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QUALITY CONTROL AND OXIDATIVE STABILITY OF SELECTED EDIBLE COLD PRESSED OILS

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ABSTRACT
The results of quality control and oxidative stability of all edible cold pressed oils showed that pumpkin oil is the most stable, while linseed oil is the most susceptible to oxidative changes. From the parameters showing the quality of the oil, the saponification number, acid number, iodine number, peroxide number, unsaponifiable matter, density and Kreis reaction were determined, and as parameters of the oxidative stability of the oil samples, the following were determined: anisidine number, totox number and thiobarbiturate number and antioxidant capacity. The values of saponification, iodine, ansidin, totox, thiobarbituric number for pumpkin and grape seed oil samples do not show significant deviations from the prescribed values, while linseed oil had slightly higher values. All samples had acid number values in accordance with the legal regulation defined by the Quality Regulation, 2010. It is noticeable that the density for all oil samples increases with the length of storage. The content of unsaponifiable matter was higher in pumpkin and linseed oil compared to grape seed oil. Buda oil samples had a higher content of polyphenolic compounds compared to other oils.

KEYWORDS: edible cold pressed oils, quality control, oxidative stability.

1. INTRODUCTION
Although the process of producing cold pressed oils is relatively simple, there are a large number of factors that are of crucial importance and that can affect the quality of the obtained oil [1]. The technological process for the production of cold pressed oils includes a pressing operation, without heating, in order to preserve the quality and nutritional value as much as possible. Before pressing, the raw material is treated in an appropriate way, depending on the type of raw material and this mainly includes the operations of cleaning, peeling and shredding the raw material. After pressing, cold pressed oils are purified exclusively by washing with water, settling, filtering and centrifuging. These oils can be used in different ways: as salad oils for direct consumption or for the preparation of special dishes, they can be mixed with other oils, in the pharmaceutical and cosmetic industry and in the chemical industry as oils and lubricants, etc. The most important indicators of the chemical quality of the raw material intended for the production of cold pressed oil are the acidity and oxidative state of the oil. Lipid autoxidation occurs due to the effect of oxygen from the air on the unsaturated bonds of fatty acids. Regardless of the type of spoilage, the consequences are always the same: decomposition products are formed that worsen the sensorial properties, giving the oil an unpleasant smell and taste (especially volatile carbonyl compounds). In addition, some of the resulting compounds (free radicals, peroxides, polymers, etc.) are also harmful to the health of consumers. Oil spoilage processes take place both in the raw material itself and in the finished product, i.e. edible oil. According to Popa et al., 2017 oxidation of fats and oils is an important indicator for performance and shelf life of oils [2]. Thus the aim of this original scientific research work is to examine the comparative quality control and oxidative stability of edible cold pressed pumpkin, linseed and grape seed oils, where two samples were analyzed, one with a shorter and one with a longer shelf life.

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2. MATERIALS AND METHODS

Materials
As materials in this original scientific research work are used three edible cold pressed oils, pumpkin oil, linseeds and grape seeds oil were within the shelf life given by the manufacturer, with one sample of each type of edible oil at the end of the shelf life. ***Table 1.*** shows the samples of the oils used in this original scientific paper, as well as the associated labels and shelf time for each sample.

Table 1. Oil samples with associated labels and shelf time

Oil samples	Label	Shelf life
Edible cold pressed pumkin oil	PS1	20.03.2019.
	PS2	09.02.2018
Edible cold pressed lanseed oil	LS1	08.05.2019.
	LS2	19.07.2017.
Edible cold pressed grape seed oil	GS1	23.03.2019.
	GS2	28.07.2017.

Methods
In this original scientific paper, a total of six oil samples were analyzed, and standard methods for the analysis of fats and oils were used for their physical and chemical analysis. Standard methods for fat analysis as described in Grujić's and Trajković's book were used to examine the selected physico-chemical properties of the oil [3], [4]. The following parameters were analyzed: basic indicators of oil quality such as: acid number, saponification number, peroxide number, iodine number, unsaponifiable matter, density, and the kreis reaction was also performed, oxidative stability: anisidine number, totox number and thiobarbiturate number and antioxidant capacity.

3. RESULTS AND DISCUSSION

The obtained results are presented Figureically and tabularly, and all tested samples of edible cold pressed pumpkin oil, linseeds and grape seeds were within the shelf life given by the manufacturer, with one sample of each type of edible oil at the end of the shelf life. Chemical analysis of the tested samples was done with three replicates, and all results were expressed numerically and in appropriate units of measure.

3.1. Saponification number

Figure 1. shows the results of determining the saponification number of selected edible cold pressed oil.

