EFFECTS OF HYDROCOLLOIDS ADDITION ON THE RETENTION AND RELEASE PROFILE OF DIACETYL AND (-)-α-PINENE IN MODEL REDUCED FAT SALAD DRESSINGS

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Background. Salad dressings due to their gustatory and nutritious advantages have been very often used in many food products. Traditional dressings usually contain large amount of fat (20-65%). Reduction of its content in such systems in most cases leads to their physical destabilization and causes worsening of sensory properties particularly because of increase in volatility of lipophilic aroma compounds which have been mostly found in food products. The objective of this study was to investigate the influence of hydrocolloid type and concentration on the retention and release profile of diacetyl and (-)-α-pinene in model reduced fat salad dressings formed with sodium caseinate.

Material and methods. Model reduced fat salad dressings containing 10 wt% vegetable fat and stabilized by both 1 wt% sodium caseinate and 0.01-0.2 wt% hydrocolloids (xanthan gum, guar gum, gum arabic, native pregelatinised rice starch – Remyline XS-DR-P and acetylated distarch phosphate – Microlys CA – produced from potato starch) were investigated. The samples were flavoured with diacetyl or (-)-α-pinene at concentration of 0.1 wt% for each flavour compound. Following measurements were done: dressings characteristics (oil droplet size and distribution, apparent viscosity, thermodynamic and kinetic stability), stability of the odorants (relative retention and release profile) and odour intensity by method using scale.

Results. The studies showed significant dependence ($\alpha \leq 0.001$) between relative retention of the investigated odorants and hydrocolloid type as well as concentration. Moreover, it was detected that the values of persistence index of flavour compounds (related to the release profile) were in majority significantly correlated ($\alpha \leq 0.05$) with viscosity and creaming stability of the dressings, whereas relatively low and mostly statistically insignificantly with mean droplet size (D[3,2]). Furthermore, significant correlation values ($\alpha \leq 0.05$) were registered between odour intensity and vapour/liquid partition coefficient of the aroma compounds (K) in salad dressings containing: xanthan gum, guar gum, and gum arabic.

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Conclusions. Xanthan gum and guar gum markedly improved stability of hydrophilic diacetyl and hydrophobic (-)-α-pinene in dressings containing 10 wt% rapeseed oil, whereas rice starch – Remyline XS-DR-P and acetylated distarch phosphate-Microlys CA increased significantly retention of hydrophilic aroma compound.

Key words: salad dressings, hydrocolloids, diacetyl, (-)-α-pinene, retention, release profile

INTRODUCTION

Salad dressings are liquid or semiliquid products used to flavour, moisturize and enrich salads. In addition they may be used as spreads for sandwiches or as ingredients in a variety of cold and hot recipes [Yang 1993, Mandala et al. 2004]. During recent years dressings have grown in popularity and many consumers have turned to them as healthy eating option [Wendin and Hall 2001, Su and Arab 2006]. Commercial salad dressings are oil-in-water emulsions (o/w) stabilized by both surface active agents and thickeners [Charles et al. 2000]. As the emulsified systems they are characterized by an intrinsic structural complexity as a consequence of the creation during processing of a unhomogeneous and compartmentalised structure and by the contemporaneous presence, in form of a uniform macroscopic or microscopic dispersed system, of at least two immiscible phases with different chemical and physical properties in which the various components could partition [Pittia et al. 2005, Dalgleish 2006]. Typical dressings usually contain 20-65% oil [Yang 1993, Paraskevopoulou et al. 2007]. However, in recent years due to increased consciousness amongst consumers there have been still calls for further decrease of fat content in foods [Rideout et al. 2004, Naknean and Meenune 2010]. The reduction of oil concentration in o/w emulsions below 60% unfortunately causes that the systems become thermodynamically and kinetically unstable [Capek 2004, Drakos and Kiosseoglou 2008]. Moreover, most aroma compounds found in foods are fat-soluble and therefore, decrease of the quantity of non-polar phase affects also perceived odour and may result in higher loss of flavour compounds during processing and storage due to increase in their volatility [De Roos 1997, Leland 1997, Giroux et al. 2007]. Proteins and hydrocolloids are very often used together to stabilize low-fat o/w emulsions [Bryant and McClements 2000, Hemar et al. 2001]. It has been reported that proteins and polysaccharides can also affect odorants release because of their ability to bind or retard mass transfer of volatiles [Fisher and Widder 1997, Godshall 1997, De Roos 2003, Guichard 2006, Reineccius 2006]. The magnitude of the reduction in aroma release depends also on the polymer type and concentration, as well as on the flavour compound physicochemical properties e.g. molecular weight, molar volume, solubility and hydrophobicity [Druaux and Voilley 1997, Philippe et al. 2003, Seuvre et al. 2006]. Moreover, some of the scientists demonstrated that interactions between polysaccharides and proteins can be either detrimental due to thermodynamic incompatibility or coacervation or beneficial to product quality [Bryant and McClements 2000, Ye et al. 2004, Pallandre et al. 2007]. Furthermore, depending on the hydrophobicity of the aroma compounds, the presence of hydrocolloids can cause that they are retained in the matrix or released in higher quantity than from water [Gijs et al. 2000, Bortnowska 2005, Seuvre et al. 2006].

The aim of this research was to study the effect of hydrocolloid type and concentration on the diacetyl and (-)-α-pinene retention and release profile in model salad dressings containing 10 wt% rapeseed oil. The hypothesis being tested was that hydrocolloids may in different extent interact with odorants as well as significantly change microstructure and texture of salad dressings and in the consequence affect aroma compounds volatility and release rate.

