TECHNICAL UNIVERSITY OF MOLDOVA

As a manuscript
C.Z.U.:
665.347.8:[634.743+634.17+582.734.4](043)

POPOVICI VIOLINA

STABILIZATION OF VEGETABLE OILS WITH BIOACTIVE COMPOUNDS FROM RENEWABLE SOURCES

253.06 Biological and chemical technologies in the food industry

Summary of the doctoral thesis in engineering sciences

CHISINAU 2022

The thesis was developed within the Department of Food Technology, Faculty of Food Technology, Technical University of Moldova. Some of the tests were performed at the Institute of Bioanalytical Chemistry, Faculty of Chemistry and Minerology, Leipzig University, Germany (Erasmus+).

Scientific supervisor / consultant:
STURZA Rodica, dr. hab., prof. univ.

Official referents:
GHENDOV-MOȘANU Aliona, dr.hab.conf.univ., TUM
COVALIOV Olga, dr.hab.prof.univ., Institute of Chemistry
NISTOR Ileana-Denisa, prof.dr.ing., Vasile Alecsandri University of Bacau, Romania

Composition of the doctoral committee:
1. TATAROV Pavel, **chairman,** PhD, hab. in technical sciences, university professor, TUM
2. GUREV Angela, **scientific secretary**, PhD, associate professor, TUM
3. STURZA Rodica, **member**, PhD, hab., university professor, TUM
4. ȚÎSLINSCAIA Natalia, **member**, PhD, associate professor, TUM
5. GHENDOV-MOȘANU Aliona, **referent,** PhD, hab., associate professor, TUM
6. COVALIOV Olga, **referent,** PhD, hab., university professor, Chemistry institute
7. NISTOR Ileana-Denisa, **referent,** prof.dr.ing., Vasile Alecsandri University of Bacau, Romania

The defense will take place on _17__June____ 2022_, at 14.00_ in the meeting of the Doctoral Committee within the Technical University of Moldova, FFT, 9/9 Studentilor Street, study block no. 5, aud. 120, MD-2045, Chisinau, Republic of Moldova.

The doctoral thesis and the abstract can be consulted at the library of the Technical University of Moldova and on the ANACEC website (www.anacip.md).
The abstract was sent on __16__ May__ 2022.

Scientific Secretary of the Doctoral Committee,
GUREV Angela, PhD, associate professor

Scientific supervisor,
STURZA Rodica, PhD, hab. university professor

Author
POPOVICI Violina

© POPOVICI Violina, 2022

CONTENTS

RESEARCH CONCEPTUAL GUIDELINES

The motivation for choosing the subject. The continuous development of society, globalization inevitably affects the food industry and the food production process. High quality foods are obtained through complex processes, and all the processes they undergo are both negatively and positively influencing the finished product, which would lead to changes in their quality. The major cause of food spoilage is oxidation (Siró et al., 2008; Kaur et al., 2011).

The oxidation of lipids in food is a complex process that is influenced by various factors such as: the chemical structure of the food; physical condition; the quantity and quality of substances with an antioxidant role in food; how the food is processed, packaged and stored.

One of the current strategies used in the food industry to inhibit the oxidation of lipids is the use of antioxidants. (Popovici et al., 2019b). Antioxidants are substances that prolong the shelf life of food by protecting it from various changes that occur as a result of the oxidation process.

The topicality and the importance of the topic. Nowadays, with the development of society and the growing needs of consumers in the food industry, there is a need to improve the sensory and organoleptic qualities of food, to obtain foods with increased biological value, oxidative and microbiological stability; safe food with an optimal shelf life.

Berries are rich in antioxidants, vitamins and minerals important from a nutritional point of view (Roman et al., 2013). In this research we have studied especially sea buckthorn fruits, hawthorn and rosehips, which represent a natural concentrate of vitamins (C, P, B_1, B_2, E, K), carotenoids, folic acid, isoramnetol, unsaturated fatty acids and phytosterols, nicotinic acid, volatile oil etc.(Crețu et al., 2005).

Regarding this paper, several researches was carried out on the evaluation of the oxidative stability of lipophilic extracts as well as functional foods with high lipid content within the Technical University of Moldova and other laboratories equipped for this purpose (Haritonov et al., 2018; Ghendov-Mosanu et al., 2020a; 2020b; Sturza et al., 2020; Ghendov-Moşanu et al., 2020; Sandulachi et al., 2021).

Purpose and objectives of the research consists in elucidating the chemical changes that take place during lipid oxidation, stabilizing vegetable oils and assessing the impact of lipophilic extracts on the oxidative stability of complex food products by optimizing manufacturing technology.

The general objective of the paper is to assess the stability of vegetable oils in dependence on chemical compounds that form in the process of lipid oxidation, stabilization of vegetable oils and assessing the impact of lipophilic extracts on oxidative stability of complex foods by optimizing manufacturing technology.

To achieve this goal, the following **specific objectives** have been proposed:

- Analysis of the lipid oxidation mechanisms of vegetable oils, including the determination of chemical changes that occur during lipid oxidation in complex foods.
- Development of technology for obtaining lipophilic extracts from sea buckthorn, hawthorn and rosehip fruits; characterization of the chemical composition and CIElab chromatic parameters.
- Stabilization of vegetable oils with lipophilic extracts of sea buckthorn, hawthorn and rosehip.
- Development of technologies for obtaining complex food products with the addition of lipophilic extracts and plant powders from sea buckthorn, hawthorn and rosehip.
- Characterization of the complex of bioactive compounds from complex fortified food products; evaluation of antioxidant activity in *in vitro* digestion conditions.
- Optimization of the manufacturing technology of complex food products based on their physico-chemical and sensory characteristics.
- Evaluation of the influence of lipophilic extracts on the oxidative stability in time of complex foods with high lipid content.

The research hypothesis is that vegetable oils and foods with high lipid content can be stabilized against the oxidation process based on biologically active compounds from natural sources.

Synthesis of the research methodology and justification of the chosen research methods. Traditional and high-performance physico-chemical methods were applied to carry out the research. For the characterization of lipophilic extracts were applied: physico-chemical quality indicators, HPLC. The antioxidant capacity was determined for the extracts obtained (DPPH, HPSA methods), and for the complex products developed. The tandem mass spectrometry method (LC-MS/MS) was applied to identify lipid oxidation products, for *in situ* research, sensory, physico-chemical methods and UV/Vis spectroscopy were used.

The theoretical importance and scientific innovation of the paper consists in arguing the possibility of using bioactive compounds from renewable sources of sea buckthorn, hawthorn, rosehip, identifying the optimal conditions for obtaining lipophilic extracts from local plant sources with high antioxidant potential; arguing the possibility of using lipophilic extracts and local plant powders to obtain complex food products. The problem has been solved by conducting the following research:

- It was shown that during the storage of sunflower oil the process of lipid self-oxidation takes place through the formation and decomposition of hydroperoxides and the formation of secondary oxidation products, predominantly the formation of aldehydes with various molecular weights. It has been found that the loss of quality of sunflower oil occurs over time following the formation of about 60 low molecular weight aldehydes;

- Was argued the possibility of using biologically active compounds from renewable plant sources of local origin to obtain lipophilic extracts with increased antioxidant potential
- Was elucidated the influence of lipophilic extracts on the oxidative stability of vegetable oils and the antioxidant activity, CIELab chromatic parameters, quality indicators of lipophilic extracts were determined;
- Was argued theoretically and experimentally the increased antioxidant potential of plant powders from local plant sources and lipophilic extracts obtained by analyzing quality indicators, antioxidant activity and CIELab chromatic parameters.
- Was obtained new scientific information about the mechanism and dynamics of the formation of lipid oxidation products during oxidative processes.
- Was developed complex manufacturing technologies with increased antioxidant potential for oxidative stabilization of food.

Theoretical significance: For the first time, the methodology for stabilizing vegetable oils from local renewable sources was developed; were obtained oils with lipophilic extracts from local plant sources with increased antioxidant potential; tandem mass spectrometry was used for the first time to determine the dynamics of lipid oxidation formation.

The work was carried out based on research and experience gained in carrying out the following national and international projects: **IntelWastes 2SOFT/1.2 /83** (2020-2022); **20.80009.5107.09** Improving food quality and safety through biotechnology and food engineering (2020-2023); **19.80012.51.09A** Functional products obtained by valorification of natural texturing agents and carotenoids (2019); **18.51.07.01A_PS** Diminishing the contamination of raw materials and food products with pathogenic microorganisms (2018-2019); **COST CA Action CA 15136** European Network to advance carotenoid research and applications in agro-food and health (EUROCAROTEN) (2018-2020); **Scholarship of Excellence of the World Federation of Scientists**. Project "The antioxidant capacity of local berries lipophilic extracts of sea buckthorn (*Hippophae rhamnoides L.),* rosehip (Rosa Canina L.), hawthorn (Crataegus)", FMS (June 2019 - May 2020); **Erasmus + Scholarship** Project "Evaluation of oxidized Phosphatidylethanolamine and Phosphatidylcholine plasmalogens", Institute of Bioanalytical Chemistry, Faculty of Chemistry and Minerology, Leipzig University, Germany (October 2020 - February 2021).

Applicative value of the work: Based on the experimental results obtained, were developed procedures for obtaining lipophilic extracts from renewable plant sources; Technologies for the manufacture of the following complex foods have been developed:

- Sauce with high lipid content based on lipophilic extracts from sea buckthorn, rosehip and hawthorn;
- Mini-cakes with sea buckthorn, hawthorn and rosehip powder;

- Donuts with sea buckthorn, hawthorn and rosehip powder;
- Candies with sea buckthorn, hawthorn and rosehips powder;

Was elucidated the impact of plant powders, lipophilic extracts of sea buckthorn, hawthorn and rosehip on quality indicators, sensory parameters, shelf life, antioxidant activity and oxidative stability of complex food products.

Approval of the paper at national and international scientific forums. The results obtained during the paper were presented and discussed at 17 national and international conferences: International Conference "Modern Technologies in the Food Industry", Chisinau (2018); "EuroAliment" International Symposium, Galați, Romania (2019); Conference of students, masters and doctoral students, Chisinau (2016, 2019, 2020); National Session of Student Scientific Communications, Natural and Exact Sciences, USM, Chisinau (2017); International Conference "Achievements and Perspectives of Modern Chemistry", Chisinau (2019); Franco-Romanian Colloquium on Applied Chemistry - COFrRoCA, Bacău, Romania (2018); International Conference "Achievements And Perspectives Of Modern Chemistry dedicated to the 60th anniversary of the foundation of the Institute of Chemistry", Chisinau (2019); International Conference "Days of the Academy of Technical Sciences of Romania", Chisinau (2019); International Scientific and Practical Conference "Resource and Energy Saving Technologies of Production and Packing of Food Products as the Main Fundamentals of Their Competitiveness", Kyiv, Ukraine (2019); International Conference "Prospects and problems of research and education integration into the European area", Cahul (2021); International Conference "Constructive Design and Technological Optimization in Machine Building", Bacău, Romania (2021); International Salon of Scientific Research, Innovation and Inventions PRO INVENT, Cluj-Napoca, Romania (2018); International Salon of Scientific Research, Innovation and Inventions INVENTICA, Iași, Romania (2018); Exhibition of Innovation and Research - UGAL, Galați, Romania (2019); International Specialized Exhibition INFOINVENT, Chisinau (2019); European Exhibition of Creativity and Innovation EUROINVENT, Iași, Romania (2021).

Thesis publications. The results of the research and the issues addressed in the thesis have been published in 23 scientific papers, including 5 scientific articles, 1 patent, 1 patent application, 16 articles and abstracts in collections of national and international scientific events.

Summary of thesis chapters. The paper is exposed on 112 pages and includes the following chapters: annotation in Romanian, Russian and English, introduction, 4 chapters, conclusions and recommendations, bibliography with 291 sources and 3 annexes. The work is illustrated with 38 tables and 41 figures.

Keywords: vegetable oil, lipophilic extract, oxidative stability, complex food, quality.

THESIS CONTENT

1. The evolution of the oxidative stability of vegetable oils and the lipid fraction in complex foods

Chapter 1 shows the general characteristics of vegetable oils, oxidative stability and the oxidation mechanism of lipids; the factors that affect the mechanism of lipid oxidation are exposed; the impact of lipid oxidation on the sensory properties of complex foods; characteristic of the antioxidant complex in local horticultural products.

