Physicochemical parameters of food emulsion products with summer savory (*Satureja hortensis* L.) essential oil

Anton Lazarov[1,*], *Stanko* Stankov[2], *Hafize* Fidan[2], *Vanya* Gandova[3], and *Albena* Stoyanova[1]

[1] Department of Technology of Tobacco, Sugar, Vegetable and Essential Oils, University of Food Technologies, 4002 Plovdiv, Bulgaria
[2] Department of Tourism and Culinary Management, University of Food Technologies, 4002 Plovdiv, Bulgaria
[3] Department of Analytical and Physical Chemistry, University of Food Technologies, 4002 Plovdiv, Bulgaria

Abstract. Summer savory (*Satureja hortensis* L.) is a plant source of essential oil belonging to the *Lamiaceae* family, widely used in the food industry. The present work aims to determine the physicochemical parameters of food emulsions containing the essential oil. The summer savory essential oil with main components carvacrol (63.71%), *γ*-terpinene (20.47%), and *p*-cymene (5.08%) was used in this study. Several model variants of emulsions have been developed with varying amounts of emulsifier (2 and 3% soy protein isolate), oil phase (20 and 40% sunflower oil), and essential oil (0.2 and 0.4%). The following physicochemical parameters of the emulsion were determined: Gibbs free energy, enthalpy, and entropy. This parameter was used to determine the thermal effect of the system. The process was determined as exothermic with the negative enthalpy. Emulsions prepared with 2% soybean protein isolate, 40% oil phase, and 0.4% essential oil were characterized by some good results with high equilibrium constants and high Gibbs energies. Model variants of salad diet dressings had also been developed, with 0.2 and 0.3% essential oil, which were qualified by sensory analysis. The overall evaluation of salad dressings showed that the evaluators perceived with best sensory properties in those with 0.2% essential oil.

1 Introduction

The summer savory (*Satureja hortensis* L.), family Lamiaceae originates from the lands around the Mediterranean Sea and the Middle East, where it has spread worldwide. Today it is a popular essential oil plant cultivated in many countries of Europe, North America, and Central Asia [1, 2].

Summer savory is a short plant that grows in dry, sunny places. They reach 15-50 cm in height and have small leaves 1 - 3 cm long. The flowers grow from the stem in circular racemes and are white to pink-violet. The stem is straight, 30 - 45 cm high, four-edged, and branched from the base [1, 2].

Summer savory essential oil is a yellow to reddish-yellow liquid with a spicy, characteristic savory odor and a sharp, mildly spicy taste. The main components are carvacrol (14.3 - 77.6%) and thymol (0.01 - 46.0%). Also found: linalool (about 26.0%), *γ*-terpinene (7.6 - 52.9%), *p*-cymene (2.8 - 16.0%), *α*-pinene (0.1 - 2.1%), *α*-terpinene (0.6-5.3%), *β*-pinene, myrcene, *etc*. [1, 3 - 11].

The oil finds application in food products [12, 13] due to its antimicrobial [3, 6, 10 - 17] and antioxidant properties [4, 5, 7, 12, 14, 17-19].

* Corresponding author: antondlazarov@gmail.com

The present work aims to develop food emulsion products with essential oil of summer savory and to monitor some of their physicochemical parameters.

2 Materials and methods

2.1 Raw materials

Summer savory essential oil was used in this study, provided by an essential oil producer in the vicinity of the city of Plovdiv.

Eighteen emulsions with different oil and water phase ratios were developed and presented in Table 1.

2.2 Determination of thermodynamic parameters

Three series of emulsions were prepared. The first sample was obtained with oil, water, and soybean protein isolate (SPI). Second – with addition of 0.2% v/v essential oil and third with 0.4% v/v.

The content of the essential oil used in the samples was determined according to our preliminary unpublished data. The smaller essential oil amounts were not influencing the smell of the final product, and with more significant amounts – a rougher smell and taste of the emulsions were obtained.

Sunflower oil was used for all emulsion preparation as a stabilizer, and was added SPI in three concentrations (Table 1). The sunflower oil was slowly added and homogenized for 2 min by mixing, and the essential oil was added in a continuous phase [20].