MATERIAL AND METHODS

Material

Spray-dried sodium caseinate (89.48 wt% protein) was bought from Duncean Sp. z o.o. (Kamień Pomorski). Xanthan gum (2.95 wt% protein), guar gum (3.01 wt% protein), gum arabic (1.62 wt% protein), native pregelatinised rice starch – Remyline XS--DR-P (0.92 wt% protein) and acetylated distarch phosphate – Microlys CA – produced from potato starch (0.56 wt% protein) were purchased from Hortimex Sp. z o.o. (Konin). The aroma compounds diacetyl and (-)-α-pinene with purities higher than 98% were bought from Sigma-Aldrich Sp. z o.o. (Poznań), their physicochemical properties are depicted in Table 1. Commercial rapeseed oil was bought from local supermarket and used without further treatment. Distilled water was applied in all solutions. Chemicals applied for analyses were of analytical grade and purchased from Hartim Sp. z o.o. (Szczecin).

Table 1. Physicochemical properties of aroma compounds

Aroma compound	Molecular weight g/mol	Hydrophobicity[a] log P[a]	Density[a] g/mL	Boiling point[a] °C	Odour descriptor[b]
Diacetyl	86.09	–0.467	0.985	89	buttery
(-)-α-Pinene	136.24	4.83	0.858	158	pine-like

[a] Received from Sigma-Aldrich (Poznań) at 20°C.
[b] Van Ruth et al. [2002].

Preparation of salad dressings

Twenty-five model salad dressings containing 10 wt% rapeseed oil and 1 wt% sodium caseinate, varying in hydrocolloid type and concentration were made (Table 2). The reference samples were formed without hydrocolloids addition. Polysaccharide solutions were prepared by dispersing hydrocolloids in buffer (disodium hydrogen phosphate-citric acid, pH 7) and continuously stirring at 80 ±0.5°C for 3 h. Oil-in-water emulsions were formed at room temperature (22 ±0.5°C) by mixing rapeseed oil into the sodium caseinate solutions (buffer, pH 7) using a MPW 302 laboratory homogeniser (Mechanika Precyzyjna, Warszawa) at a speed of 14 000 rpm for 30 s. Salad dressings were produced by mixing polysaccharide solutions with freshly prepared emulsions to obtain a final concentration of hydrocolloids as shown in Table 2, then 0.02 wt%

Table 2. Dressings codes, composition and characteristics

Dressing code	Hydrocolloid		DC	D [3,2] μm	D [4,3] μm	η_a mPa·s	ES %
	type	concentration wt%					
R[a]	–	–	3.20	0.64	0.78	2.24	11.95
A 1	xanthan gum	0.01	2.30	0.65	0.78	2.25	12.01
A 2		0.05	2.95	0.60	0.70	3.53	12.93
A 3		0.10	2.20	0.55	0.66	4.42	13.19
A 4		0.15	2.19	0.54	0.63	5.43	13.27
A 5		0.20	2.85	0.62	0.72	7.57	14.23
LSD$_{0.05}$		–	0.32	0.04	0.06	0.97	1.06
B 1	guar gum	0.01	2.76	0.59	0.72	2.48	12.41
B 2		0.05	2.47	0.48	0.56	3.82	11.16
B 3		0.10	2.18	0.46	0.56	4.92	13.22
B 4		0.15	2.20	0.51	0.59	6.21	13.94
B 5		0.20	2.22	0.46	0.58	8.67	14.28
LSD$_{0.05}$		–	0.26	0.03	0.05	1.06	0.93
C 1	gum arabic	0.01	3.07	0.56	0.69	2.37	13.08
C 2		0.05	3.08	0.41	0.51	2.63	13.23
C 3		0.10	3.56	0.66	0.79	2.65	13.17
C 4		0.15	2.94	0.52	0.58	2.69	13.18
C 5		0.20	2.76	0.61	0.73	2.74	13.21
LSD$_{0.05}$		–	0.16	0.05	0.07	0.84	0.84
D 1	remyline XS-DR-P	0.01	2.56	0.47	0.55	2.48	12.43
D 2		0.05	2.74	0.61	0.73	2.72	13.09
D 3		0.10	2.39	0.60	0.72	2.89	13.34
D 4		0.15	2.48	0.58	0.69	3.12	13.21
D 5		0.20	2.53	0.60	0.77	3.38	13.42
LSD$_{0.05}$		–	0.22	0.03	0.04	0.98	0.54
E 1	microlys CA	0.01	3.52	0.66	0.78	2.82	12.57
E 2		0.05	2.52	0.59	0.75	2.97	13.92
E 3		0.10	5.43	0.61	0.73	3.12	13.09
E 4		0.15	4.26	0.63	0.72	3.28	13.46
E 5		0.20	3.47	0.66	0.77	3.32	13.51
LSD$_{0.05}$		–	0.73	0.04	0.06	0.69	0.78

[a] Reference sample prepared without hydrocolloid addition.
    DC – dispersion coefficient, D[3,2] – volume-surface average diameter, D[4,3] – weight mean diameter, η_a – apparent viscosity, ES – creaming stability.

sodium azide as the antimicrobial agent was added. For the relative retention, release profile and sensory analyses, salad dressings were flavoured with diacetyl or (-)-α--pinene and the final concentration of each aroma compound was 0.1 wt%.