Oxidative stability is an important indicator to determine oil quality and shelf life (Hamilton, 1994) because low molecular weight compounds (LPPs) that are produced during oxidation. The oxidation process is one of the most common processes of food spoilage, especially those with high lipid content. This process can be slowed down with the help of bioactive compounds with antioxidant capacity, which are found in abundance in local fruits and berries.

The use of local raw materials is a great advantage to significantly reduce production prices, so that the market price of the final product will be affordable. The possibility of developing the technology for obtaining lipophilic extracts from vegetable powders with antioxidant capacity is a good possibility to replace synthetic additives with natural ones in order to obtain complex food that are safe and with a longer shelf life.

2. Materials and methods

Chapter 2 describes the raw materials and reagents used in the research; are described the physico-chemical methods for the analysis of lipophilic extracts from plant sources and for the identification of lipid oxidation products; are described the methodology for determining the quality indicators of lipophilic extracts and complex food products developed.

The main research objects are vegetable oils, berries: sea buckthorn, hawthorn and rosehip harvested during the years 2016-2019, the lipophilic extracts obtained, as well as complex foods made with the addition of extracts and/or powders from berries.

3. Research on the physico-chemical characteristics and antioxidant potential of lipophilic extracts

Chapter 3 describes the technology for obtaining lipophilic extracts from renewable plant sources; were determined the quality indicators, chromatic parameters, antioxidant activity and oxidative stability of the extracts during storage; were investigated the intensity of the formation of lipid oxidation products over time.

3.1. Physico-chemical characteristic of lipophilic extracts from berries

In the lipophilic extracts of rosehip, sea buckthorn, hawthorn analyzed, the content of chlorophyll α and *β*, *β*-carotene, lycopene and zeaxanthin was determined spectrophotometrically. The results obtained show that the lipophilic extracts of rosehip, hawthorn and sea buckthorn researched are characterized by a rich carotenoid content. ELM contains an essential amount of β-carotene (17.04 mg / L), while ELP contains 1.6 times less and ELC 2.6 times less. After a shelf life of 3 months, the β-carotene content decreased for ELM by 15%, ELC by 5% and ELP by 30%. After 3 months of storage of lipophilic extracts, the amount of carotenoids changed non-essential due to storage conditions. Quantitative changes in carotenoids can occur due to oxidative processes that occur along the way, but are slowed down if the extracts are stored in airtight containers to exclude access to oxygen, at low temperatures and in dark spaces.

The *L*-ascorbic acid content determined for all three types of extracts (fig. 3.1) was close to the results previously reported by other researchers. The differences can be attributed to cultivation conditions, maturity, ascorbic acid extraction methods and methods for its determination (Hernández et al., 2006). The values obtained are for sea buckthorn extract - 19.32 ± 0.70 mg/100g plant; hawthorn extract - 12.04±0.70 mg/100g plant; rosehip extract - 10.75±0.70 mg/100g plant.

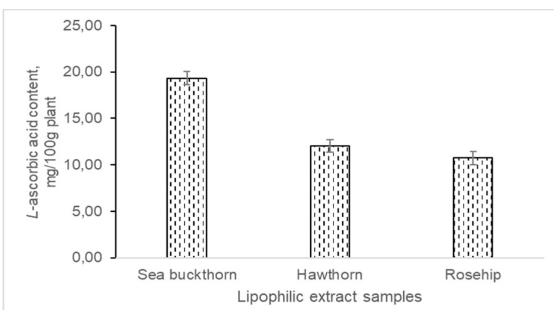


Fig. 3.1. *L*-ascorbic acid content in researched lipophilic extracts of sea buckthorn, hawthorn and rosehip

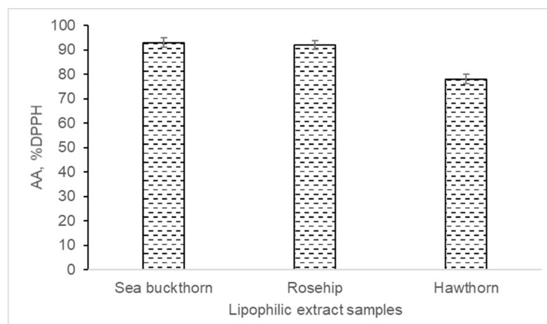


Fig. 3.2. Antioxidant activity in lipophilic extracts of sea buckthorn, hawthorn and rosehip

In order to estimate the antioxidant potential of the lipophilic extracts from studied plant sources, the analysis of the antioxidant activity was performed with the help of the free radical DPPH, and the obtained results are presented in fig.3.2.

Oxidative processes can be evaluated with the help of lipid quality indicators, which characterize the state of lipid matter. For this reason, it is important to study the evolution of physico-chemical and quality parameters of oils with lipophilic extracts during storage for 3 months. The results obtained are presented in table 3.1:

After a period of 3 months of storage, there is an increase in AV values for all samples examined for oil and lipophilic extracts, but which do not exceed the maximum value of 0.6 mg KOH/g oil, provided according to the technical regulations for vegetable oil.

Table 3.1. Quality and safety indicators of oils with lipophilic extracts of berries ***

Nr.	Quality parameter**		PM	ELM	ELC	ELP
1	**Acid Value, mg KOH/g**	0 month	0,07±0,01	0,17±0,01	0,21±0,01	0,13±0,01
		3 month	0,48±0,04	0,58±0,04	0,55±0,04	0,42±0,04
2	**Peroxide Value, m_{echiv} O_2 activ/kg**	0 month	2,30±0,05	1,70±0,04	1,30±0,05	1,70±0,05
		3 month	4,68±0,13	4,13±0,13	3,66±0,13	3,68±0,13
3	**Content of conjugated dienes – DC, u.c.**	0 month	13,81 ±0,11	6,13±0,11	7,66±0,11	9,76±0,11
		3 month	18,96±0,11	14,22±0,11	14,30±0,11	15,03±0,11
4	**Content of conjugated triene – TC, u.c.**	0 month	4,63±0,11	4,68±0,11	4,33±0,11	7,50±0,11
		3 month	8,39±0,11	5,34±0,11	4,96±0,11	6,42±0,11
5	***p*-anisidine Value, u.c.**	0 month	9,65±0,12	9,93±0,13	8,49±0,13	9,32±0,13
		3 month	13,97 ±0,13	10,61±0,13	9,83±0,13	10,94±0,13

*Note: results are presented as mean ± standard deviation; ** PM – control sample; ELM - lipophilic rosehip extract; ELP - lipophilic hawthorn extract; ELC - lipophilic sea buckthorn extract; *** t extraction 45 ° C; Extraction τ 180 min.*

The peroxide value for sunflower oil is within the permissible limits (max 10 m_{echiv} O_2/kg). In the examined extracts IP is considerably lower - in the case of rosehip extract - by 0.5 m_{echiv} O_2/kg, and in the case of lipophilic extracts of sea buckthorn and hawthorn - by about 1.0 m_{echiv} O_2/kg compared to the peroxide value for sunflower oil.

After a storage period of 3 months, it was observed that the PV values for the lipophilic extracts of hawthorn, sea buckthorn and rosehip are lower compared to PM. For lipophilic extracts PV increased for ELM by 40%; for ELC by 35%; for EPC by 46% and for PM by 49%.

Following the research of the content of conjugated dienes and trienes in the studied vegetable oils and lipophilic extracts, it was established that during 3 months of storage PM attests a considerable variation in the content of dienes (13.81-18.96 u.c.) and conjugated trienes (4,63-8.39 u.c.) compared to samples enriched with plant extract. Extract samples are characterized by much lower values, which vary insignificantly and express that the process of formation of primary oxidation products is slowed down. The results obtained show that the lipophilic extracts of rosehip, sea buckthorn and hawthorn can be used to obtain foods with high lipid content.

AA was determined in terms of gastric and intestinal digestion *in vitro*. Gastric and intestinal digestion was simulated *in vitro* for 2 hours. During the simulation, aliquots were extracted, which were subsequently subjected to research and AA determination by reaction with the free radical DPPH, and the results obtained are presented in fig.3.3.

Evaluation of antioxidant activity following induced gastric digestion (acidic environment) shows an essential increase for oils with lipophilic extracts of sea buckthorn, hawthorn and rosehip compared to PM whose values are 17.58±0.90%. For oils enriched with lipophilic extracts the values are: for ELC-46.43±0.90%; for ELM-37.08±0.90% for ELP-39.29±0.90%. The high values of antioxidant activity for lipophilic extracts compared to PM after 2 hours of digestion are explained by the gradual release of biologically active compounds in the process of gastric digestion (Pavan et al., 2014).

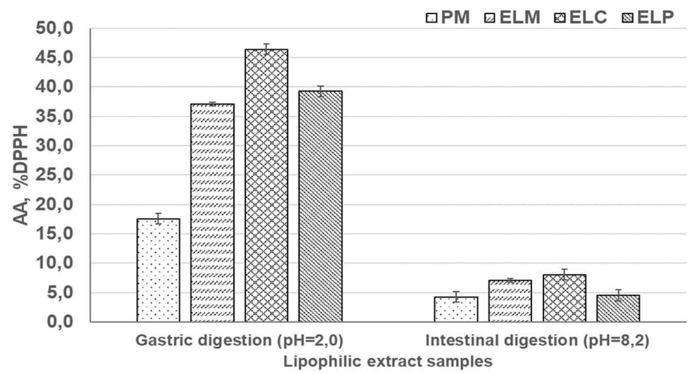


Fig. 3.3. Antioxidant activity of oil with lipophilic extracts *in vitro*: PM - control sample; ELC - lipophilic sea buckthorn extract; ELM - lipophilic rosehip extract; ELP - lipophilic hawthorn extract.

The results obtained (fig.3.3) show that the antioxidant activity of the oil with lipophilic extracts of sea buckthorn, hawthorn and rosehip is higher compared to PM. AA of sunflower oil is 4.26 ± 0.3%, while for oils with lipophilic extracts, AA values are: for sea buckthorn-8.09±0.3%; for rosehips-7.06±0.3% for hawthorn 4.56±0.3%. Following the intestinal digestion, a gradual decrease in antioxidant activity is observed within 2 hours for both the samples with the addition of extract and for PM. This can be explained by the low stability of biologically active compounds in alkaline conditions (pH=8.2±0.1) and the formation of metabolites that inhibit the antioxidant activity of biologically active compounds in the products studied.

3.2. Research on the formation intensity of lipid oxidation products

The oxidation by-products were analyzed by mass spectrometry. Both high molecular weight and low molecular weight products have been identified. As the by-products of oxidation are extremely volatile and undetectable, an additional step of derivatization with CHH was performed. All lipid oxidation products were manually identified by detailed analysis of MS2 spectra generated by XCalibur software. Below in fig. 3.4 and 3.5 was exemplified several spectra for the identification of both low molecular weight and high molecular weight reaction products.

The tandem mass spectra (fig. 3.4.) of the CHH-derived hydroxy-hexanal (m/z = 374.2077) showed a signal at m/z = 366.1966 indicating the water loss (-18 Da) corresponding to the OH group. Intense signal at m/z = 244.0966; another signal at m/z = 262.1072 and m/z = 276.1339 confirms CHH derivatization. The signal at m/z=114.0916 represents the ion fragment for hydroxy-hexanal ($C_6H_{12}O_2$). The accumulation of hydroxy-hexenal in the investigated samples imprints to the analyzed samples an unpleasant smell of grass, rancid, and paint (Sarolić et al., 2014).

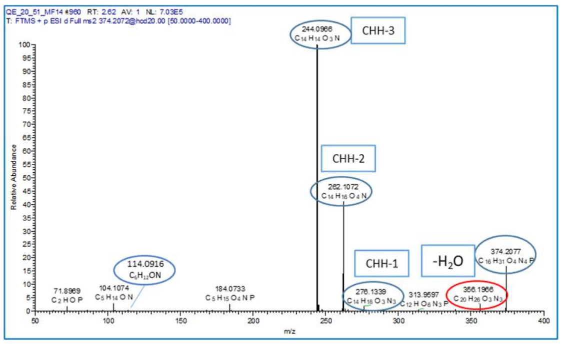


Fig. 3.4. MS2 spectra for hydroxy-hexanal

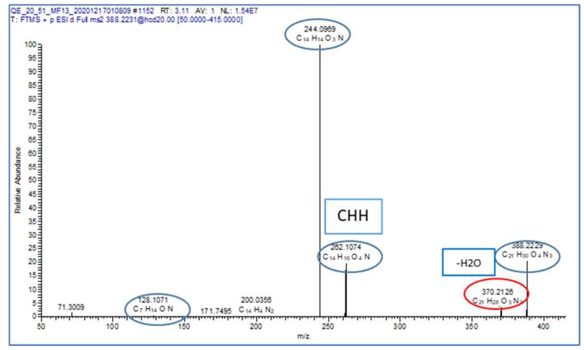


Fig. 3.5. MS2 spectrum for hydroxy-heptanal

The tandem mass spectrum (fig. 3.5.) of the CHH-derived hydroxy-heptanal (m/z = 388.2229) showed a signal at m/z = 370.2126 indicating the water loss (-18 Da) corresponding to the OH group. Intense signal at m/z = 244.0968; another signal at m/z = 262,1074 confirms CHH derivatization. The signal at m/z = 128,1071 represents the ion fragment for hydroxy-heptanal ($C_7H_{14}O_2$).

