins produced emulsions with a smaller droplet size than OSA-inulins. The minimum droplet size was achieved when the % hydrophobe incorporation was above ~8 mol% for both OSA- and DDSA-modified inulins and it was concluded that stabilisation was achieved mainly through electrostatic repulsive forces created by the presence of a carboxylate ion present in the surfactant head group. It is evident that alkenylated inulins have considerable potential as emulsifiers in the Food Industry.

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References

Alvarez-Sabatel, S., de Maranon, I. M., & Arboleya, J.-C. (2015). Impact of high pressure homogenisation (HRH) on inulin gelling properties, stability and development during storage. *Food Hydrocolloids, 44*, 333–344.

Bhandari, P. N., & Singhal, R. S. (2002). Studies on the optimisation of preparation of succinate derivatives from corn and amaranth starches. *Carbohydrate Polymers, 47*(3), 277–283.

Evans, M., Gallagher, J. A., Ratcliffe, I., & Williams, P. A. (2014). Physicochemical characterisation of inulin and ryegrass fructan. In P. A. Williams, & G. O. Phillips (Eds.), *Gums and stabilisers for the Food Industry 17* (pp. 73–78). Cambridge: The Royal Society of Chemistry. Special Publication 346.

Evans, M., Gallagher, J. A., Ratcliffe, I., & Williams, P. A. (2015). Determination of the degree of polymerisation of fructans from ryegrass and chicory using MALDI-TOF Mass Spectrometry and Gel Permeation Chromatography coupled to multiangle light scattering. *Food Hydrocolloids*. http://dx.doi.org/10.1016/j.foodhyd.2015.01.015 (in press).

Franck, A. (2002). Technological functionality of inulin and oligofructose. *British Journal of Nutrition, 87*, S287–S291.

Franck, A. (2006). Chapter 10: Inulin. In A. M. Stephen, G. O. Phillips, & P. A. Williams (Eds.), *Food polysaccharides and their application* (2nd ed.). (pp. 335–351). Boca Raton: CRC Press, LLC.

Gibson, G. R., & Roberfroid, M. B. (1995). Dietary modulation of the human colonic microbiota: introducing the concept of prebiotics. *The Journal of Nutrition, 125*(6), 1401–1412.
van Kempen, S. E. H. J., Schols, H. A., van der Linden, E., & Sagis, L. M. C. (2014). Effect of variations in the fatty acid chain on functional properties of oligofructose fatty acid esters. *Food Hydrocolloids, 40*, 22–29.
Kokubun, S., Ratcliffe, I., & Williams, P. A. (2013). Synthesis, characterization and self-assembly of biosurfactants based on hydrophobically modified inulins. *Biomacromolecules, 14*(8), 2830–2836.
van Loo, J., Coussement, P., de Leenheer, L., Hoebregs, H., & Smith, G. (1995). On the presence of inulin and oligofructose as natural ingredients in the western diet. *Critical Reviews in Food Science and Nutrition, 35*(6), 525–552.
Meyer, D. (2009). Chapter 30: Inulin. In G. O. Phillips, & P. A. Williams (Eds.), *Handbook of hydrocolloids* (2nd ed.). (pp. 829–848). Boca Raton: CRC Press, LLC.
Meyer, Bayarri, S., Tarrega, A., & Costell, E. (2011). Inulin as texture modifier in dairy products. *Food Hydrocolloids, 25*, 1881–1890.
Solowiej, B., Glibowski, P., Muszynski, S., Wydrych, J., Gawron, A., & Jelinski, T. (2015). The effect of fat replacement by inulin on the physicochemical properties and microstructure of acid casein processed cheese analogues with added whey protein polymers. *Food Hydrocolloids, 44*, 1–11.
Teeuwen, H., Thone, M., & Vandorpe, J. (1992). Inulin: a versatile fibre ingredient. *International Food Ingredients, 4*(5), 10–14.
Verraest, D. L., Peters, J. A., Batelaan, J. G., & van Bekkum, H. (1995). Carboxymethylation of inulin. *Carbohydrate Research, 271*(1), 101–112.
Wang, H., Williams, P. A., & SenanC. (2014). Synthesis, characterization and emulsification properties of dodecenyl succinic anhydride derivatives of gum Arabic. *Food Hydrocolloids, 37*, 143–148.
Ward, F. M.. Water soluble esterified hydrocolloids Patent US 2002/6455512.
Wurzburg, O. B. (2006). Chapter 3: modified starches. In A. M. Stephen, G. O. Phillips, & P. A. Williams (Eds.), *Food polysaccharides and their applications* (2nd ed.). (pp. 87–118). , Boca Raton: CRC Press Taylor and Francis Group.