Methods

Salad dressing characteristics. Sample droplet size and distribution were measured using a Matic®B1 microscope equipped with a built in camera (Carlzeiss Jena, Germany). The objective lens calibrated with an objective micrometer and an appropriate software (Multiscan v. 11. 06, Computer Scanning Systems) were used. The mean droplet size was characterized by two average diameters: $D[3,2] = \sum n_i d_i^3 / \sum n_i d_i^2$ (volume-surface average diameter) and $D[4,3] = \sum n_i d_i^4 / \sum n_i d_i^3$ (weight mean diameter), where: n_i – number of droplets of diameter d_i [Dickinson and James 1999, Quintana et al. 2002]. Dispersion coefficient (DC) being a measure of the with of the size distribution was calculated from the equation $DC = (D_{90} - D_{10})/D_{50}$, where: D_{90} – diameter under which 90% of the droplets in the cumulative distribution fall, D_{10} – diameter corresponding to 10% of the droplets and D_{50} – diameter corresponding to 50% of the droplets [Joscylene and Trägärdh 1999]. Thermodynamic stability of the emulsions was characterized in terms of changes in the average particle size parameter $D[4,3]$ [Dickinson and James 1999, Capek 2004], whereas kinetic stability was assessed in relation to the apparent particle-to-particle distance (δ) as a function of storage time [Hemar et al. 2001].

The parameter δ was calculated from equation $\delta = d \cdot [(0.64/\Phi_C)^{1/3} - 1]$, where: d – weight mean diameter ($D[4,3]$), $\Phi_C = (H_T/H_C) \cdot \Phi_O$, H_T and H_C – initial and remaining emulsion heights, Φ_O – initial volume fraction of oil in the dressings. Stability of the emulsions towards creaming (ES) was determined using accelerated ageing. Aliquots of the emulsion (8 ±0.01 mL) were centrifuged at 1983.6 g for 10 min at 22 ±0.5°C using a MPW-350 laboratory centrifuge (Med. Instruments, Warszawa). Creaming stability was calculated from equation $ES\ (\%) = (H_C/H_T) \cdot 100$, where: H_C and H_T – as explained above [Huang et al. 2001]. Apparent viscosity of the dressings was measured at room temperature (22 ±0.5°C) using a viscometer Rheotest 2-50 Hz – type RV 2 (Medingen, Germany) equipped with S/S1 cylinder, at a shear rate of 1312 s⁻¹. Total nitrogen present in sodium caseinate and hydrocolloids was determined by the Kjeldahl procedure with a Tecator Kjeltec System-1026 Distilling Unit (Tecator AB, Höganäs, Sweden). The conversion factors of 6.38 and 6.25 for sodium caseinate and hydrocolloids, respectively were used [AOAC 1995].

Static headspace analysis. Gas chromatography-mass spectrometry (GC-MS) analyses were performed on a Perkin-Elmer AutoSystem XL GC apparatus coupled with TurboMass MSD (Mass Selective Detector Quadrupole type). For the analyses of aroma compounds relative retention, salad dressings (5 ±0.01 mL) were transferred into 22.3 mL headspace vials and the vials were immediately sealed. Then the samples were preequilibrated in a ST1 thermostat (Pol-Eko-Aparatura, Wodzisław Śl.) at 37 ±0.5°C. Preliminary experiments showed no increase in headspace concentrations after 24 h equilibration. Flavour compounds release and persistence measurements were performed with following procedures. Headspace vials (not closed) containing salad dressings (5 ±0.01 mL) were stored in a refrigerator at 4 ±0.5°C for 1-38 days and at fixed time intervals the samples were removed from refrigerator in order to measure the re-

sidual amount of (-)-α-pinene or diacetyl in salad dressings. For chromatographic analyses, the vials containing dressings were placed into a Perkin-Elmer TurboMatrix 16 autosampler and the headspace sample was automatically withdrawn and injected into a gas chromatograph. Only one sample per vial was made. The inlet was operated in the splitless mode and the carrier gas was helium, at a flow rate of 0.7 mL/min. Separation was done using a PE-5MS capillary column (30 m × 0.25 mm × 0.25 μm) by increasing oven temperature from 50 to 150°C at a rate of 10°C/min. Volatile compounds were identified by comparison of their retention times and mass spectra with pure reference aroma compounds. Quantitative chromatographic analyses were performed using an external standard method [Kolb and Ettre 1997].

Aroma compounds retention and persistence index calculations. Aroma compounds relative retention ($R_{relative}$) in dressings corresponded to the percentage of volatility decrease relatively to buffer and calculated from the following formula $R_{relative}$ (%) = $(1 - K_{matrix}/K_{buffer}) \cdot 100$, where: K_{matrix} – vapour/matrix partition coefficient and K_{buffer} – vapour/buffer partition coefficient, expressed in mass fractions [Seuvre et al. 2006, Nongonierma et al. 2007]. The intensity (quantity) of flavour released from the dressing (I) was monitored as a function of time (t) and data obtained during storage were fitted to a 1st-order kinetic equation $I = I_0 \cdot EXP(-ct)$, where: I_0 – maximum intensity and c – decay rate constant for flavour release. A persistence index (PI) was calculated from the decay rate constant according to the equation $PI = 1/c$ [Giroux et al. 2007].