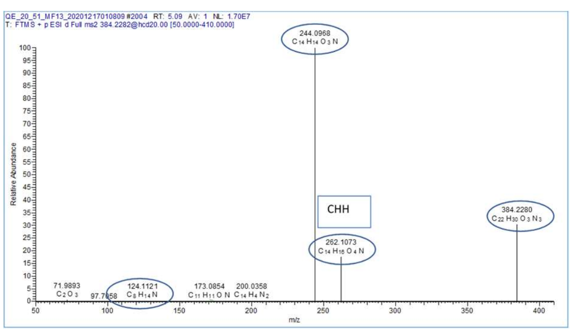


Fig. 3.6. MS2 spectra for octenal

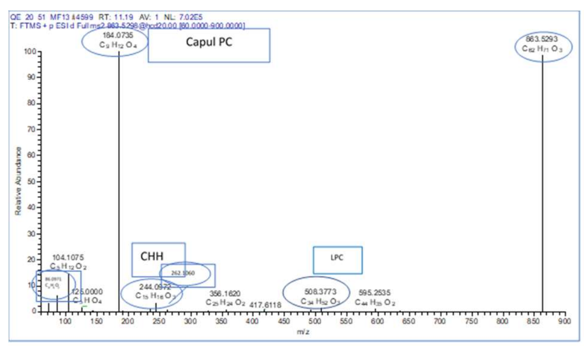


Fig. 3.7. MS2 spectra for PC(P-18:1/5:0<oxo@C5>)

The tandem mass spectra (fig. 3.6.) for octenal derived with CHH (m/z = 384.2280) showed an intense signal at m/z=244.0968 and another minor signal at m/z=262.1073 which confirms the derivatization with CHH. The signal at m/z=124.1121 represents the fragment ion for octenal ($C_8H_{14}O$).

The tandem mass spectra (fig.3.7.) for the CHH-derivatized PC(P-18:1/5:0<oxo@C5>) (m/z=863.5293) showed a relatively strong signal at m/z=184.0735 representing the PC head. The intense signal at m/z=244.0972 and another minor signal m/z=262.1060 confirms the derivatization with CHH. The signal at m/z=508.3773 represents the fragment ion for 2-LysoPC ($C_{25}H_{51}NO_6P$). The m/z=86.0972 indicates the structure of sn-2 5C-carbonyl.

Table 3.5. Modifications for CHH-Derived Low Molecular Lipid Oxidation Products (positive mode) *

Modification	PC/PE/ oxoLPP	Type of ionization	Precursor	Chemical formula (neutral)	Chemical formula (ion)	m/z	MS2 product	Chemical formula (ion)	m/z
Truncation	oxoLPP	$[M+H]^+$	Pentanal	$C_5H_{10}O$	$C_{19}H_{26}N_3O_3$	344,1970	CHH-2	$C_{14}H_{16}N_2O_3$	262,1074
							CHH-3	$C_{14}H_{12}NO_3$	244,0967
							Ion fragment	$C_5H_{10}N$	84,0812
Truncation	oxoLPP	$[M+H]^+$	Hexanal	$C_6H_{12}O$	$C_{20}H_{28}N_3O_3$	358,2126	CHH-2	$C_{14}H_{16}N_2O_3$	262,1074
							CHH-3	$C_{14}H_{12}NO_3$	244,0970
							Ion fragment	$C_6H_{12}N$	98,0969
Truncation, OH adittion	oxoLPP	$[M+H]^+$	Hydroxy-hexanal	$C_6H_{12}O_2$	$C_{20}H_{28}N_3O_4$	374.2072	Loss of H_2O	$C_{20}H_{26}N_3O_3$	356.1966
							CHH-1	$C_{14}H_{18}N_3O_3$	276.1339
							CHH-2	$C_{14}H_{16}N_2O_3$	262.1072
							CHH-3	$C_{14}H_{12}NO_3$	244.0966
							Ion fragment	$C_6H_{12}NO$	114.0916
Truncation	oxoLPP	$[M+H]^+$	Heptenal	$C_7H_{12}O$	$C_{21}H_{28}N_3O_3$	370,2126	CHH-2	$C_{14}H_{16}N_2O_3$	262,1074
							CHH-3	$C_{14}H_{12}NO_3$	244,0968
							Ion fragment	$C_7H_{12}N$	110,0970
Truncation	oxoLPP	$[M+H]^+$	Octanal	$C_8H_{16}O$	$C_{22}H_{32}N_3O_3$	386,2438	CHH-2	$C_{14}H_{16}N_2O_3$	262,1073
							CHH-3	$C_{14}H_{12}NO_3$	244,0968
							Ion fragment	$C_8H_{16}N$	126,1277
Truncation, OH adittion	oxoLPP	$[M+H]^+$	Hydroxy-octanal	$C_8H_{16}O_2$	$C_{22}H_{32}N_3O_4$	402.2380	Loss of H_2O	$C_{22}H_{30}N_3O_3$	384.2279
							CHH-1	$C_{14}H_{18}N_3O_3$	276.1335
							CHH-2	$C_{14}H_{16}N_2O_3$	262.1070
							CHH-3	$C_{14}H_{12}NO_3$	244.0965
Truncation, OH adittion	oxoLPP	$[M+H]^+$	Hydroxy-nonenal	$C_9H_{16}O_2$	$C_{23}H_{32}N_3O_4$	414,2390	Loss of H_2O	$C_{23}H_{30}N_3O_3$	396,2282
							CHH-2	$C_{14}H_{16}N_2O_3$	262,1074
							CHH-3	$C_{14}H_{12}NO_3$	244,0969
							Ion fragment	$C_9H_{17}N$	139,1118
Truncation, Epoxidation	oxoLPP	$[M+H]^+$	Epoxy-nonenal	$C_9H_{14}O_2$	$C_{23}H_{30}N_3O_4$	412.2223	CHH-2	$C_{14}H_{16}N_2O_3$	262.1074
							CHH-3	$C_{14}H_{12}NO_3$	244.0968
							Ion fragment	$C_9H_{14}NO$	152.1067
Truncation, OH adittion	oxoLPP	$[M+H]^+$	Hydroxy-nonadienal (PC)	$C_9H_{14}O_2$	$C_{23}H_{30}N_3O_4$	412.2232	Loss of H_2O	$C_{23}H_{28}N_3O_3$	394.2201
							CHH-2	$C_{14}H_{16}N_2O_3$	262,1074
							CHH-3	$C_{14}H_{12}NO_3$	244,0969
							Ion fragment	$C_9H_{17}N$	152.1100
Truncation, Epoxidation	oxoLPP	$[M+H]^+$	Epoxy undecadienal	$C_{11}H_{16}NO_2$	$C_{25}H_{32}N_3O_4$	438,2389	CHH-2	$C_{14}H_{16}N_2O_3$	262,1073
							CHH-3	$C_{14}H_{12}NO_3$	244,0968
							Ion fragment	$C_{11}H_{16}ON$	178,1225

Lipid oxidation is propagated by various pathways which include: Russell reaction, Hock rearrangement, H abstraction from the structure of unmodified adjacent lipids etc. Due to the diversity and complexity of lipid compounds in nature, no analysis protocol has yet been able to extract all classes of lipids with the same efficiency (Lange et al., 2019). Separation of LPPs from oxidized lipids was performed by reverse phase liquid chromatography on column C18. Evaluation of oxoPE and oxoPC plasmalogens was successfully performed in both negative-mode ESI ionization and positive-mode ESI ionization. CHH derivation allows the identification of both low molecular weight LPP and high molecular weight LPP.

Following the tests, lipid oxidation products formed as a result of the cleavage of alkyl chains of hydroperoxides were identified, namely: pentanal, hydroxy-hexanal, heptanal, heptenal, hydroxy-nonenal or hydroxy-decadienal, etc. Reverse phase liquid chromatography allowed the separation of lipid oxidation products depending on their hydrophobicity which is influenced by the length of the acyl chain and the number and position of the double bonds. Efficient separation of LLP was ensured by using the stationary phase C18 and the mobile phase composed of bidistilled water, acetonitrile and isopropanol in the gradient. The identification of lipid oxidation products was possible due to the presence of distinct signals with a certain mass/charge ratio (m/z) specific for each identified compound as well as the presence of CHH derivatization confirmed by the signals m/z=262.1074 and m/z =244 , 0967. The ionic fragments for each identified compound were confirmed by distinct signals such as for octanal the signal m/z=126.1277; for hydroxy-nonenal the signal m/z=139.1188; for heptadecanal the signal m/z=226.7829 etc.

As a result of the tests by the method of liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) 83 products of lipid oxidation were identified.

The results presented above demonstrate the diversity of lipid oxidation products formed by the addition of oxygen (epoxidation, OH addition) and oxidative cleavage (aldehydes and corresponding carboxylic acids). The rate of lipid oxidation is determined by a complex set of factors that include the fatty acid composition of the analyzed lipids or the presence of antioxidant compounds (ex. tocopherol). The identification of LPP allowed the study of lipid oxidation mechanisms and the analysis of the quantitative evolution of lipid oxidation products that formed in the oxidation process.

3.3. Quantitative evolution of lipid oxidation products

Was analyzed the amount of LPP formed for 30 hours by the oxidation mechanism induced by the Fenton Reaction at 45°C. The primary products of the oxidation reaction are unstable, decompose and lead to homolytic cleavage and the formation of volatile compounds, which are by-products of oxidation and include aldehydes and ketones. These components negatively affect the quality of the food by forming a rancid odor.

Oxidation of lipids, especially phospholipids containing unsaturated fatty acids, leads to the formation of a wide range of aldehyde compounds. In this context, the reaction products of the oxidation of phospholipids, namely PE (phosphotidyl-ethanolamine) and PC (phosphotidyl-choline), were further studied.

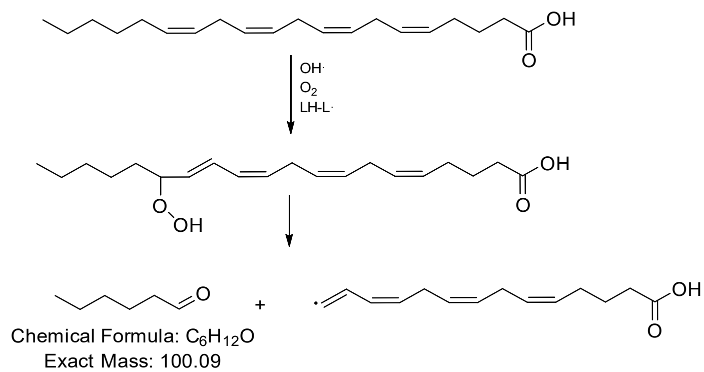
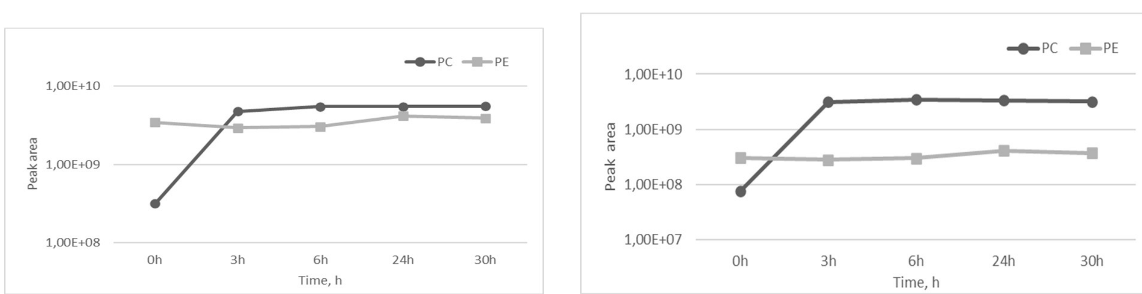


Fig. 3.8. The mechanism of hexanal formation (după Coliva et al., 2020)

Analyzing the dynamics of hexanal formation during the oxidation of PC and PE phospholipids, we notice that the hexanal formed following the oxidation of PE lipids has a constant evolution throughout the 30 hours. Initial values at 0 h of oxidation The values for PC lipids are considerably lower compared to PE, but during 3h there is a significant increase in the hexanal content formed (fig.3.8.; fig.3.9.a).



a) b)

Fig. 3.9. Dynamics of lipid oxidation products for phosphatidylcholine (PC) and phosphatidylethanolamine (PE): a-hexanal; b-hydroxy-nonenal

The hydroxy-nonenal compound (HNE) is a mutagenic and cytotoxic product of linoleic acid oxidation. The evolution of this compound formed after the oxidati on of PE lipids shows a stable growth throughout the period of exposure to high temperatures. The increase in HNE content in the case of PC lipids shows a considerable evolution in the first 3 hours of exposure to high temperatures. After 24 hours of exposure, there is a slight decrease in HNE content, which can be explained by the subsequent degradation of aldehydes and the formation of new compounds due to high temperatures (fig. 3.9.b; fig. 3.10).

