МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ
Федеральное государственное автономное образовательное учреждение
высшего образования
«Дальневосточный федеральный университет»

ШКОЛА БИОМЕДИЦИНЫ

Департамент пищевых наук и технологий

Дарвиш Фади Самир Юсра

Разработка способов стабилизации качества и сохраняемости растительных масел с использованием натуральных антиоксидантов

МАГИСТЕРСКАЯ ДИССЕРТАЦИЯ
по образовательной программе подготовки магистров
по направлению 19.04.05 «Высокотехнологичные производства пищевых продуктов функционального и специализированного назначения»

г. Владивосток
2018

Автор работы студент гр. М 7209 _____
подпись

«25» июня 2018 г.

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«_____»_____ 2018 г

Защищена в ГЭК с оценкой

_____

Секретарь ГЭК

_____ _____
подпись И.О. Фамилия

«_____» _____ 2018 г.

УТВЕРЖДАЮ
Ю.С. Хотимченко / _____ /
Ф.И.О. Подпись

Директор Школы биомедицины
«__» _____ 2018 г.

В материалах данной выпускной квалификационной работы не содержатся сведения, составляющие государственную тайну, и сведения, подлежащие экспортному контролю.

Ю.С. Хотимченко / _____ /
Ф.И.О. Подпись

Уполномоченный по экспортному контролю
«__» _____ 2018 г.

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Департамент пищевых наук и технологий

З А Д А Н И Е
на выпускную квалификационную работу

студенту (ке) Дарвиш Фади Самир Юсра (фамилия, имя, отчество) группы *М 7209*

на тему Разработка способов стабилизации качества и сохраняемости растительных масел с использованием натуральных антиоксидантов

Вопросы, подлежащие разработке (исследованию):
Conducting a process of extraction of different herbs (thyme, ginger, rosemary, sage) using different solvents (ethanol 95%, ethanol 70%, propylene glycol 95%, ethanol 95%, and propylene glycol 95%) and measuring the total amount of phenolic compounds and the free radical scavenging activity (DPPH) of herbs extract.Comparison between the acid and peroxide values after the addition of each single herb extract or the addition of a mixture of herb extract to sunflower oil and the acid and peroxide value of either the sample of sunflower oil without additions or the sample of sunflower oil with BHT.

Основные источники информации и прочее, используемые для разработки темы:
Books, Scientific Articles, Textbooks, Master Thesis, Electronic Resources, Normative documents (GOST ,TP TC)

Срок представления работы «22» июня 20 г.

Дата выдачи задания «31» октября 20 г.

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Задание получил (подпись) Дарвиш Ф.С. (и.о.ф)

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ
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Департамент пищевых наук и технологий

ГРАФИК

подготовки и оформления выпускной квалификационной работы

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на тему Разработка способов стабилизации качества и сохраняемости растительных масел с использованием натуральных антиоксидантов

№ п/п	Выполняемые работы и мероприятия	Срок выполнения	Отметка о выполнении
1	Выбор темы и согласование с руководителем	11.09.2017	Выполнено
2	Составление плана работы. Подбор первичного материала, его изучение и обработка. Составление предварительной библиографии	20.09.2017	Выполнено
3	Разработка и представление руководителю первой части работы	18.11.2017	Выполнено
4	Составление задания на преддипломную практику и сбору материала для выполнения ВКР	20.11.2017	Выполнено
5	Разработка и представление руководителю второй части работы	10.02.2018	Выполнено
6	Разработка и представление руководителю третьей части работы	22.04.2018	Выполнено
7	Подготовка и согласование с руководителем выводов, введения и заключения. Подготовка презентации работы	02.05.2018	Выполнено
8	Доработка ВКР в соответствии с замечаниями руководителя	15.05.2018	Выполнено
9	Первая проверка ВКР в системе «Антиплагиат»	25.05.2018	Выполнено
10	Исправление возможных фрагментов плагиата	04.06.2018	Выполнено
11	Предзащита ВКР	07.06.2018	Выполнено
12	Доработка ВКР в соответствии с замечаниями, высказанными на предзащите	15.06.2018	Выполнено
13	Вторая проверка ВКР в системе «Антиплагиат» и представление руководителю на проверку для получения отзыва	20.06.2018	Выполнено
14	Загрузка ВКР в ЭБС	25.06.2018	Выполнено
15	Завершение подготовки к защите (доклад, раздаточный материал, презентация в Power Point)	25.06.2018	Выполнено

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«22» 04 2019 20 г.

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«25» 04 2019 20 г.

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ
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ОТЗЫВ РУКОВОДИТЕЛЯ

на выпускную квалификационную работу студента (ки) _ Дарвиш Фадир Самир Юсра
(фамилия, имя, отчество)

Направление подготовки 19.04.05 Высокотехнологичные производства пищевых продуктов функционального и специализированного назначения

Профиль _Технология функциональных продуктов питания
Научный руководитель __д.т.н., профессор Табакаева О.В. _____
(ученая степень, ученое звание, и.о. фамилия)

На тему_ Разработка способов стабилизации качества и сохраняемости растительных масел с использованием природных антиоксидантов
Дата защиты ВКР «14» июня 2018 г.

В настоящее время процессам свободно-радикального окисления уделяется все более пристальное внимание в связи с доказанным их влиянием на различные процессы метаболизма организма человека. Количественное изучение антирадикальных свойств различных веществ является актуальным направлением исследований, позволяющим определить пути практического использования веществ с антирадикальной активностью. В связи с этим тема работы является актуальной.

Для данной работы было использовано более 100 источников и публикаций. Экспериментально установлено что введение экстрактов трав в растительное масло замедляет процессы окисления и гидролиза и увеличивает срок хранения.

Работа выполнена на современном уровне, задачи решены в полном объеме, полученные в ходе работы данные обобщены и проанализированы, выводы соответствуют поставленным задачам.

Материал в выпускной квалификационной работе изложен грамотно и последовательно. Результаты имеют конкретное практическое значение. Существенных замечаний по выполненной выпускной квалификационной работе нет. Выпускная квалификационная работа студента Дарвиш Фадир Самир Юсра в полной мере соответствует требованиям, предъявляемым к ВКР студентов, обучающихся по специальности 19.04.05 «Высокотехнологичные производства пищевых продуктов функционального и специализированного назначения». Выпускная квалификационная работа студента Дарвиш Фадир Самир Юсра заслуживает положительной оценки и присвоения степени «Магистр».

Руководитель ВКР _д.т.н., профессор___ _____ Табакаева О.В. ___
(должность, уч.звание) (подпись) (и.о.ф)

«25» июня 2018 г.

МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ
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ШКОЛА БИОМЕДИЦИНЫ
Департамент пищевых наук и технологий

РЕЦЕНЗИЯ

на подготовленную выпускную квалификационную работу (диссертацию) магистранта Дарвиш Фадир Самир Юсра

Направление подготовки 19.04.05 Высокотехнологичные производства пищевых продуктов функционального и специализированного назначения

Профиль _Технология функциональных продуктов питания

Научный руководитель __д.т.н., профессор Табакаева О.В. _____
(ученая степень, ученое звание, и.о. фамилия)

На тему_ Разработка способов стабилизации качества и сохраняемости растительных масел с использованием природных антиоксидантов

1. Актуальность выпускной квалификационной работы (диссертации), ее научное, практическое значение
Работа посвящена актуальной проблеме процессов окисления липидов и гидролиза триацилглицеринов в растительных маслах, так как процессы свободнорадикального окисления влияют на процесс старения и сохранения здоровья. Разработка оксистабильных композиций растительных масел является одним из наиболее перспективных способов создания безопасных продуктов питания.
2. Достоинства работы:
Магистрант в ходе работы демонстрирует умение работать с научной литературой, справочной, нормативной документацией, планировать и ставить эксперименты, обобщать их результаты, обрабатывать полученные данные, формировать задачи и выводы по результатам работы, разрабатывать нормативно-техническую документацию. Тема диссертации раскрыта, задачи выполнены в полном объеме, полученные в ходе работы данные обобщены и проанализированы, выводы соответствуют поставленным задачам. Материал в диссертации изложен грамотно и последовательно_____
3. Недостатки и замечания
Существенных замечаний по выполненной работе нет.
4. Рекомендации по использованию результатов и выводов научно-квалификационной работы (диссертации) _ Результаты диссертации рекомендованы к внедрению в учебный процесс и в производство с учетом разработки системы управления качеством, основанной на принципах ХАССП__
5. Общий вывод: (о присвоении соответствующей квалификации (невозможности присвоить соответствующую квалификацию) и оценка: отлично, хорошо, удовлетворительно, неудовлетворительно)
Присвоить квалификацию исследователь, преподаватель-исследователь, оценка «отлично»

Рецензент ____Смертина Е.С._____
(Ф.И.О.)

_доцент кафедры товароведения ШЭМ ДВФУ, к.т.н., доцент _____ 21.06.2018 г.

ABSTRACT

The work contains 3 chapters, outlined on 91 pages, 27 tables, 25 figures, 102 bibliographic sources.

Keywords**:** sunflower oil, synthetic antioxidants, natural antioxidants, herbs and spices.

Purpose of work is the development of ways to stabilize the quality and the maintain of vegetable oils using natural antioxidants.

The results of research proved the usefulness of using herbal extracts as natural antioxidants to reduce the process of oxidation of vegetable oils and used as substitutes for industrial antioxidants. After making extracts of different herbs (thyme, ginger, rosemary,sage) using different solvents(ethanol 95%, ethanol 70%, propylene glycol 95%, ethanol 95%, and propylene glycol 95%) we measure the total amount of phenolic compounds and the free radical scavenging activity (DPPH) of herbs extract. These extracts were either added separately or added a mixture of these extracts to refine sunflower oil and after measuring the value of peroxide and the acid values of the different oil samples every 15 days for two months and comparing with the acid and peroxide value of either the sample of sunflower oil without additions or the sample of sunflower oil with BHT. The results of experiments show that all the extracts have an antioxidant effect higher than the industrial antioxidant. In addition, the sample containing the rosemary and thyme extract had the lowest peroxide and acid value by comparing it with other oil samples, and this shows that this mixture of extracts has the ability in delaying the occurrence of the oxidation process of refined sunflower oil. Therefore, we suggest that the rosemary and thyme extract can be used as a potential natural antioxidant for vegetable oils rather than industrial antioxidants

CONTENT

INTRODUCTION

Relevance of the topic. The oxidation of vegetable oils is considered one problem in the food industry, thus, are added antioxidants in food [1].

The oils and fats are exposed to the phenomenon of rancidity which lead to a decline in value and quality deterioration oils and lipid containing foods, especially when exposed to elevated temperature, light and oxygen [2].

Long time ago synthetic anti-oxidants such as butylated hydroxyanisole (BHA) and (BHT) were used, to lengthen the period of food oils conservation but it was found that these antioxidants have negative effects on the health of the consumer[3].

So there is a need to look for antioxidants from natural sources as an alternative to prevent the degradation of fats and oils and safe for the consumer.

There are many of the plant extracts containing natural antioxidants, such as, ginger, spices, herbs, seeds, rosemary, cereals, cocoa shell, grains, fruits, catnip, hyssop, oregano, sage and thyme and other natural sources[4].

Where the interest in the use of herbs and spices has increased as a source of natural antioxidants because they contain many phytochemical compounds such as phenolic diterpenes, flavonoids, alkali, tannins and phenolic acids [5].

From the consumer's perspective, these antioxidants are safe in terms of health and did not need to safety followed tests as synthetic anti-oxidation because they are consumed from natural sources long ago [2, 6].

Purpose of work–Development of ways to stabilize the quality and the maintain of vegetable oils using natural antioxidants.

CHAPTER 1 LITERATURE REVIEW

1.1 Lipids oxidation

The oxidation of lipids affects not only the nutritional value and life of food products containing oils, destruction of contained vitamins (the fat-soluble A, D and E), but may also affects human health [7].

Oxidative rancidity takes place in oils when these oils are exposed to elevated temperature, oxygen and light or other catalysts cause unsaturated fatty acids to turn into free radicals. This happens when hydrogen is lost from the a-methylenic carbon in the fatty acid group [8].

Oxidation reactions lead to the production of free radicals which may in turn begin chain reactions that give rise to more oxidation by chain reaction [9].

These free radicals are easily oxidized to produce hydroperoxides and organic compounds, which are responsible for the obnoxious odors and flavors characteristic of rancid fats in vegetable oils [10].

The oxidation of lipids which takes place in the triacylglycerol molecules includes 3steps [11].

The first phase of fat oxidation is called initiation .This phase is called the phase of the production of free radicals fatty acids. This process occurs when the hydrogein atom is removed from unsaturated fatty acids specifically from the group of methylene alkylic. This reaction is often caused by the presence of light, transition metals or high temperature [12].

The interactions and changes that occur at this stage are explained in the following equations (1, 2).

The second phase of fat oxidation is called propagation .The spread of fat free radical in oxidation processes occurs by a chain reaction that consumes oxygen and

produces new radical types such as peroxyl radicals, ROO or by forming peroxides, ROOH .Products R • and ROO• can increase the propagation of free radical reaction and ROO• Initiate chain reaction with other molecules creating hydropyroxides fat and free fat radical.

This reaction is repeated several times so that it produces and accumulates large amounts of heproperoxides and stops only when the unsaturated fat or fatty acid molecules are depleted. The interactions and changes that occur at this stage are explained in the following equations (3, 4,5,6,7,8).

The final phase of fat oxidation is called termination .Radical interaction ends when radicals react and produce a non-radical product. This happens because radicals are very reactive and when there is a decrease in the amount of fatty acids, the bonds are radical to each other and form a non-stable stable compound. This will terminate the interaction [13].

The interactions and changes that occur at this stage are explained in the following equations (9, 10, 11).

(1) RH →R•+H•

(2) ROOH+ RH → R•+H_{2O+}RO•

(3) R• + O2 →ROO•

(4) ROO• + RH →ROOH + R•

(5) ROO• + R → ROOR•

(6) ROOR•→RO•+RO•

(7) RO• +RH→ROH +R•

(8) RO• +O2→R"O+HO_2•

(9) ROO• +ROH → ROOH + R"O +HO•

(9) R• + R• →R-R

(10) ROO•+R•→ROOR

(11) ROO• + ROO• →ROH + R"COR + O2

The mainly oxidation compound are hydroperoxides [14]. These compounds quickly are transformed into other compounds because they are unstable such as aldehydes alkanes, alcohols, and acids which called secondary products [9].

There are other ways to explain the mechanism of fat oxidation:

The first method is called autoxidation. Autoxidation is the most common reaction to explain the mechanism of fat oxidation. This reaction occurs through the incorporation of unsaturated fatty acids with molecular oxygen to produce hydroperoxides.

The other way occurs in the presence of oxygen, when unsaturated fats are exposed to light and a sensitizer this leads to the production of alkyl hydroperoxide. This interaction is called photooxidation[15].

1.2 Antioxidants

There are several ways to inhibit the oxidation process such as denial of access to oxygen, use of lower temperature, inhibition of enzymes catalyzing oxidation reduce the oxygen pressure and the use of suitable packaging [16].

Another way to protect against oxidation use specific additives called antioxidants [17].

Antioxidants are substances obtained from natural sources or industrial sources added in small quantities to vegetable oils to improve oxidative stability, reduce the oxidation rate or delaying the occurrence of auto-oxidation process by preventing free radicals formation [9, 8,18].

Antioxidants lengthen the induction period of oxidation, or slow the rate of oxidation. Antioxidants disable free radicals, such as alkyl or peroxyl fat radicals, inhibit the effect of transitional metals, put out the shirt, oxygen and disrupt the sensitizers [19].

Antioxidant additives must be chosen to edible oils for the purpose of keeping unsaturated fatty acids to get better stability to thermal degradation which takes place between 150 and 220 °C [20, 21].

Antioxidants can give a hydrogen atom to free radicals and turn it into a more stable non-radical product. The main contributors to antioxidants and hydrogen are mono or polyhydroxenolic compounds with different substitutes in the aromatic nucleus. The standard recovery capacity of one of the alkyl, peroxyl and alkoxy radicals of PUFA is 600, 1000, 1600 mph, respectively. Usually the usual recovery of antioxidants is 500 mph or less.

This clearly indicates that antioxidants interact with radical peroxyl prior to a radical pyroxyl reaction with another fatty molecule leading to the formation of other free radicals. Any radical of antioxidants formed by interaction with the peroxyl radical of fat has less energy than radical peroxyl.

Antioxidants are divided into two types depending on its source natural antioxidants and industrial antioxidants [22].

Because of high performance and low cost for synthetic antioxidants, they are widely used in food oil to reduce rancidification such as butylated hydroxyanisole (BHA),octalgallate(OG), butylated hydroxytoluene (BHT) and 2,4,5-trihydroxybutyrophenone (THBP) , but it was found that these antioxidants have negative effects on the health of the consumer [9,23].

There are many plants which have antioxidant properties such as ginger, spices, herbs, teas, rosemary, cereals, cocoa shell, grains, fruits, catnip, hyssop, oregano, sage and thyme and other. Antioxidant effects are due mainly to contain these plants on phenolic compounds [24, 25].

Antioxidants depending on the mechanism of action are divided into primary and secondary antioxidant [26, 27].

In order to get a synergistic effect both types can be mixed with each other. However some antioxidants have more than one way of action [28].

So it was important to use antioxidants that have the ability to delay and protect the oil from the emergence of rancidity in fatty foods; they are working to remove the active

oxygen forms, which are considered the first step oxidize or demolition oxidative, through interact the free radical of fatty acids with antioxidants mutant to stable form.

These antioxidants should be safe to use, and have no odor or flavor, and added in very small quantities, low costs [14].

In the initiation stage the antioxidants function prevent the formation of free radicals. However in the propagation stage antioxidants function by donating hydrogen to terminate the free radical chain [10].

The primary antioxidants act as follows:

-It can end the free radicals chain through donation hydrogen to free radicals and turn them into stable compounds.

-By reacting with lipid radicals they are able to form lipid-antioxidant complexes.

-By reacting with a lipid free radical they are able to inhibit the initiation step.

-By reacting with proxy they are able to delay propagation step [9].

The Secondary antioxidants act as follows:

-Convert hydroperoxide to non-radical type.

-Disrupt singlet oxygen.

-Oxygen scavengers.

-By absorbing ultraviolet radiation.

-By giving primary antioxidants H+[9].

Table 1 – Different classes of antioxidants [29]

Class of antioxidants	Examples	Function
Free radical scavengers	BHA BHT TBHQ Propyl gallate tocopherols Extracts from spices and herbs (rosemary, clove, sage, oregano)	Block free radicals by donating a hydrogen atom
Oxygen scavenger	Ascorbic acid	React with oxygen

	Erythorbic acid Ascorbate Sulfites, bisulfites Ascorbic palmitate	
Chelating agents	Citric acid EDTA Phosphates	React with metal ions capable of catalyzing oxidation

1.2.1 Antioxidants found in Edible oils

Some antioxidants naturally exist in edible oils such as phenolic compounds tocopherols, sterols, carotenoids, and tocotrienols.

Tocopherols were considered the mainly antioxidants exist in edible oils. Some vegetable oils, such as sunflower, soybean, corn oils, and canola contain high concentrations of tocopherols [30].

During the process of removing odor from the oils part of the tocopherols removed, the remaining amount of tocopherol remains sufficient to protect against oxidation.α-tocopherol comparison of the types of tocopherol it is considered more active antioxidant [31, 32].

Other antioxidants present in some oil belong to group of lignans which contain phenolic acids. During processing of oil seeds many of them are insoluble.

During processing of oil seeds, natural antioxidants are found in oil seeds partition into hydrophilic fractions or liposoluble.

Through the solvent extraction or expeller pressing many of lipophilic antioxidants are transported into crude oil by extraction [31].

Many previous research has indicated that oil peroxy radicals are able to interact with tocopherols faster ($104–109 M^{-1}.S^{-1}$) this is compared to their interaction with lipids ($10–60 M^{-1}. S^{-1}$), so they are able to chain breakers and radicals scavengers [33].

10^3 to 10^8 polyunsaturated fatty acid can be protected by1 tocopherol molecule at low pv (peroxide value).H atom at the 6-OH on tocopherols ring can transfer to oil peroxy radical subsequently scavenge this peroxy radicals [30].

Effectiveness of tocopherols as antioxidants related to its concentration and isomers [30].

Phenolic antioxidants through interaction with ROO• can produce ROOH and phenoxyl radical which is relatively stable.

ROO· +PhH → ROOH + Ph·

Ph· through interaction with ROO• can produce non-radical products

ROO·+ Ph· → Non radical products

Where ROO•: peroxyl radicals

Ph·: phenolic antioxidants [33].

Carelli and others found that when a- tocopherol added to sunflower oil for the purpose of increasing oxidative stability. When the amount of tocopherol is increased, the oxidative stability increased. Compared with the industrial antioxidant (BHT) show that its effectiveness similar to the effectiveness of industrial anti-oxidant in sunflower oil [34].

Table 2 – Main classes, compounds and mechanisms of action of antioxidants present in edible vegetable oils [35]

Classes of antioxidants and selected compounds	Antioxidant mechanism
Tocols α-tocopherol c-tocopherol	Primary or chain breaking antioxidants
Phenolic compounds Hydroxytyrosol (α) Tyrosol	Primary or chain breaking antioxidants; Also secondary or preventive antioxidants2 acting as chelators of metal ions; Might stabilize and prevent decompositionof hydroperoxides.

Carotenoids β-carotene	Secondary or preventive antioxidants acting as singlet oxygen quenchers; Also primary or chain breaking antioxidants.
Phytosterols β -sitosterol	Possible primary or chain breaking antioxidant

1.2.2 Synthetic Antioxidants

In many countries, industrial antioxidants are used, but there are many uncertainties about their health effects.

The main reasons in adding these substances to food oils are because of the ability of industrial antioxidant to prolong the life of food oils by delaying or inhibiting the process of oxidation [36].

BHT and BHA these antioxidants can be added alone to food or with other chemicals that have the properties of antioxidants such as ascorbic acid, phosphoric acid, propyl gallate and citric acid.

(Butylated hydroxyanisole; C11H16O2) and (butylated hydroxytoluene; C15H24O), as mentioned earlier, are commonly used preservatives in foods with fats and oils [38]. Their purpose is mainly to delay the oxidation of foods so that they do not change color, flavor, or odor over time. They do this by reacting with oxygen before they react with fats and oils so that fats and oils do not oxidize and spoil.

Long time ago compounds such as TBHQ, BHT and BHA have been known to be antioxidants from unnatural sources, they were produced in laboratories [37, 38].

BHA the scientific name is butylated hydroxyanisole is one of the most widely used antioxidants due to its high solubility in fats and oils and is able to stabilize at high temperatures. And it is added to many foods including vegetable oil, frying oil.

The use of BHA as an antioxidant increased because it has the ability to stabilize at high temperatures. Even though it is used less than BHT [33] .

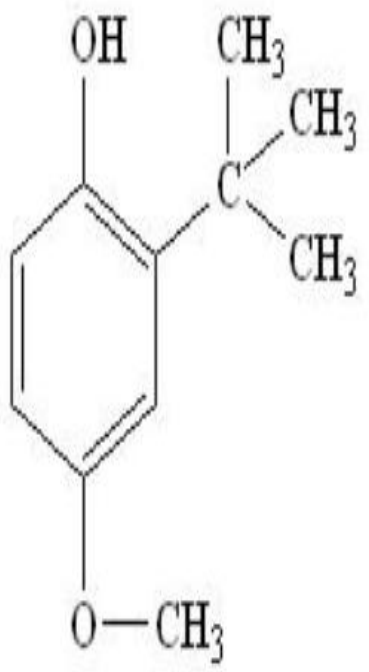

Figure 1 - Chemical Composition of BHA

BHT the scientific name is butylated hydroxytoluene. Although all the benefits of BHT and its derivatives, this family of interesting aromatic compounds very well known as promising antioxidants.

There are more than publications are discussed exclusively on the properties of antioxidants Of BHT and its derivatives.

Currently, BHT is one of the antioxidants widely used in the food industry.

It is used in low-fat food, fish products. It is also widely used in combination with other antioxidants such as, propyl gels, and citric acid to stabilize of oils and high-fat foods.