Sensory analysis. Odour intensity of the salad dressings was detected by orthonasal perception with the method using scale. The internal panel consisted of 12 assessors (8 females and 4 males), 20-24 years old selected according to PN-ISO 8586-1 [1996]. The reference samples contained buffer and were aromatized with diacetyl or (-)-α- -pinene at concentrations of: 0.00, 0.05 and 0.10 wt%. The appropriate odour intensity of the sample was quantified as: 0.0, 5.0 and 10 points, whereas intermediate values were calculated using linear interpolation. Samples were marked by a three-digit code and served in glass jars with metal lids. The equilibration of the salad dressings was done with the same procedures as were applied for studies of aroma compounds relative retention. Detected values of odour intensity were compared with vapour/liquid partition coefficients of diacetyl and (-)-α-pinene (K) in salad dressings. The partition coefficient (K) was calculated as the ratio of flavour compound concentrations in vapour and liquid phases at equilibrium, according to the method described by Kolb and Ettre [1997].

Statistical analysis. Three replicates were conducted for all measured parameters and data were statistically treated using STATISTICA for Windows (version 6.0, Copyright© Statsoft, Inc. 2003). A two-way ANOVA with interactions was applied to evaluate influence of the hydrocolloid type and concentration on vapour/matrix partition coefficient (K_{matrix}) of the odorants in studied salad dressings. Significant differences between means were identified by the least significant difference (LSD) procedure, using Tukey's multiple comparison test (α = 0.05). The extent of correlation between investigated parameters was determined by Pearson's correlation coefficient and Student's test was applied to estimate significance level.

RESULTS AND DISCUSSION

Effect of composition of model salad dressings on the relative retention of diacetyl and (-)-α-pinene. In all studied samples positive values of relative retention of hydrophilic diacetyl and hydrophobic (-)-α-pinene were recorded what means that the investigated aroma compounds were retained in reduced fat salad dressings (Fig. 1). Moreover, results from the two-way ANOVA indicate that hydrocolloid type and concentration as well as interactions affected significantly (α ≤ 0.001) vapour/matrix partition coefficient (K_{matrix}) of odorants in examined systems (Table 3). Relative retention of hydrophilic aroma compound was in the range of 47.6-77.8%, whereas this one of hydrophobic odorant ranged from 62.2 to 95.3% (Fig. 1). The higher (-)-α-pinene than diacetyl retention may be attributed to the fact that lipophilic (-)-α-pinene was dissolved in oil droplets (lipophilic environment) which are internal phase of the salad dressings and to be released in the headspace it had first to diffuse to the aqueous phase
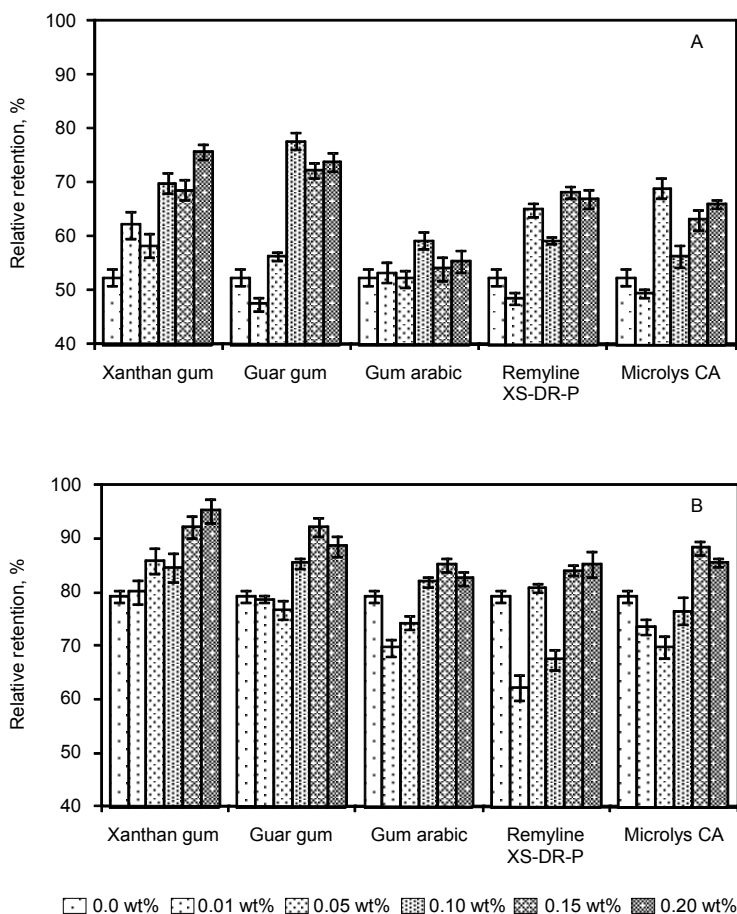

Fig. 1. Relative retention of diacetyl (A) and (-)-α-pinene (B) as a function
of hydrocolloid type and concentration in model salad dressings

Table 3. ANOVA table of the effects of hydrocolloid type and concentration on vapour/matrix partition coefficient (K_{matrix}) of diacetyl and (-)-α-pinene in model salad dressings

Attribute	Hydrocolloid type (HT)		Hydrocolloid concentration (HC)		(HT × HC)	
	F	df	F	df	F	df
K_{matrix}						
Diacetyl	71.48*	4	199.54*	5	48.87*	20
(-)-α-Pinene	748.23*	4	903.17*	5	138.39*	20

*Significance level α ≤ 0.001.