Table. 1 Composition of emulsions - pure and with the addition of essential oil

Emulsion	Compositions in mass, %		
No	Sunflower oil	Water	SPI
Control emulsions			
1	20	79	1
2	40	59	1
3	20	78	2
4	40	58	2
5	20	77	3
6	40	57	3
addition of 0.2% essential oil			
7	20	79	1
8	40	59	1
9	20	78	2
10	40	58	2
11	20	77	3
12	40	57	3
addition of 0.4% essential oil			
13	20	79	1
14	40	59	1
15	20	78	2
16	40	58	2
17	20	77	3
18	40	57	3

With spectrophotometer measurements of absorbance equilibrium constant was estimated for all samples using the so-called "dilution method" [21]. The investigations were performed using a Camspec M107 UV/VIS spectrophotometer. Measurements were done at 385 nm. The following equation calculated the Gibbs free energy

$$\Delta G = -RT \ln K \qquad (1)$$

where:
R is the universal gas constant (R = 8.314 J/K. mol),
T is the absolute temperature (K), and
K is equilibrium constant.

The enthalpy of emulsions calculated by applying the Vant-Hoff equation.

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta H}{R} \qquad (2)$$

where:
ΔH is enthalpy of formation (kJ/mol).

The entropy was determined by classical thermodynamic equation (3) [20]:

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \qquad (3)$$

where:
ΔS is entropy (kJ/(K. mol)).

2.3 Salad dressings

The salad dressings are prepared using the following technology: The necessary raw materials are placed in a beaker and subjected to pureeing using a blender (SOLAC BA5607) at maximum speed for 5 min.

The essential oil quantity was determined according to the yield of the dressing (160 g) and are based on our preliminary unpublished data – at higher concentrations, the residual aftertaste was unpleasant, while at lower concentrations – the unpleasant effect in taste was not determined.

2.4 Analysis of salad dressings

pH measurement was provided by direct pH meter.

Sensory assessment – 20 trained assessors conducted the sensory evaluation. The tested products were at a temperature of 10 ± 1°C, and equal amounts (5 g) of the sample were placed in plastic cups coded with three-digit random numbers and provided to the assessors in random order. The evaluation conditions are standard – at room temperature (25 ± 1°C) and in daylight.

The food products' characteristics and specific indicators were defined: color, smell, taste, aroma, consistency, and residual taste.

Each indicator is quantified in terms of perceptual intensity (amplitude) with a numerical value from 0 to 10, corresponding from "no stimulus" to "extremely strong stimulation."

A separate scale is made for each indicator, and after mathematical processing, the obtained results are presented graphically.

The sensory profiles of the products are presented.

2.5 Statistical analysis

The experiment was provided with three parallel analysis and presented as ± standard deviation values. Statistical analysis was carried out using Excel software.

3 Results and discussion

The summer savory essential oil had a carvacrol content of 63.71% [2, 16].

The carvacrol content determines the typical aroma profile of savory oil and the broad spectrum of its application in food practice [2].

The thermodynamic parameters, the Gibbs free energies, enthalpies, and entropies of all emulsions were calculated, and their values are presented in Table 2.

The classical thermodynamics equations were used [22]. The first equilibrium constant (K) was estimated. K values differ from 6.15 to 15.088, but all were positive. In the Van't Hoff equation, lnK is used. The values less than 1 (K < 1) after logarithm presented negative values, and this result connected with an unstable system, but in this case, all K > 1.

The Gibbs free energy used for the criterion of emulsion stability was calculated using the classical thermodynamic equation. The emulsification process influences the oil phase and protein quantity. Emulsions prepared with 2% soybean protein isolate and 40% oil phase showed good results with high equilibrium constants and Gibbs energies. The hydrophobic interactions of the high oil phase stabilized the emulsions, so emulsions prepared with 40% oil were more stable. Emulsions with a high amount of protein and a lower oil phase were characterized by good stability, too, since there were also hydrophobic interactions in the proteins that stabilized them.