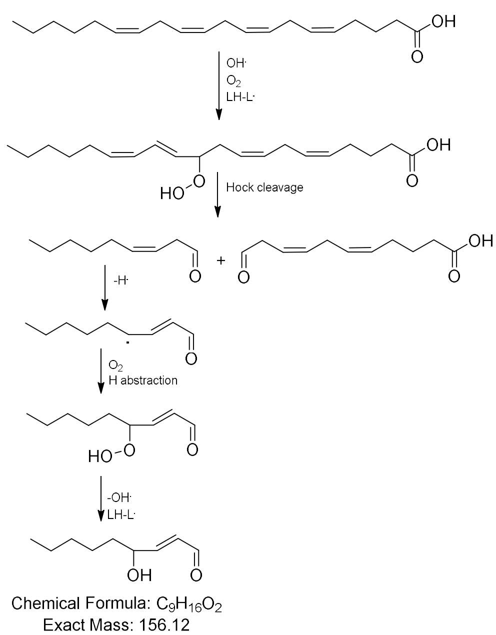


Fig. 3.10. The mechanism of hydroxy-nonenal formation (după Coliva et al., 2020)

During the research, more than 63 PE and PC lipid oxidation products were identified, including low molecular weight products, which were identified by derivatization with CHH. Likewise, were identified products with high molecular weight, both in negative and positive ion mode.

4. Technologies for the manufacture of complex products based on lipophilic extracts and berry powder

Chapter 4 describes the technologies for manufacturing complex foods with increased antioxidant potential; were studied quality indicators, chromatic parameters, antioxidant activity and oxidative stability of complex foods.

4.1. Technology for high lipid content sauce enriched with lipophilic extracts

In order to investigate the stability of the lipid complex in lipid-based foods, it was proposed to manufacture sauce with a fat content of ~ 30%. For research, lipophilic extracts from plant sources were used: sea buckthorn, hawthorn and rosehip by substituting vegetable sunflower oil in the recipe.

For the sensory analysis, 5 basic parameters were assessed, namely: color, taste, consistency, appearance, smell. The evaluation of each parameter was assessed with a score scale of 1-5 points. The sauce enriched with sea buckthorn extract attests to an average score of 18.51 - non-essential lower, which is due to the sour-astringent taste specific to sea buckthorn fruits. The sauce samples with rosehip and hawthorn extract attest to non-essential changes in taste, smell, consistency compared to

PM. It was established that the samples examined with sea buckthorn extract, hawthorn and rosehip are pleasant in taste and smell, with a homogeneous consistency and some inclusions of air bubbles that are admissible according to the regulations. Following the findings, it was established that the samples examined are positively assessed and as a result represent potential functional foods that can be intended for consumption. The use of lipophilic extracts enriched with sea buckthorn, hawthorn and rosehip presents a good possibility to increase the biological value of the food product, in this case sauces in a natural way and without risk to the health of consumers.

The main quality indicators of foods with high lipid content were analyzed. The results obtained are presented in table 4.3. After a period of 3 months of storage, there is an increase in AV values for all samples tested. The AV values for PM (0.78 ± 0.04 mgKOH/g) and SEC (0.65±0.04 mgKOH/g) exceed the maximum limit of 0.6 mgKOH/g provided by the technical regulations and it is recommended to keep sea buckthorn sauce for up to 2 months. In the case of SEM (0.58±0.04 mgKOH/g) and SEP (0.52±0.04 mgKOH/g), the AV values do not exceed the maximum permissible value according to the regulations and it is recommended to keep them up to 3 months.

Table 4.3. Quality indicators of sauce enriched with lipophilic extracts*

Nr.	Quality parameter	Shelf life	PM	SEM	SEC	SEP
1	**Acid Value, mg KOH/g**	0 month	0,38±0,01	0,40±0,01	0,41±0,02	0,35±0,02
		3 month	0,78±0,04	0,58±0,04	0,65±0,04	0,52±0,04
2	**Peroxide Value, m_{echiv} O_2 activ/kg**	0 month	2,33±0,05	1,11±0,04	1,78±0,05	1,00±0,05
		3 month	5,68±0,13	3,85±0,13	4,06±0,13	4,28±0,13
3	**Content of conjugated dienes – DC, u.c.**	0 month	15,21 ±0,11	7,53±0,11	8,96±0,11	10,26±0,11
		3 month	20,16±0,11	11,92±0,11	14,30±0,11	16,83±0,11
4	**Content of conjugated triene – TC, u.c.**	0 month	9,83±0,11	6,18±0,11	5,33±0,11	8,08±0,11
		3 month	12,69±0,11	7,34±0,11	6,56±0,11	9,02±0,11

*Note: PM - witness test; SEC - sea buckthorn sauce sauce; SEP - hawthorn extract sauce; SEM - sauce with rosehip extract. * extraction t 45 ° C; Extraction τ 180 min*

After a storage period of 3 months, it is observed that the PV values for SEC (4.06 ± 0.13 m_{echiv} O_2/kg), SEM (3.85 ± 0.13 m_{echiv} O_2/kg) and SEP (4.28 ± 0.13 m_{echiv} O_2/kg) is lower compared to PM. The lipophilic extracts of sea buckthorn, hawthorn and rosehip are antioxidant due to their biologically active compounds (carotenoids, ascorbic acid, polyphenols) from renewable plant sources.

Following the research of the content of conjugated dienes and trienes in the emulsified sauce with the addition of vegetable oils and lipophilic extracts, it was established that during 3 months of storage PM shows a considerable variation in the content of conjugated dienes and trienes compared to samples of sea buckthorn, hawthorn and rosehip extract. The content of conjugated dienes for SEM increased 1.5 times, for SEC and SEP 1.6 times. The content of conjugated trienes in PM increased 1.3 times, and for SEM and SEP 1.1 times and for SEC 1.2 times.

Based on the data obtained, it was established that the samples of sauce with lipophilic extract are characterized by much lower values, which vary insignificantly between them and express the fact that the process of formation of primary oxidation products is slowed down. The concentration of 18% extract is recommended for the manufacture of the emulsified sauce with the addition of lipophilic extract of sea buckthorn, hawthorn and rosehip. The optimum shelf life of sauces with lipophilic extract of sea buckthorn, hawthorn and rosehip is 2 months at storage temperature + 4°C.

4.2. Technology for candies enriched with berry powder

Candies are confectionery products that are widely used and adored by consumers of all ages. But it is good to know the harmful effects of refined or processed sugars on health. Thus, the technology for obtaining candies was developed where the vegetable powder of sea buckthorn, hawthorn and rosehip was used as a natural ingredient with antioxidant potential (table 4.4).

Tabelul 4.4 Recipe for making candies with berry powder

Raw materials	Raw material consumption per 100 kg of finished product						
Cashew nuts, kg	62,5						
Natural honey, kg	5,00						
Cinnamon, kg	2,50						
Ground hazelnuts, kg	25,00						
Cocoa, kg	4,50			4,75			5,00
Sea buckthorn powder, kg	0,50	-	-	0,25	-	-	-
Hawthorn powder, kg	-	0,50	-	-	0,25	-	-
Rosehip powder, kg	-	-	0,50	-	-	0,25	-
Total:	100,00	100,00	100,00	100,00	100,00	100,00	100,00

Following the evaluation of the sensory parameters, it was established that the samples examined with the addition of rosehip, sea buckthorn or hawthorn powder or hawthorn have a pleasant taste and smell, with a homogeneous consistency, color from yellow-orange to reddish, which is characteristic for the researched berries..

Table 4.5 Evaluation of sensory parameters* of berry powder candies.

Parameter	PM	BPM		BPC		BPP	
		5%	10%	5%	10%	5%	10%
Appearance and shape	4,95±0,05	4,89±0,05	4,67±0,04	4,76±0,03	4,65±0,05	4,60±0,04	4,40±0,05
Consistency	4,97±0,05	4,79±0,05	4,45±0,04	4,65±0,03	4,35±0,04	4,70±0,04	4,55±0,05
Color	4,50±0,05	4,32±0,03	4,80±0,05	4,50±0,05	4,70±0,04	4,60±0,03	4,55±0,04
Taste	4,38±0,05	4,75±0,04	4,25±0,04	4,80±0,05	4,50±0,05	4,78±0,04	4,50±0,04
Smell	4,90±0,05	4,95±0,05	4,35±0,03	4,70±0,04	4,20±0,06	4,60±0,05	4,50±0,04
Total	23,03±0,12	22,61±0,13	23,5±0,13	21,96±0,13	23,02±0,10	23,28±0,10	23,4±0,13

** average, according to the 5-point scale, according to ISO 6658: 2017; p <0.05. Note: PM – control sample; BPC - sea buckthorn powder candies; BPP - hawthorn powder candies; BPM - rosehip powder candy.*

The addition of sea buckthorn, hawthorn and rosehip powders has a positive influence on sensory parameters, especially taste, smell and color (table 4.5). For candies with added vegetable powders, it was recommended to replace walnuts with 5% sea buckthorn powder, hawthorn and rosehip.

On the fifth day after the preparation of the candies with berry powder, the content of chlorophyll α and β, β-carotene, lycopene and zeaxanthin was determined spectrophotometrically. The results obtained are presented in table 4.6.

Tabelul 4.6. Carotenoid content in candies with fruit powder

Carotenoids	BPM	BPC	BPP
Adaos – 5%			
Chlorophyll α, mg / L	0,68±0,02	0,75±0,01	0,85±0,02
Chlorophyll β, mg / L	1,39±0,04	1,56±0,01	1,98±0,04
β-carotene, mg / L	17,18±0,01	16,58±0,03	14,58±0,01
Lycopene, mg / L	18,13±0,04	17,23±0,05	16,15±0,01
Zeaxanthin, mg / L	18,02±0,02	17,56±0,01	15,99±0,04
Adaos 10 %			
Chlorophyll α, mg / L	0,79±0,01	0,84±0,01	0,99±0,01
Chlorophyll β, mg / L	1,75±0,02	2,02±0,01	2,54±0,01
β-carotene, mg / L	20,16±0,01	19,34±0,01	17,85±0,05
Lycopene, mg / L	22,11±0,04	21,06±0,01	19,25±0,04
Zeaxanthin, mg / L	21,98±0,01	21,56±0,03	18,33±0,03

Note: PM – control sample; BPC - sea buckthorn powder candies; BPP - hawthorn powder candies; BPM - rosehip powder candy.

After increasing the administered vegetable powder content, it was found that the β-carotene content increased significantly for BPM10% and BPC10% - 1.2 times and for BPP10% - 1.3 times. The content of chlorophyll α and chlorophyll β increased on average by 15% and 28%, respectively. The lycopene content increased for BPM10%, BPC10% and BPP10% - 1.2 times. Likewise, the content of zeaxanthin for the researched samples BPM10%, BPC10% and BPP10% attests values 1.2 times higher.

In order to study the evolution of the antioxidant activity of complex products with the addition of vegetable powders, a simulation of gastric and intestinal digestion over time was performed. The results obtained are shown in fig. 4.1.