Table 4. Correlation values between relative retention of aroma compounds and hydrocolloid concentration in model salad dressings

Aroma compound	Xanthan gum	Guar gum	Gum arabic	Remyline XS-DR-P	Microlys CA
Diacetyl	0.902*	0.858*	0.466	0.816*	0.632
(-)-α-Pinene	0.966**	0.868*	0.737	0.544	0.722

*Significant correlations α ≤ 0.05.
**Significant correlations α ≤ 0.01.

(hydrophilic environment) [De Roos 1997]. In general, detected higher relative retention of the investigated flavour compounds with increasing concentration of hydrocolloids and the highest rise regarding diacetyl (52.4-75.8%, r = 0.902, α ≤ 0.05) and (-)-α-
-pinene (79.3-95.3%, r = 0.966, α ≤ 0.01) was found in dressings formed with xanthan gum (A1-A5; Fig. 1, Table 4). Moreover, significant correlation values (α ≤ 0.05) were noticed in samples aromatized with diacetyl and containing guar gum (B1-B5) and rice starch-Remyline XS-DR-P (D1-D5), whereas regarding (-)-α-pinene in dressings prepared with guar gum (B1-B5). Conversely, the lowest influence of hydrocolloid addition on the relative retention of diacetyl and (-)-α-pinene was observed in samples formed with gum arabic (Fig. 1). The relatively very high retention of (-)-α-pinene in dressings stabilized by xanthan gum may be attributed to several factors. First, decrease in volatility of (-)-α-pinene could be associated with the composition and physicochemical properties of interfacial membrane formed around oil droplets [Druaux and Voilley 1997, Dalgleish 2006]. Proteins adsorbed at the interface have been known that produce cationic emulsion droplets [Hu et al. 2005], therefore the anionic hydrocolloid xanthan gum could form with proteins electrostatic e.g. ionic bonds, which are stronger than hydrogen bonds or hydrophobic interactions that could be established between proteins and guar gum or starches [McClements et al. 2007, Sikorski 2007]. Secondly, polysaccharides can interact with lipophilic odorants in the bulk phase e.g. forming inclusion complexes and retain them in hydrophobic interiors due to hydrophobic interactions [Godshall 1997]. Xanthan gum has a more distinctive hydrophobic character compared to other hydrocolloids [Naknean and Meenune 2010] what could also contribute to the increase of retention of the non-polar aroma compound. On the other hand, another

mechanism probably prevailed regarding dressings formed with gum arabic. This polysaccharide being a complex mixture of hydrophilic carbohydrate and hydrophobic protein components [Paraskevopoulou et al. 2007, Lelon et al. 2010], probably in bigger extent was adsorbed at the oil-water interface, increasing thermodynamic stability of the emulsion (Table 2). However, its ability to retain aroma compounds in the bulk phase through steric phenomena was probably very low [Secouard et al. 2003]. The results concerning reduction of headspace diacetyl by xanthan and guar gums agree with the opinion shared by Rankin and Bodyfelt [1996] as well as Yven et al. [1998]. On the contrary, Lo et al. [1996] suggested that addition of guar gum in a commercial concentration range of 0.1 to 0.5% did not significantly change the distribution of diacetyl from that in products without guar gum. The results regarding decrease in diacetyl volatility are consistent with those reported by Boland et al. [2004] and partly with Boutboul et al. [2002] who also demonstrated that pregelatinised starches affected more retention of hydrophilic aroma compound than the acetylated ones. Conversely, Seuvre et al. [2006] reported that diacetyl was "repulsed" from mixtures containing waxy corn starch. Increase of diacetyl retention after hydrocolloids addition may be explained as the result of its adsorption at the oil/water interfacial region and specific interactions with carbohydrates [Pittia et al. 2005, Reineccius 2006]. Diacetyl has no ionizable groups but localized charges associated with the electron withdrawing effect of adjacent carbonyl group may provide δ– and δ+ regions that could function as binding sites [Rankin and Bodyfelt 1996]. On the other hand, carbohydrates depending on the molecular structure, offer ionizable groups, peptides or proteins or lipophilic sites for chemical interactions [Huang et al. 2001, Reineccius 2006]. Rankin and Bodyfelt [1996] reported that binding of diacetyl may result from: covalent bond formation (Schiff's base), hydrogen bonding, hydrophobic interactions or inclusion complexes. However, the presence of hydroxyl groups of hydrocolloids may suggest that the hydrogen bonding between hydrocolloids and diacetyl was mainly responsible for its registered relative retention in investigated salad dressings [Yven et al. 1998, Boutboul et al. 2002, Boland et al. 2004].