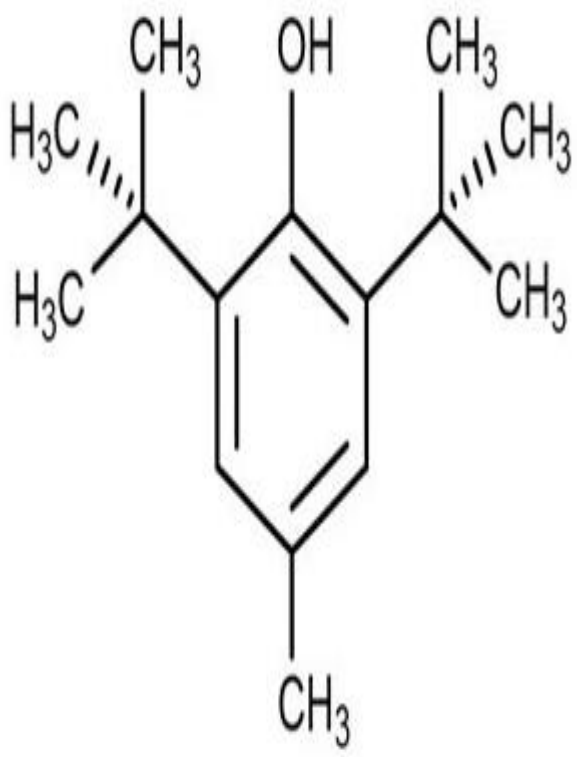

Figure 2 - Chemical Composition of BHT

The action of this industrial antioxidant is similar to BHA as it works to reduce oxygen radicals and stop the spread of oxidation operations. But its use in food oil is lower compared to BHA.

Because it is unstable at high temperatures this makes it suitable for use in food oils at moderate temperatures [33].

TBHQ the scientific name is tert-butylhydroquinone. TBHQ this compound can be especially used as an antioxidant for oils with high content of unsaturated fatty acids and can be added alone or added with other antioxidants such as BHA or BHT.

It possesses some advantages compared with other antioxidants in prolonging the storage period of edible oils [37].

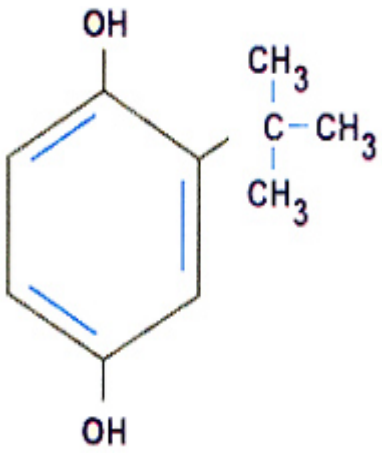

Figure 3 - Chemical Composition of TBHQ

Propyl gallate this type can get from natural gallic acid .It has high antioxidant activity in vegetable oils. Compared with BHT and BHA which has low solubility in oils.

Antioxidant activity of (PG) belongs to its content of trihydroxy substitutions and the para-OH group and ester group is considered the most important one.

Similar to other antioxidants gallate esters prevent fat peroxidation through the transfer (h) atom from a phenolic (oh) group to lipid radicals.

During this process relatively stable compounds will be formed due to the ability of free radicals of (pg) to correlate with lipid radicals. For this reason this compound can be considered effective antioxidant [39].

1.3 Natural antioxidants

1.3.1 Spices and herbs

Spices and herbs are added to food in order to give them flavor [40].Interest has increased in the use of these substances in the food industry because of their ability to delay oxidative degradation of oil and increase nutritional and life of food because of their

antioxidant properties which are superior to many of the natural anti-oxidants and synthetic antioxidants currently used [41].

Because of high contents of phenolic compounds, they have a high ability to donate hydrogen atoms [40].

These advantages are due to many compounds, including, carotenoid sterpenoids, vitamins, flavonoids, minerals, phytoestrogens which make spices and herbs used for food preservation [16].

There are natural antioxidants that are added to foods such as tocopherols, citric acid, tocotrienols, ascorbic acid, and enzymatic antioxidants.

Nevertheless these natural antioxidants have some flaws, synthetic antioxidants higher antioxidant activity as compared with natural antioxidants.

Although they have advantages such as consumers readily accept them and consider to be safe, natural antioxidants are accepted and currently available by health experts [42].

Herbs and spices such as, oregano, clove, savory, marjoram, sage, garlic, thyme, cinnamon, basil, nutmeg, pepper, turmeric, cumin and rosemary are considered a good source of antioxidants.

Table 3 – Antioxidants isolated from herbs and spice [43, 44]

Spice/herb	Scientific name	Antioxidant compounds	Mode of action
Rosemary	*Rosemarinus officinalis*	Carnosol, carnosic acid, rosmanol, rosmadial, diterpenes (epirosmanol, isorosmanol, rosmaridiphenol), rosmariquinone, rosmarinic acid	Scavenge superoxide radicals, lipid antioxidant, and metal chelator

Sage	*Salvia officinalis L.*	Carnosol, carnosic acid, rosmanol, rosmadial, methyl and ethyl esters ofcarnosol,rosmarinic acid	Free radical scavenger
Oregano	*Origanum vulgaris*	Rosmarinic acid, caffeic acid, protocatechuic acid, 2-caffeoyloxy-3-[2-(4-ydroxybenzyl)-4,5-dihydroxy] phenylpropionic acid; flavonoids—apigen, eriodictyol, dihydroquercetin, dihydrokaempherol; cavacrol, thymol	Free radical scavenger
Thyme	*Thymus vulgaris L.*	Thymol, cavacrol, *p*-Cumene-2,3-diol, phenolic acids (gallic acid, caffeic acid, rosmarinic acid), phenolic diterpenes, flavonoids Gingerol,shogaol, zingerone	Free radical scavenger

Active components are found in herbs and spices such as phenolic diterpenes and mono (carnosol,carnosic acid, thymol rosmadial, cavacrol, and rosmanol,) derivatives and phenolic acids such as caffeic, gallic, protocatechuic, ferulic, and rosemarinic.

Components belong to gingerol such as shagoal and gingerol, diarylheptanoids cassamunin A, B, C and curcumin, phenolic amides compounds such as capsaicinol and capsaicin and flavonoids components (isoharmnetin , kaempferol ,luteolin, apigenin, , and quercetin) [45].

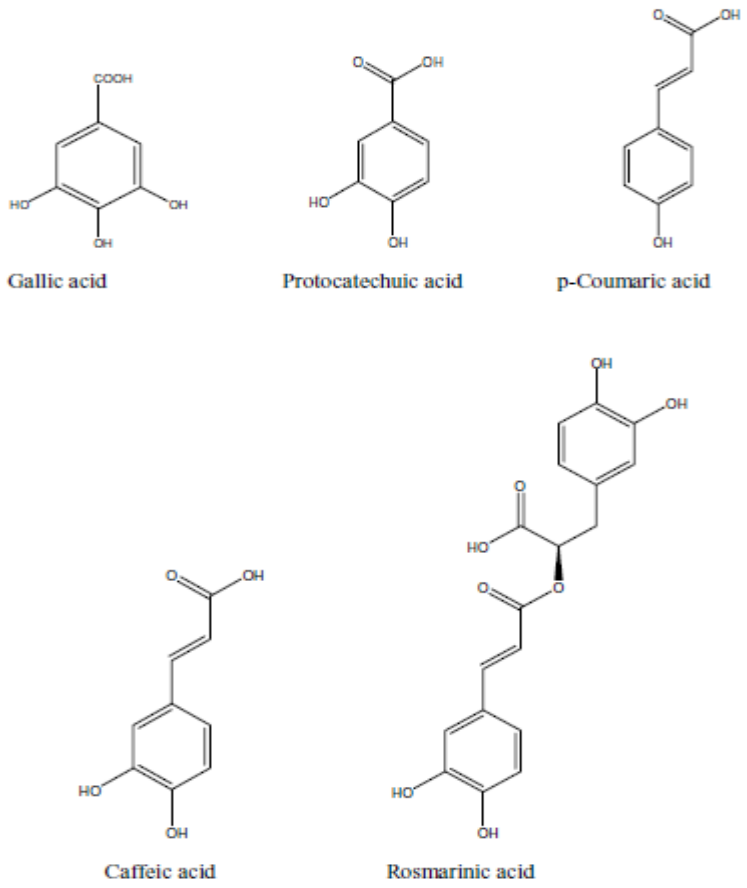

Figure 4-Antioxidative phenolic found in plants

Herbs which belong to lamiaceae family contain a compound called rosmarinic acid .This composite is capable of scavenging (DPPH potential) that's because it contains 4-OH. This compound is present at a high concentration in oregano about 500ppm, 30000 ppm in peppermint and 37000 ppm in lemon balm [33].

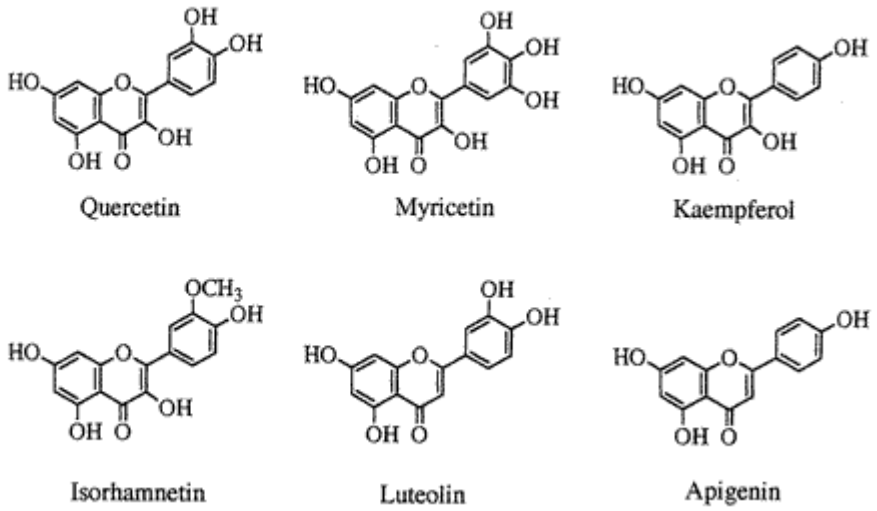

Figure 5 -flavonoids components found in plants [95]

1.3.2 Natural antioxidants properties

Natural antioxidants must have the following properties:

-Must be safe to eat by the consumer.

- Should not leave harmful effects after ingestion.

- Should not leave any odor or taste unacceptable in the oils that are added to it.

- They should be effective when used with low concentrations.

- They must maintain its stability during the processing and conservation of the oils to which it is added.

- They must be cheaply priced.

- They should be easy to use and easy to handle.

- They must be able to dissolve in the oils that are added to it.

- They should be able to prolong the life of the oils that are added to it [43].

1.4 Oxidative stabilization of vegetable oil by adding natural antioxidants

Allam and others conducted experiments to measure the thermal stability of sunflower oil heated to 180 degrees celsius for an hour after adding a combination of natural antioxidants (mixed mono- acylglycerol citrate and tocopherols) and industrial antioxidants such as (TBHQ, AP, BHA, PG, and BHT) the results showed that the oil containing TBHQ has the highest thermal stability while the least is the oil containing AP [46].

Several previous studies have indicated that the peroxide value of sunflower oil containing rosemary extract and stored for 8 hours at 98 ^{0}C(16meq O2/kg of oil) is less than twice the value of peroxide of sunflower oil without adding (32meq O2/kg of oil).

Babović and others found that the effectiveness of the industrial antioxidant (BHA) and sage extract after adding each of them to the heated sunflower oil for temperature 98 for 12 hours have the same effectiveness [47].

Saba Ajeena and others found that after measuring radical scavenging of the extracts of each, cumin fruits, black pepper seeds, and sage leaves and Industrial antioxidants (BHT and BHA) the results showed that the sage extract has the best ratio (49.97%) then fruits of cumin 47.88%, while BHA 36.77 and BHT 46.97% while the lowest ratio was black pepper seeds 2.95% [48].

When adding the extract of nigella seeds to sunflower oil at temperatures 60 and 100 and room temperature, this extract showed oxidation activity, which may be due to containing phenol compounds. Also adding this extract in 1000 ppm has been shown to be most effective as an antioxidant [49].

Khalil Dhouib and others found that the effectiveness of the industrial antioxidant (BHT) at 200 ppm and basil extract at 300-400 ppm after adding each of them to the sunflower oil have the same effectiveness [50].

Marinova and others concluded that the addition of myricetin extract to sunflower oil at temperature 100 showed activity as an antioxidant better than α-tocopherol [15].

Some previous studies have indicated that the extract of garlic extracted by methanol when added to sunflower oil at concentrations 500 and 1000 ppm and compared to industrial antioxidants (BHA and BHT) at 200 ppm that were added to the same oil.

The extract with concentrations 1000 ppm has been shown more effective as an antioxidant than industrial antioxidants [51].

Imran and others found through the experiments that the addition of extracts of Fenugreek, Liquorice and Mint to sunflower oil stored at room temperature to increase the stability of this oil have shown almost equal effectiveness of industrial antioxidants (BHA and BHT) [52].

Mostafa Taghvaei and others found that the addition of extracts of olive cake with concentrations 200ppm to sunflower oil stored at room temperature in order to increase the stability of this oil against oxidation and prolong the life of this oil has shown more effective than BHT [51].

Several studies have indicated that when adding the extract of sesame cake to sunflower oil. This extract has an antioxidant effect higher than industrial antioxidants [51, 53, 54].

Sameera and others found that when adding the extracts of oleoresin curcuminoids , lecithin and capsicum to sunflower oil ,these extracts have been shown to be effective as an antioxidant similar to the industrial antioxidant TBHQ which was added to the same oil with a concentration200ppm [55].

Sesamin, sesamol, and sesaminol are considered as lignan compounds present in sesame oil. Many previous studies have indicated that comparison between effectiveness of sesamol and sesaminol as an antioxidant in sunflower oil and effectiveness of sesamin

found that the latter is less effective in autoxidation of sunflower oil and it is also less at scavenge radicals. Not only in the light but also in the dark, sesamol plays the role of anti-oxidation during the oxidation process [40].

Some studies have indicated that carnosic acid, camphor, rosmarinic acid and carnosol, are responsible for the efficacy of sage extracts as antioxidants [56].

Some studies have indicated that several antioxidant compounds can be obtained from sage such as luteolin-7-O- β -glucopyranoside, 6-O-caffeoyl- β -D-fructofuranosyl-(2→1)- α -D-glucopyranoside, 1-O-caffeoyl- β -D-apiofurano-syl-(1→6)- β -D-glucopyranoside, and 9-ethylrosmanol ether. But the more active compounds are rosmarinic acid carnosic acid and carnosol [57].

Tea is an evergreen tree belong to the theaceae family, exist in several countries [58, 21].

Polyphenols of tea at a concentration 200 mg/kg have been added to salad oil, then they were stored for45 days have shown efficacy in preventing oil degradation, but there was a change in color [43].

Green tea has antioxidant effectiveness as a result of containing compounds such as flavonoids, vitamins, and tannins. This activity is mainly due to the phenol compounds it contains which is estimated at 450 mg/g as a catechins which consists mainly of derivatives of gallic acid [40].

Taghvaei and others have found through experiments that when added green tea extract with concentration100, 200, 500 and 1,000 ppm to each of the menhaden and seal blubber oil and in comparison with the addition of both BHA, TBHQ and BHT with 200 ppm and α-tocopherol at 500 ppm, the efficacy of green tea extract at concentration 200ppm as an antioxidant is better than α-tocopherol, BHT and BHA but less than TBHQ [59].

Chen and others have found through experiments that when added green tea extract at a concentration of 0.02% to rapeseed oil and in comparison with the addition of both BHT and rosemary extract.

They found that the efficacy of green tea extract at concentration 0.02% as an antioxidant is better than BHT and rosemary extract.

Anna Gramza and others found that extract of green tea extracted by ethanol and when added to sunflower oil with concentration1000ppm show antioxidant activity better than α-tocopherol [58].

Basil this type of spices belongs to a family *Lamiaceae*. It is usually used for cooking or for medical purposes. There are many compounds that are highly active as antioxidants found in high concentrations in basil extract such as phenolics and eugenol. It is also found some phenolic acids such as caffeic, vanillic, p-coumaric, syringicand ferulic acid [60].

KritiSoni and Kanchan Kohli found that rosmarinic acid is the main phenolic compound found in basil leaves and was believed to be responsible for the effectiveness of basil as an antioxidant.

It was also found that essential oil of basil contains some compounds such as, epi-α-cadinol, γ –cadinene, α-bergamotene and, linalool [61].

Khalil Dhouib and others through experiments found that the basil extract has the ability to increase the stability of sunflower oil when added to it because it has the ability to improve hydrolytic stability and prevent the double bond conjugation.

When added basil extract at concentrations 200–500 ppm to sunflower oil, the results showed that has the ability to maintain the stability of this oil more than industrial antioxidants such as BHT [62].

Some previous studies have indicated that when added basil extract to soybean oil, it has the ability to protect this oil from oxidation more than industrial antioxidants such as TBHQ [60].

Svitlana and others found that when added basil extract to sunflower oil, when increase the amount of added extract from 2 to 10 % this led to increased antioxidant activity by 1.57 times [63].

1.4.1 Using the rosemary extract as a natural antioxidant for vegetable oil

This type of herb belongs to the *Lamiaceae* family .Rosemary was first planted in the vicinity of the Mediterranean Sea but today it is cultivated in many parts of the world as an ornamental and aromatic plant.

Leaves of this plant It is usually added to foods to improve the taste, but this plant has also been widely used for various medicinal purposes in traditional medicine [64].

The leaves of rosemary used as ingredient for giving flavor for food productsandbecause of health useful properties such as antirheumatic, antialgesic and antimicrobia effects has been known as beneficial plant for the health.

Studies have indicated that antioxidant activity of α-tocopherol is less than rosemary extract [65].

Because of components such as rosmaridiphenol, rosmanol, carnosoand rosmariquinone,which are present in rosemary oleoresin the effectiveness of anti-oxidants BHA are less four times than rosemary as antioxidant [66].

Carnosic acid this component, according to several previous studies, indicates that it is more active as antioxidant compared to other component found in rosemary extract [72, 67].

Some previous studies have indicated that the extract of rosemary when added to vegetable oil at concentrations 400 ppm and compared to industrial antioxidants (BHA and BHT) at 200 ppm that were added to the same oil.

The extract at concentrations 400 ppm has been shown more effective as an antioxidant more than industrial antioxidants [67].

Because of higher concentration of phenolic compounds antioxidant activity of rosemary isattributed to contain the phenolic compounds such as osmanolcarnosic acid, isorosmanoepirosmanol and carnosol.

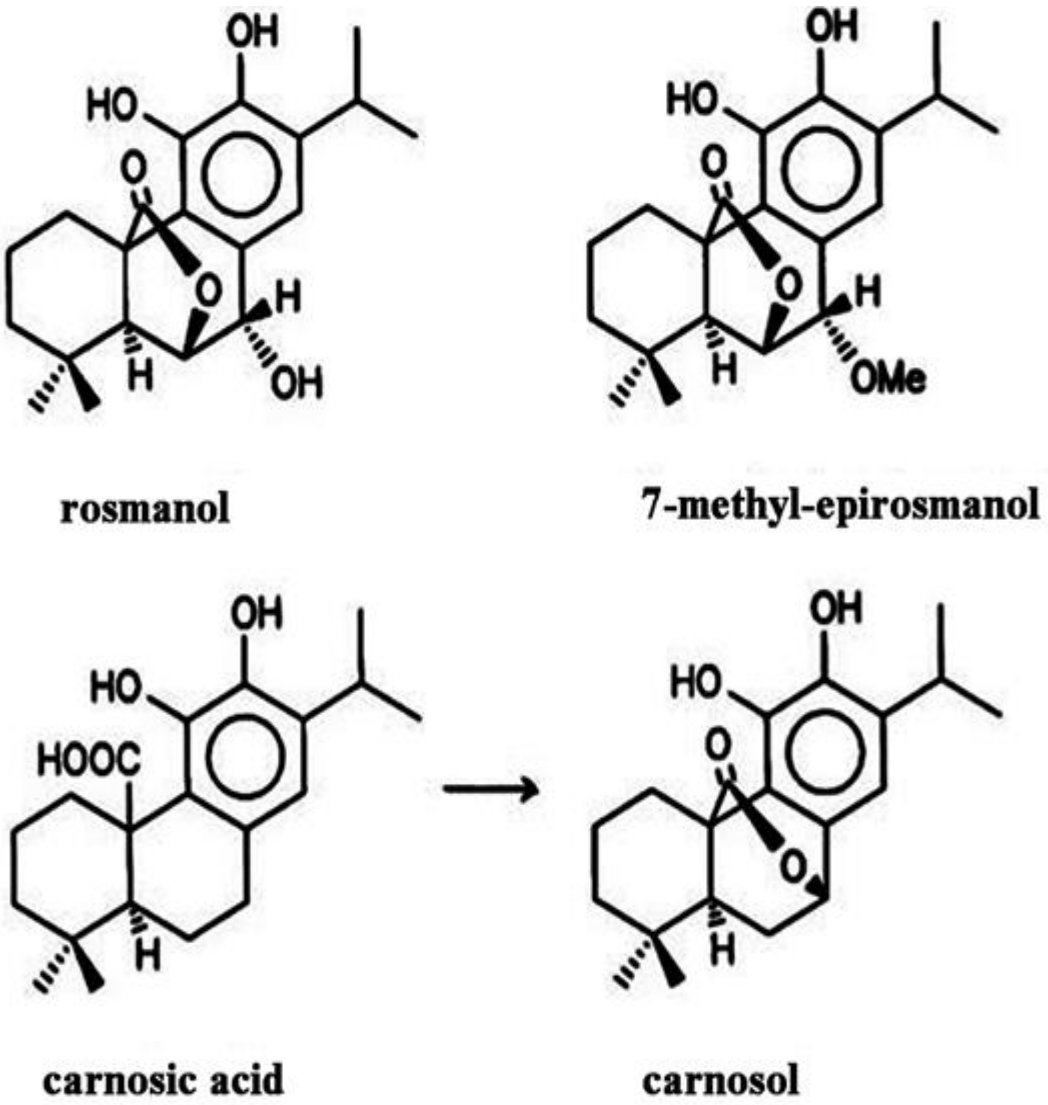

Figure 6 -Some anti-oxidant compounds are present in rosemary [68]

BHA and BHT known as synthetic antioxidants are able to donate hydrogen found in a group oh in a single aromatic ring. However carnosic acid contains a single aromatic ring with two groups OH and that are able to donate H [40].

Xiaoqiang Chen and Ying Zhang found through experiments that the extract of rosemary when added to sunflower oil at concentrations 200 ppm and compared to industrial antioxidants (BHA and BHT) at 200 ppm that were added to the same oil.

The extract at concentrations200 ppm has been shown more ability to prevent the formation of free radicals than industrial antioxidants [69].

And also according to other studies Jang-HyukAhn and Young-Pil Kim found after adding herbal extracts (rosemary, broccoli sprout and citrus) to sunflower oil, these extracts have the potential to prevent the oxidation of fat found in sunflower oil [70].

1.4.2 Using the sage extract as a natural antioxidant for vegetable oil

Some previous studies have indicated that sage and rosemary contain similar types of phenolic compounds. Antioxidative activity attributed to their contain on rosmarinic acid and carnosic .

Other studies have indicated that sage contain more active compounds such as phenolic acids, flavonoids and terpenoids [71].

Relative to rosemary, sage is especially prolific in the outputting of phenolics and other flavonoids derivatives, particularly those structurally regarding the rosmarinic acid.

Some previous studies have indicated that rosmarinic acid is responsible for antioxidant activity of sage [72].

In general, sage produces lower amount of phenolics ,carnosic acid and other compounds than does rosemary [40].

Abdalla and Roozen found through experiments that sunflower oil contains 570 ppm natural α-tocopherol added to it sage extract showed high antioxidant activity through secondary and primary oxidation [73].

Salvia officinalis is a kind of sage its extract has a high ability to radical scavenging.

Sage extract had almost 2 times the amount of diterpenoidphenolics less than rosemary extract, and about 2.7 the level of carnosic acid and carnosol.

Many of the researches indicated that carnosic acid is powerful antioxidant in rosemary.

This is the main reason that sage extract is less used than rosemary as an antioxidant [43].