The evaluation of the antioxidant activity following the induced gastric digestion (pH=2.0±0.1) attests an essential increase for the samples with the addition of powder compared to PM whose values constitute: for PM-30.18 ± 1.20%; for BPM-70.07±0.80%; for BPC-64.26±1.20%; for BPP-58.45±1.20%. The changes that occur during gastric digestion and the considerable increase in antioxidant activity for samples enriched with vegetable powder are due to the biologically active compounds in the composition of the ingested food mold. Following the gastrointestinal digestion process, the simulation of the intestinal digestion phase induced by incubating the samples in an alkaline environment (pH =8.2±0.1) and determining the antioxidant activity after a period of 2 hours was performed. The data obtained show that the antioxidant activity of the samples with the addition of vegetable powder decreased for PM by 1.6 times; for BPM -2.69 times; for PCB-2.37 times; for BPP-2.93 times.

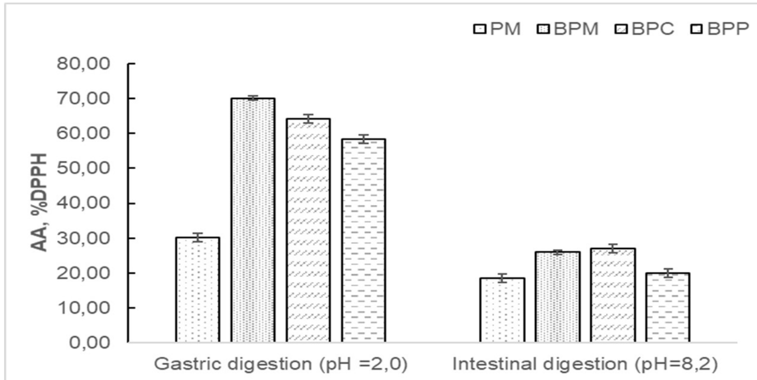


Fig. 4.1 Antioxidant activity of candies in the conditions of gastric and intestinal digestion: BPC - candies with sea buckthorn powder; BPM - candies with rosehip powder; BPP - candies with hawthorn powder.

This can be explained by the low stability of biologically active compounds in alkaline conditions (pH=8.2±0.1) and the formation of metabolites that inhibit the antioxidant activity of biologically active compounds in the researched products. (Lucas-González et al., 2018).

4.3. Technology for donuts enriched with berry powder

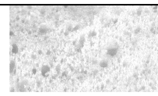
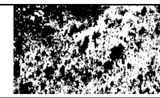
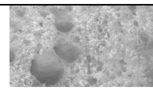
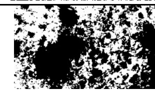
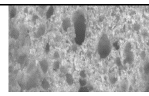
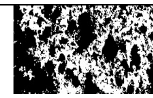
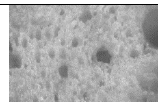
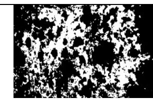
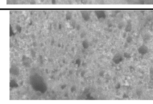
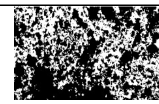
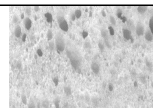
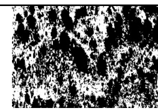
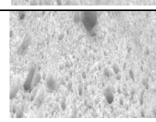
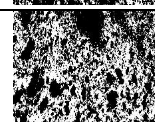
As people prefer fast food and those products that require a short preparation time, the use of products with high nutritional value is becoming increasingly important (Saraf et al., 2019). Thus, it was proposed to replace wheat flour with sea buckthorn powder, hawthorn and rosehip in a ratio of 5 and 10%.

The results of the sensory analysis show that the addition of 5% rosehip and sea buckthorn powder favorably influenced the sensory parameters of the samples obtained. The total scores for the sensory analysis of the samples of 5% and 10% of rosehip powder, hawthorn and sea buckthorn are in the range of 26.00 to 30.00, which means that the products are of good quality and can be offered for consumption. For donuts with added vegetable powders, it is recommended to replace wheat flour with 5% sea buckthorn powder, hawthorn and rosehip.

The porosity of complex products is determined with the electronic imaging software, which measures the size of the pores, their number, and the result is presented as a percentage. In the case of donuts, porosity is a significant feature, so it is important that the addition of fruit powder does not negatively influence this factor (table 4.9).

After determining the porosity of complex products all samples have a good porosity, can be concluded that samples with the addition of fruit powder have a higher porosity than the control sample, this is a benefit, the highest porosity (67.87%) is in the sample with the addition of 5% powder. Vitamins and simple carbohydrates in fruit powder stimulate the fermentative activity of baking yeast, positively influencing the porosity of donuts. This is an important factor because porosity contributes to the digestibility of bakery products. The higher the porosity, the easier it is to digest by the human body.

Table 4.9 Donut porosity analysis using ImageJ software

Nr.	Sample name	RGB Image	Binary image	Porosity, %
1	PM			52,9±1,6
2	GPP5%			57,7±1,9
3	GPP10%			58,6±2,1
4	GPM5%			67,9±2,0
5	GPM10%			61,2±1,5
6	GPC5%			61,3±1,4
7	GPC10%			61,7±1,5

Note: PM - witness test; GPC - donuts with sea buckthorn powder; GPP - donuts with hawthorn powders; GPM - donuts with rosehip powder.

The physical properties of the donuts with the addition of 10% fruit powder until and after the frying process were investigated in order to study the changes that take place during the frying process. The results obtained are shown in fig. 4.2.

According to the research conducted by (Ragaee et al., 2011) the partial substitution of wheat flour with some cereals can cause a reduction in the volume of bakery products. Therefore, the value of the volume change for PM varies from 1.75 to 3.86%; for GPC-from 1.30 to 2.25%; for GPM- from 1.33 - 2.17% and respectively GPP- 1.29 - 2.07%.

Samples of donuts fried in vegetable oil at t=180°C were obtained by the deep-fry method. The results obtained from the extraction of fats by the Soxhlet method are presented in fig. 4.3. and shows that the samples with the addition of vegetable powders show a low content of oil absorbed during frying compared to PM, whose values are -17.67±0.40%. Samples with added vegetable powders are characterized by the following values: GPP -15.47±0.20%; GPC -14.82±0.10% and GPM - 14.03±0.40% respectively. The decrease in the oil content absorbed during frying is due to the diversification of the recipe for obtaining donuts by adding vegetable powders.

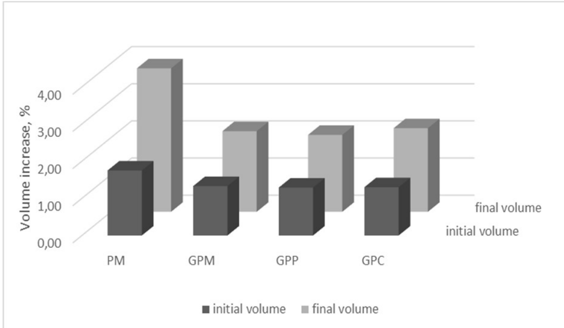


Fig. 4.2 Increase in volume of donuts during frying,%. PM – control sample; GPM - donuts with rosehip powder, GPP - donuts with hawthorn powder; GPC - donuts with sea buckthorn powder.

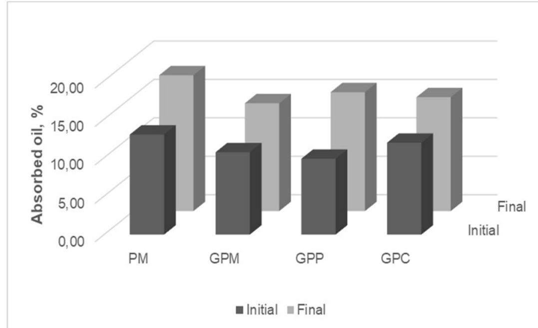


Fig. 4.3 The decrease of absorbed oil content during frying,%. PM – control sample; GPM - donuts with rosehip powder, GPP - donuts with hawthorn powder; GPC - donuts with sea buckthorn powder, p<0,05

In the study of the evolution of the antioxidant activity of complex products with the addition of sea buckthorn, hawthorn and rosehip powder, the simulation of gastric digestion as well as intestinal digestion *in vitro* was performed for the donuts with the addition of 5% fruit powder. The obtained results are presented in fig. 4.4. Evaluation of antioxidant activity following gastric digestion shows an essential increase for samples with added powder compared to PM whose values are: for PM - 19.08±0.70%; for GPM -51.57±1.30%; for GPC -50.26±1.30%; for GPP -36.45±1.30%. The changes that occur during gastric digestion and the considerable increase in antioxidant activity for the samples enriched with vegetable powder are due to the biologically active compounds in the composition of the ingested food (Rodríguez-Roque et al., 2013)

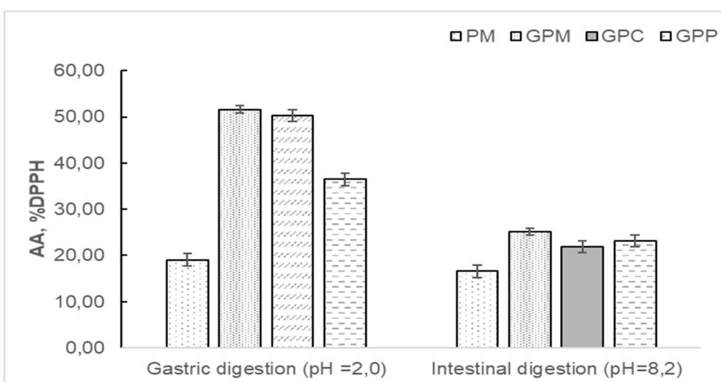


Fig. 4.4 Antioxidant activity of donuts in the conditions of gastric and intestinal digestion: GPC - donuts with sea buckthorn powder; GPM - donuts with rosehip powder; GPP - donuts with hawthorn powder.

Following the gastrointestinal digestion process, the intestinal digestion phase simulation was performed and the data obtained show that the antioxidant activity of the samples with added vegetable powder shows an essential decrease for the samples with added powder compared to PM whose values are: for PM -16.58±0.80%; for GPM - 25.15±0.80%; for GPC - 21.84±0.80%; for GPP- 23.16±0.80%. There is a gradual decrease in antioxidant activity after 2 hours of incubation for both powder and control samples due to pH changes, from acidic environment (gastric digestion) to alkaline medium (intestinal digestion) (Lucas-González et al., 2018). This can be explained by the low stability of biologically active compounds in alkaline conditions (pH=8.2±0.1) and the formation of metabolites that inhibit the antioxidant activity of biologically active compounds in the researched products.

4.4. Technology for mini-cakes enriched with berry powder

In order to be able to estimate the physico-chemical and sensory characteristics of complex products with the addition of vegetable powder, the preparation of mini-cakes with fruit powder was performed. In order to perform physico-chemical and sensorial analysis of berry powders of sea buckthron, hawthorn and rosehip and their impact upon bakery products where proposed to replace wheat flour with 5% and 10% berry powder.

Table 4.12. The content of carotenoids in mini cakes with fruit powder

Carotenoids	CPM	CPC	CPP
5% Addition			
Chlorophyll α, mg/L	2,68±0,02	2,15±0,01	1,32±0,02
Chlorophyll β, mg/L	4,39±0,04	3,88±0,02	2,75±0,04
β-carotene, mg/L	37,18±0,01	34,36±0,01	30,38±0,01
Lycopene, mg/L	35,13±0,04	33,29±0,02	29.25±0,01
Zeaxanthin, mg/L	27,02±0,02	29,23±0,01	24,79±0,04
10% Addition			
Chlorophyll α, mg/L	4,02±0,01	3,75±0,03	2,51±0,04
Chlorophyll β, mg/L	5,98±0,01	5,06±0,04	3,99±0,01
β-carotene, mg/L	58,34±0,09	52,48±0,04	49,68±0,05
Lycopene, mg/L	53,59±0,10	48,32±0,05	47,06±0,04
Zeaxanthin, mg/L	42,18±0,07	44,71±0,07	40,37±0,01

Note: PM – control sample; CPC - mini-cakewith sea buckthorn powder; CPP - mini-cake with hawthorn powder; CPM - mini-cake with rosehip powder.

Following the estimation of the sensorial parameters, it was established that the mini-cakes with the addition of 5% sea buckthorn powder, hawthorn and rosehip have a pleasant color and smell and can be suitable for the market.

Following the research of mini-cakes with sea buckthorn powder, or hawthorn, or rosehips, we determined the content of zeaxanthine, β-carotene, lycopene, chlorophyll β and chlorophyll α. The results obtained (table 4.12) confirm the increased carotenoid content in the mini-cakes enriched with rosehip, sea buckthorn and hawthorn powder, which increases its bioactivity and thus improves its nutraceutical properties (Olawuyi et al., 2019).

The elasticity of the core is the property of it to return to its original shape, after the action of the press force (Ciumac et al., 2019). In the research of the mini-cakes with the addition of sea buckthorn powder, hawthorn and rosehip powder, the elasticity for the obtained samples was determined. The results obtained are shown in fig. 4.5.