Effect of salad dressings characteristics on the release profile of diacetyl and (-)-α--pinene. In order to quantify release profile (expressed by persistence index) of diacetyl and (-)-α-pinene from salad dressings experimental data obtained during storage were fitted to a 1st-order kinetic equation. It was detected that (-)-α-pinene demonstrated higher values of persistence index than diacetyl (Fig. 2) what could be associated with higher resistance to mass transfer in oil droplets than in water [De Roos 1997]. The highest increase of the hydrophilic odorant persistence index, with increasing concentration of thickener, was identified in samples containing guar gum (B1-B5), whereas regarding (-)-α-pinene in dressings formed with xanthan gum (A1-A5). In contrast, the lowest rise of this parameter was evidenced in samples prepared with gum arabic (C1-C5) and rice starch – Remyline XS-DR-P (D1-D5) in relation to diacetyl and (-)-α--pinene, respectively (Fig. 2). The decrease of the rate of odorants release with increasing concentration of biopolymers was reported by Bakker et al. [1998] as well as Wendin and Hall [2001] and may be explained as the result of the decrease of effective diffusion. These findings are also in good agreement with the Maxwell and Mackie--Meares models demonstrated by Malone et al. [2000]. Moreover, it was found that in all investigated samples, the values of persistence index were positively and statistically significantly correlated with appropriate salad dressings viscosity (Table 5). The highest correlation values between these parameters regarding diacetyl (r = 0.940, α ≤ 0.01) and
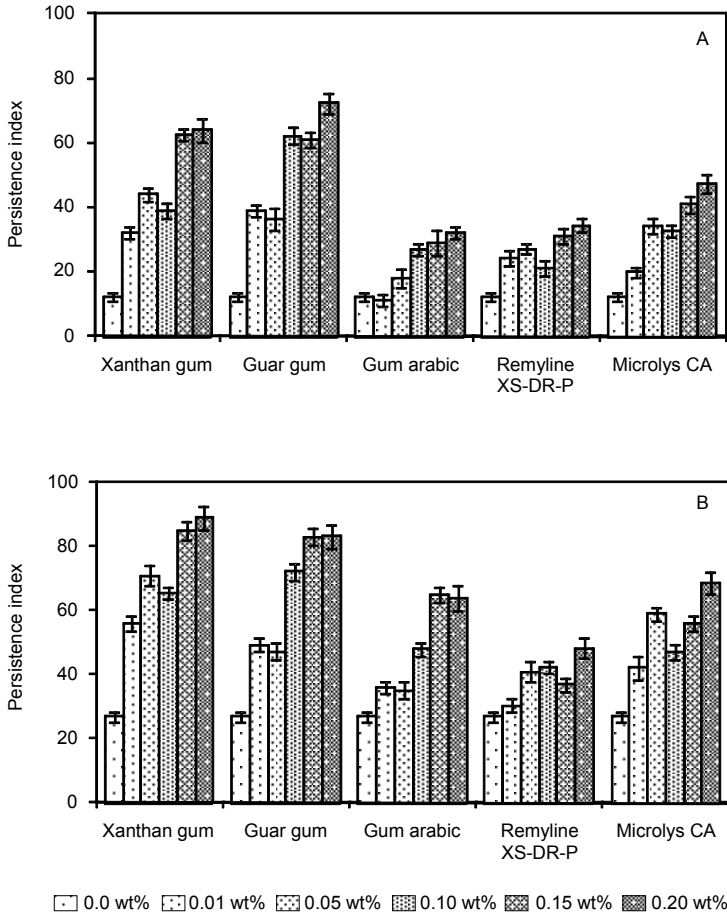
Fig. 2. Persistence index of diacetyl (A) and (-)-α-pinene (B) as a function
of hydrocolloid type and concentration in model salad dressings

(-)-α-pinene (r = 0.892, α ≤ 0.05) were detected in salad dressings prepared with potato starch-Microlys CA (E1-E5), whereas the lowest ones in samples stabilized by xanthan gum (A1-A5; r = 0.874, α ≤ 0.05) and gum arabic (C1-C5; r = 0.821, α ≤ 0.05) regarding diacetyl and (-)-α-pinene, respectively (Table 5). These results are consistent with those obtained by Roberts et al. [1996] and Secouard et al. [2003] and may be explained by the fact that presence of the entangled polymer network in thickened systems inhibited transport of aroma compounds from within the gel system to the surface, reducing diffusion of flavour molecules as predicted by the Stokes-Einstein equation [Bylaite et al. 2003, Boland et al. 2004]. Furthermore, significant correlation values were also noticed between persistence indexes and stability of the dressings measured towards creaming (Table 5). The highest correlation for diacetyl (r = 0.874, α ≤ 0.05) was found in samples stabilized by xanthan gum (A1-A5), whereas this one regarding (-)-α-pinene (r = 0.929, α ≤ 0.01) in dressings formed with rice starch-Remyline XS-DR-P (D1-D5).

Table 5. Correlation values between persistence indexes of aroma compounds and model salad
dressings characteristics

Hydrocolloid	Viscosity		Creaming stability		Droplet size	
	diacetyl	(-)-α-pinene	diacetyl	(-)-α-pinene	diacetyl	(-)-α-pinene
Xanthan gum	0.874*	0.838*	0.874*	0.865*	−0.518	−0.523
Guar gum	0.878*	0.885*	0.827*	0.870*	−0.827*	−0.769
Gum arabic	0.899*	0.821*	0.569	0.605	0.132	0.060
Remyline XS-DR-P	0.875*	0.872*	0.784	0.929**	−0.232	0.244
Microlys CA	0.940**	0.892*	0.861*	0.915*	−0.105	−0.102

*Significant correlations $\alpha \leq 0.05$.
**Significant correlations $\alpha \leq 0.01$.