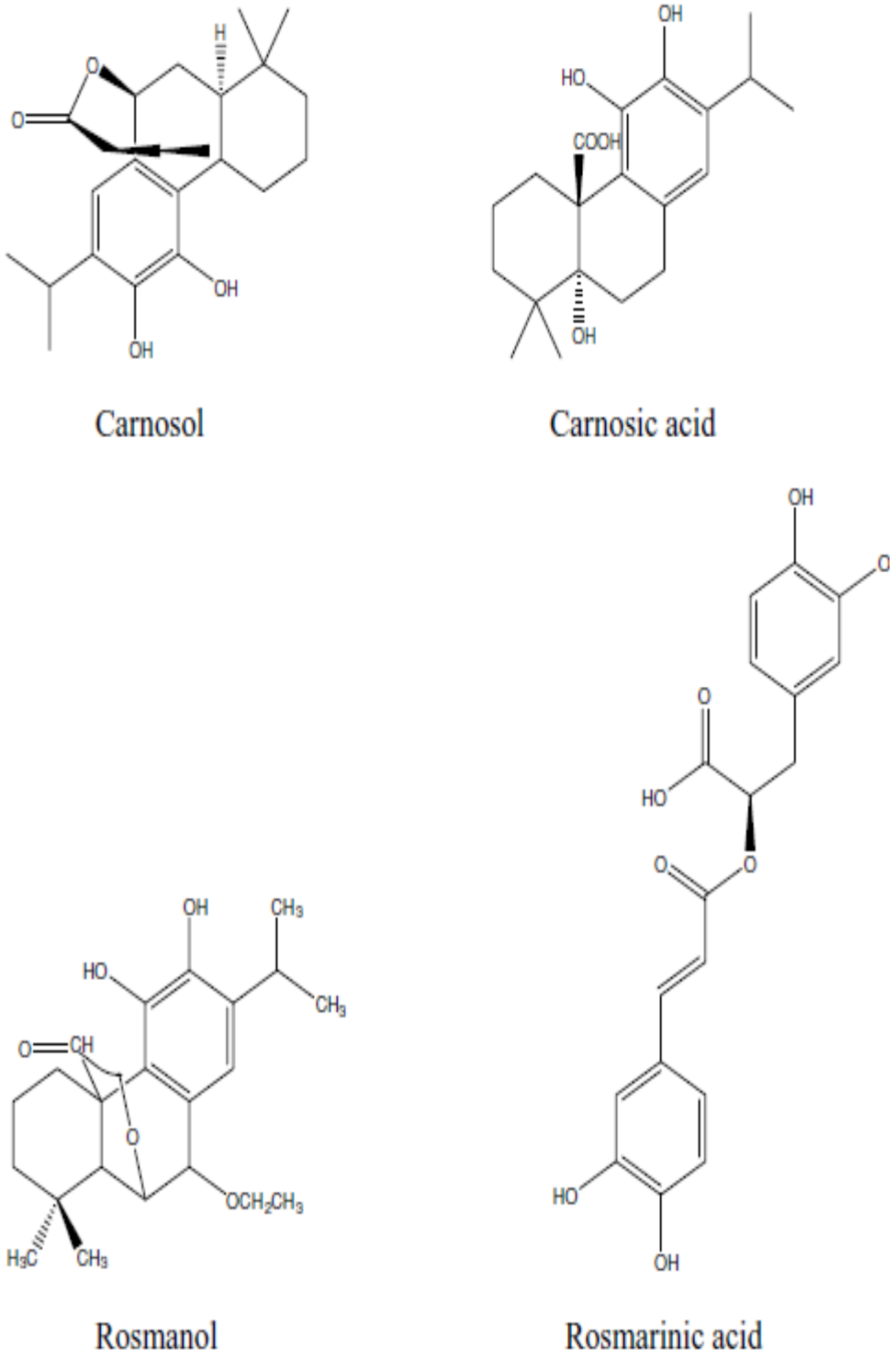

Figure 7 -Some anti-oxidant compounds are present in sage

1.4.3 Using the thyme extract as a natural antioxidant for vegetable oil

This type belongs to the aromatic herbs that are usually added to foods to give flavor and aroma.As a spice it can be used dry or fresh leaves [74].

Thyme contains rosmarinic acid eriodyctiol, luteolinglycosides,luteolin, and glycuronids of apigenin which are the major phenolic compounds.

Several types of thyme such as mastichina, caespititius and camphorate are showed antioxidant activity similar to BHT and α-tocopherol [40].

Thyme extract whichis added at concentration of 1%to sunflower oil prevent oxidation operation through its storage for 29 days in different temperature conditions [75].

Turek and Stintzing indicated that thyme extracts has an antioxidant activities which were determined by measuring the pv (peroxide value) which are present in in sunflower oil at 60 ° C and found that when adding thyme extract at concentration 6000 mg/kg oil to sunflower oil shown effective as an antioxidant almost equal1000 mg BHA/kg oil that were added to the same oil [76].

Many of the researches indicated that essential oil of this herb contents high of carvacrol and thymol which have strong antioxidant activity [77].

1,8-cineole, α-terpineol,carvacrol, and thymol considered as the mainly aroma compounds found in thyme.

Thymol is the highest effective antioxidative compounds and is considered as the mainly aroma component in thyme [78].

Thymol and carvacrol each one of them has1 aromatic ring with1 −OH group,p-cymene contains1 aromatic group and 1-terpineol contains1 −OH group, existence of aromatic ring and OH groups which is responsible for the anti-oxidant properties of these compounds [40].

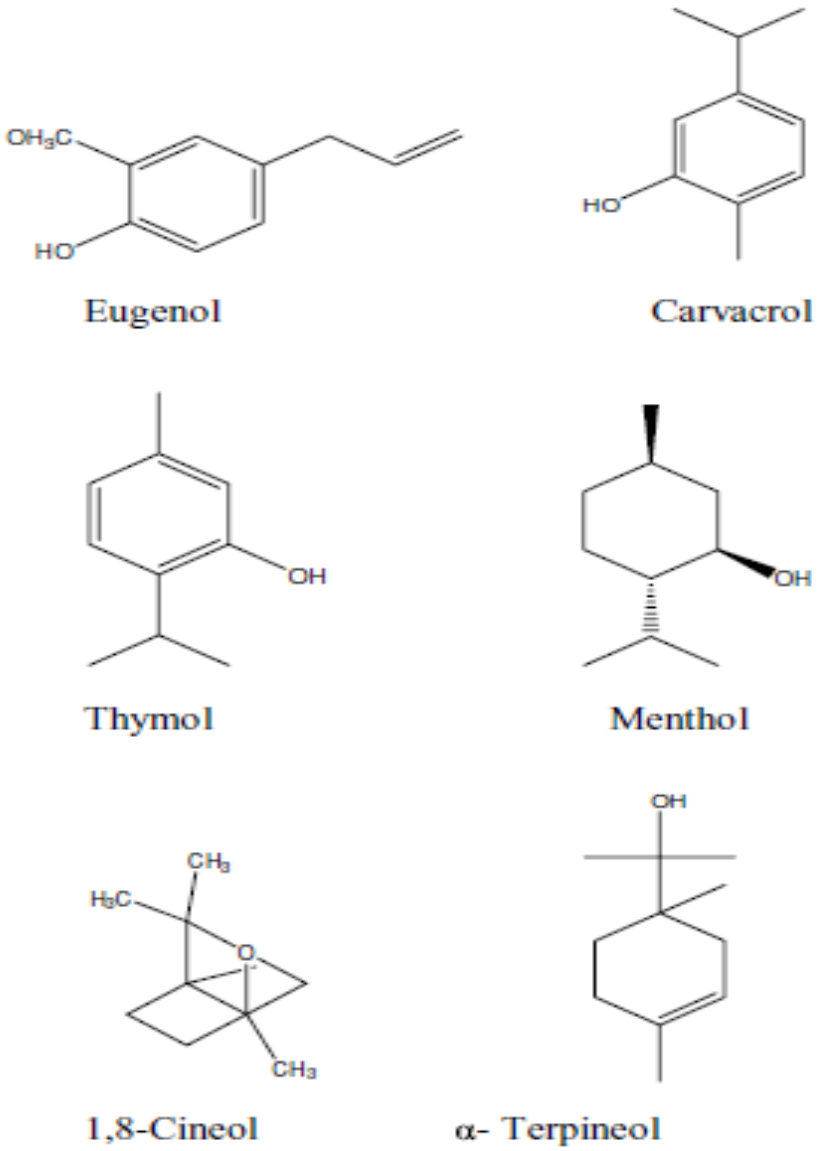

Figure 8 -Some anti-oxidant compounds are present in thyme

1.4.4 Using the ginger extract as a natural antioxidant for vegetable oil

This type of spices was added to foods to give flavor [79] and it also possesses the properties of anti-oxidant materials [80]. These properties are because it contains gingeronesshogaols and gingerols.

Dried and fresh ginger contain high amounts of the camphene, volatile oils , p-cineole, zingiberene, pentadecanoic acid and alpha-terpineol [81].

Zingiberofficinale as a type of ginger contains several antioxidants such as, ascorbic acid, terpenoids, as terpenoids beta-carotene, alkaloids, flavones, flavonoids, rutin, and glycosides. Because of its high content of antioxidants, it can be considered main source of natural antioxidants [82, 83].

Brewer the researcher concluded that ginger extract when added to sunflower oil the resultsshown that its antioxidant activity was nearly too synthetic antioxidants (BHT and BHA).Antioxidative activity of compounds which separated from ginger such as 8diarylheptanoids and 5 compounds related to ginger shown higher than α-tocopherol[40].

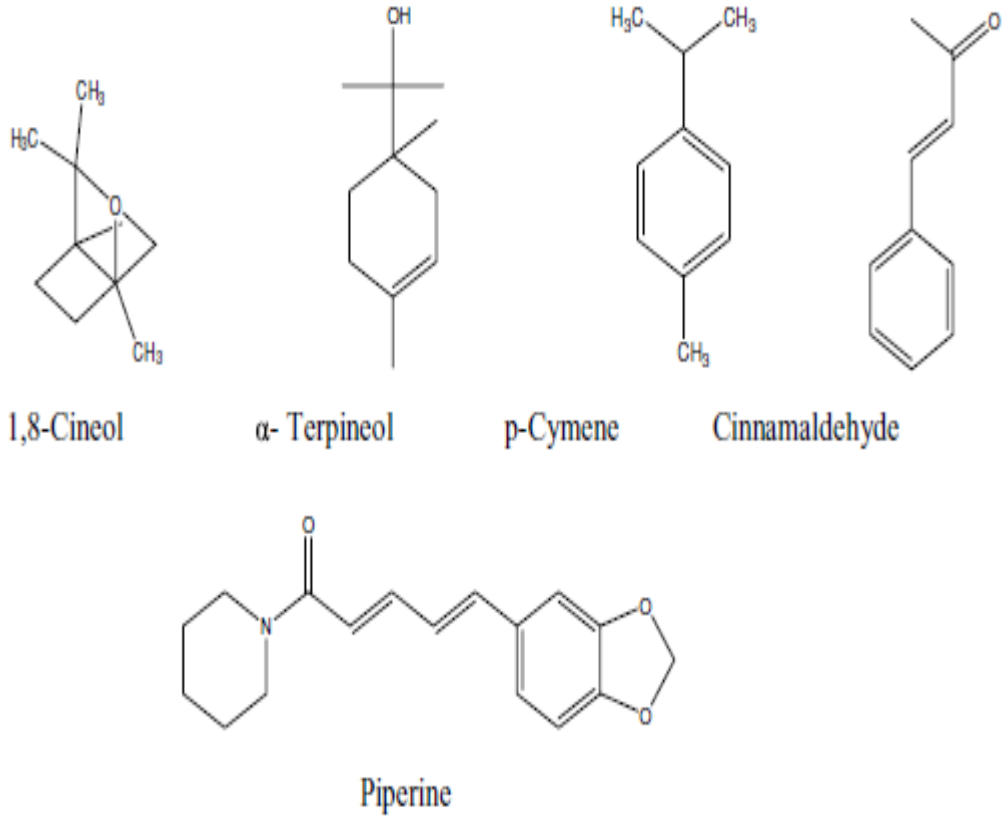

Figure 9 -Some anti-oxidant compounds are present in ginger

Salariya and Habib the researchers concluded that the solution obtained from ginger which was added to sunflower oil which storage for 60 days appeared good thermal stability [84].

When ginger extract was added with concentrations 1600 and 2400ppm to sunflower oil, the results showed that the process of out-oxidation was largely prevented and there is no difference between using ginger extract with 1600 and 2400ppm and synthetic antioxidants with 200 ppm [85].

Some previous studies have indicated that effectiveness of antioxidants BHA at 2400 and1600 ppm were less effective than the effective of ginger extract but it is almost equal to efficiency of BHT at 2400ppm when added to sunflower oil [84].

1.4.5 Using the oregano extract as a natural antioxidant for vegetable oil

This type of herb belongs to the *Lamiaceae*family [86].

Because it contains compounds such carvacrol, thymol, c-terpinene, linalol, p-cymene, and sesquiterpenes and other monoterpenes. This makes it possess anti-oxidant and anti-bacterial properties [87].

Origanum vulgare ssp and *hirtum,origanum* and *P. longiflora* are types of oregano which contain high phenolic compounds. Antioxidant efficacy of tocopherol is less effective of these compounds.

Hydroxycinnamic acid and rosmarinicacid ascompounds are present at high concentrations in oregano extracts and have a high antioxidant activity [88, 89].

Some previous studies have indicated that the essential oil which was extracted from oregano contain thymol and carvacrol. Perhaps these substances are responsible for the antioxidant effect of oregano [90, 91].

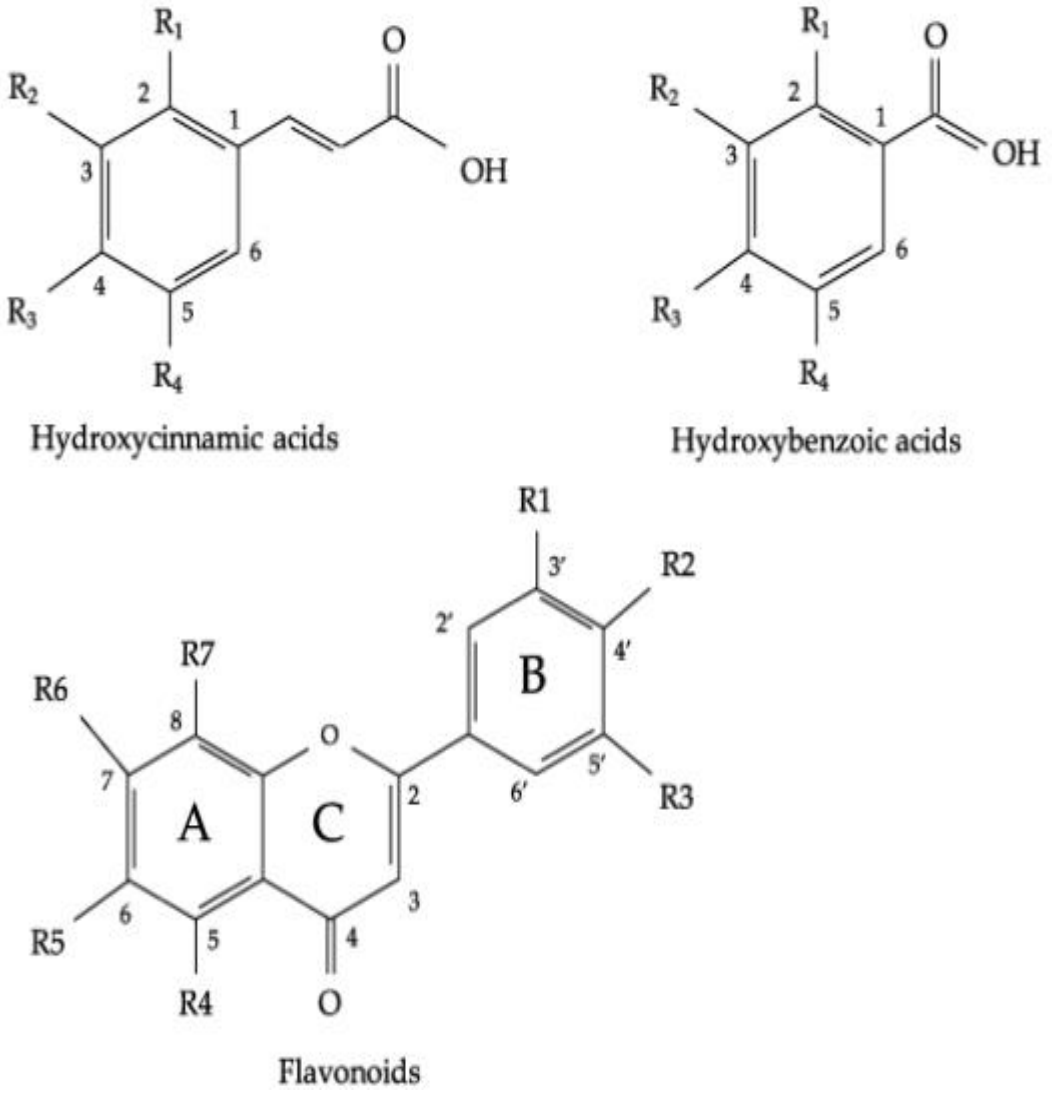

Figure 10 -Some anti-oxidant compounds are present in Oregano

Oregano extract which was extracted by using acetone is highly active in sunflower oil in comparison with 20 % oil-in-water emulsion through oxidation at 60 °C in the dark [92].

Jorge and Veronezi found that oregano showed a high effect in preventing the formation of polar compounds compared with antioxidant TBHQ. In addition, when added it at 3,000 mg/kg concentration, antioxidant protection has been shown to be better than industrial antioxidants [93].

CHAPTER 2 OBJECTS AND METHOD OF RESEARCH

2.1 Research objectives

-Conducting a process of extraction of herbs used (thyme, ginger, rosemary, sage) by the use of ethanol at a concentration of 95% and 70%.

-Conducting a process of extraction of herbs used (thyme, ginger, rosemary, sage) by the use of (ethanol 95%, propylene glycol 95%) and propylene glycol at a concentration of 95%.

-Determination of the content of polyphenols for herbal extracts (thyme, ginger, rosemary, sage).

-Measuring the free radical scavenging activity (DPPH) of herbal extracts (thyme, ginger, rosemary, sage).

-Measure both the peroxide value and the acid value in sunflower oil after adding each extract obtained from the herb used every 15 days for two months.

-Measure both the peroxide value and the acid value in sunflower oil after adding a mixture of extract obtained from the herbs used every 15 days for two months.

-Comparison between the peroxide values and acid values after the addition of each single herb extract and the addition of a mixture of herb extract.

- Comparison between the effectiveness of herbal extracts and the effectiveness of industrial antioxidants on the process of oxidation of sunflower oil when adding each extract separately.

- Comparison between the effectiveness of herbal extracts and the effectiveness of the industrial antioxidant on the process of oxidation of sunflower oil when adding a mixture of extracts from these herbs.

-Comparison between the effect of adding herb extracts separately and adding a mixture of extracts to sunflower oil on the oxidation process of sunflower oil.

2.2 The preparation of herbs extracts using ethanol 95%

Materials and equipment used:

- Dried herbs (thyme, ginger, rosemary, sage).
- Solvent ethanol 95%.
-Filter paper in order to filter the herb extract.
-Balance for weighing samples.

Conduct extraction: dried herbs (thyme, ginger, rosemary , sage) used .The grinding of the leaves was done using a small electric mill and was put the leaves powder in small glass containers until extraction. Then 5 grams of each sample was weighed. Then they were put in erlenmeyer flasks .Then 100 ml of solvent ethanol 95%were added to the herbs samples, and direct extraction was performed at the boiling point of the ethanol for 6 hours.

Then the centrifuged process was performed for 10 minutes.

The filtration process was done for sample using filter paper. Then the extract obtained from the herb was placed in the fridge until usage.

When conducting the first experiment on herbal extracts separately. The solution containing each sample of herbal extract was added to 100 ml of sunflower oil at a concentration of 1%.

When conducting the second experiment on a mixture of herbal extracts, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger- rosemary, sage- rosemary) was added at concentration 1% to 100 ml of refined sunflower oil sample.

2.3 The preparation of herbs extracts using ethanol 70%

Materials and equipment used:

- Dried herbs (thyme, ginger, rosemary, sage).
- Solvent ethanol 70%.

-Filter paper in order to filter the herb extract.

-Balance for weighing samples.

Conduct extraction: dried herbs (thyme, ginger, rosemary , sage) used .The grinding of the leaves was done using a small electric mill and was put the leaves powder in small glass containers until extraction. Then 2 grams of each sample was weighed. Then they were put in erlenmeyer flasks .Then 15 ml of solvent ethanol 70%were added to the herbs samples. The mixture was then placed in a water bath at 70 ° C for 30 min. The filtration process was done for sample using filter paper. Then the extract obtained from the herb was placed in the fridge until usage.

When conducting the first experiment on herbal extracts separately. The solution containing each sample of herbal extract was added to 100 ml of sunflower oil at a concentration of 1%.

When conducting the second experiment on a mixture of herbal extracts, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger- rosemary, sage- rosemary) wasadded at concentration 1% to 100 ml of refined sunflower oil sample.

2.4 The preparation of herbs extracts using propylene glycol 95%

Materials and equipment used:

- Dried herbs (thyme, ginger, rosemary, sage).
- Solvent propylene glycol 95%.

-Filter paper in order to filter the herb extract.

-Balance for weighing samples.

-Oven for solvent evaporation.

Conduct extraction: dried herbs (thyme, ginger, rosemary , sage) used .The grinding of the herbs was done using a small electric mill and was put the leaves powder in small glass containers until extraction. Then 10 grams of each sample was weighed. Then they

were put in erlenmeyer flasks, and then 100 ml of solvent propylene glycol 95% was added to the herbs samples .The mixture was left at room temperature for one day .The filtration process was done for the mixture using filter paper. The solvent was evaporated by placing it in the oven at 40 ° C. Then the extract obtained from the herb was placed in the fridge until usage.

When conducting the first experiment on herbal extracts separately. The solution containing each sample of herbal extract was added to 100 ml of sunflower oil at a concentration of 1%.

When conducting the second experiment on a mixture of herbal extracts, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger- rosemary, sage- rosemary) wasadded at concentration 1% to 100 ml of refined sunflower oil sample.

2.5 The preparation of herbs extracts using propylene glycol 95% and ethanol 95%

Materials and equipment used:

- Dried herbs (thyme, ginger, rosemary, sage).
- A mixture of solvents (50 ml ethanol 95% and 50 ml propylene glycol 95%).
-Filter paper in order to filter the herb extract.
-Balance for weighing samples.
-Oven for solvent evaporation.

Conduct extraction: dried herbs (thyme, ginger, rosemary , sage) used .The grinding of the leaves was done using a small electric mill and was put the leaves powder in small glass containers until extraction. Then 10 grams of each sample was weighed into one erlenmeyer flasks, and then 100 ml of a mixture of solvents (50 ml ethanol 95% and 50 ml propylene glycol 95%) was added to the herbs samples .The mixture was left at room temperature for one day .The filtration process was done for the mixture using filter paper.

The solvent was evaporated by placing it in the oven at 40 ° C. Then the extract obtained from the herb was placed in the fridge until usage.

When conducting the first experiment on herbal extracts separately. The solution containing each sample of herbal extract was added to 100 ml of sunflower oil at a concentration of 1%.when conducting the second experiment on a mixture of herbal extracts, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger- rosemary, sage-rosemary) was added at concentration 1% to 100 ml of refined sunflower oil sample.

2.6 Determination of the content of polyphenols for herbs extracts

Materials and equipment used:

-Herbal extracts (thyme, ginger, rosemary , sage) .

- Folin–Ciocalteu phenol reagents.

- Gallic acid: prepare a standard series of Gallic acid with concentrations (10, 20,40, 60, 80 mg /ml).

-Sodium carbonate: A solution of sodium carbonate is prepared at a concentration of 7.5%.

-Spectrophotometer device to measure the absorption of samples.

Conduct the experiment: polyphenol content was determined for herbal extracts used according to the Folin–Ciocalteu method .By adding 0.5 ml of each extract from the herbs to 10 ml of distilled water and then adding 2.5 ml of (Folin–Ciocalteu phenol reagents). After five minutes 2 ml of 7.5 %sodium carbonate solution was added to the previous mixture .The solution is then left in the dark for sixty minutes.

The absorbance of the solution is then measured using the spectrophotometer at 750nm and the results were expressed as mg of Gallic acid equivalent per ml [97].

After we dissolve 0.1 mg of Gallic acid in distilled water in a 100 mL calibrated balloon and prepare a standard series of Gallic acid at concentrations (10,20,40, 60, 80 mg / ml) and complete the volume with distilled water up to 100mL.

Then, the absorbance is measured at a 750 nm for the samples of Gallic acid and drew the calibration curve of the Gallic acid.