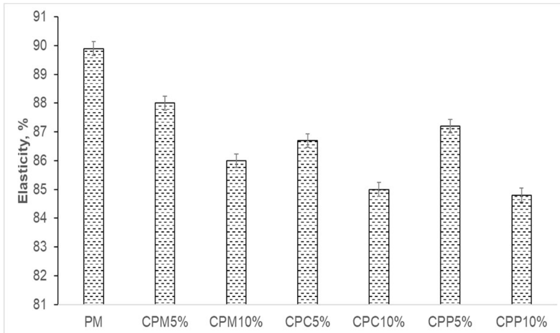


Fig. 4.5 Elasticity of mini-cakes with fruit powder additives: CPC - mini-cake with sea buckthorn powder; CPP - mini-cake with hawthorn powder; CPM - mini-cake with rosehip extract.

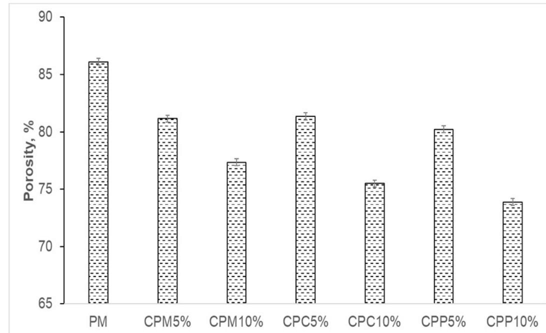


Fig. 4.6 Porosity of mini-cakes with fruit powder additives: CPC - mini-cake with sea buckthorn powder; CPP - mini-cake with hawthorn powder; CPM - mini-cake with rosehip extract.

Mini-cakes with added vegetable powders are characterized by the following values: for CPM - 86.00 - 88.00%; for CPC - 75.50 - 81.35%; for CPP -73.89 - 80.23%. Based on the results obtained, there is a significant decrease in the elasticity of the mini-cakes with the addition of vegetable powder proportional to the amount of vegetable powder substituted. This is explained by the decrease in gluten content in the composition of the dough as a consequence of substituting wheat flour with vegetable powder from sea buckthorn, hawthorn and rosehip.

The porosity of the mini-cakes with the addition of vegetable powder was analyzed, and the obtained results are presented in fig. 4.6. Following the analysis of the results from the diagram above, it was established that the porosity of the researched samples includes the following values: for CPM - 77.35 - 81.15%; for CPC - 81.35 - 75.50%; for CPP - 73.89 - 80.23%. It has been observed that increasing the content of substituted powder decreases the porosity of the mini-cakes researched. This can be explained by the low gluten-free network during the formulation of the dough and its baking, so CO_2 formed during fermentation will not be retained and as a result a product with a lower volume and low porosity is obtained (Rathnayake et al., 2018).

For cakes with the addition of hawthorn and rosehip powder, it is recommended to replace wheat flour with 10% powder, for mini-cakes with sea buckthorn powder it is recommended to replace wheat flour with 5% vegetable powder.

OVERVIEW AND RECOMMENDATIONS

The problems related in the thesis refers to the stabilization of vegetable oils with biologically active compounds from renewable sources, by elucidating the chemical, physico-chemical, biochemical transformations that take place under conditions of extraction, storage, incorporation of biologically active compounds and formulation based on food results. complex. The main results of the research were formulated by the following conclusions:

1. The by-products of lipid oxidation were analyzed by tandem mass spectrometry (LC-MS/MS), electrospray ionisation mode (ESI) with negative and positive polarization. The evaluation of oxPE and oxPC plasmalogens was performed by both polarization modes. CHH derivatization allowed the identification of both low molecular weight LPP and high molecular weight LPP. More than 63 lipid oxidation products were identified, the predominant being hexanal (m/z=98.2021), octenal (m/z=124.1121), hydroxynonenal (m/z=154.2390) and hydroxyoctadecanal (m/z=282.2792). The method applied allowed to determine the chemical changes that occur during lipid oxidation and to confirm the oxidation mechanisms studied, subchapter 3.3. și 3.4. (Subotin et al., 2021).

2. The physico-chemical parameters of fortified vegetable oils with lipophilic extracts of sea buckthorn, hawthorn and rosehip indicate that the oxidation process is considerably slowed down, compared to the control sample. During 3 months of storage of fortified oils they showed stable characteristics, PV being considerably lower: by 0.5 $m_{echiv}O_2$/kg in the case of rosehip extract, by about 1.0 $m_{echiv}O_2$/kg for sea buckthorn and hawthorn extracts ; the value of the *p*-anisidine value for oil with lipophilic extracts varies between 10.61 - 10.94 u.c., and for unfortified oil varies between 9.65 - 13.97 u.c., subchapter 3.1. (Popovici et al., 2018d; 2020).

3. The antioxidant activity (AA) of fortified vegetable oils under conditions of induced gastric digestion (pH=2.0 ±0.1) shows a significant increase for samples with lipophilic extracts compared to the control sample (17.58±0.90%), constituting respectively: for sea buckthorn-46.43±0.90%; for rosehips: 37.08±0.90%, and for hawthorn -39.29±0.90%. The acidic environment favors the release of biologically active compounds, which also influences the antioxidant capacity. In the phase of intestinal digestion induced by the incubation of samples in an alkaline environment (pH =8.2±0.1) the AA of sunflower oil is 4.26±0.3%, and for fortified oils the AA values vary respectively from 8.09±0.3% for sea buckthorn; 7.06±0.3% (rosehip) and 4.56±0.3% (hawthorn). Most bioactive compounds are extremely sensitive to slightly alkaline conditions, being susceptible to interaction with other released food components, such as dietary fiber and protein, subchapter 3.2. (Popovici et al., 2021c; 2021b)

4. Were developed technologies for obtaining complex food products with the addition of lipophilic extracts and vegetable powders from sea buckthorn, hawthorn and rosehip: functional sauces with the addition of ELC, ELP and ELM; mini-cakes and donuts with the addition of sea buckthorn

powder, hawthorn and rosehip; functional candies with sea buckthorn, hawthorn and rosehip vegetable powders. Quality parameters of processed products - PV, AV, CD and CT confirmed the slowdown of oxidative processes during storage of foods with high lipid content, chapter 4 (Popovici, 2018; Popovici et al., 2019d).

5. Complex foods with the addition of lipophilic extracts and vegetable powders are characterized by a rich content of carotenoids and plant pigments: chlorophyll α-0.68-0.99 mg/L; chlorophyll β-1.39-2.54 mg/L; β-carotene-17.18-20.16 mg/L; lycopene-16.15-22.11 mg/L; zeaxanthin-15.99-21.98 mg/L (candy). As a result of *in vitro* gastrointestinal digestion, an essential increase in antioxidant activity was attested: for PM-30.18 ±1.20%, and for BPM - 70.07 ± 0.80%; BPC -64.26±1.20%; BPP -58.45 ±1.20%, subchapter 4.2.3 (Popovici et al., 2019d; 2019e).

6. The technological parameters of the manufacturing process of flour products with high lipid content were evaluated. Samples with vegetable additives (donuts) show a low oil content absorbed during frying (14.03-15.47%) compared to PM-17.67%, due to the diversification of the recipe by the addition of hydrocolloids from vegetable matter. The analysis of the CIELab color space and the sensory analysis showed that the optimum concentration of 5% plant additives is optimal, subchapter 4.3.2.

7. It was argued that lipophilic extracts, fortified oils with sea buckthorn extracts and powders, hawthorn and rosehips could be used to make high-lipid confectionery and pastries products. The analysis of the oxidative stability over time of the complex products obtained showed that the vegetable powders of sea buckthorn, hawthorn and rosehip, characterized by a high content of carotenoids and chlorophylls, provide a sufficient antioxidant potential to slow down the oxidative processes and alteration of fats in the food matrix., subchapter 4.2.2. (Popovici et al., 2019c; 2019a).

PRACTICAL RECOMMENDATIONS

Within the thesis was developed a series of processes for the manufacture of complex foods with the addition of lipophilic extracts and vegetable powders of sea buckthorn fruit, hawthorn and rosehip that are recommended for their implementation in the food industry:

1. **Process for stabilizing vegetable oils with lipophilic extracts of sea buckthorn, hawthorn and rosehip**, according to the patent (Popovici, 2019b; Popovici et al., 2020).
2. **Technology for making emulsified sauce with the addition of lipophilic extracts from sea buckthorn, hawthorn and rosehip,** according to the patent (Popovici, 2018; Popovici et al., 2021a).
3. **Technology for the manufacture of functional candies with sea buckthorn powder, hawthorn and rosehip** (Popovici et al., 2019c).

The addition of sea buckthorn, hawthorn and rosehip powders has a positive influence on sensory parameters, especially taste, smell and color. The positive influence of sea buckthorn, hawthorn and rosehip vegetable powders on the *in vitro* antioxidant activity has been demonstrated, which is considerably higher compared to the control sample. For candies with added vegetable powders, it is recommended to replace walnuts with 5% sea buckthorn powder, hawthorn and rosehip.

4. Technology for the manufacture of donuts with sea buckthorn, hawthorn and rosehip powder

The addition of sea buckthorn, hawthorn and rosehip powders has a positive influence on sensory indices, especially taste and color. The positive influence of sea buckthorn, hawthorn and rosehip vegetable powders on the *in vitro* antioxidant activity has been demonstrated, which is considerably higher compared to the control sample for both gastric and intestinal digestion. It was found that the oil content absorbed during frying does not vary significantly for GPP and decreases by approx. 15% for GPM and GPC. For donuts with added vegetable powders, it is recommended to replace wheat flour with 5% sea buckthorn powder, hawthorn and rosehip.

5. Technology for the manufacture of mini-cakes with sea buckthorn, hawthorn and rosehip powder

The addition of sea buckthorn, hawthorn and rosehip powders has a positive influence on sensory parameters, especially taste, smell and color. There has been an increase in the content of biologically active compounds in mini-cakes with the addition of sea buckthorn powder, hawthorn and rosehip, which can provide an increased antioxidant potential. For mini-cakes with the addition of hawthorn and rosehip powder it is recommended to replace wheat flour with 10% powder, for mini-cakes with sea buckthorn powder it is recommended to replace wheat flour with 5% vegetable powder.

BIBLIOGRAPHY

CIUMAC, J., REȘITCA, V., CHIRSANOVA, A., et al. *Tehnologia generală a produselor alimentare:Indicații metodice privind efectuarea lucrărilor de laborator*. Chişinău: Tehnica-UTM, 2019.

COLIVA, G., LANGE, M., COLOMBO, S., et al. Sphingomyelins Prevent Propagation of Lipid Peroxidation—LC-MS/MS Evaluation of Inhibition Mechanisms. *Molecules* 25 (8), 2020: pp.1925. https://doi.org/10.3390/molecules25081925.

CREȚU, L., și DOMAŞENCO, L. *Plantele alimentare care ne apără sănătatea*. Arc, 2005.

GHENDOV-MOSANU, A., CRISTEA, E., PATRAS, A., et al. Rose Hips, a Valuable Source of Antioxidants to Improve Gingerbread Characteristics. *Molecules* 25 (23), 2020a: pp.5659. https://doi.org/10.3390/molecules25235659.

GHENDOV-MOSANU, A., CRISTEA, E., PATRAS, A., et al. Potential Application of Hippophae Rhamnoides in Wheat Bread Production. *Molecules* 25 (6), 2020b: pp.1272. https://doi.org/10.3390/molecules25061272

GHENDOV-MOȘANU, A., STURZA, R., OPRIŞ, O., LUNG, I., POPESCU, L., **POPOVICI, V.,** et al. Effect of Lipophilic Sea Buckthorn Extract on Cream Cheese Properties. *Journal of Food Science and Technology* 57 (2), 2020: pp.628–37. https://doi.org/10.1007/s13197-019-04094-w.

HARITONOV, S., și STURZA, R. IN VITRO BIOAVAILABILITY OF SUNFLOWER OIL FORTIFIED WITH IODINE, decembrie, 2018. https://doi.org/10.5281/ZENODO.2576750.

HERNÁNDEZ, Y., LOBO, M.G., și GONZÁLEZ, M. Determination of Vitamin C in Tropical Fruits: A Comparative Evaluation of Methods. *Food Chemistry* 96 (4), 2006: pp.654–64. https://doi.org/10.1016/j.foodchem.2005.04.012.