In contrast, the lowest correlation values were detected in dressings containing gum
arabic (C1-C5) irrespectively of the aroma compound hydrophobicity (Table 5).
The influence of the creamed layer on the release rate of flavour compounds could be
associated with the fact that tightly packed emulsion droplets could form natural hin-
drance and retard diffusion of the aroma compounds in the headspace. The release pro-
file of (-)-α-pinene probably was also affected by the extent of phase separation of
the dressings, because with bigger particle-to-particle distance (Fig. 3), higher values
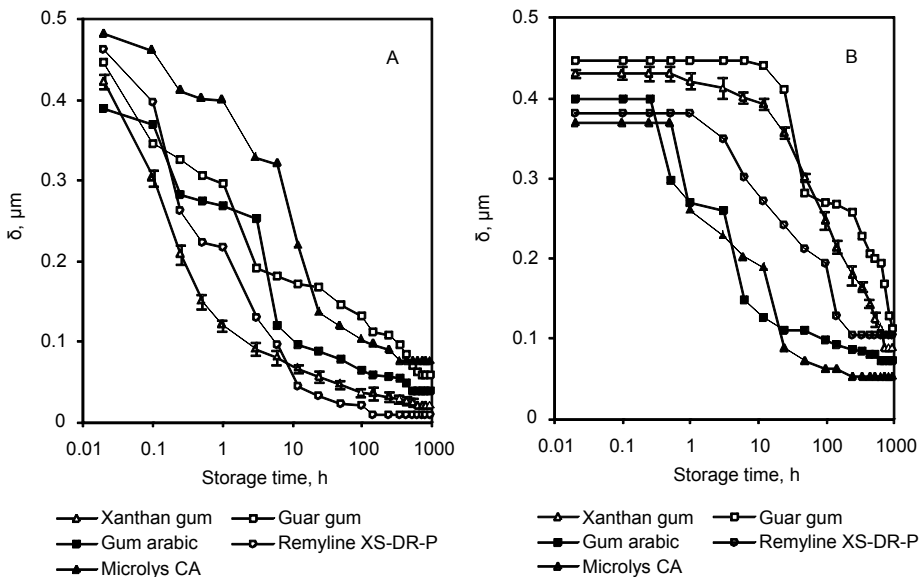

Fig. 3. Apparent particle-to-particle distance (δ) as a function of storage time for model
salad dressings containing 0.01 wt% (A) and 0.20 wt% (B) hydrocolloids. Typical
standard deviations are reported for salad dressings formed with xanthan gum

of persistence index were observed (Fig. 2). There was not clear dependence between mean droplet size of the emulsions (expressed as volume-surface average diameter- D[3,2]) and the rate of aroma compounds release (Table 5). It was reported, that increase of the droplet size leads to slower release of lipophilic flavour compounds, due to increase in the diffusional pathlength. On the other hand, changes in droplet diameter may also affect viscosity of the system and as the result release rate of both lipophilic and hydrophilic odorants [Harrison et al. 1997, Malone et al. 2000]. However, in this experiment, the phenomenon of flavour compounds release was also influenced by some of the other factors e.g. viscosity and interactions with biopolymers. Therefore, probably the presented results are only partly in good agreement with those demonstrated by Charles et al. [2000] and van Ruth et al. [2002] who concluded that oil droplet diameter had a considerably effect on the thermodynamic component of aroma release.

Comparison of odour intensity and vapour/liquid partition coefficient of diacetyl and (-)-α-pinene in model salad dressings. The relationships between vapour/ /liquid partition coefficients (K) and odour intensities of diacetyl and (-)-α-pinene in salad dressings are illustrated in Figure 4. It was registered that with increase values of vapour/liquid partition coefficient assessors also reported higher appropriate odour intensities of studied aroma compounds (Fig. 4, Table 6). Comparison of the measured instrumentally and detected orthonasally parameters showed higher correlation (R^2 = 0.7874) regarding (-)-α-pinene-flavoured salad dressings than in those aromatized with diacetyl (R^2 = 0.5149; Fig. 4). The differences between correlation values probably were associated with low detection threshold and specific sensory properties of diacetyl. Moreover, the relatively low correlation values may have been due to the fact that intensity of the aroma above dressings containing small concentration of thickener or those exhibiting low viscosity, was probably very abundant and assessors could have some problems to correctly use the scale what also reported González-Tomás et al. [2004]. On the other hand, taking into account hydrocolloid type, significant correlation values
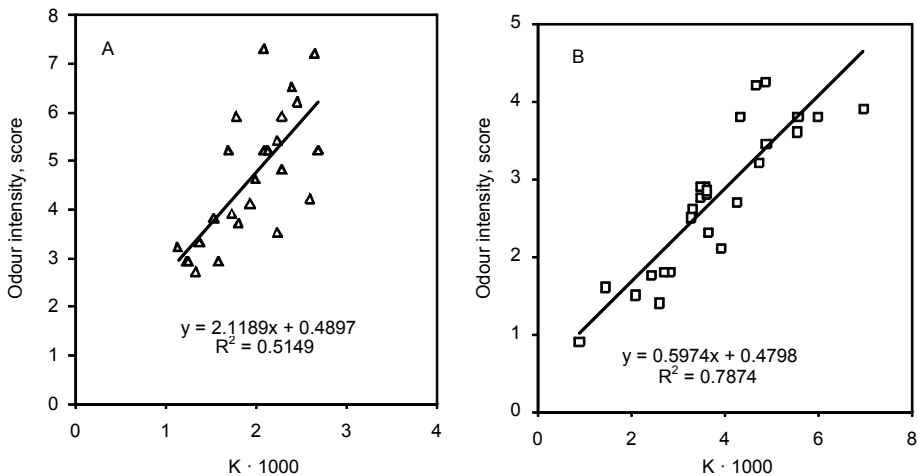

Fig. 4. Correlation between odour intensity and vapour/liquid partition coefficient of (A) diacetyl and (B) (-)-α-pinene in model salad dressings

Table 6. Correlation values between odour intensity and vapour/liquid partition coefficient of aroma compounds in model salad dressings

Aroma compound	Xanthan gum	Guar gum	Gum arabic	Remyline XS-DR-P	Microlys CA
Diacetyl	0.962**	0.931**	0.810*	0.601	0.487
(-)-α-Pinene	0.889*	0.858*	0.823*	0.718	0.758

*Significant correlations $\alpha \leq 0.05$.
**Significant correlations $\alpha \leq 0.01$.