2.7 Measuring the free radical scavenging activity (DPPH) of herbal extracts

Materials and equipment used:

- Herbs extracts (thyme, ginger, rosemary , sage) .
- DPPH(1,1-diphenyl-2-picrylhydrazyl).
-Spectrophotometer device to measure the absorption of samples.
-Methanol.

Conduct the experiment: the determining of total free radical scavenging capacity of extracts from different plant samples was estimated according to the following method. A solution of radical is prepared by adding 2.4 mg DPPH in 100 mL methanol. Test solution(0.5µl of herbs extract)was added to 3.995 ml of methanol- DPPH. The mixture was vigorously shaken and kept in the dark at room temperature for 30 minutes. Absorption was measured using a spectrophotometer at 515nm.

Absorption was also measured for the same solution(DPPH)but without the presence of the sample blank.

The measurement was done three times per sample [98].

The capability to scavenge the DPPH radical was calculated using the following equation:

DPPH Scavenged (%) = ((AB–AA)/AB) ×100

Where is AB - is absorbance of solution but without the presence of the sample.

AA - absorbance of solution of the sample.

2.8 Determine the peroxide value of oil samples

The peroxide value was determined according to GOST P 51487-99[99].

Preparation of solutions:

-A solution of potassium iodide is prepared at concentration 55%.

-The starch solution is prepared as follows: 5 g of a soluble starch is mixed with 30 cm of water, add this mixture to 1000 mm boiling water and boil for 3 minutes.

-A solution of sodium thiosulfate with a molar concentration of 0.1 M.

Conduct the experiment: in a flask with a 5 g of sample, add 10 cm of chloroform, rapidly dissolve the sample, add 15 cm of acetic acid and 1 cm of 55% solution of potassium iodide, after that the flask is immediately closed, the contents are stirred for 1 minute and left for 5 minutes in a dark place at a temperature of 15-25 ° C.

Add 75 ml of distilled water to the flask, carefully stir and add the starch solution until we see weak homogeneous violet-blue color.

Isolated iodine is titrated with a solution sodium thiosulfate to milky-white color, stable for 5 seconds.

The peroxide value was calculated using the following formula:

$$x = \frac{1000(v - v0)c}{m}$$

Where is V- the volume of sodium thiosulfate solution used for oil sample definition, mm.

V0 -The volume of sodium thiosulfate solution used for control definition, mm.

c -The actual concentration of the used thiosulfate sodium solution.

m -Weight of the sample of the product, g.

2.9 Determine the acid value of oil samples

The acid value was determined according to GOST R 50457-92 [100].

Materials used:

-Refined sunflower oil.

-Phenolic phenols: weighs 1 gram of phenolic phenols and melts in 100 ml of ethanol.

- Potassium hydroxide: carefully weigh5.61 grams of sodium hydroxide and place in a 1000 ml flask. Then the distilled was added until the mark.

-Ether.

Conduct the experiment: in a conical flask with a capacity of 250 mm, 5 g of sunflower oil was weighed. Then add 50 mm of ether to the sample. The contents of the flask are stirred by shaking the flask by hand. If the oil does not dissolve, it is heatedto (50) ° C in a water bath, then cooled to 20 ° C. A few drops of phenolphthalein are added to the solution. Then the solution is calibrated with a solution of potassium hydroxide at a concentration 0.1 N until a slightly pink color is obtained and stable for 30 s.

The acid value was calculated using the following formula:

$$\mathrm{AV}=\frac{v.56{,}1.c}{\mathrm{m}}$$

Where is v - volume of a solution of potassium hydroxide in a molar concentration (KOH) = 0.1 mol / dm3, expended on titration, mm.

C - The actual concentration of potassium hydroxide.

56.1 - Is the KOH mass in 1 cm of the molar concentration solution (KOH) = 0.1mol / dm3 (0.1 N).

m - Weight of the sample, g.

CHAPTER 3 RESULTSAND DISCUSSION

3.1 The amount of phenolic compounds for herbs extracts

The amount of phenolic compounds was determined by the linear regression equation which is obtained from the calibration curve of Gallic acid as a standard y = 0.009x + 0.0768 ؛R^2 = 0.9869 based on the Gallic acid percentage. In the regression equation of the calibration curve of Gallic acid, Y is the absorption rate that was read at a wavelength of 765 nm and X is the concentration of phenolic compounds based on mg gallic acid/mL.

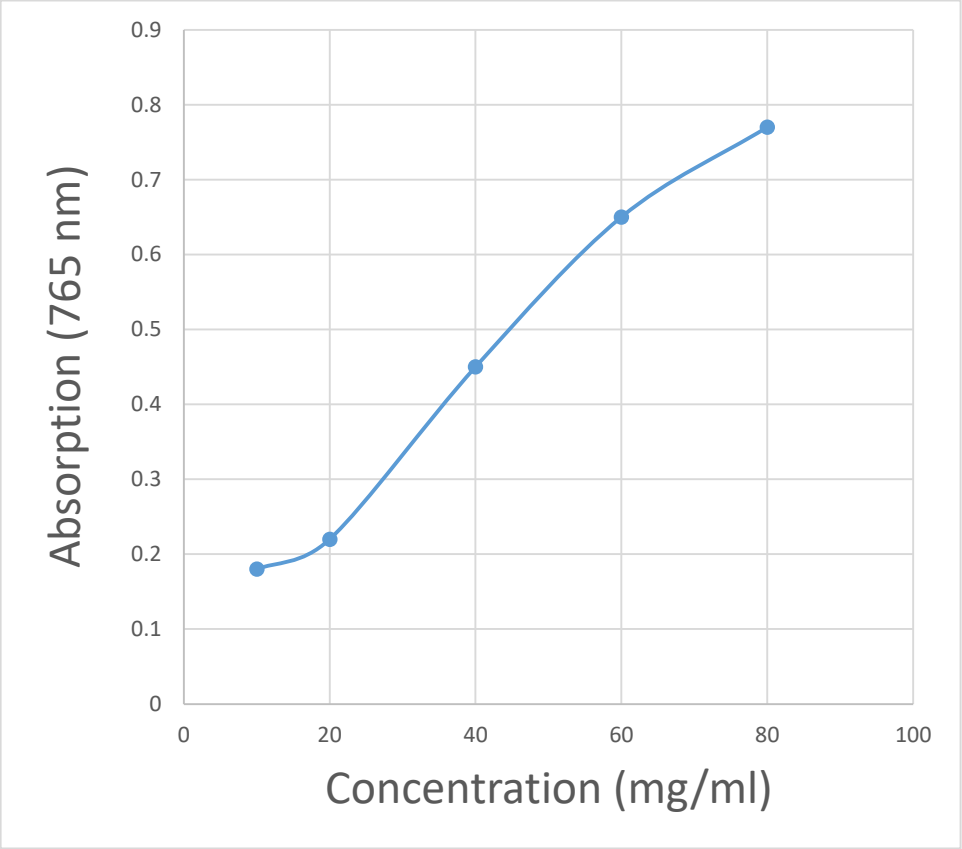

Figure 11 - Standard curve of Gallic acid

The amount of phenolic compounds for various extracts ranged from 11.12 to 45.17. The Total polyphenol content of the extracts can be ranked in the order rosemary (45.17)>thyme (36.15) > sage (25.74) > ginger (11.12).The results show that the rosemary extract contains the highest value of polyphenols.

Table 4 – The amount of phenolic compounds for various extracts extracted with ethanol 95%

Herbs	Total polyphenol content (mg Gallic acid/mL)
Rosemary	45.17 mg/ml
Thyme	36.15 mg/ml
Ginger	11.12 mg/ml
Sage	25.74 mg/ml

3.2 The DPPH radical scavenging ability of the herbs extracts

The DPPH is a stable radical with a maximum absorption at 517 nm that can readily undergo scavenging by antioxidant. It has been widely used to evaluate the antioxidative activity of plant extracts .All the extracts showed different levels of DPPH radical scavenging activity.

Table 5 – DPPH free radical scavenging activity of different extracts from herbs extracted with ethanol 95%

Herbs	inhibition DPPH radical%
Rosemary	85.15
Thyme	76.55
Ginger	36.44
Sage	55.64

The results show that the DPPH radical scavenging ability of the extracts can be ranked in the order rosemary (85.15%) >thyme (76.55%) > sage (55.64 %) > ginger (36.44%). The observed differential scavenging activities of the extracts against the DPPH system could be due to the presence of different compounds in the extract.

3.3 The peroxide values and acid values of refined sunflower oil samples

3.3.1 Effect of adding herb extracts extracted with ethanol 95% separately or BHT on the peroxide values and on acid values of refined sunflower oil samples

In this experiment, extracts were added separately at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg.

Initially, the peroxide value of refined sunflower oil was determined without any addition and the result was 3.66 meq/kg.

Every 15 days for two months the peroxide value of the oil samples containing the plant extracts or the industrial antioxidant was measured and the results shown in the table 6.

Table 6 – The effects of (BHT), thyme extract, ginger extract, rosemary extract, added to the refined sunflower oils, on peroxide values

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Peroxide value (meq/kg)						
1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.74	3.72	3.75	3.77	3.79
30days	5.3	3.84	3.82	3.88	3.89	3.98
45days	5.95	3.92	3.91	4.03	4.05	4.3
60days	6.5	4	3.97	4.012	4.015	4.4

Through the results, we note that the values of peroxide of the sample of sunflower oil without any additions have increased from 3.66 to 6.5.While the oil samples- whether

containing the herbal extracts or the industrial antioxidant- the increase in the values of peroxide were few. The results were represented on a diagram showing the changes in the peroxide values of the various oil samples.

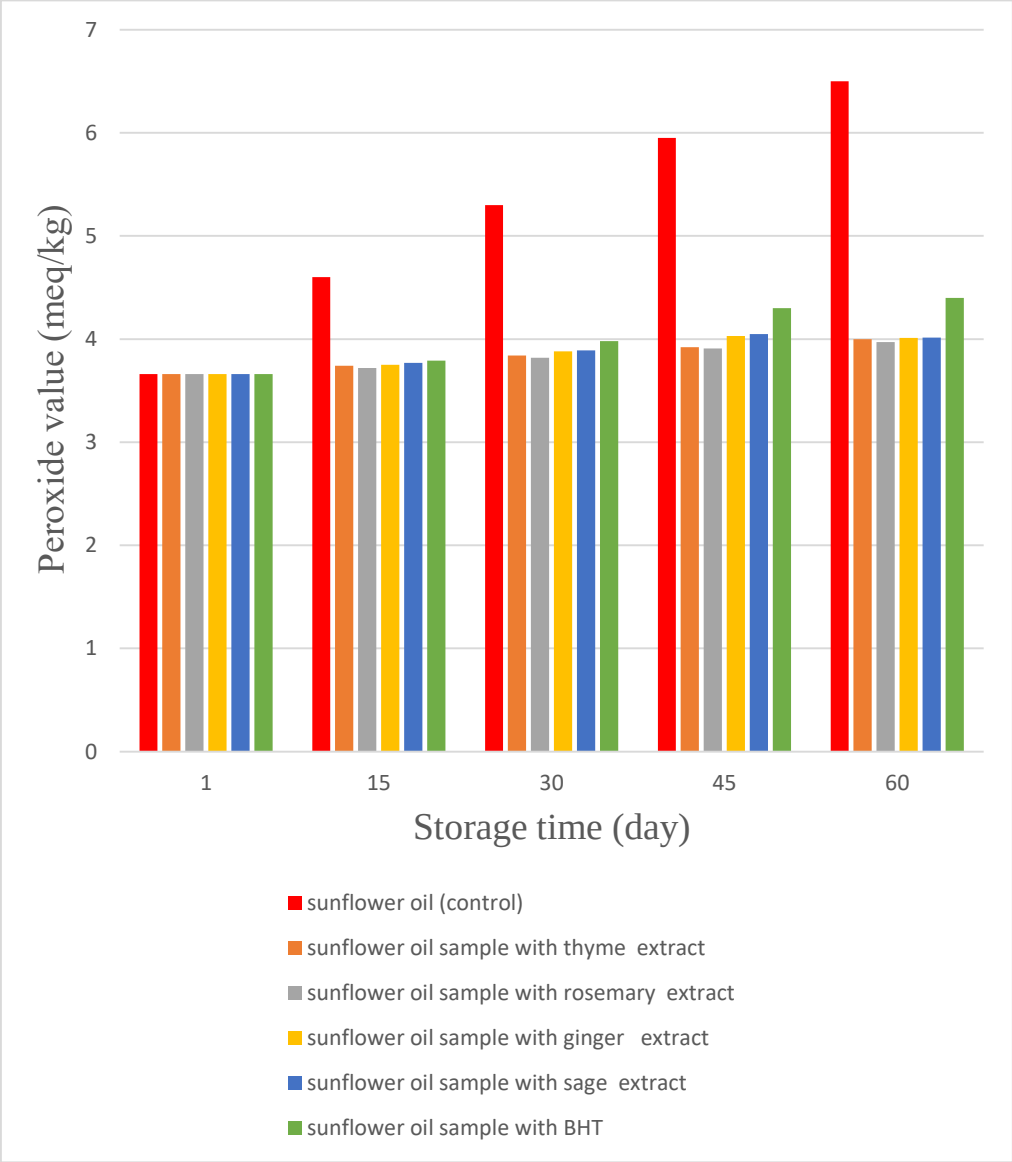

Figure 12 - Effect of adding BHT and herbal extracts extracted with ethanol 95% on peroxide value of sunflower oil

In comparing the different samples, we note that the lowest peroxide value was for the sample of sunflower oil containing the rosemary extract. This is due to the high percentage of polyphenols. On the other hand, the peroxide values of all samples

containing herb extracts were lower than the peroxide value of the oil sample containing the industrial antioxidant.

Thus, we conclude that herbal extracts have a higher effectiveness in preventing the oxidation of sunflower oil than the industrial antioxidant.

First, the acid value of the refined sunflower oil was determined without any additives and the result was 0.114 mg KOH / g.

The acid value of refined sunflower oil samples- whether free of additives or containing (BHT) or the herbal extracts added separately at concentration 1% to the oil- were determined every 15 days for two months, and the results were shown in table 7.

Table 7 – The effects of (BHA), thyme extract, ginger extract, rosemary extract, added to the refined sunflower oils, on its acid values

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.2	0.18	0.22	0.24	0.24
30days	0.47	0.28	0.24	0.32	0.34	0.36
45days	0.65	0.33	0.3	0.41	0.43	0.47
60days	0.87	0.4	0.38	0.48	0.53	0.58

From the results, we can observe the increase in the acidity value of the sample of refined sunflower oil, which is free of any additives, was big.

But other oil samples whether containing (BHT) or the herbal extracts added separately to the oil the change in acidity values was small.

The results were represented on a diagram showing the changes in the acid values of the various oil samples.

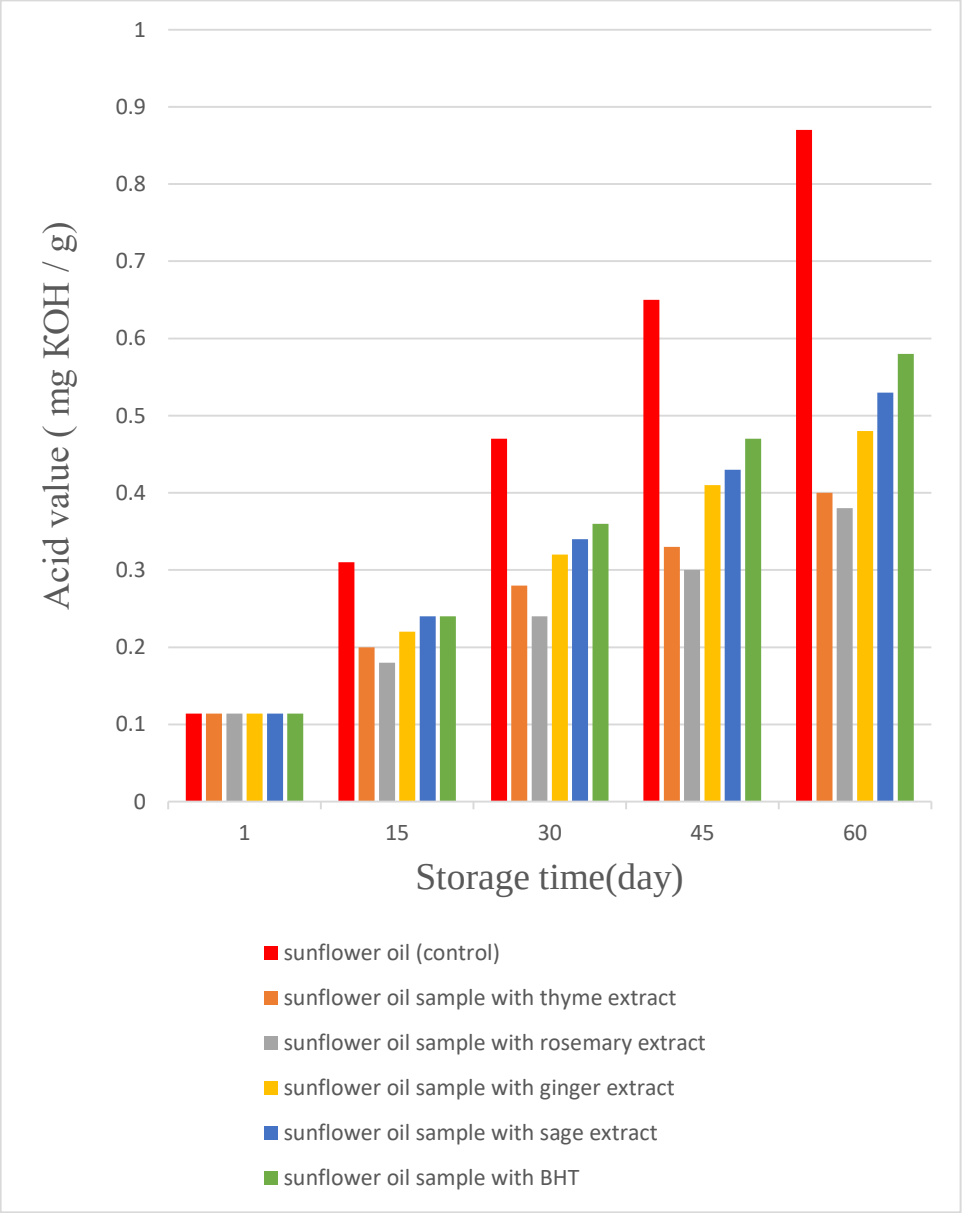

Figure 13 – Effect adding of BHT and herbal extracts extracted with ethanol 95%on acid value of sunflower oil

After comparing the different samples, we note that the sample with the lowest acid value is the sample containing the rosemary extract, because it contains a higher proportion of polyphenols than other samples.

Furthermore, the acid value of the oil sample containing the industrial antioxidant was greater than the acid values of all samples containing herb extracts.Thus, we conclude that the industrial antioxidant has a lower effectiveness in preventing the oxidation of sunflower oil than herbal extracts.

3.3.2 Effect of adding a mixture of herb extracts extracted with ethanol 95% or BHT on the peroxide values and on acid values of refined sunflower oil samples

In this experiment, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger-rosemary, sage- rosemary) was added at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg.

In the beginning, the peroxide value was measured for the refined sunflower oil sample, which did not contain any additives, and the result was 3.66 meq/kg. The peroxide values were then measured for different oil samples containing either a mixture of herb extracts or synthetic antioxidant every 15 days for two months. The results were as follows in table 8.

Table 8 – Effect of adding a mixture of herbal extracts or synthetic antioxidants on the peroxide values of refined sunflower oil.

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The sample of sunflower oil with BHT
Peroxide value (meq/kg)						
1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.72	3.70	3.74	3.75	3.79

30days	5.3	3.81	3.76	3.83	3.86	3.98
45days	5.95	3.9	3.83	3.92	4.01	4.3
60days	6.5	3.96	3.88	4.02	4.10	4.4

After examining the results we noted, an increase in the peroxide value of the sample of sunflower oil that does not contain additives was larger than other samples.

On the other hand, the peroxide values of refined sunflower oil samples containing either a mixture of herb extracts or synthetic antioxidant have not changed significantly.The results in the table were represented on figure 14 showing the increase in peroxide values for all oil samples.

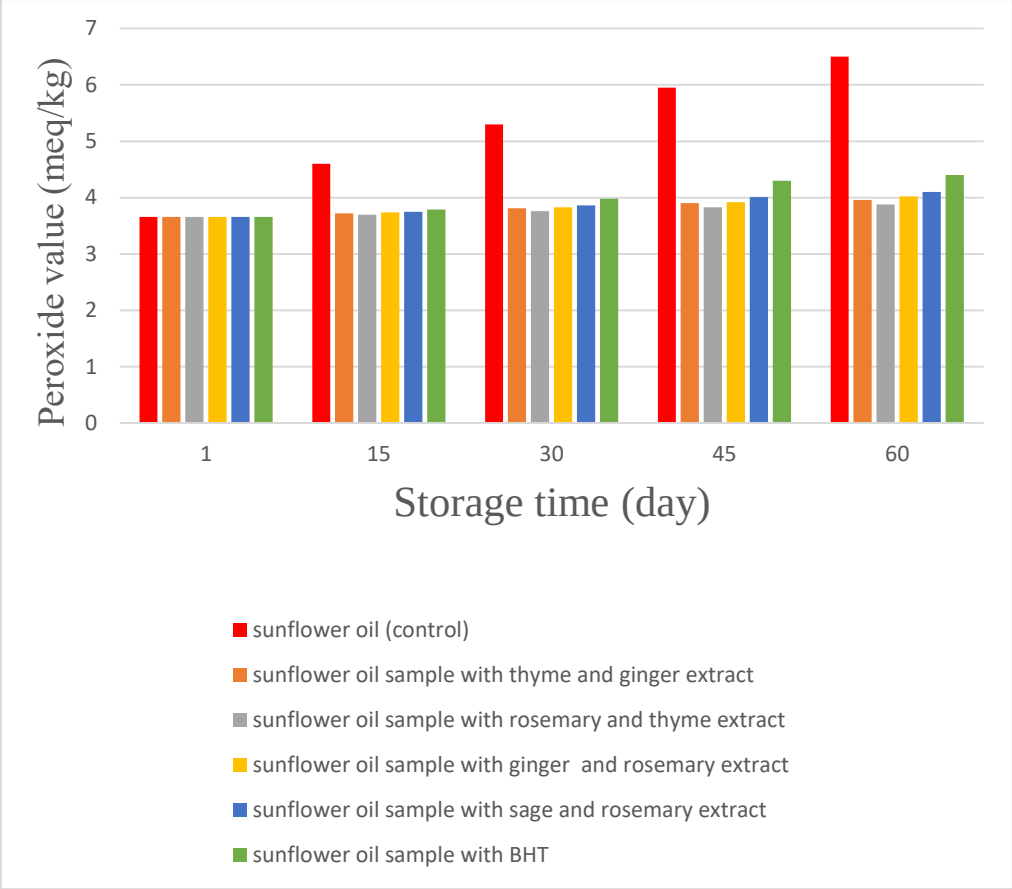

Figure 14 -Effect of adding BHT and a mixture of herbal extracts extracted with ethanol 95% on peroxide value of sunflower oil

The comparison between the different samples shows that the sample containing the rosemary-thyme extract had the lowest peroxide value. The peroxide value for this

sample (3.88 meq/kg) was less than the limit of acceptable values (10 meq/kg), stipulated by the standard GOST 1129-2013 for sunflower oil [101] because, rosemary and thyme extract contained the highest concentration of phenolic substances. It was also found that all the samples of oil containing a mixture of herbal extracts have lower peroxide values than the sample containing the synthetic antioxidant.

We can conclude that the mixture of herbal extracts has a greater effectiveness in delaying the occurrence of the process of oxidation of refined sunflower oil than the synthetic antioxidant.

At first, the acid value was measured for the refined sunflower oil sample, which did not contain any additives, and the result was as follows 0.114 mg KOH / g.

Every 15 days for two months, the acid value of the oil samples containing a mixture of herbal extracts or the industrial antioxidant was measured and the results were as follows in the table 9.

Table 9 – Effect of adding a mixture of herbal extracts or industrial antioxidants on the acid values of refined sunflower oil.

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.19	0.17	0.21	0.22	0.24
30days	0.47	0.25	0.22	0.3	0.34	0.36
45days	0.65	0.31	0.27	0.38	0.4	0.47

60days	0.87	0.37	0.31	0.44	0.51	0.58

Through the results, we note that the acid value of the sample of sunflower oil without any additions have increased from 0.114 to 0.87.However, the oil samples, whether containing the synthetic antioxidant or the mixture of herbal extracts, the increase in the values of acid were few. The results in the table were represented in figure 15 showing the increase in acid values for all oil samples.