KAUR, D., WANI, A.A., SINGH, D.P., et al. Shelf Life Enhancement of Butter, Ice-Cream, and Mayonnaise by Addition of Lycopene. *International Journal of Food Properties* 14 (6), 2011: pp.1217–31. https://doi.org/10.1080/10942911003637335.

LANGE, M., NI, Z., CRISCUOLO, A., et al. Liquid Chromatography Techniques in Lipidomics Research. *Chromatographia* 82 (1), 2019: pp.77–100. https://doi.org/10.1007/s10337-018-3656-4.

LUCAS-GONZÁLEZ, R., VIUDA-MARTOS, M., PÉREZ ÁLVAREZ, J.A., et al. Changes in Bioaccessibility, Polyphenol Profile and Antioxidant Potential of Flours Obtained from Persimmon Fruit (Diospyros Kaki) Co-Products during in Vitro Gastrointestinal Digestion. *Food Chemistry* 256 (august), 2018: pp.252–58. https://doi.org/10.1016/j.foodchem.2018.02.128.

OLAWUYI, I.F., și LEE, W.Y. Quality and Antioxidant Properties of Functional Rice Muffins Enriched with Shiitake Mushroom and Carrot Pomace. *International Journal of Food Science & Technology* 54 (7), 2019: pp.2321–28. https://doi.org/10.1111/ijfs.14155.

PAVAN, V., SANCHO, R.A.S., și PASTORE, G.M. The Effect of in Vitro Digestion on the Antioxidant Activity of Fruit Extracts (Carica Papaya, Artocarpus Heterophillus and Annona Marcgravii). *LWT - Food Science and Technology* 59 (2), 2014: pp.1247–51. https://doi.org/10.1016/j.lwt.2014.05.040.

POPOVICI, V. The impact of hawthorn lipophilic extract on oxidative stability of food products. În *MTFI-2018 International Conference, Book of Abstracts*, pp.198–202. Chisinau, 2018.

POPOVICI, V., GHENDOV-MOSANU, A., PATRAŞ, A., DESEATNICOVA O., STURZA R.,. *Procedeu de obținere a sosului funcțional*, Cerere de brevet de invenție de scurtă durată, nr. intrare 2225, data intrare 2021.07.29

POPOVICI V., GHENDOV-MOȘANU A., STURZA R., DESEATNICOVA O. *Procedeu de stabilizare a uleiurilor vegetale.* Brevet de invenție de scurtă durată, 9670, 2020.12.02.

POPOVICI, V., KOVALIOV, E., CAPCANARI T., POPOVICI C., O. RADU, *Evolution of total carotenoid content in food products enriched with rosehip (rosa canina) powder*, Resource and Energy Saving Technologies of Production and Packing of Food Products as the Main Fundamentals of Their Competitiveness, Proceedings of the 8th International Specialized Scientific and Practical Conference September 12, 2019, pp. 170, Kyiv, Ukraine, ISBN 978-966-612-227-1.

POPOVICI, V., RADU O., HUBENIA V., COVALIOV E., CAPCANARI T., POPOVICI C., *Physico-chemical and sensory properties of functional confectionery products with Rosa Canina powder,* Ukrainian Food Journal, Volume 8, Issue 4, Kiev 2019, ISSN 2313-5891, pp. 815 – 827.

RAGAEE, S., GUZAR, I., DHULL, N., et al. Effects of Fiber Addition on Antioxidant Capacity and Nutritional Quality of Wheat Bread. *LWT - Food Science and Technology* 44 (10), 2011: pp.2147–53. https://doi.org/10.1016/j.lwt.2011.06.016.

RATHNAYAKE, H.A., NAVARATNE, S.B., și NAVARATNE, C.M. Porous Crumb Structure of Leavened Baked Products. *International Journal of Food Science* 2018 (august), 2018: pp.1–15. https://doi.org/10.1155/2018/8187318.

RODRÍGUEZ-ROQUE, M.J., ROJAS-GRAÜ, M.A., ELEZ-MARTÍNEZ, P., et al. Changes in Vitamin C, Phenolic, and Carotenoid Profiles Throughout in Vitro Gastrointestinal Digestion of a Blended Fruit Juice. *Journal of Agricultural and Food Chemistry* 61 (8), 2013: pp.1859–67. https://doi.org/10.1021/jf3044204.

ROMAN, I., STĂNILĂ, A., și STĂNILĂ, S. Bioactive Compounds and Antioxidant Activity of Rosa Canina L.Biotypes from Spontaneous Flora of Transylvania. *Chemistry Central Journal* 7 (1), 2013: pp.73. https://doi.org/10.1186/1752-153X-7-73.

SANDULACHI, E., BULGARU, V., GHENDOV-MOSANU, A., et al. Controlling the Risk of Bacillus in Food Using Berries. *Food and Nutrition Sciences* 12 (06), 2021: pp.557–77. https://doi.org/10.4236/fns.2021.126042.

SARAF, S., SINGH, A., și DESAI, B.G. Estimation of Porosity and Pore Size Distribution from Scanning Electron Microscope Image Data of Shale Samples: A Case Study on Jhuran Formation of Kachchh Basin, India. *ASEG Extended Abstracts* 2019 (1), 2019: pp.1–3. https://doi.org/10.1080/22020586.2019.12073197.

SAROLIĆ, M., GUGIĆ, M., TUBEROSO, C.I.G., et al. Volatile Profile, Phytochemicals and Antioxidant Activity of Virgin Olive Oils from Croatian Autochthonous Varieties Mašnjača and Krvavica in Comparison with Italian Variety Leccino. *Molecules (Basel, Switzerland)* 19 (1), 2014: pp.881–95. https://doi.org/10.3390/molecules19010881.

SIRÓ, I., KÁPOLNA, E., KÁPOLNA, B., et al. Functional Food. Product Development, Marketing and Consumer Acceptance—A Review. *Appetite* 51 (3), 2008: pp.456–67. https://doi.org/10.1016/j.appet.2008.05.060.

STURZA, RODICA, DRUȚĂ, RAISA, COVACI, ECATERINA, et al. MECHANISMS OF SUNFLOWER OIL TRANSFORMING INTO FORCED THERMAL OXIDATION PROCESSES, septembrie, 2020. https://doi.org/10.5281/ZENODO.3949716.

SUBOTIN, I., DRUTA, R., **POPOVICI, V.**, et al. Kinetic of Forced Oxidation of Grape Seeds, Walnuts and Corn Germs Oils in the Presence of Antioxidants. *Food and Nutrition Sciences* 12 (12), 2021: pp.1326–39. https://doi.org/10.4236/fns.2021.1212097.

LIST OF THE AUTHOR'S PUBLICATIONS ON THE SUBJECT OF THE THESIS

1. Articles in scientific journals

- in journals in the Web of Science and SCOPUS databases:

1. SUBOTIN, I., DRUTA, R., **POPOVICI, V.**, COVACI, E., STURZA, R. *Kinetic of Forced Oxidation of Grape Seeds, Walnuts and Corn Germs Oils in the Presence of Antioxidants,* Food and Nutrition Sciences, 2021, nr. 12, pp. 1326-1339. doi: 10.4236/fns.2021.1212097. (WoS – ESCI)

2. GHENDOV-MOSANU A., STURZA R., OPRIS O., LUNG I., POPESCU L., **POPOVICI V.**, SORAN M. L., PATRAS A., *Effect of lipophilic sea buckthorn extract on cream cheese properties,* Journal of Food Science and Technology. 2020, nr. 2(57), pp. 628-637. ISSN 0022-1155. DOI:10.1007/s13197-019-04094-w. (WoS – ESCI – IF=1,849)

3. **POPOVICI V.**, RADU O., HUBENIA V., COVALIOV E., CAPCANARI T., POPOVICI C., *Physico-chemical and sensory properties of functional confectionery products with Rosa Canina powder*, Ukrainian Food Journal, Volume 8, Issue 4, Kiev 2019, ISSN 2313-5891, pp. 815 – 827. (WoS – ESCI)

- in journals from the National Register of profile journals (indicating the category)

4. **POPOVICI, V.**, *Evaluation of the oxidative stability of sea buckthorn (hippophae rhamnoides l.) lipophilic extract*. In: Journal of Engineering Sciences. 2018, nr. 3, pp. 111-115. ISSN 2587-3474. DOI: 10.5281/zenodo.2557344. (DOAJ – cat. B+)

5. **POPOVICI V.**, STURZA R., GHENDOV-MOȘANU A., SORAN L., LUNG I., PATRAȘ A., *Influența condițiilor de extracție asupra compoziției și activității antioxidante a extractelor liposolubile de măceșe,* Meridian ingineresc, vol. 1, 2018, 23-27. ISSN 1683-853X. (IBN/IDSI – cat. C)

2. Articles in the proceedings of conferences and other scientific events

- in the works of scientific events included in other databases accepted by ANACEC

6. **POPOVICI, V.** *Evaluarea activității antioxidante in vitro a extractelor liposolubile din fructe de pădure*. In: The closing conference of the Intelligent valorisation of agro-food industrial wastes project, 2SOFT/1.2/83: proc., 24 February 2022, Chisinau, Republica Moldova: Book of abstracts, 2022, p. 43. ISBN 978-9975-3464-6-7.

7. **POPOVICI V.,** STURZA R., GHENDOV-MOȘANU A., *Physico-chemical characteristics of lipophilic extracts of rosehip (rosa canina) and hawthorn (crataegus) fruits,* International Conference INTELLIGENT VALORISATION OF AGRO-INDUSTRIAL WASTES, Book of abstracts, Chișinău, 7-8 octombrie 2021, ISBN 978-9975-3464-2-9. (IBN)

8. **POPOVICI V.,** STURZA R., GHENDOV-MOȘANU A., *The impact of hawthorn (Crataegus) lipophilic extract on the oxidative stability of vegetable oils,* The 16th International Conference of Constructive Design and Technological Optimization in Machine Building Field, OPROTEH 2021, Conference Proceedings, Bacău, 25-27 mai 2021, ISSN 2457 - 3388. (IBN)

9. **POPOVICI V.,** STURZA R., GHENDOV-MOȘANU A., SORAN M. L., LUNG I., *Total carotenoid content evaluation of functional food products with rosehip powder (Rosa Canina),* International Conference Achievements And Perspectives Of Modern Chemistry dedicated to the 60th anniversary from the foundation of the Institute of Chemistry, 9-11 October 2019, Chisinau, Republic of Moldova, p.236, ISBN 978-9975-62-428-2. (IBN/IDSI)

10. **POPOVICI V.**, BOAGHI E., RADU O., CAPCANARI T., POPOVICI C., *Evaluation of total carotenoid content in functional food products enriched with rosehip powder (Rosa Canina)*, International Conference Achievements And Perspectives Of Modern Chemistry dedicated to the 60th anniversary from the foundation of the Institute of Chemistry, 9-11 October 2019, Chisinau, Republic of Moldova, p.186, ISBN 978-9975-62-428-2. (IBN/IDSI)

11. POPOVICI V., COVALIOV E., CAPCANARI T., POPOVICI C., O. RADU, *Evolution of total carotenoid content in food products enriched with rosehip (rosa canina) powder*, Resource and Energy Saving Technologies of Production and Packing of Food Products as the Main Fundamentals of Their Competitiveness, Proceedings of the 8th International Specialized Scientific and Practical Conference September 12, 2019, pp. 170, Kyiv, Ukraine, ISBN 978-966-612-227-1. (IBN)

12. POPOVICI V., *Evaluation of the oxidative stability of rosehip (Rosa Canina) lipophilic extracts*, Papers of the international symposium EURO-ALIMENT, 5-6 September 2019, Galati, Romania, p.43-44,. ISSN 1843-5114. (IBN)

13. POPOVICI V., *The impact of hawthorn lipophilic extract on oxidative stability of food products*, MTFI-2018 International Conference, TUM, Chisinau, 2018, p.198-202, ISBN 978-9975-87-428-1. (IBN/IDSI)

14. POPOVICI V., STURZA R., GHENDOV-MOSANU A., ROSCA I., SORAN L., LUNG I., OPRIS O., *Total carotenoid content of local berries lipophilic extracts**, MTFI-2018 International Conference, TUM, Chisinau, 2018, p. 228, ISBN 978-9975-87-428-1. (IBN/IDSI)

15. POPOVICI V., STURZA R., *Antioxidant capacity of local berries in complex food products*, Food and Environment Safety - Journal of Faculty of Food Engineering, Ştefan cel Mare University - Suceava Volume XVII, Issue 1, 2018; p.32-36. ISSN – 2068-6609. (IBN)