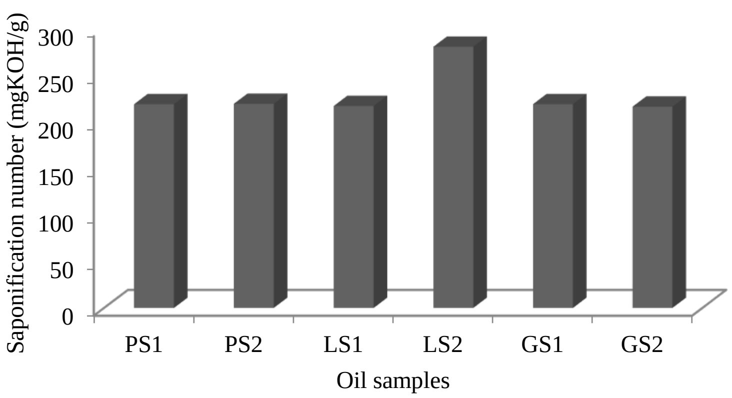

Figure 1. Saponification number of selected edible cold pressed oils

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Saponification number is of considerable importance as it measure the chemical nature of the oil and determine the final quality of the oil [5]. Alfawaz, 2004 reported that the saponification number in pumpkin oil was 185.20±5.84 mg of KOH/g of oil [6a]. Ahmed & Elfaki, 2013 reported that the saponification number in pumpkin seed oil was 240.50 mg of KOH/g of oil [7a]. Popa at all., 2012 reported that the saponification value of linseed oil was 190.50 mg of KOH/g of oil [8a]. Based on the obtained results, it can be concluded that the values of the saponification number in all samples were approximate. The highest value was for the linseed oil sample (LS2) and that value was 280.48 mg of KOH/g of oil which could be a consequence of the longer shelf life of this oil. This means that saponification, that is, the formation of glycerol and fatty acid salts through the hydrolysis process, took place to the greatest extent.

3.2. Iodine number

Figure 2. shows the results of determining the iodine number of selected edible cold pressed oils.

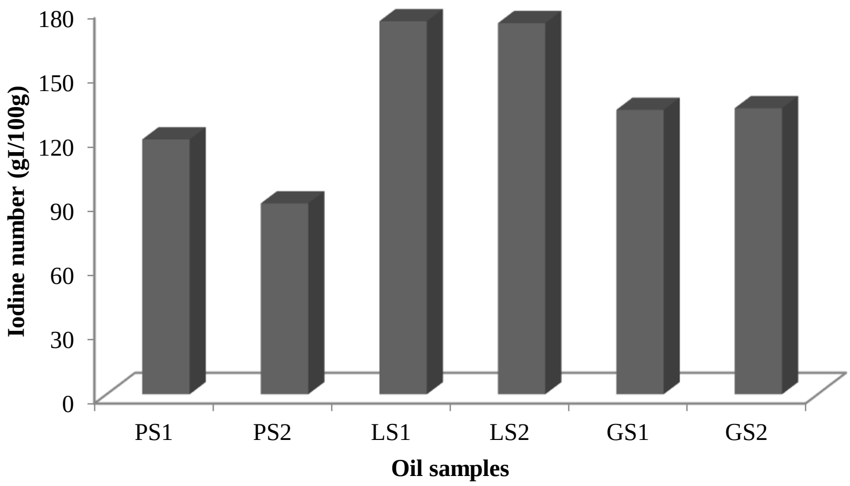

Figure 2. Iodine number of selected edible cold pressed oils

Alfawaz, 2004 reported that the iodine number in pumpkin oil was 105.12±5.83 mg of I_2/100g of oil [6b]. Both examined samples of linseed oil (LS1 and LS2) had iodide number values of 174.33 and 173.45 mg of I_2/100g, which is close to the results obtained by Popa at all., 2012, where it was reported that the iodine number of linseed oil was 177 mg of I_2/100g of oil [8b]. This is the reason for the presence of polyunsaturated fatty acids, which is characteristic of this type of oil, that is, more iodide was needed to bind to the double bonds in the fatty acid chain. The iodide number in the grape seed oil that was fresher was 132.92 mg of I_2/100g, and in the longer stored oil it was 133.68 mg of I_2/100g, respectively.

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3.3. Acid number

Figure 3. shows the results of determining the acid number of selected edible cold pressed oils.