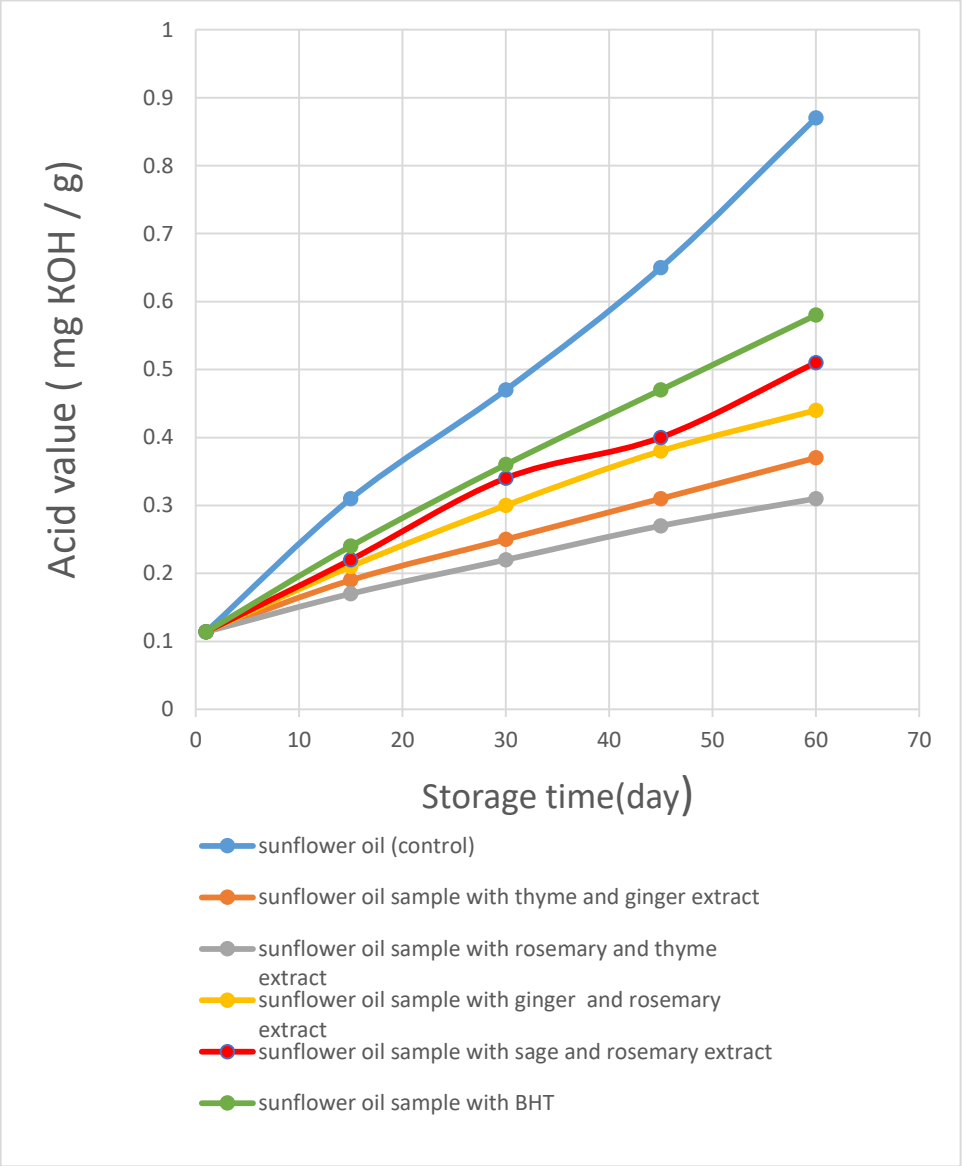

Figure 15 -Effect of adding BHT and a mixture of herbal extracts extracted with ethanol 95% on acid value of sunflower oil

Table 10 – Regression equations describing the change in acid value for the samples of sunflower oil within two months

The sample of sunflower oil	The regression equation	Coefficient of approximation
The sample of sunflower oil without additions	y = 0.0125x + 0.1049	R^2 = 0.9972
The sample of sunflower oil with thyme and ginger extract	y = 0.0043x + 0.1179	R^2 = 0.9959
The sample of sunflower oil with rosemary and thyme extract	y = 0.0033x + 0.1165	R^2 = 0.9954
The sample of sunflower oil with ginger and rosemary extract	y = 0.0055x + 0.1212	R^2 = 0.9908
The sample of sunflower oil with sage and rosemary extract	y = 0.0066x + 0.1186	R^2 = 0.9902
The sample of sunflower oil with BHT	y = 0.0078x + 0.1158	R^2 = 0.9981

y-Acid value (mg KOH / g);x- Storage time(day).

After comparing the different samples, we note that the sample with the lowest acid value is the sample containing the rosemary-thyme extract.

The acid number for this sample (0.31 mg KOH / g of oil) was less than the limit of acceptable values (0.4 mg KOH / g of oil), stipulated by the standard GOST 1129-2013 for sunflower oil, because they contain compounds such as rosmanol, rosmaridiphenol, and carnosol which are effective as antioxidants.

After adding both herbal extracts and industrial antioxidants to refined sunflower oil samples, the sample containing the industrial antioxidant has the highest acid value among other samples containing herbal extracts.

Therefore, we conclude that the synthetic antioxidant has a less effectiveness in delaying the occurrence of the process of oxidation of refined sunflower oil than a mixture of herbal extracts.

3.3.3 Effect of adding herb extracts extracted with ethanol 70% separately or BHT on the peroxide values and on acid values of refined sunflower oil samples

In this experiment, extracts were added separately at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg.

At the first day, the peroxide value of the oil sample was determined without any additions and the value was 3.66 meq/kg. After every 15 days for 60 days, the peroxide values of the oil samples, whether containing the synthetic antioxidant or herb extracts, was measured and the results were as in the table 11.

Table 11 – Effect of adding herbal extracts or BHT on the peroxide values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Peroxide value (meq/kg)						
1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.74	3.72	3.76	3.78	3.79
30days	5.3	3.86	3.83	3.89	3.9	3.98
45days	5.95	3.97	3.94	4.05	4.07	4.3
60days	6.5	4.09	3.99	4.14	4.15	4.4

Among all oil samples, refined sunflower oil sample without any additives showed the highest increased in peroxide value. When comparing different samples, the increased of peroxide value during 60 days storage were small for oil samples containing the herbal extracts or BHT. The results were represented on the following chart.

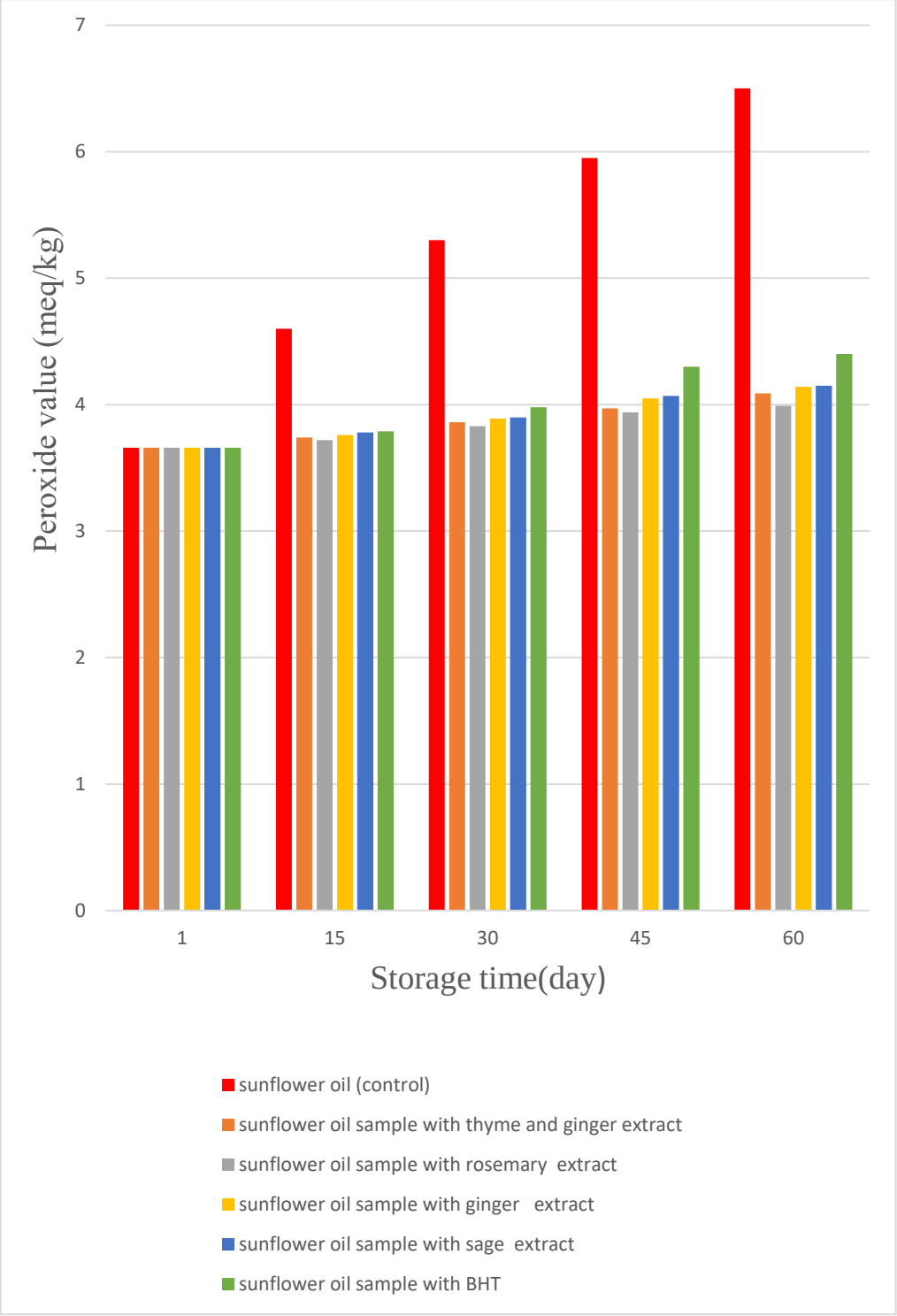

Figure 16 -Effect of adding BHT and herbal extracts extracted with ethanol 70% on peroxide value of sunflower oil

We note from the results that the oil sample containing the rosemary extract had the lowest peroxide value, due to their high content of polyphenols.

The results show that after the addition of plant extracts to refined sunflower oil samples, the peroxide values of these samples were lower than the value of peroxide when adding BHT.

Thus, we conclude that the BHT antioxidant had the potential to inhibit the oxidation process of refined sunflower oil less than herbal extracts.

At the beginning of the experiment, the acid value of the refined sunflower oil sample was measured; it was0.114 mg KOH / g. After the addition of BHT antioxidant or the herb extracts to the refined sunflower oil samples, the acid values of these samples were determined every 15 days for 60 days.

Table 12 – The effect of herbal extracts or industrial antioxidants on the acid values of refined sunflower oil when each was added separately

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The Sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.2	0.19	0.22	0.24	0.24
30days	0.47	0.31	0.27	0.31	0.33	0.36
45days	0.65	0.39	0.33	0.43	0.44	0.47
60days	0.87	0.47	0.39	0.52	0.54	0.58

From the results, we note that the sample that has the highest acid value after 60 days is the sample of oil free of additives.

From the results in table 12 we note that the increased of acid value during 60 days storage were small for oil samples containing the herbal extracts or BHT. These results were represented on the chart.

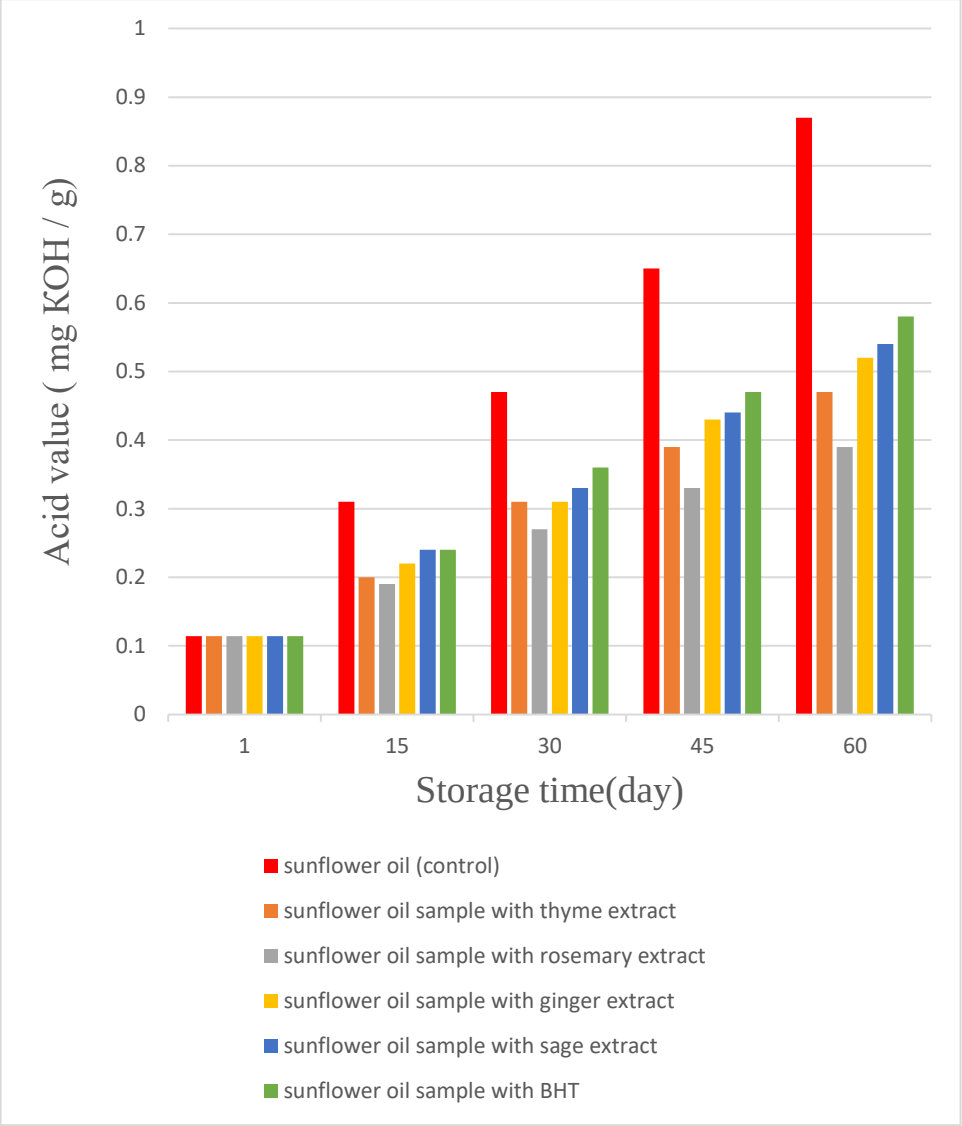

Figure 17 -Effect of adding BHT and herbal extracts extracted with ethanol 70%on acid value of sunflower oil

Among all oil samples, refined sunflower oil sample with rosemary extract showed the lowest increase in acid value. This may be because it contains more polyphenols than other samples. The increase in the acid values of the oil samples containing the herb extract is less than the increase in the acid value of the oil sample containing the synthetic antioxidant.

Therefore, we conclude that herbal extracts have the potential to inhibit the oxidation process of refined sunflower oil more than the industrial antioxidant.

3.3.4 Effect of adding a mixture of herb extracts extracted with ethanol 70% or BHT on the peroxide values and on acid values of refined sunflower oil samples

In this experiment, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger-rosemary, sage- rosemary) was added at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg.

On the first day, the peroxide value of oil sample without additions was measured and the value was 3.66 meq/kg. Every 15 days for two months, the peroxide value of the oil samples containing the plant extracts or the synthetic antioxidant was measured and the results were as in the table 13.

Table 13 – Effect of adding a mixture of herbal extracts or industrial antioxidants on the peroxide values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The Sample of sunflower oil with BHT
Peroxide value (meq/kg)						
1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.72	3.71	3.74	3.75	3.79
30days	5.3	3.83	3.78	3.86	3.88	3.98
45days	5.95	3.92	3.86	3.99	4.02	4.3
60days	6.5	3.98	3.92	4.09	4.12	4.4

A sample of refined sunflower oil free from herb extracts or BHT increased its peroxide value more than other samples as it increased from3.66 to6.5.

The peroxide values of the oil samples did not change much after 60 days except for the oil sample free from any additives; the results were represented on the following chart.

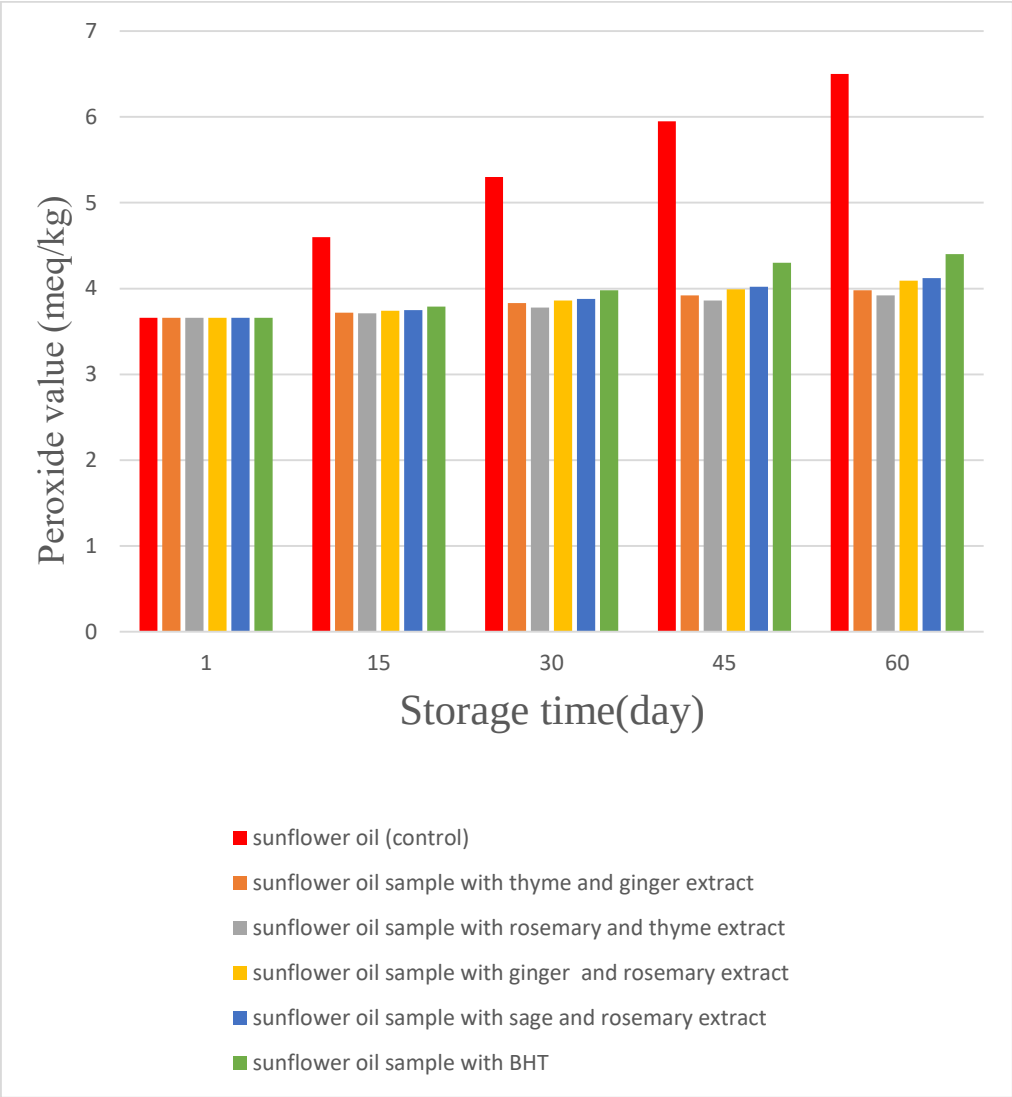

Figure 18 -Effect of adding BHT and a mixture of herbal extracts extracted with ethanol 70% on peroxide value of sunflower oil

From the results, we note that, the sample containing the rosemary-thyme extract has the lowest peroxide value among the other samples. The peroxide value for this sample (3.92 meq/kg) was less than the limit of acceptable values (10 meq/kg), stipulated by the standard TP TC 024/2011 for technical regulations for oil and fat products [102].

This may be because they contain a higher percentage of compounds that are effective as antioxidants.

By observing the results in table 13, we observe that the increase in the peroxide values of all the oil samples containing the herb extracts is less than the increase in the peroxide value of the oil sample containing the industrial antioxidant.

Thus we can conclude that herbal extracts that have been added to sunflower oil have the potential to delay the occurrence of oxidation of oil more than the industrial antioxidant.

At first, the acid value was measured for the refined sunflower oil sample, which did not contain any addition, and the result was as follows 0.114 mg KOH / g.

After adding a mixture of herbal extracts and BHT to the oil samples and measuring the acid values for each sample after 15 days and for two months. The results were as in the table14.

Table 14 – Effect of adding a mixture of herbal extracts or industrial antioxidants on the acid values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The Sample of sunflower oil with BHT
	Acid value (mg KOH / g)					
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.2	0.19	0.23	0.24	0.24
30days	0.47	0.26	0.24	0.32	0.34	0.36
45days	0.65	0.32	0.29	0.42	0.44	0.47
60days	0.87	0.38	0.34	0.49	0.51	0.58

In the table we note that the change in the value of the acid of the sample of the oil containing no addition is much greater compared to the change in the values of acid of the oil samples, whether containing a mixture extracts of herbs or industrial antioxidant.

However, the oil samples, whether containing the synthetic antioxidant or the mixture of herbal extracts, the increase in the values of acid were few. The change in the peroxide values was represented on the chart.