Table 2. Equilibrium constant and thermodynamic parameters

K	ΔG	ΔH	ΔS
Control emulsions			
7.738± 0.07	-5.069± 0.06	-19.545± 0.01	-0.049± 0.09
8.563± 0.04	-5.320± 0.11	-19.654± 0.12	-0.048± 0.07
9.863± 0.02	-5.671± 0.07	-19.806± 0.10	-0.047± 0.02
14.588± 0.02	-6.640± 0.04	-20.227± 0.08	-0.046± 0.08
11.800± 0.05	-6.115± 0.01	-19.999± 0.04	-0.047± 0.06
7.975± 0.06	-5.144± 0.01	-19.577± 0.01	-0.048± 0.08
Addition of 0.2% essential oil			
6.150± 0.01	-4.500± 0.05	-19.297± 0.02	-0.050± 0.04
11.613± 0.08	-6.075± 0.09	-19.981± 0.06	-0.047± 0.07
10.900± 0.01	-5.918± 0.12	-19.913± 0.02	-0.047± 0.03
15.088± 0.02	-6.724± 0.02	-20.263± 0.01	-0.045± 0.01
14.750± 0.02	-6.661± 0.02	-20.239± 0.01	-0.046±0.03
11.750± 0.07	-6.104± 0.01	-19.994± 0.01	-0.047± 0.02
Addition of 0.4% essential oil			
7.463± 0.11	-4.980± 0.02	-19.506± 0.04	-0.049± 0.06
8.388 ±0.01	-5.269± 0.12	-19.631± 0.09	-0.048± 0.03
8.763 ±0.08	-5.378± 0.05	-19.678± 0.02	-0.048± 0.07
16.050± 0.06	-6.918± 0.09	-20.260± 0.02	-0.045± 0.04
15.933± 0.01	-6.898± 0.07	-20.252± 0.13	-0.045± 0.04
9.513± 0.03	-5.581± 0.01	-19.767± 0.07	-0.048± 0.09

Legend: K - equilibrium constant; ΔG - Gibbs free energy, kJ/mol; ΔH - enthalpy, kJ/mol; ΔG - entropy, kJ/(K.mol)

Emulsions prepared by adding essential oil presented some highest values of equilibrium constant and Gibbs energies. The emulsions' stability was increased when the ΔG increased in negative value. Different emulsions showed different energy values; the highest values were observed for those prepared with 0.4% essential oil. The results obtained in this study showed that all processes in emulsions were spontaneous ($\Delta G < 0$).

Subsequently, by equation (Van't Hoff) the enthalpy of emulsions was calculated and obtained as negative. This parameter was used for determining the system's thermal effect, and with the negative enthalpy, the process was determined as exothermic. Entropy is the parameter that presents the order in emulsions. The foods usually observed minimal negative values connected with phase separation of emulsion.

A model recipe of dietary salad dressing was developed, including summer savory essential oil. The model recipe with the inclusion of essential oil and products purchased from the commercial market is presented in Table 3.

Table 3. Model recipes of dietary salad dressings with summer savory essential oil

Raw, g	Control sample	Sample 0.2%	Sample 0.3%
Pine nuts	0.100	0.100	0.100
Lemon juice	0.024	0.024	0.024
Water	0.035	0.035	0.035
NaCl	0.001	0.001	0.001
Essential oil	-	0.032	0.048

The results of the chemical analysis were directly related to the sensory evaluation of the dressings obtained. The presence of carvacrol is associated with the odor typical of savory, which is why the essential oil obtained from it is a suitable flavouring in roasted meat and vegetable dishes, soft chews, soft drinks, chewing gum, and sauces. Due to its specific aroma and taste, its application in the food industry is limited to lower ranges of quantitative participation.

Dietary salad dressings were used to flavor various meat products and were prepared several hours before use. The application of cold dressings, both in the composition of cold dishes and in warm vegetable foods, is based on the refreshing and complementary effect when combining them.

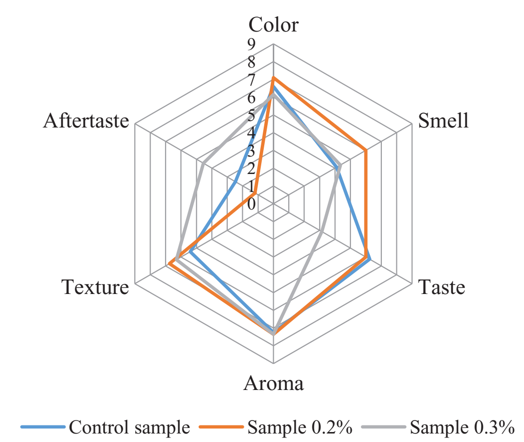

Fig. 1. Sensory profiles of dietary salad dressings with summer savory essential oil.

The results of the sensory evaluations of the assortments are shown in Fig. 1. With the most intense smell, evaluators defined a dressing containing 0.2% essential oil.

The ratings of the control and dressing samples with 0.2% essential oil flavouring are close, with the lowest being for the 0.3% dressing. The sour and salty taste is rated equally for all three assortments due to the identical amounts of salt and citric acid used in their composition. After consumption, the aftertaste of the dressing with 0.3% essential oil is more pronounced, and the bitter aftertaste is hardly noticeable in all three assortments.