16. POPOVICI V., I. ROSCA, C. CIOBANU, L. SORAN, I. LUNG, *Stabilite oxydative et activite antioxydante des extraits liposolubes d'eglantier* –COFrRoCA - 2018 Tenth French-Romanian Colloquium of Applied Chemistry 27-29 June 2018, Bacau, ROMANIA; p.95. ISSN 2068-6382. (IBN)

17. POPOVICI V., *Evaluarea impactului extractelor horticole asupra stabilității oxidative a complexului lipidic din alimente*, Sesiunea națională de comunicări științifice studențești: Științe ale naturii și exacte, USM, 4-5 mai 2017, Chisinau, p.31-33. (IBN/IDSI)

- **in the works of scientific events included in the Register of materials published on the basis of organized scientific events in the Republic of Moldova**

18. POPOVICI V., *The impact of berry powders on the quality parameters of functional food products,* Conferința științifică internațională „Perspectivele și Problemele Integrării în Spațiul European al Cercetării și Educației", Ediția a VIII-a, Cahul 4 iunie 2021. (IBN)

19. POPOVICI V., *The oxidative stability of seabuckthorn lipophilic extracts,* Conferința Studenților, Masteranzilor și Doctoranzilor, Volum I, UTM, Chișinău, 1-3 aprilie 2020, p.411-414, ISBN 978-9975-45-632-6. (IBN/IDSI)

20. POPOVICI V., BOAGHI E., RADU O., CAPCANARI T., RUBȚOV S., *Evaluation of total carotenoid content in functional food products with rosehip powder (R.Canina),* International Conference Days of the Academy of Technical Sciences of Romania 2019, 14th Edition, October 17-18, 2019, Chisinau. (IBN)

21. POPOVICI V., *The oxidative stability of vegetable oils enriched with caratenoids***,** Conferința Studenților, Masteranzilor și Doctoranzilor, Volum I, UTM, Chișinău, 26-29 martie 2019, p.509-510. ISBN 978-9975-45-588-6. (IBN/IDSI)

22. POPOVICI V., ROȘCA ILIE, GANŢA DOMNIŢA-LAURA, EŞANU NATALIA, *Diminuarea impactului oxidării lipidelor cu adaosuri vegetale de antioxidanţi*, Conference of students, master students and doctoral students of TUM, Chisinau, 2016. (IBN/IDSI)

3. Patents and other intellectual property objects (IPO)

- **issued by the State Agency for Intellectual Property**

1. POPOVICI, V., GHENDOV-MOSANU, A., PATRAŞ A., DESEATNICOVA O., STURZA R., *Procedeu de obținere a sosului funcțional.* Cerere de brevet de invenție de scurtă durată, nr. intrare 2225, data intrare 2021.07.29.

2. POPOVICI V., GHENDOV-MOȘANU A., STURZA R., DESEATNICOVA O. *Procedeu de stabilizare a uleiurilor vegetale.* Brevet de invenție de scurtă durată, 9670, 2020.12.02.

ADNOTARE

Popovici Violina: Stabilizarea uleiurilor vegetale cu compuși biologic activi din surse regenerabile, teză de doctor în științe inginerești, Chișinău, 2022.

Structura tezei: constă din introducere, 4 capitole, concluzii și recomandări, bibliografie cu 291 titluri 3 anexe. Textul de bază conține 112 pagini, inclusiv 41 figuri și 38 de tabele. Rezultatele obținute sunt publicate în 23 lucrări științifice.

Cuvinte-cheie: ulei vegetal, extract liposolubil, stabilitate oxidativă, alimente complexe, calitate.

Scopul lucrării: constă în elucidarea modificărilor chimice care au loc pe parcursul oxidării lipidice, stabilizarea uleiurilor vegetale și evaluarea impactului extractelor liposolubile asupra stabilității oxidative a produselor alimentare complexe prin optimizarea tehnologiei de fabricație.

Obiectivele cercetării prevăd: obținerea extractelor liposolubile din surse vegetale regenerabile autohtone, determinarea indicatorilor de calitate, parametrilor cromatici și activitatea antioxidantă; elaborarea tehnologiilor de fabricare a unor produse alimentare complexe; determinarea indicatorilor de calitate, parametrilor cromatici, biodisponibilitatea compușilor biologic activi și activitatea antioxidantă.

Noutatea și originalitatea științifică constă în argumentarea posibilității de utilizare a compușilor biologic activi din surse regenerabile de cătină, păducel, măceșe, identificarea condițiilor optime de obținere a extractelor liposolubile din surse vegetale autohtone cu potențial antioxidant sporit; argumentarea posibilității de utilizare a extractelor liposolubile și pudrelor vegetale autohtone pentru obținerea unor produse alimentare complexe.

Rezultatele principale: S-a demonstrat că pe parcursul depozitării uleiului vegetal se desfășoară procesul de autooxidare a lipidelor și s-a constatat că se formează peste 60 de aldehide cu masă moleculară mică. S-a argumentat posibilitatea de utilizare a compușilor biologic activi din surse vegetale regenerabile de origine autohtonă pentru obținerea extractelor liposolubile cu potențial antioxidant sporit; a fost elucidată influența extractelor liposolubile asupra stabilității oxidative a uleiurilor vegetale; s-a determinat activitatea antioxidantă, parametrii cromatici CIELab, indicatorii de calitate a extractelor liposolubile; au fost obținute informații științifice noi despre mecanismul și dinamica formării produșilor oxidării lipidice pe parcursul proceselor oxidative; au fost elaborate tehnologii de fabricare a unor alimente complexe cu determinarea indicatorilor de calitate; a fost evaluată stabilitatea oxidativă în timp a produselor alimentare complexe obținute și s-a constatat că pudra vegetală asigură potențialul antioxidant necesar pentru a încetini procesele oxidative și de alterare a grăsimilor din componența produselor complexe.

Semnificația teoretică: Pentru prima dată a fost elaborată metodologia de stabilizare a uleiurilor vegetale din surse regenerabile autohtone; au fost obținute uleiuri cu extracte liposolubile din surse vegetale autohtone cu potențial antioxidant sporit; pentru prima dată a fost utilizată spectrometria de masă tandem pentru stabilirea dinamicii de formare a produșilor oxidării lipidice.

Valoarea aplicativă: Au fost propuse și realizate procedee de obținere și stabilizare a uleiurilor vegetale; tehnologii de fabricare a unor alimente complexe. A fost obținut 1 brevet de invenție și 1 cerere de brevet.

Implementarea rezultatelor științifice: Rezultatele cercetărilor au fost implementate la SRL "Rose Line", Țaul, Dondușeni.

АННОТАЦИЯ

Попович Виолина: Стабилизация растительных масел биологически активными соединениями из возобновляемых источников, докторская диссертация по техническим наукам, Кишинев, 2022.

Структура диссертации: состоит из введения, 4 глав, выводов и рекомендаций, библиографии из 291 источников, 3 приложения. Основной текст содержит 112 страницы, 41 рисунков и 38 таблиц. Полученные результаты опубликованы в 23 научных статьях.

Ключевые слова: растительное масло, жирорастворимый экстракт, окислительная стабильность, комплексные пищевые продукты, показатели качества.

Цель диссертации: состоит в выяснении химических изменений, происходящих во время окисления липидов, стабилизации растительных масел и оценке воздействия жирорастворимых экстрактов на окислительную стабильность сложных пищевых продуктов путем оптимизации технологии производства.

В **задачи исследования** входят: получение жирорастворимых экстрактов из возобновляемых растительных источников местного происхождения, определение их показателей качества, хроматических параметров и антиокислительной активности; разработка технологий производства сложных пищевых продуктов; определение их показателей качества, хроматических параметров, биодоступности биологически активных соединений и антиокислительной активности.

Научная новизна и оригинальность заключаются в обосновании использования биологически активных соединений из возобновляемых источников (облепихи, боярышника, шиповника), определении оптимальных условий получения жирорастворимых экстрактов из местных растительных источников с повышенным антиокислительным потенциалом; аргументации использования жирорастворимых экстрактов и растительных порошков для получения сложных пищевых продуктов.

Основные результаты: Доказано, что при хранении растительного масла происходит процесс самоокисления и установлено, что образуется более 60 низкомолекулярных альдегидов. Обоснована возможность использования биологически активных соединений из возобновляемых растительных источников местного происхождения для получения жирорастворимых экстрактов с повышенным антиокислительным потенциалом; выяснено влияние жирорастворимых экстрактов на окислительную стабильность растительных масел; определена антиокислительная активность, хроматические параметры CIELab, показатели качества жирорастворимых экстрактов; получены новые научные сведения о механизме и динамике образования продуктов окисления липидов при окислительных процессах; разработаны комплексные технологии производства пищевых продуктов и определены их показатели качества.

Теоретическая значимость: впервые разработана методика стабилизации растительных масел из возобновляемых источников местного происхождения; получены масла с жирорастворимыми экстрактами из местных растительных источников с повышенным антиоксидантным потенциалом; впервые тандемная масс-спектрометрия была использована для установления динамики образования продуктов окисления липидов.

Прикладное значение: Предложены и выполнены процедуры получения и стабилизации растительных масел; сложные технологии производства пищевых продуктов. Получен 1 патент и 1 заявку на патент.

Внедрение научных результатов: Результаты исследований внедрены на ООО «Rose Line», г. Цаул, Дондюшаны..

ANNOTATION

Popovici Violina:. Stabilization of vegetable oils with biologically active compounds from renewable sources, doctoral thesis, Chisinau, 2022.

Thesis structure: consists of introduction, 4 chapters, conclusions and recommendations, bibliography with 291 titles 3 annexes. The basic text contains 112 pages, including 41 figures and 38 tables. The obtained results are published in 23 scientific papers.

Key-words: vegetable oil, lipophilic extract, oxidative stability, complex foods, quality

The purpose of the work: consists in elucidating the chemical changes that take place during lipid oxidation, stabilizing vegetable oils and evaluating the impact of lipophilic extracts on the oxidative stability of complex foods by optimizing manufacturing technology.

The research objectives include: obtaining lipophilic extracts from local renewable plant sources, determining quality indicators, chromatic parameters and antioxidant activity; elaboration of technologies for manufacturing complex food products; determination of quality indicators, chromatic parameters, bioavailability of biologically active compounds and antioxidant activity.

The scientific novelty and originality consists in arguing the possibility of using bioactive compounds from renewable sources of sea buckthorn, hawthorn, rosehip, identifying the optimal conditions for obtaining lipophilic extracts from local plant sources with increased antioxidant potential; arguing the possibility of using lipophilic extracts and local vegetable powders to obtain complex foods.

Main results: It was shown that the autoxidation process that takes place during storage of vegetable oil and are formed more than 60 low molecular weight aldehydes. It was argued the possibility of using biologically active compounds from renewable plant sources of local origin to obtain lipophilic extracts with increased antioxidant potential; the influence of lipophilic extracts on the oxidative stability of vegetable oils was elucidated; the antioxidant activity was determined, the CIELab chromatic parameters, the quality indicators of the lipophilic extracts; new scientific information has been obtained on the mechanism and dynamics of the formation of lipid oxidation products during oxidative processes; complex food manufacturing technologies have been developed to determine quality parameters; the oxidative stability over time of the complex foods obtained was evaluated and it was found that the plant powder provides the antioxidant potential necessary to slow down the lipid oxidation in the composition of the complex products.

Theoretical significance: For the first time, the methodology for stabilizing vegetable oils from local renewable sources was developed; oils with lipophilic extracts were obtained from local plant sources with increased antioxidant potential; For the first time, tandem mass spectrometry was used to establish the dynamics of the formation of lipid peroxidation products.

Applicative value: Procedures for obtaining and stabilizing vegetable oils have been proposed and performed; complex food manufacturing technologies. 1 patent was obtained and 1 patent application was registered.

Implementation of scientific results: The research results were implemented at LTD "Rose Line", Țaul, Dondușeni.

POPOVICI VIOLINA

STABILIZATION OF VEGETABLE OILS WITH BIOACTIVE COMPOUNDS FROM RENEWABLE SOURCES

253.06 Biological and chemical technologies in the food industry

Summary of the doctoral thesis in engineering sciences

Approved for printing: date	Paper size 60x84 1/16
Offset paper. Offset printing.	Circulation 50 ex.
Printing sheets:…	Order no. .

TUM, MD 2004, mun. Chisinau, bd. Stefan cel Mare si Sfant, no. 168. “TEHNICA-UTM” Publishing House, MD-2045, Chisinau mun., 9/9 Studenţilor street

CHISINAU 2022