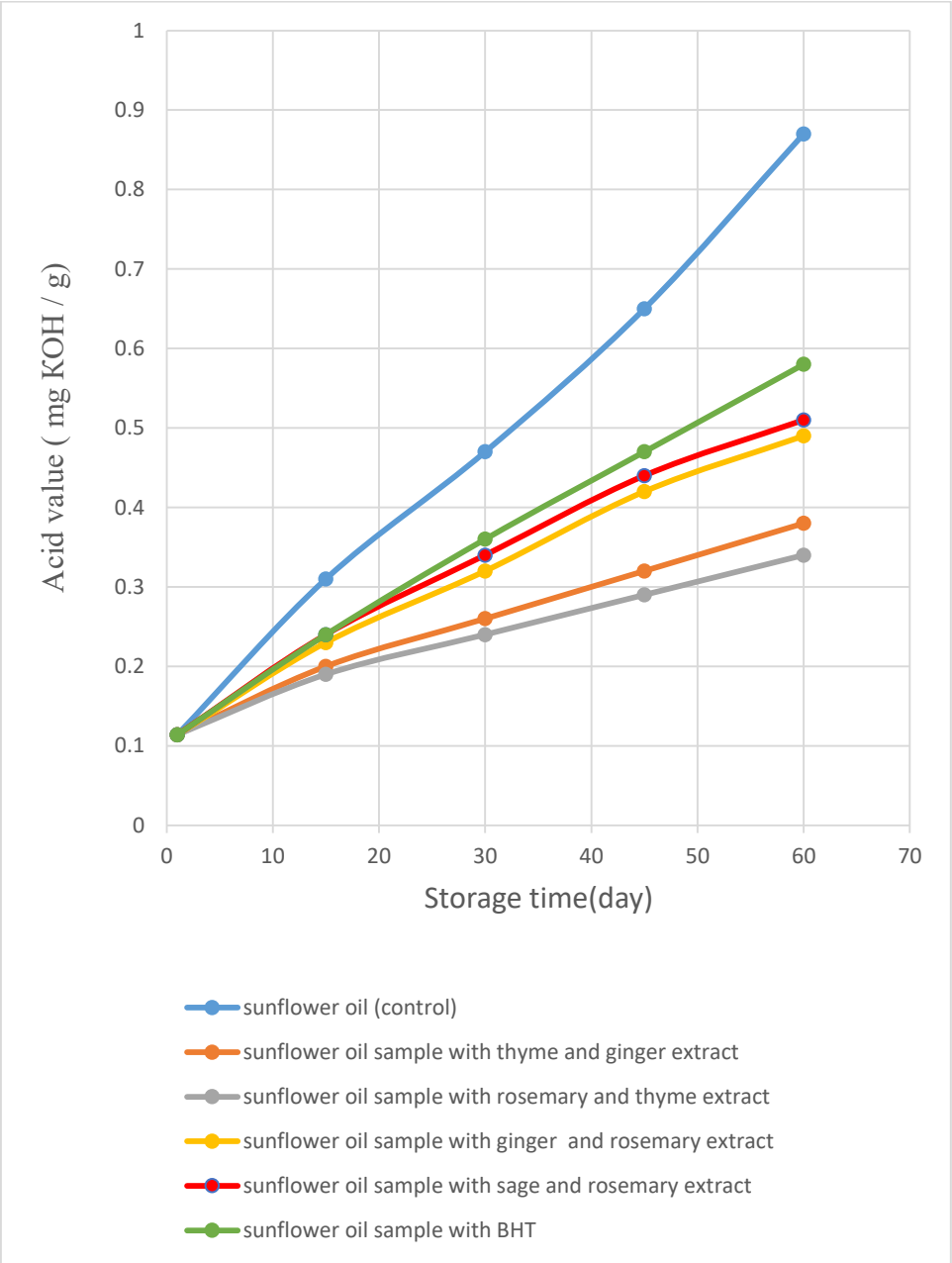

Figure 19 - Effect of adding BHT and a mixture of herbal extractsextracted with ethanol 70% on acid value of sunflower oil

Table 15 – Regression equations describing the change in acid value for the samples of sunflower oil within two months

The sample of sunflower oil	The regression equation	Coefficient of approximation
The sample of sunflower oil without additions	y = 0.0125x + 0.1049	$R^2 = 0.9972$
The sample of sunflower oil with thyme and ginger extract	y = 0.0044x + 0.1219	$R^2 = 0.9914$
The sample of sunflower oil with rosemary and thyme extract	y = 0.0037x + 0.1223	$R^2 = 0.9885$
The sample of sunflower oil with ginger and rosemary extract	y = 0.0064x + 0.1228	$R^2 = 0.9917$
The sample of sunflower oil with sage and rosemary extract	y = 0.0067x + 0.1266	$R^2 = 0.9881$
The sample of sunflower oil with BHT	y = 0.0078x + 0.1158	$R^2 = 0.9981$

y-Acid value (mg KOH / g); x- Storage time (day).

The results of the experiment showed that the sample that has the least acidity value is the oil sample container of the rosemary-thyme extract.

This may be because they contain a higher percentage of polyphenols than other samples.

The acid number for this sample (0.34 mg KOH / g of oil) was less than the limit of acceptable values (0.6 mg KOH / g of oil), stipulated by the standard TP TC 024/2011 for technical regulations for oil and fat products.

From the results in table 14 we note that increase in the acid value of the oil sample containing BHT is greater than the increase in the acid values of all the oil samples containing the herb extracts.

Therefore, we can conclude that the industrial antioxidant that added to sunflower oil has the potential to delay the occurrence of oxidation of oil less than herbal extracts.

3.3.5 Effect of adding herb extracts extracted with ethanol 95%and propylene glycol 95% or BHT on the peroxide and on acid values of refined sunflower oil samples

In this experiment, extracts were added separately at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg.

Firstly, the peroxide value of refined sunflower oil was determined without any addition and the value was 3.66 meq/kg.

Then the herbal extracts and the industrial antioxidant were added separately to the oil samples. Peroxide values were measured for each sample after 15 days and for two months. The results were as follows in the table16.

Table 16 – The effects of (BHA), thyme extract, ginger extract, rosemary extract, added to the refined sunflower oils, on peroxide values respectively were

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Peroxide value (meq/kg)						
1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.76	3.74	3.77	3.78	3.79
30days	5.3	3.88	3.85	3.91	3.93	3.98
45days	5.95	3.99	3.96	4.07	4.09	4.3
60days	6.5	4.11	4	4.16	4.17	4.4

From the results, we can observe the increase in the peroxide value of the sample of refined sunflower oil, which is free of any additives, as follows from 3.66 to6.5.

While the oil samples, whether containing the herbal extracts or the industrial antioxidant, the increase in the values of peroxide were few. These results were represented on the chart.

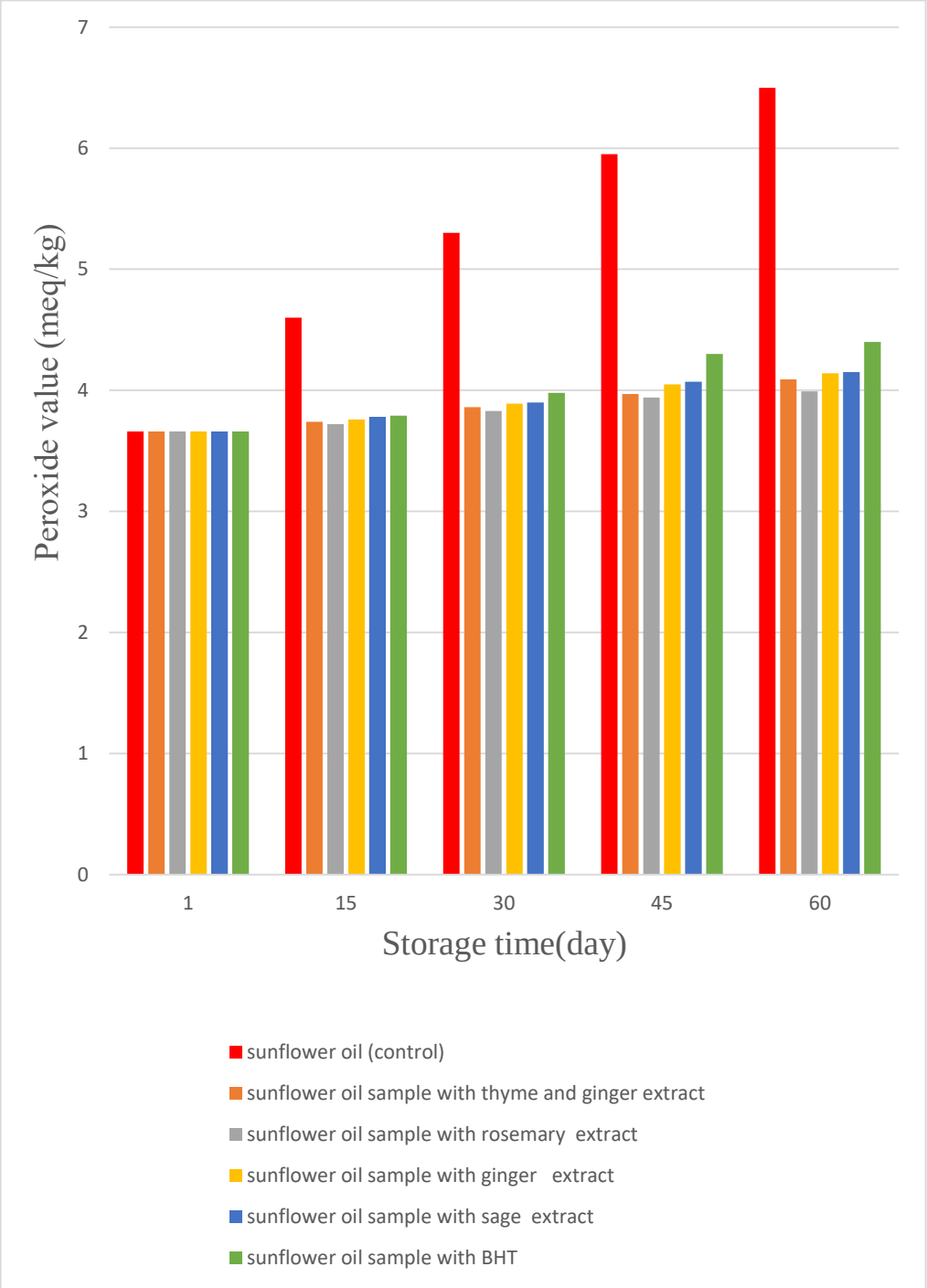

Figure 20 - Effect of adding BHT and herbal extracts extracted with ethanol 95% and propylene glycol 95% on peroxide value of sunflower oil

The comparison between the different samples shows that the sample that has the least peroxide value is the oil sample containing the rosemary extract because, rosemary extract contained the highest concentration of phenolic substances.

Furthermore, the increase in the peroxide values of the oil samples containing the herb extract is less than the increase in the peroxide value of the oil sample containing the industrial antioxidant.

Thus, we conclude that herbal extracts have the potential to inhibit the oxidation process of refined sunflower oil more than the industrial antioxidant.

In the beginning, the acid value was measured for the refined sunflower oil sample, which did not contain any additives, and the result was 0.114 mg KOH / g.

Then the acid values were measured for different oil samples either containing herb extracts or an industrial antioxidant every 15 days for two months. The results were as follow in the table17.

Table 17 – The effects of (BHA), thyme extract, ginger extract, rosemary extract, added to the refined sunflower oil, on its acid values

Day	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.24	0.22	0.24	0.25	0.24
30days	0.47	0.3	0.28	0.33	0.34	0.36
45days	0.65	0.36	0.34	0.44	0.45	0.47
60days	0.87	0.48	0.4	0.53	0.56	0.58

Through the results, we note that the acid value of the sample of sunflower oil without any additions have increased from 0.114 to 0.87.On the other hand, the acid values of refined sunflower oil samples containing either a mixture of herb extracts or an industrial antioxidant have not changed significantly. The change in the acid values was represented on the chart.

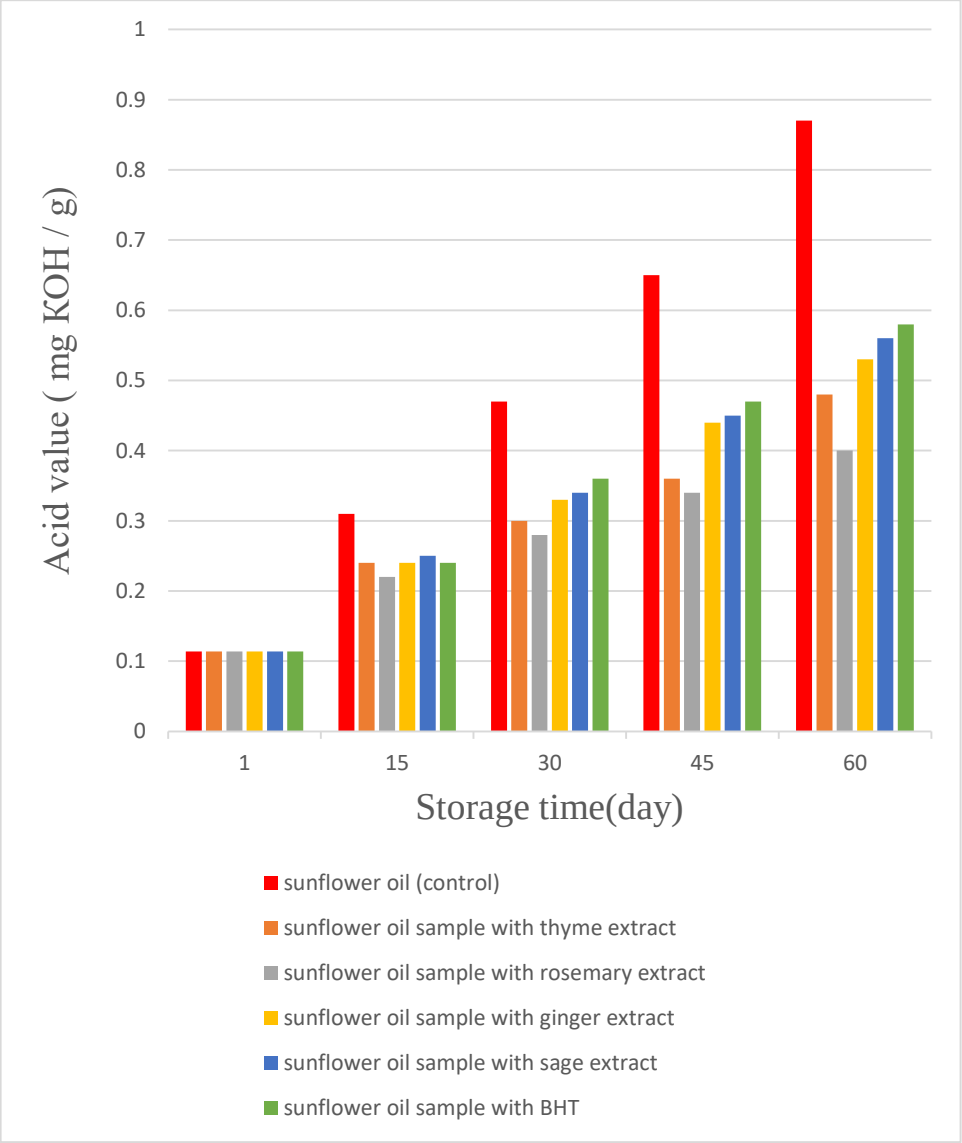

Figure 21 -Effect of adding BHT and herbal extracts extracted with ethanol 95% and propylene glycol 95% on acid value of sunflower oil

When comparing different samples, the sample that has the least acid value is the oil sample containing the rosemary extract. This may be because it contains a higher

percentage of compounds that are effective as antioxidants. From the results in table17, we note also that increase in the acid value of the oil sample containing BHT is greater than the increase in the acid values of all the oil samples containing the herb extracts.

Wherefore, we suggest that the BHT has a less effectiveness in delaying the occurrence of the process of oxidation of refined sunflower oil than herbal extracts.

3.3.6 Effect of adding a mixture of herb extracts extracted with ethanol 95%and propylene glycol 95% or BHT on the peroxide values and on acid values of refined sunflower oil samples

In this experiment, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger-rosemary, sage- rosemary) was added at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg .In the beginning, the peroxide value was measured for the refined sunflower oil sample, which did not contain any addition, and the value was 3.66 meq/kg. After the addition of BHT or a mixture of the herb extracts to the refined sunflower oil samples, the peroxide values of these samples were determined every 15 days for 60 days. The results were as follow in thetable18.

Table 18 – Effect of adding synthetic antioxidants or a mixture of herbal extracts on the peroxide values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The sample of sunflower oil with BHT
Peroxide value (meq/kg)						

1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.74	3.73	3.76	3.78	3.79
30days	5.3	3.85	3.8	3.89	3.91	3.98
45days	5.95	3.93	3.86	4.01	4.03	4.3
60days	6.5	4	3.94	4.11	4.14	4.4

From the results, after 60 days we note that the sample that has the highest peroxide value the sample of oil free of additives. While we note that the peroxide values of the oil samples containing either the BHT or a mixture of herbal extracts did not exhibit a considerable increase during sixty days of storage. The increase in the peroxide values was represented on the chart.

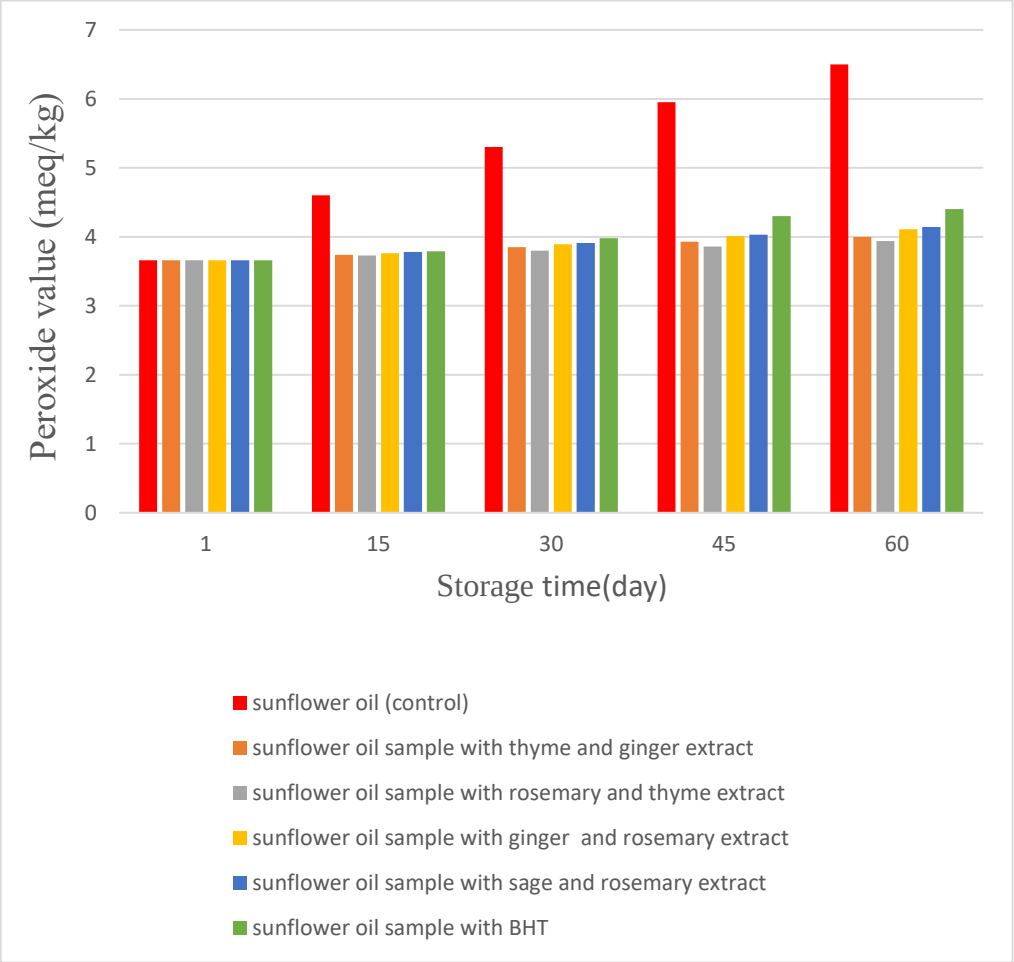

Figure 22 -Effect of adding BHT and a mixture of herbal extracts extracted with ethanol 95% and propylene glycol 95% on peroxide value of sunflower oil

The results of the experiment showed that the oil sample containing the rosemary-thyme extract had the lowest peroxide values. The peroxide value for this sample (3.94meq/kg) was less than the limit of acceptable values (10 meq/kg), stipulated by the standard GOST 1129-2013 for sunflower oil, because they contain compounds such as rosmanol, rosmaridiphenol, and carnosol which are effective as antioxidants. The increase in the peroxide values of the oil sample containing BHT antioxidant is more than the increase in the peroxide value of the oil samples containing the mixture of herb extract. Thus we conclude that a mixture of herbal extracts has the antioxidant efficacy in stabilizing the oils by delaying the hydroperoxides formation more than the industrial antioxidant.

At first, the acid value was measured for the refined sunflower oil sample, which did not contain any additives; it was 0.114.Every 15 days for two months, the acid value of the oil samples containing mixture of herbal extracts or the synthetic antioxidant was measured and the results were as follows in the table19.

Table 19 – Effect of adding a mixture of herbal extracts or BHT on the acid values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.19	0.18	0.22	0.2	0.24
30days	0.47	0.28	0.26	0.33	0.34	0.36

45days	0.65	0.37	0.31	0.43	0.44	0.47
60days	0.87	0.44	0.36	0.5	0.52	0.58

The results show that after2monthsthe sample that had the highest acid value the sample of oil without any addition. While the oil samples- whether containing the mixture of herbal extracts or BHT- the increase in the values of acid were few. The in creasein the acid values was represented on the chart.

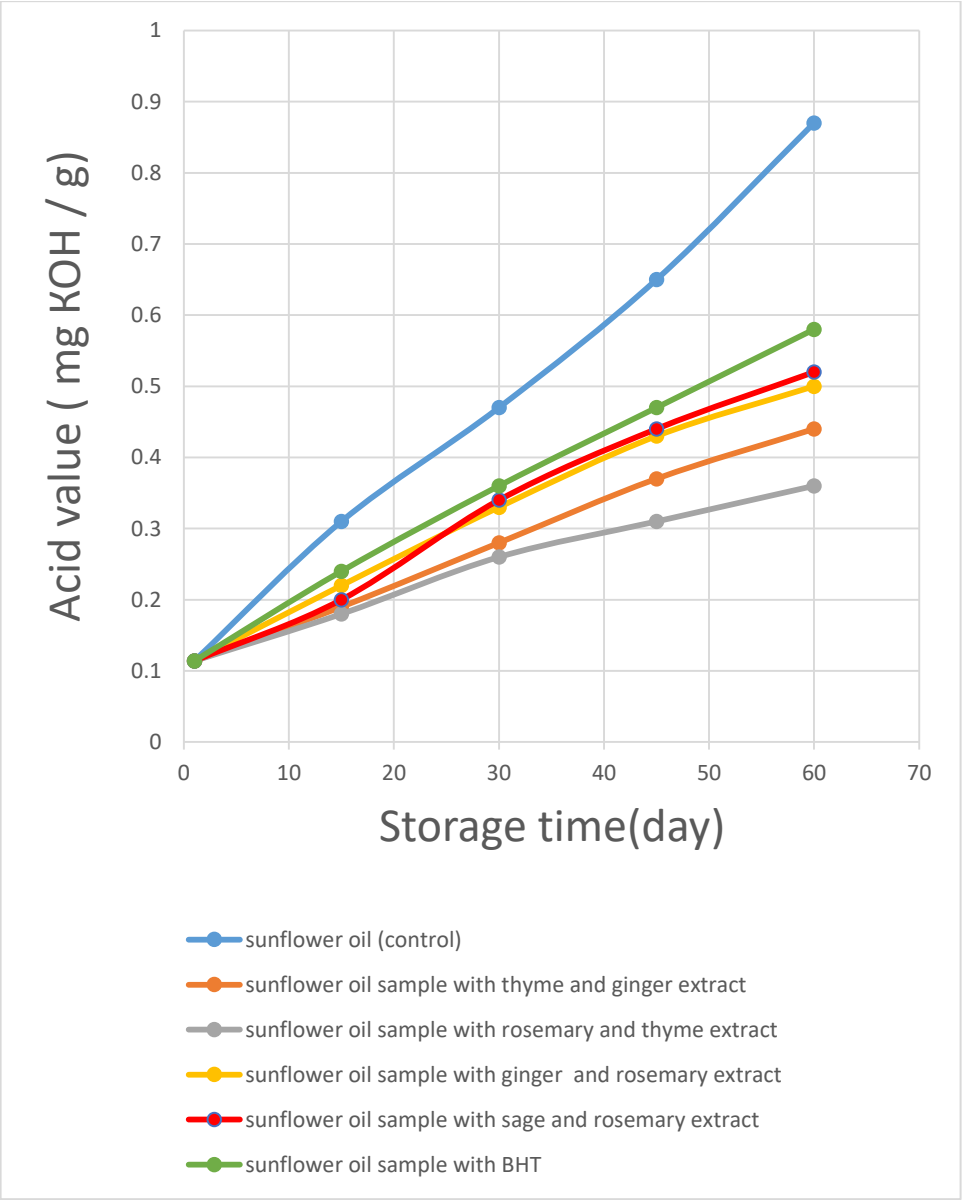

Figure 23 -Effect of adding BHT and a mixture of herbal extracts extracted with ethanol 95% and propylene glycol 95% on acid value of sunflower oil

Table 20– Regression equations describing the change in acid value for the samples of sunflower oil within two months

The sample of sunflower oil	The regression equation	Coefficient of approximation
The sample of sunflower oil without additions	y = 0.0125x + 0.1049	R^2 = 0.9972
The sample of sunflower oil with thyme and ginger extract	y = 0.0071x + 0.1082	R^2 = 0.9917
The sample of sunflower oil with rosemary and thyme extract	y = 0.0042x + 0.118	R^2 = 0.9889
The sample of sunflower oil with ginger and rosemary extract	y = 0.0066x + 0.1186	R^2 = 0.9925
The sample of sunflower oil with sage and rosemary extract	y = 0.0056x + 0.109	R^2 = 0.9983
The sample of sunflower oil with BHT	y = 0.0078x + 0.1158	R^2 = 0.9981

y-Acid value (mg KOH / g); x- Storage time (day).

The comparison between the different samples shows that the sample that has the least acidity value is the oil sample containing the rosemary-thyme extract, because they contain compounds such as rosmanol, rosmaridiphenol, and carnosol which are effective as antioxidants

The acid number for this sample (0.36 mg KOH / g of oil) was approaching the limit of acceptable values (0.4 mg KOH / g of oil), stipulated by the standard GOST 1129-2013 for sunflower oil.