The overall perception of the three products showed that the evaluators perceived the one with 0.2% essential oil as the best.

4 Conclusion

Different variants of food emulsions with summer savory essential oil (0.2% and 0.4%) have been development. Physicochemical parameters Gibbs free energy, enthalpy, and entropy were calculated. The results showed that these food products usually observed minimal negative values connected with phase separation of emulsion.

In this study, dietary salad dressings have been developed with the participation of summer savory essential oil in amounts of 0.2 and 0.3%.

The general perception of the dressings results showed that the summer savory essential oil in the amount of 0.2% was a suitable technological ingredient for producing dietary salad dressings, improving their sensory evaluation.

References

1. I. Fierascu, C.-E. Dinu-Pirvu, R. Claudiu Fierascu, B. Velescu, V. Anuta, A. Ortan, V. Jinga, Molecules. **23**, 10 (2018)
2. A. Stoyanova, *A Guide for the specialist in the aromatic industry* (UFT, Plovdiv, 2022) [In Bulgarian]
3. Y. Alan, A. Savci, B. Çakmak, H. Kurt, Yüzüncü Yıl Üniversitesi Fen Bilimleri Enstitüsü Dergisi. **21**, 167 (2016)
4. A. Alizadeh, M. Khoshkhui, K. Javidnia, O. Firuzi, E. Tafazoli, A. Khalighi, J. Med. Plants Res. **4**, 33 (2010)
5. D. Chambre, C. Moisa, A. Lupitu, L. Copolovici, G. Pop, D.-M. Copolovici, Sci. Rep. **10**, 21322 (2020)
6. M. Farzaneh, H. Kiani, R. Sharifi, M. Reisi, J. Hadian, Postharvest Biol. Technol. **109**, 145 (2015)
7. A. Fathi, M. Sahari, M. Barzega, H. Naghdi Badi, J. Med. Plants. **1**, 51 (2013)
8. D. Katar, O. Kacar, N. Kara, Z. Aytaç, E. Göksu, S. Kara, N. Katar, S. Erbas, I. Telci, M. Elmastas, J. Appl. Res. Med. Arom. Plants. **7**, 131 (2017)
9. S. Mohtashami, V. Rowshan, L. Tabrizi, M. Babalar, A. Ghani, Ind. Crop Prod. **111**, 226 (2018)
10. A. Nabigol. J. Horticult, Sci. Biotechnol. **86**, 371 (2011)
11. A. Sharifzadeh, A. Khosravi, S. Ahmadian, Microb. Pathog. **96**, 1 (2016)
12. D. Djenane, M. Aboudaoub, M. Amine Ferhatc, A. Ouelhadja, A. Ariño, J. Essent. Oil Res. **31**, 444 (2019)
13. G. Ghalamkari, M. Toghyani, E. Tavalaeian, N. Landy, Z. Ghalamkari, H. Radnezhad, Afr. J. Biotechnol. **10**, 13318 (2011)
14. D. Abou Bakera, M. Al-Moghazyb, A. ElSayeda. Bioorg. Chem. **95**, 103559 (2020)
15. D. Blažeković, V. Kakurinov, S. Stojanovski, Acta Biologica. **17**, 618 (2010)
16. L. Jirovetz, K. Wlcek, G. Buchbauer, V. Gochev, T. Girova, A. Stoyanova, E. Schmidt, Int. J. Essent. Oil Therap. **1**, 153 (2007)
17. S. Valizadeh, T. Fakheri, R. Mahmoudi, F. Katiraee; P. Gajarbeygi. Biotechnol. Health Sci. **1**, e24733 (2014)
18. G. Yaldiz, M. Çamlica, Indian J. Pharm. Educ. Res. **51**, 258 (2017)
19. N. Yanishlieva, E. Marinova. Nahrung. **39**, 458 (1995)
20. V. Gandova, I. Genov, Food Sci. Appl. Biotechnol. **3**, 9 (2019)
21. L. Wang, M. Peng, Y. Zhu, S. Tong, X. Cao, X. Xu and J. Yu, Iranian J. Pharm. Res. **13**, 1157 (2014)
22. C. Kendrow, J.-C. Baum, C.-J. Marzzacco. J. Chem. Educ. **86**, 1330 (2009)