($\alpha \leq 0.05$) were found in samples containing xanthan gum (A1-A5), guar gum (B1-B5) and gum arabic (C1-C5), irrespectively of the odorant hydrophobicity (Table 6). The results regarding release of hydrophilic odorant agree with those reported by Guyot et al. [1996] as well as Cook et al. [2003] and may suggest that in salad dressings exhibiting relatively high viscosity (Table 2) results received from instrumental analyses are comparable with those detected in sensory evaluations (Table 6).

CONCLUSIONS

1. Relative retention of hydrophilic diacetyl was in the range of 47.6-77.8%, whereas concerning hydrophobic (-)-α-pinene ranged from 62.2 to 95.3% and was clearly dependent on the hydrocolloid type and concentration.

2. Release profile of diacetyl and (-)-α-pinene mostly depended on the viscosity of salad dressings, whereas oil droplet diameter did not affect significantly this parameter.

3. Increase of hydrocolloid concentration in salad dressings markedly improved stability of investigated odorants particularly in samples prepared with xanthan gum or guar gum.

4. Odour intensity was higher correlated with vapour/liquid partition coefficient in salad dressings flavoured with (-)-α-pinene than in those aromatized with diacetyl.

5. It seems, that xanthan and guar gums may be utilized as very suitable thickeners by manufacturing salad dressings flavoured with both hydrophilic and hydrophobic aroma compounds, whereas modified rice and potato starches should be rather applied in systems aromatized with polar odorants.

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WPŁYW DODATKU HYDROKOLOIDÓW NA RETENCJĘ ORAZ PROFIL UWALNIANIA SIĘ DIACETYLU I (-)-α-PINENU W MODELOWYCH DRESSINGACH O ZREDUKOWANEJ ILOŚCI TŁUSZCZU

Wstęp. Sosy sałatkowe typu dressing ze względu na walory smakowe i odżywcze są stosowane bardzo często w wielu produktach spożywczych. Dressingi o składzie tradycyjnym zwykle zawierają znaczną ilość tłuszczu (20-65%). Zmniejszenie jego zawartości w takich układach najczęściej prowadzi do ich destabilizacji fizycznej oraz obniżenia właściwości sensorycznych, szczególnie w wyniku zwiększenia lotności lipofilowych substancji zapachowych w większości zidentyfikowanych w żywności. Celem badań była ocena wpływu rodzaju i stężenia hydrokoloidu na retencję oraz profil uwalniania się diacetylu oraz (-)-α-pinenu w modelowych dressingach o zmniejszonej ilości tłuszczu przygotowanych z użyciem kazeinianu sodu.

Materiał i metody. Materiałem do badań były modelowe dressingi zawierające 10% (w/w) tłuszczu roślinnego, które stabilizowano kazeinianem sodu (1% w/w) oraz hydrokoloidami (0,01-0,2% w/w): gumą ksantanową, gumą guar, gumą arabską, natywną poddaną wstępnemu żelowaniu skrobią ryżową – Remyline XS-DR-P oraz acetylowanym fosforanem dwuskrobiowym – Microlys CA (produkowanym ze skrobi ziemniaczanej). Próby aromatyzowano diacetylem lub (-)-α-pinenem (0,1% w/w). Zakres badań obejmował: charakterystykę dressingów (wielkość i rozkład cząstek zdyspergowanej fazy olejowej, stabilność kinetyczną i termodynamiczną, lepkość pozorną), pomiar stabilności substancji zapachowych (retencję względną, profil uwalniania) oraz ocenę intensywności zapachu metodą skalowania.

Wyniki. Wykazano istotną zależność ($\alpha \leq 0,001$) pomiędzy retencją względną badanych substancji zapachowych a rodzajem i stężeniem użytego hydrokoloidu. Stwierdzono również, że indeks trwałości badanych substancji zapachowych (odnoszony do profilu uwalniania) w większości analizowanych układów istotnie był skorelowany ($\alpha \leq 0,05$) z lepkością oraz stabilnością emulsji mierzoną w kierunku podstawania, natomiast w większości statystycznie nieistotnie – ze średnią średnicą cząstek fazy zdyspergowanej (D[3,2]). Korelację istotną ($\alpha \leq 0,05$) zauważono także pomiędzy intensywnością zapachu i współczynnikiem podziału substancji zapachowych (K) w dressingach zawierających gumę ksantanową, gumę guar oraz gumę arabską.

Wnioski. Guma ksantanowa i guma guar wyraźnie poprawiały stabilność hydrofilowego diacetylu i hydrofobowego (-)-α-pinenu w dressingach zawierających 10% (w/w) oleju rzepakowego, natomiast skrobia ryżowa – Remyline XS-DR-P oraz acetylowany fosforan dwuskrobiowy – Microlys CA zwiększały retencję hydrofilowej substancji zapachowej.

Słowa kluczowe: dressingi, hydrokoloidy, diacetyl, (-)-α-pinen, retencja, profil uwalniania