On the other hand, the acid value of the oil sample containing the synthetic was greater than the acid values of all samples containing a mixture of herbal extracts.

Therefore, we conclude that synthetic antioxidant has the antioxidant efficacy in stabilizing the oils by delaying the free fatty acid formation less than a mixture of herbal extracts.

3.3.7 Effect of adding herb extracts extract with propylene glycol 95% separately or BHT on the peroxide values and on acid values of refined sunflower oil samples

At the beginning of the experiment, the peroxide value of the refined sunflower oil sample was measured; the value was 3.66 meq/kg.In this experiment, extracts were added separately at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg.

After adding herbal extracts and industrial antioxidants to the oil samples separately and measuring the peroxide values for each sample after 15 days and for two months, the results were as in the table 21.

Table 21 – The effect of herbal extracts or industrial antioxidants on the acid values of refined sunflower oil when each was added separately

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of sunflower oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Peroxide value (meq/kg)						
1day	3.66	3.66	3.66	3.66	3.66	3.66
15 days	4.6	3.78	3.76	3.78	3.79	3.79
30days	5.3	3.9	3.88	3.93	3.95	3.98
45days	5.95	4.01	3.98	4.09	4.11	4.3
60days	6.5	4.14	4.05	4.17	4.19	4.4

A sample of refined sunflower oil free from herb extracts or BHT increased its peroxide value more than other samples as it increased from 3.66 to 6.5.

On the other hand, the peroxide values of refined sunflower oil samples containing either of herb extracts or an industrial antioxidant have not changed significantly. The change in the peroxide values was represented on the chart.

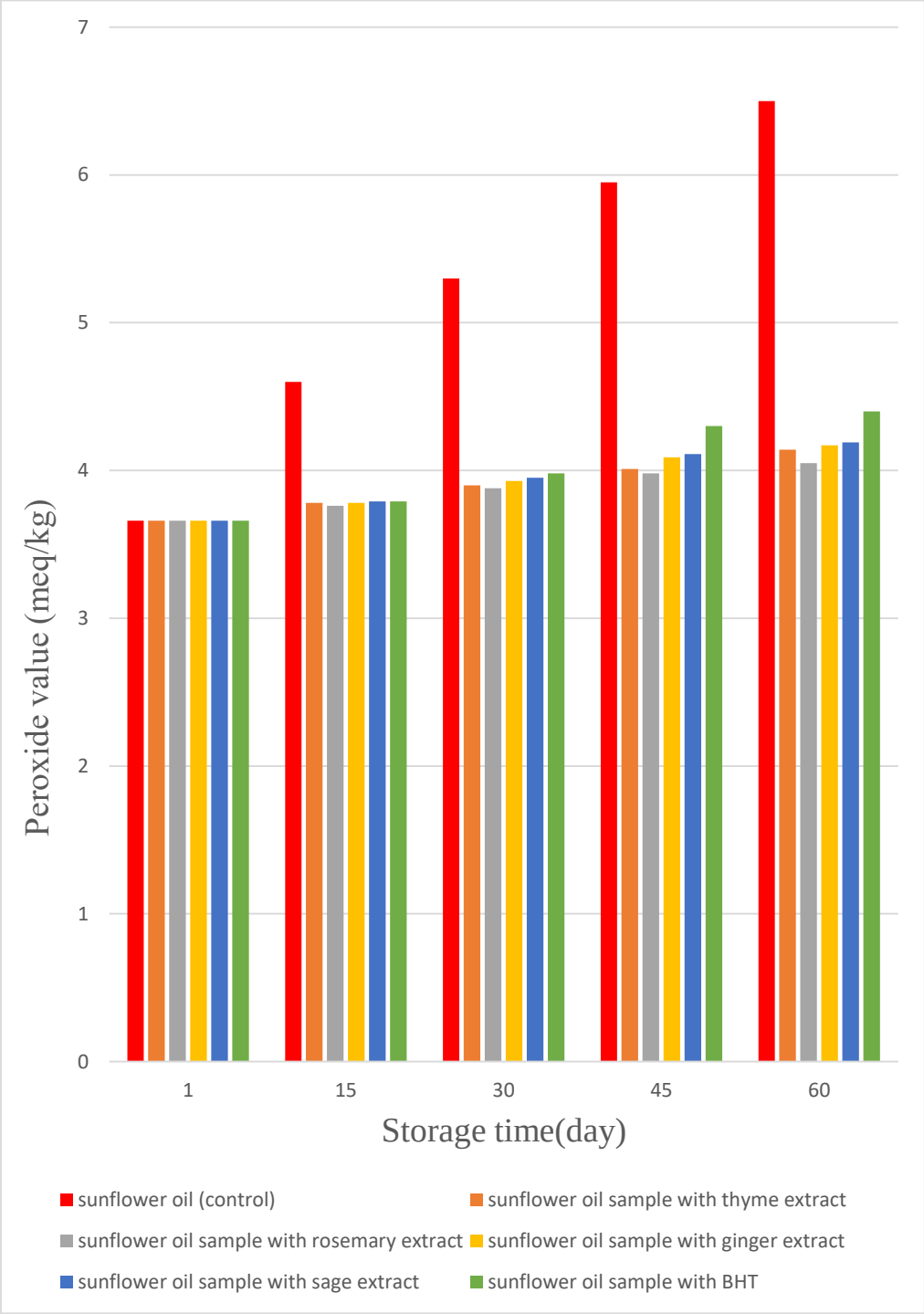

Figure 24 -Effect of adding BHT and herbal extracts extracted with propylene glycol 95% on peroxide value of sunflower oil

The sample containing rosemary extracts had the lowest peroxide value. This may be because it contains a higher percentage of polyphenols than other samples.

It was also found that all the samples of oil containing herbal extracts have lower peroxide values than the sample containing the synthetic antioxidant.

We can conclude that herbal extracts that have been added to sunflower oil have the potential to delay the occurrence of oxidation of oil more than the industrial antioxidant.

First, the acid value of the refined sunflower oil was determined without any additives and the result was 0.114 mg KOH / g.

The acid value of refined sunflower oil samples- whether free of additives or containing (BHT) or the herbal extracts added separately at concentration 1% to the oil- were determined every 15 days for two months, and the results were shown in table22.

Table 22 – The effect of herbal extracts or BHT antioxidants on the acid values of refined sunflower oil when each was added separately

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme extract	The sample of oil with rosemary extract	The sample of sunflower oil with ginger extract	The sample of sunflower oil with sage extract	The sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.25	0.24	0.26	0.27	0.24
30days	0.47	0.32	0.3	0.35	0.36	0.36
45days	0.65	0.38	0.36	0.46	0.47	0.47
60days	0.87	0.5	0.42	0.56	0.57	0.58

Among all oil samples, refined sunflower oil sample without any additives showed the highest increased in acid value.

The acid values of the oil samples did not change much after 60 days except for the oil sample free from any additives, the results were represented on the following chart.

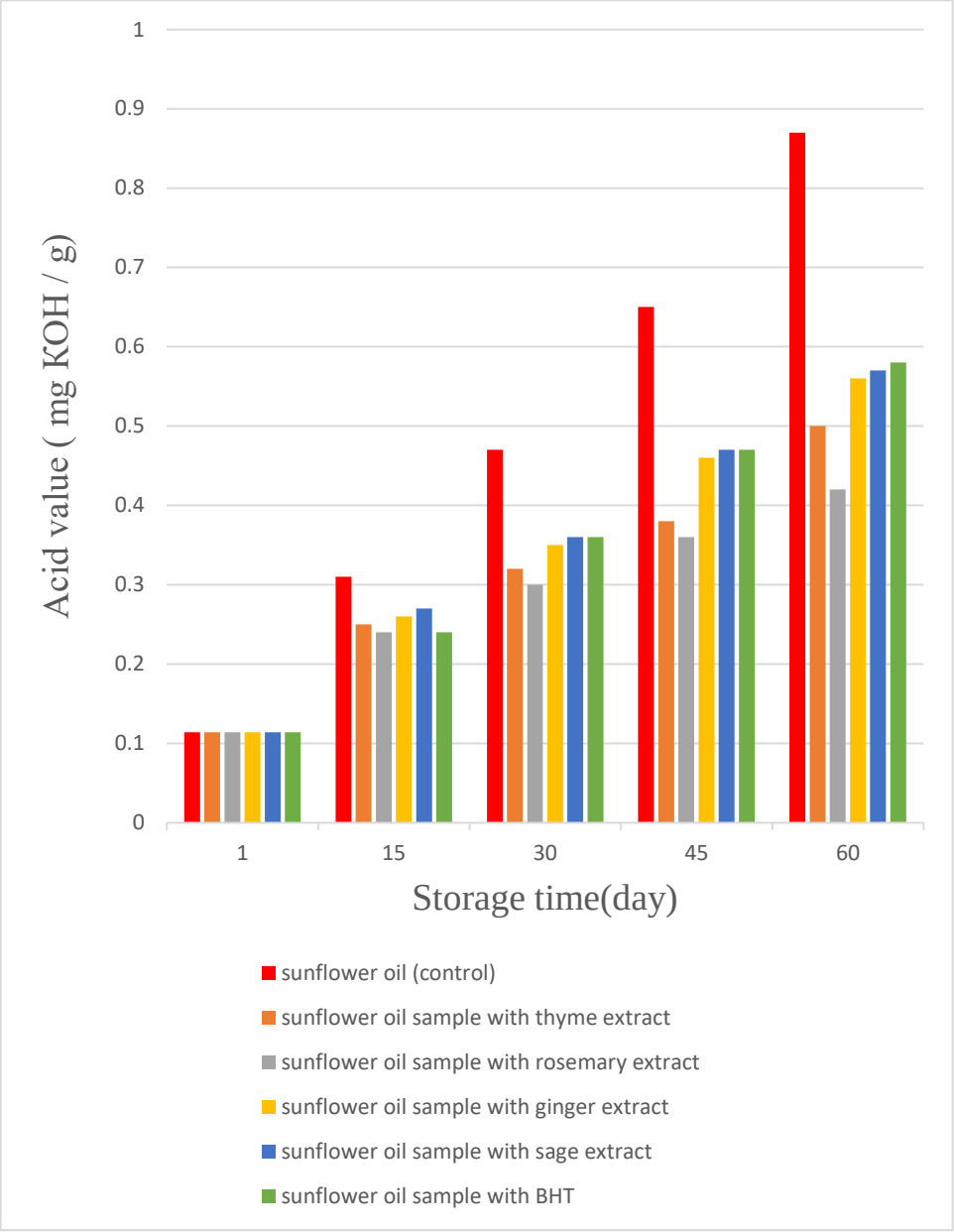

Figure 25 -Effect of adding BHT and herbal extracts extracted with propylene glycol 95%on acid value of sunflower oil

After comparing the different samples, we note that the sample with the lowest acid value is the sample containing the rosemary extract. This is due to the high percentage of

polyphenols. The results show that after the addition of plant extracts to refined sunflower oil samples, the acid values of these samples were lower than the value of acid when adding the BHT antioxidant. Wherefore, we suggest that the BHT antioxidant had the potential to inhibit the oxidation process of refined sunflower oil less than herbal extracts.

3.3.8 Effect of adding a mixture of herb extracts extract with propylene glycol 95% or BHT on the peroxide values and on acid values of refined sunflower oil samples

In this experiment, a mixture of extracts (thyme- ginger, rosemary- thyme, ginger-rosemary, sage- rosemary) was added at concentration 1% to 100 ml of refined sunflower oil sample and BHT at concentration 180 mg / Kg. Firstly, the peroxide value of refined sunflower oil was determined without any addition the value was 3.66 meq/kg. Then the synthetic antioxidant or a mixture of herbal extracts were added to the oil samples. Peroxide values were measured for each sample after 15 days and for two months. The results were as follows in the table 23.

Table 23 – Effect of adding a mixture of herbal extracts or industrial antioxidants on the peroxide values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of sunflower oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The sample of sunflower oil with BHT
	Peroxide value (meq/kg)					
1day	3.66	3.66	3.66	3.66	3.66	3.66

15 days	4.6	3.75	3.74	3.77	3.78	3.79
30days	5.3	3.86	3.83	3.91	3.93	3.98
45days	5.95	3.95	3.89	4.03	4.07	4.3
60days	6.5	4.02	3.97	4.14	4.17	4.4

Among all oil samples, refined sunflower oil sample without any additives showed the highest increased in peroxide value. On the other hand, the peroxide values of refined sunflower oil samples containing either a mixture of herb extracts or BHT antioxidant have not changed significantly. The change in the peroxide values was represented on the chart.

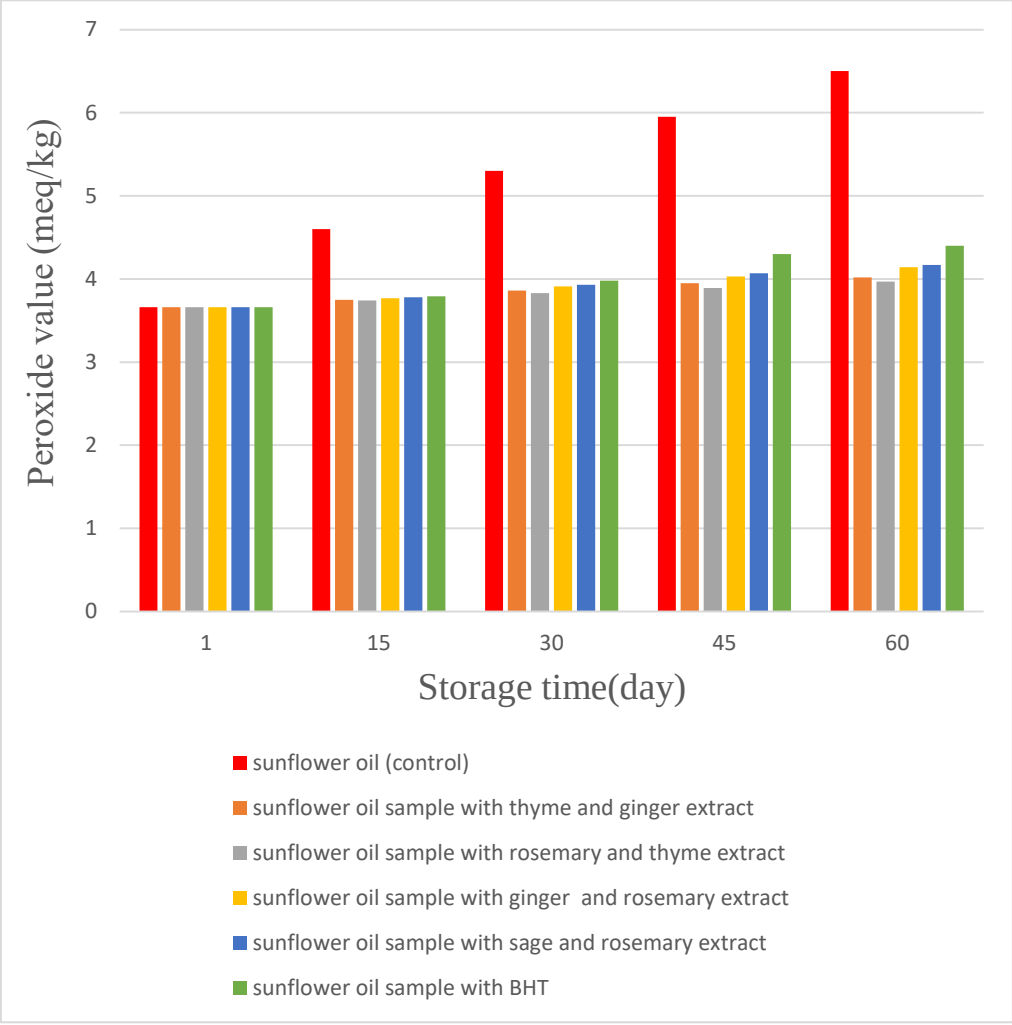

Figure 26 -Effect of adding BHT and a mixture of herbal extracts extracted with propylene glycol 95% on peroxide value of sunflower oil

The comparison between the different samples shows that the sample containing the rosemary-thyme extract had the lowest peroxide value. The peroxide value for this sample (3.97meq/kg) was less than the limit of acceptable values (10 meq/kg), stipulated by the standard TC 024/2011 for technical regulations for oil and fat products, because they contain a higher proportion of polyphenols than other samples.

The results show that all the samples of oil containing a mixture of herbal extracts have lower peroxide values than the sample containing the synthetic antioxidant.

We can conclude that the mixture of herbal extracts has a greater effectiveness in delaying the occurrence of the process of oxidation of refined sunflower oil than BHT.

At the beginning of the experiment, the acid value of the refined sunflower oil sample was measured sample; it was0.114 mg KOH / g. Every 15 days for two months, the acid value of the oil samples containing the synthetic antioxidant or a mixture of herbal extracts was measured and the results were as follows in the table 24.

Table 24 – Effect of adding a BHT or a mixture of herbal extracts on the acid values of refined sunflower oil

Days	The sample of sunflower oil without additions	The sample of sunflower oil with thyme and ginger extract	The sample of oil with rosemary and thyme extract	The sample of sunflower oil with ginger and rosemary extract	The sample of sunflower oil with sage and rosemary extract	The sample of sunflower oil with BHT
Acid value (mg KOH / g)						
1day	0.114	0.114	0.114	0.114	0.114	0.114
15 days	0.31	0.21	0.2	0.2	0.23	0.24
30days	0.47	0.3	0.28	0.34	0.36	0.36
45days	0.65	0.39	0.34	0.44	0.46	0.47
60days	0.87	0.47	0.39	0.52	0.53	0.58

The results show that after 2months the sample that had the highest acid value the sample of oil without any addition. While the oil samples, whether containing the mixture of herbal extracts or BHT, the increase in the values of acid were few. The results were represented on the following chart.

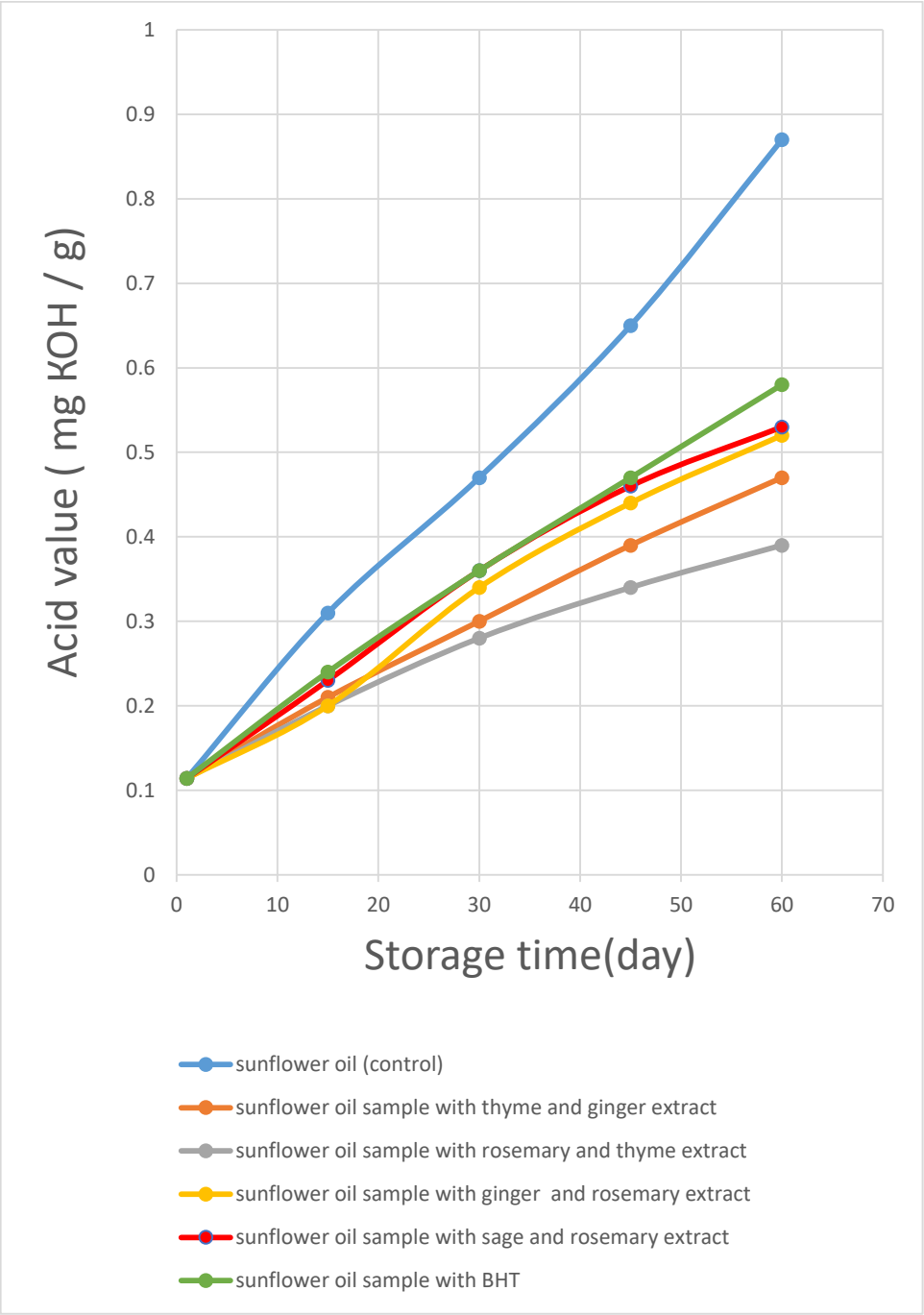

Figure 27 -Effect of adding BHT and a mixture of herbal extracts extracted with propylene glycol 95% on acid value of sunflower oil

Table 25 – Regression equations describing the change in acid value for the samples of sunflower oil within two months

The sample of sunflower oil	The regression equation	Coefficient of approximation
The sample of sunflower oil without additions	y = 0.0125x + 0.1049	R^2 = 0.9972
The sample of sunflower oil with thyme and ginger extract	y = 0.0072x + 0.1223	R^2 = 0.987
The sample of sunflower oil with rosemary and thyme extract	y = 0.0071x + 0.1082	R^2 = 0.9917
The sample of sunflower oil with ginger and rosemary extract	y = 0.006x + 0.1149	R^2 = 0.9982
The sample of sunflower oil with sage and rosemary extract	y = 0.0047x + 0.1238	R^2 = 0.9848
The sample of sunflower oil with BHT	y = 0.0078x + 0.1158	R^2 = 0.9981

y-Acid value (mg KOH / g); x- Storage time (day).

The results of the experiment showed that the sample that has the least acid value is the oil sample container of the rosemary-thyme extract.

The acid number for this sample (0.39 mg KOH / g of oil) was less than the limit of acceptable values (0.6 mg KOH / g of oil), stipulated by the standard TP TC 024/2011 for technical regulations for oil and fat products.

This may be because they contain more polyphenols than other samples.

From the results in the table 24 we note that the acid value of the oil sample, which is added to it, BHT was higher than the acid values of the oil samples containing a mixture of the plant extracts.

Wherefore, we conclude that a mixture of herbal extracts has the potential to inhibit the oxidation process of refined sunflower oil more than BHT.

CONCLUSIONS

1.The results show that amount of phenolic compounds for various extracts ranged from11.12to45.17. The total polyphenol content of the extracts can be ranked in the order rosemary (45.17)>thyme (36.15) > sage (25.74) > ginger (11.12).The results show that the rosemary extract contains the highest value of polyphenols.

2. The results show that the DPPH radical scavenging ability of the extracts can be ranked in the order rosemary (85.15%) >thyme (76.55%) > sage (55.64 %) > ginger (36.44%). The observed differential scavenging activities of the extracts against the DPPH system could be due to the presence of different compounds in the extract.

3. In comparing the different samples, we note that the lowest peroxide value was for the sample of sunflower oil containing the rosemary extract.

On the other hand, the peroxide values of all samples containing herb extracts that were added separately to these samples were lower than the peroxide values of the oil sample containing the industrial antioxidant.Thus, we conclude that herbal extracts have a higher effectiveness in preventing the oxidation of sunflower oil than the industrial antioxidant.

4. After comparing the different samples, we note that the sample with the lowest acid value is the sample containing the rosemary extract.

Furthermore, the acid value of the oil sample containing the industrial antioxidant was greater than the acid values of all samples containing herb extracts that were added separately to these samples.Thus, we conclude that the industrial antioxidant has a lower effectiveness in preventing the oxidation of sunflower oil than herbal extracts.

5. The comparison between the different samples shows that the sample containing the rosemary-thyme extract had the lowest peroxide value.It was also found that all the samples of oil containing a mixture of herbal extracts have lower peroxide values than the sample containing the synthetic antioxidant, and as well as below the peroxide values of

sunflower oil samples containing extracts that were added separately to these samples .We can conclude that the mixture of herbal extracts has a greater effectiveness in delaying the occurrence of the process of oxidation of refined sunflower oil than the synthetic antioxidant.

6. After comparing the different samples, we note that the sample with the lowest acid value is the sample containing the rosemary-thyme extract. On the other hand, all the samples of oil containing a mixture of herbal extracts have lower acid values than the sample containing the synthetic antioxidant, and as well as below the acid values of sunflower oil samples containing herbal extracts that were added separately to these samples.

So, we conclude that the synthetic antioxidant has a less effectiveness in delaying the occurrence of the process of oxidation of refined sunflower oil than a mixture of herbal extracts. Therefore, we suggest using a mixture of thyme and rosemary extract as a natural antioxidant for vegetable oils.

LIST OF SOURCES USED

1. Jorge, N. Antioxidant Effect of Thyme (Thymus vulgaris L.) and Oregano (Origanum vulgare L.) Extracts in Soybean oil underThermoxidation/N. Jorge, et al //Journal of food processing and preservation. – 2015. – VOL. 39. – №. 6. – P. 1399-1406.

2. Decker, E. A. Oxidation in foods and beverages and antioxidant applications: management in different industry sectors/E. A Decker, R. J .Elias.–Elsevier, 2010. –52 P.

3. Gallego, M. G. Antioxidant properties of three aromatic herbs (rosemary, thyme and lavender) in oil-in-water emulsions/M.G. Gallego, et al //Journal of the American Oil Chemists' Society. – 2013. – Vol. 90. – №. 10. – P. 1559-1568.

4. Aladedunye, F. A. Natural antioxidants as stabilizers of frying oils/F.A. Aladedunye //European journal of lipid science and technology. – 2014. – Vol. 116. – №. 6. – P. 688-706.

5. Kim, I. S. Antioxidant activities of hot water extracts from various spices /I.S.Kim,et al //International journal of molecular sciences. – 2011. – Vol. 12. – №. 6. – P. 4120-4131.

6. Charles, D. J. Antioxidant properties of spices, herbs and other sources/D. J. Charles.– Springer Science & Business Media, 2012. –105-108 P.

7. Decker, E. A.Oxidation in Foods and Beverages and Antioxidant Applications. Understanding Mechanisms of oxidation and antioxidant/E. ADecker,R. J.Elias.–Elsevier, 2010. –2 P.

8. Sayyari, Z. Stabilization of sunflower oil with pussy willow (Salix aegyptiaca) extract and essential oil/Z.Sayyari,R.Farahmandfar //Food science & nutrition. – 2017. – Vol. 5. – №. 2. – P. 266-272.

9. Patil, D. Role of antioxidants in stability of edible oil/D.Patil //Trends in Post-Harvest Technology. – 2013. – P. 68-73.

10. Aluyor, E. O. The use of antioxidants in vegetable oils–A review/E.O. Aluyor, M. Ori-Jesu //African Journal of Biotechnology. – 2008. – Vol. 7. – №. 25. p. 4836-4842.

11. Turek, C. Stability of essential oils: a review/C.Turek,F. C. Stintzing //Comprehensive Reviews in Food Science and Food Safety. – 2013. – Vol. 12. – №. 1. – P. 40-53.

12. Baek, N. Effects of natural antioxidants on lipid oxidation of menhaden oil/N.Baek. – Master Thesis, Virginia Tech, 2013. – 10P.

13. Caeiro, R. A. Antioxidant effect of caffeic acid alkyl esters in sunflower oil and their combination with other antioxidants/R.A. Caeiro. –Master Thesis, 2014.– 2 P.

14. Kostik, V. Fatty acid composition of edible oils and fats/V.Kostik, S.Memeti //Journal of Hygienic Engineering and Design. – 2013. – Vol. 4. – P. 112-116.

15. Shrestha,R. Occurrence of epoxy fatty acids in oils and their formation during photo-oxidation in o/w emulsion / R. Shrestha. – Master Thesis, 2016. – 5 P.

16. Tavasalkar, S. U. Evaluation of antioxidant efficacy of natural plant extracts against synthetic antioxidants in sunflower oil/S.U.–Tavasalkar,H.N Mishra, S.Madhavan //Scientific Reports. – 2012. – Vol. 1. – P. 504.

17. Roby, M. H. H. Evaluation of antioxidant activity, total phenols and phenolic compounds in thyme (Thymus vulgaris L.), sage (Salvia officinalis L.), and marjoram (Origanummajorana L.) extracts/M.H.HRoby,et al //Industrial Crops and Products. – 2013. – Vol. 43. – P. 827-831.

18. Wilson, D. W. The Role of Food Antioxidants, Benefits of Functional Foods, and Influence of Feeding Habits on the Health of the Older Person: An Overview/D.W.Wilson,et al //Antioxidants. – 2017. – Vol. 6. – №. 4. – P. 81.

19. Oroian, M. Antioxidants: characterization, natural sources, extraction and analysis/M.Oroian,I.Escriche //Food Research International. – 2015. – Vol. 74. – P. 10-36.

20. Reda, S. Y. Evaluation of antioxidants stability by thermal analysis and its protective effect in heated edible vegetable oil /S.Y.Reda //Food Science and Technology. – 2011. – Vol. 31. – №. 2. – P. 475-480.

21. Muniandy, P. Influence of green, white and black tea addition on the antioxidant activity of probiotic yogurt during refrigerated storage/P. Muniandy , A.B. Shori , A.S. Baba //Food Packaging and Shelf Life. – 2016. – Vol. 8. – p. 1-8.

22. Brar, S. K. Biotransformation of waste biomass into high value biochemical /K.S.Brar,S.G.Dhillon. – Springer Science & Business Media, 2013. –118 P.

23. Sana, M. Antioxidant effect of essential oils of Thymus, Salvia and Rosemarinus on the stability to auxidation of refined oils/M.Sana,et al //Ann Bio Res. – 2012. – Vol. 3. – P. 4259-4263.

24. Gaweł-Bęben, K. Stevia rebaudiana Bert. Leaf extracts as a multifunctional source of natural antioxidants/K.Gaweł-Bęben,et al //Molecules. – 2015. – Vol. 20. – №. 4. – P. 5468-5486.

25. Dubey, N. K. Plants as a source of natural antioxidants/N.K.Dubey. –CABI, 2014.– 2 P.

26. Mehta, S. K. Members of Antioxidant Machinery and Their Functions/S.K.Mehta, S.J.Gowder. –Basic Principles and Clinical Significance of Oxidative StressInTech, 2015.– 60-85 P.

27. Daramola,B.Bitter Kola (Garcinia kola) seeds and health management potential/B.Daramola,G.O.Adegoke. – Nuts and Seeds in Health and Disease Prevention, 2011. – 213-220P.

28. Shalaby, E. A., Shanab S. M. M. Antioxidant compounds, assays of determination and mode of action/Shalaby E.A, S.M.Shanab//African journal of pharmacy and pharmacology. – 2013. – Vol. 7. – №. 10. – p. 528-539.

29. Lieu, H. K. Effect of black and white sesame cake extracts on retarding lipid oxidation in catfish fat / H.K.Lieu, T.Q.Dang //Journal of Food and Nutrition Sciences. – 2015. – Vol. 3. – №. 1-2. – p. 39-44.

30. Shahidi, F. Tocopherols and tocotrienols in common and emerging dietary sources: Occurrence, applications, and health benefits/F.Shahidi,A.C.de Camargo//International journal of molecular sciences. – 2016. – Vol. 17. – №. 10. – P. 1745.

31. Minatelli, J. A. Composition using seed oil extracts and phospholipids to enhance absorption of carotenoids and associated methods/J.A.Minatelli,et al. –U.S. Patent Application, 2015.–No. 14/706,092. –P.1-4.

32. Lampi, A. M. Analysis of tocopherols and tocotrienols by HPLC/A.M.Lampi //The AOCS (American Oil Chemists' Society) Lipid Library, (Aug. 3, 2011) available online at http://lipidlibrary. aocs. org/topics/tocopherols/index. htm. – 2011.P1-2.

33. Fishbein, J. C. Advances in molecular toxicology/J.C.Fishbein, J.M.Heilman. – Academic Press, 2012. – vol. 6.

34. Martínez-Force, E. Sunflower: chemistry, production, processing, and utilization/E.Martínez-Force,N.T.Dunford,J.J.Salas. –Elsevier, 2015.–476P.

35. Castelo-Branco, V. N. Potential application of antioxidant capacity assays to assess the quality of edible vegetable oils /V.NCastelo-Branco,A.G.Torres //Lipid technology. – 2009. – Vol. 21. – №. 7. – P. 152-155.

36. Hamdo, H. H. The antioxidant activity of tocotrienols compared with some synthetic antioxidant /H.H.Hamdo,W.Khayata,Z.Al-Assaf //Pharmacology & Pharmacy. – 2014. – Vol. 5. – №. 7 special issue. – P. 612.

37. Race, S. Antioxidants: The truth about BHA, BHT, TBHQ and other antioxidants used as food additives/S. Race. – Tigmor Book: London, 2009. –7-8 P.

38. Carocho, M. A review on antioxidants, prooxidants and related controversy: natural and synthetic compounds, screening and analysis methodologies and future perspectives/M.Carocho,I.C.Ferreira //Food and chemical toxicology. – 2013. – Vol. 51. – P. 15-25.

39. Medina, M. E. Antioxidant activity of propyl gallate in aqueous and lipid media: a theoretical study/M.E.Medina,C.Iuga,J.RAlvarez-Idaboy //Physical Chemistry Chemical Physics. – 2013. – Vol. 15. – №. 31. – P. 13137-13146.

40. Brewer, M. S. Natural antioxidants: sources, compounds, mechanisms of action, and potential applications / M.S.Brewer //Comprehensive reviews in food science and food safety. – 2011. – Vol. 10. – №. 4. – P. 221-247.

41. Nanditha, B. Antioxidants in bakery products: a review/B. Nanditha,P. Prabhasankar //Critical reviews in food science and nutrition. – 2008. – Vol. 49. – №. 1. – p. 1-27.

42. Eça, K. S. Films and edible coatings containing antioxidants-a review/K.S.Eca, T.Sartori,F.Menegalli //Brazilian Journal of Food Technology. – 2014. – Vol. 17. – №. 2. – P. 98-112.

43. Shahidi, F. (Ed.).Handbook of food preservation/F. (Ed.).Shahidi. –CRC press, 2007. –3-10P.

44. Saxena,M.Flavonoids and phenolic acids as antioxidants in plants and human health/M.Saxena,J.Saxena,A.Pradhan //International Journal of Pharmaceutical Sciences Review and Research. – 2012. – Vol. 16. – №. 2. – P. 130-134.

45. Aladedunye, F. A. Natural antioxidants as stabilizers of frying oils/F.A.Aladedunye //European journal of lipid science and technology. – 2014. – Vol. 116. – №. 6. – P. 688-706.

46. Gunstone, F. (ed.). Vegetable oils in food technology: composition, properties and uses/F.(ed.).Gunstone. – John Wiley & Sons, 2011. – 159 p.

47. Babović, N. Oxidative stabilization of sunflower oil by antioxidant fractions from selected Lamiaceae herbs/N.Babović,et al //Chemical Industry and Chemical Engineering Quarterly/CICEQ. – 2010. – Vol. 16. – №. 4. – P. 287-293.

48. Ajeena, S. Studying the Antioxidant Activity of Some Plants Extracts Tested by Hydroxyl Radical Scavenging/S.Ajeena,M.Hindi,JArkawazi//International Conference on Energy and Environmental Science,2013.Vol.54. P.12.

49. Kiralan, M. Effect of Nigella Seed Extract on Oxidative Stability of Refined Sunflower Oil/M.Kiralan, et al //Asian Journal of Chemistry. – 2008. – Vol. 20. – №. 5. – P. 3313.

50. Ben-Ali, M. Stabilization of sunflower oil during accelerated storage: use of basil extract as a potential alternative to synthetic antioxidants/M.Ben-Ali,et al //International journal of food properties. – 2014. – Vol. 17. – №. 7. – P. 1547-1559.

51. Taghvaei, M. Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives/M.Taghvaei,S.M.Jafari //Journal of food science and technology. – 2015. – Vol. 52. – №. 3. – P. 1272-1282.

52. Niamat, I. Stabilization of sunflower oil with extracts from fenugreek, mint and liquorice/I.Niamat, et al //Bulgarian chemical communication. – 2016. – Vol. 48. – №. 4. – P. 753-757.

53. Lieu, H. K. Effect of black and white sesame cake extracts on retarding lipid oxidation in catfish fat/H.K.Lieu,T.Q.Dang //Journal of Food and Nutrition Sciences. – 2015. – Vol. 3. – №. 1-2. – p. 39-44.

54. Abdelazim, A. Oxidative stability of vegetable oils as affected by sesame extracts during accelerated oxidative storage/A. Abdelazim ,et al //Journal of food science and technology. – 2013. –Vol. 50. – №. 5. – p. 868-878.

55. Rege, S. A.Synergistic Antioxidant Activity of Capsicum Oleoresin, Lecithin and Curcuminoids in Sunflower Oil/S.A.Rege,S.A.Momin //International Journal. – 2017. – Vol. 4. – №. 1. – P. 7.

56. Rasmy, N. M. Assessment of the antioxidant activity of sage (Salvia officinalis L.) extracts on the shelf life of mayonnaise/N.M.Rasmy,et al //World Journal of Dairy & Food Sciences. – 2012. – Vol. 7. – №. 1. – P. 28-40.

57. Decker, E. A. Oxidation in foods and beverages and antioxidant applications: management in different industry sectors / E. A.Decker,R. J.Elias.– Elsevier, 2010.Vol. 2.

58. Yin, J. Green tea extract as food antioxidant. Synergism and antagonism with α-tocopherol in vegetable oils and their colloidal systems/J.Yin, et al //Food chemistry. – 2012. – Vol. 135. – №. 4. – p. 2195-2202.

59. Taghvaei, M. Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives/M. Taghvaei,S.M. Jafari //Journal of food science and technology. – 2015. – Vol. 52. – №. 3. – P. 1272-1282.

60. Veronezi, C. M. Basil (Ocimumbasilicum L.) as a natural antioxidant /C.M.Veronezi, T.Costa,N.Jorge//Journal of food processing and preservation. – 2014. – Vol. 38. – №. 1. – P. 255-261.

61. Kukreja, B. K. Current market trends and regulatory aspects of herbal antioxidants and natural dietary supplements: A boon for health and treatment of diseases/B.K.Kukreja, K.Soni, K.Kohli //World J. Pharm. Pharm. Sci. – 2015. – Vol. 4. – №. 10. – P. 2373-2406.

62. Ben-Ali, M. Stabilization of sunflower oil during accelerated storage: use of basil extract as a potential alternative to synthetic antioxidants/M. Ben-Ali,et al //International journal of food properties. – 2014. – Vol. 17. – №. 7. – p. 1547-1559.

63. Usatiuk,S. Chlorophyll content and antioxidant activity of sunflower oil with aromatic raw materials/S.Usatiuk, L.pelekhova //Food and Environment Safety Journal. – 2016. – Vol. 13. – №. 4.

64. Abozid, M. M. Chemical composition, antioxidant and antimicrobial activity of the essential oil of the thyme and rosemary /M.M Abozid,M. Asker //International Journal of Academic Research. – 2013. – Vol. 5. – №. 3– p. 186-195.

65. Fan, L. The use of antioxidants in the preservation of edible oils/ L.Fan, N.A.M.Eskin. – Handbook of Antioxidants for Food Preservation, 2015. – 373-388 P.

66. Gad, A. S. Antioxidant properties of rosemary and its potential uses as natural antioxidant in dairy products—A review/A.S.Gad,A.F.Sayd //Food and Nutrition Sciences. – 2015. – Vol. 6. – №. 01. – P. 179.

67. Yang, Y. Rosemary extract can be used as a synthetic antioxidant to improve vegetable oil oxidative stability/Y.Yang,et al //Industrial Crops and Products. – 2016. – Vol. 80. – P. 141-147.

68. Brewer, M. S. Natural antioxidants: sources, compounds, mechanisms of action, and potential applications / M.S. Brewer //Comprehensive reviews in food science and food safety. – 2011. – Vol. 10. – №. 4. – p. 221-247.

69. Chen, X. Antioxidant effects of rosemary extracts on sunflower oil compared with synthetic antioxidants/X.Chen, et al //International Journal of Food Science & Technology. – 2014. – Vol. 49. – №. 2. – P. 385-391.

70. Ahn, J. H. Antioxidant effect of natural plant extracts on the microencapsulated high oleic sunflower oil/J.H.Ahn, et al //Journal of Food Engineering. – 2008. – Vol. 84. – №. 2. – P. 327-334.

71. Hamidpour, M. Chemistry, pharmacology, and medicinal property of sage (Salvia) to prevent and cure illnesses such as obesity, diabetes, depression, dementia, lupus, autism, heart disease, and cancer/M.Hamidpour, et al //Journal of traditional and complementary medicine. – 2014. – Vol. 4. – №. 2. – P. 82-88.

72. Erdogan, S. S.The Determination of Antioxidant Activity of Some Sage Populations of In The Marmara Region/ S.S .Erdogan, U. karik , K.H.C. Baser //Türk Tarım ve Doğa Bilimleri. – 2014. – Vol. 7. – №. 7. – P. 1877-1882.

73. Sunil, L. Oryzanol as natural antioxidant for improving sunflower oil stability/L. Sunil, et al //Journal of food science and technology. – 2015. – Vol. 52. – №. 6. – P. 3291-3299.

74. Dashti, N. G. Antioxidant Effect of Thyme Essential Oil on Oxidative Stability of Chicken Nuggets/N.G.Dashti,et al//Int J Food Eng. – 2015. – Vol. 1. – №. 2. – P. 115-20.

75. Zaborowska, Z. Antioxidative effect of thyme (Thymus vulgaris) in sunflower oil/ Z. Zaborowska, K. Przygoński, A. Bilska //ACTA Scientiarum Polonorum Technologia Alimentaria. – 2012. – Vol. 11. – №. 3. – P. 283-291

76. Babović, N. Oxidative stabilization of sunflower oil by antioxidant fractions from selected Lamiaceae herbs/N.Babović, et al //Chemical Industry and Chemical Engineering Quarterly/CICEQ. – 2010. – Vol. 16. – №. 4. – p. 287-293.

77. Komaki, A. Study of the effect of extract of Thymus vulgaris on anxiety in male rats/A.Komaki,et al //Journal of traditional and complementary medicine. – 2016. – Vol. 6. – №. 3. – P. 257-261.

78. Nikolić, M. Chemical composition, antimicrobial, antioxidant and antitumor activity of Thymus serpyllum L., Thymus algeriensisBoiss. andReut and Thymus vulgaris L. essential oils/M.Nikolić,et al //Industrial Crops and Products. – 2014. – Vol. 52. – P. 183-190.

79. Mashhadi, N. S. Anti-oxidative and anti-inflammatory effects of ginger in health and physical activity: review of current evidence/N.SMashhadi,et al //International journal of preventive medicine. – 2013. – Vol. 4. – №. Suppl 1. – P. S36.

80. Tohma, H. Antioxidant activity and phenolic compounds of ginger (ZingiberofficinaleRosc.) determined by HPLC-MS/MS/H.Tohma,et al //Journal of Food Measurement and Characterization. – 2017. – Vol. 11. – №. 2. – P. 556-566.

81. Stoilova, I. Antioxidant activity of a ginger extract (Zingiber officinale) / I. Stoilova, et al // Food chemistry. – 2007. – Vol. 102. – №. 3. – P. 764-770.

82. Ghasemzadeh, A. Antioxidant activities, total phenolics and flavonoids content in two varieties of Malaysia young ginger (Zingiberofficinale Roscoe)/A.Ghasemzadeh,H.Z.Jaafar,A.Rahmat //Molecules. – 2010. – Vol. 15. – №. 6. – P. 4324-4333.

83. Prakash, J. Chemical composition and antioxidant properties of ginger root (Zingiberofficinale)/J. Prakash //Journal of Medicinal Plants Research. – 2010. – Vol. 4. – №. 24. – P. 2674-2679.

84. Devi,A. Ginger extract as a nature based robust additive and its influence on the oxidation stability of biodiesel synthesized from non-edible oil/A.Devi,V.K.Das, D.Deka//Fuel. – 2017. –Vol. 187. – P. 306-314.

85. Bardsley, K. Ginger (Zingiberofficinale): Antioxidants and their use in stabilizing lemon oil /K. Bardsley, Dissertation directorsRutgers The State University of New Jersey-New Brunswick, 2013.– 7-8 p.

86. Nacaroglu, H. T. Angioedema Due to Lamiaceae Allergy/H.T. Nacaroglu ,et al //Iranian Journal of Allergy, Asthma and Immunology. – 2018. – Vol. 17. – №. 1. – p. 97-99.

87. Pitaro, S. Antioxidant activity of basil and oregano extracts added to soybean oil for accelerated storage test /S.Pitaro,L.Fiorani,N.Jorge //Journal of Food Biochemistry. – 2013. – Vol. 37. – №. 4. – P. 485-490.

88. Yashin, A. Antioxidant activity of spices and their impact on human health: A Review/A.Yashin,et al //Antioxidants. – 2017. – Vol. 6. – №. 3. – P. 70.

89. Derakhshani, Z. Evaluation of phenolic content and antioxidant capacity in some medicinal herbs cultivated in Iran /Z.Derakhshani, et al //Botanica Serbica. – 2012. –Vol. 36. – №. 2. – P. 117-22.

90. Al-Hijazeen, M. Effect of oregano essential oil (Origanum vulgare subsp. hirtum) on the storage stability and quality parameters of ground chicken breast meat/M. Al-Hijazeen , et al //Antioxidants. – 2016. – Vol. 5. – №. 2. – P. 18.

91. Suntres, Z. E. The bioactivity and toxicological actions of carvacrol/Z.E.Suntres,J.Coccimiglio,M.Alipour //Critical reviews in food science and nutrition. – 2015. – Vol. 55. – №. 3. – P. 304-318.

92. Turan, S. Effects of some plant extracts on the oxidative stability of canola oil and its purified triacylglycerols/S.Turan //Journal of food quality. – 2014. – Vol. 37. – №. 4. – P. 247-258.

93. Jorge, N. Antioxidant Effect of Thyme (Thymus vulgaris L.) and Oregano (Origanum vulgare L.) Extracts in Soybean Oil UnderThermoxidation/N.Jorge,et al //Journal of food processing and preservation. – 2015. – Vol. 39. – №. 6. – P. 1399-1406.

94. Zaborowska, Z. Antioxidative effect of thyme (Thymus vulgaris) in sunflower oil/Z. Zaborowska, K. Przygoński, A. Bilska //ACTA Scientiarum Polonorum Technologia Alimentaria. – 2012. – Vol. 11. – №. 3. – P. 283-291.

95. Pereira D. Rosemary as natural antioxidant to prevent oxidation in chicken burgers/D. Pereira, et al //Food Science and Technology (Campinas). – 2017.– Vol. 37 – №. AHEAD. – P.5.

96. Sayyari, Z. Stabilization of sunflower oil with pussy willow (Salix aegyptiaca) extract and essential oil/Z.Sayyari, R.Farahmandfar//Food science & nutrition. – 2017. – Vol. 5. – №. 2. – p. 266-272.

97. Shahi, M. M. N. Study of antioxidant activity and free radical scavenging power of Physalisalkekengi flower extract/M.M.N Shahi, et al. //Journal of Fundamental and Applied Sciences. – 2016. – Vol. 8. – №. 2. – P. 547-557.

98. Rajurkar, N. S. Estimation of phytochemical content and antioxidant activity of some selected traditional Indian medicinal plants /N.S. Rajurkar ,S.M. Hande//Indian journal of pharmaceutical sciences. – 2011. – Vol. 73. – №. 2. – P. 146.

99. ГОСТ Р 51487-99. Масла растительные и жиры животные. Методопределенияперекисногочисла.

100. ГОСТ Р 50457-92 Государственный стандарт Российской Федерации. Жиры и масла животные и растительные. Определение кислотного числа и кислотности.

101. ГОСТ 1129-2013 Масло подсолнечное. Технические условия (с Поправкой).

102. ТР ТС 024/2011Технический регламент на масложировую продукцию.