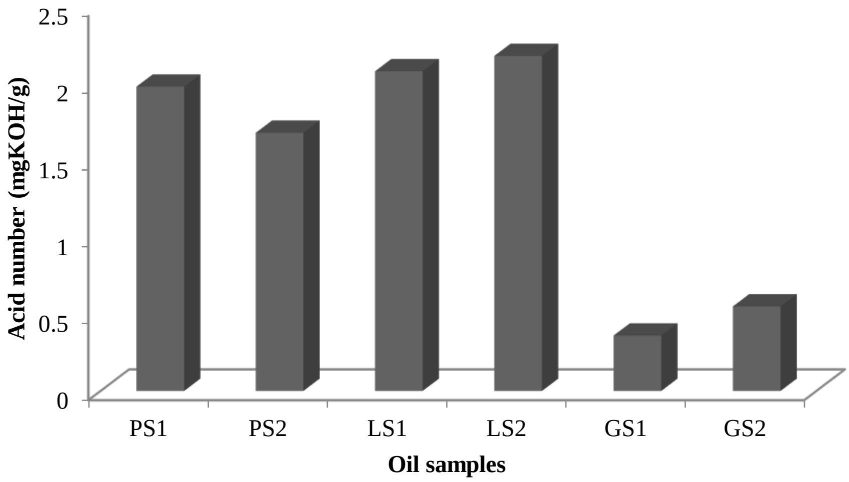

Figure 3. Acid number of selected edible cold pressed oils

Acid value represent free fatty acid content due to enzymatic activity, and is usually indicative of spoilage. Its maximum acceptable level 4 mg KOH/g oil. The lowest value was GS1 0.36 mg of KOH/g of oil. Alfekaik & AL-Hilfi, 2016 obtained a somewhat higher acid number for grape seed oil, and that number was 0.72 mg of KOH/g of oil [9]. Alfawaz, 2004 reported that the acid number in pumpkin oil was 0.53±0.25 mg of KOH/g of oil [6c]. Ahmed & Elfaki, 2013 reported that the acid number in pumpkin seed oil was 0.27 mg of KOH/g of oil [7b]. The highest content of acid number was in LS2 and that number was 2.18 mg of KOH/g of oil, however Popa et al., 2012 reported that the value of linseed oil is 0.80 mg of KOH/g of oil [8c]. All obtained results of the acid number test, as one of the most important indicators of quality, are in accordance with the legal regulation defined by the Rulebook on Quality, 2010 for edible unrefined oils, where the maximum allowed value of the acid number is 4.0 mg of KOH/g of oil [10].

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3.4. Ester number

*Figure 4.*shows the results of determining the ester number of selected edible cold pressed oils.

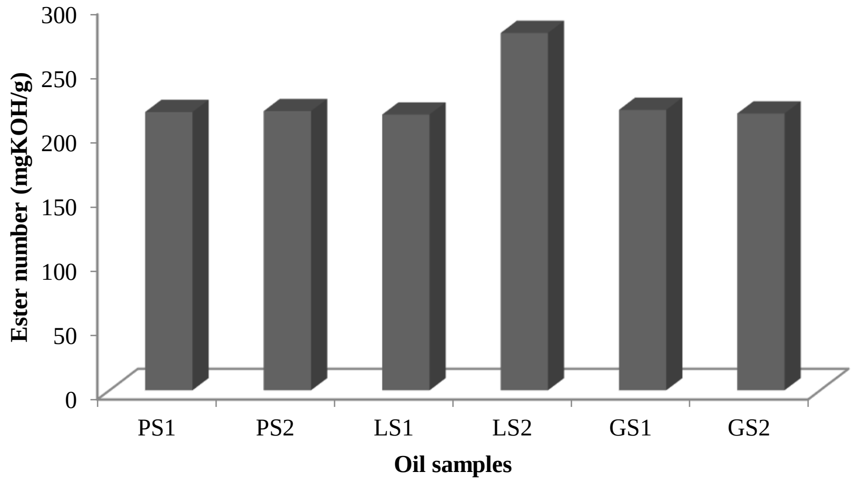

Figure 4. Ester number of selected edible cold pressed oils

Ester number = Saponification number - Acid number. Higher ester number in linseed oil with a more recent production date, compared to other samples. Saponification of fatty acid esters in 1 g of linseed oil requires the most mg of KOH, which results in the highest ester number. This means that linseed oil contains the most fatty acid esters in 1 g of oil.

3.5. Peroxide number

Figure 5. shows the results of determining the peroxide number of selected edible cold pressed oils.

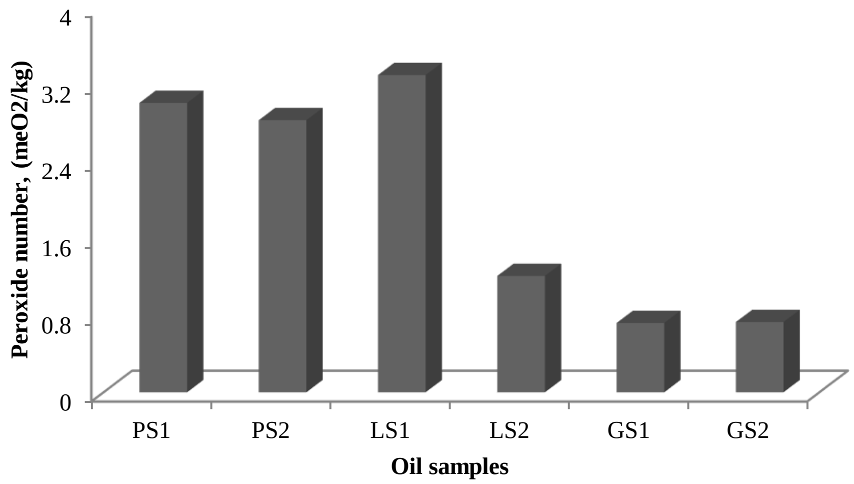

Figure 7. Peroxide number of selected edible cold pressed oils

The highest peroxide number was recorded for linseed oil of recent production date (LS1) and this value was 3.30 meO_2/kg of oil, while the lowest value was recorded for grape seed oil (GS1), 0.72 meO_2/kg of oil. Both samples of pumpkin oil had higher values than other oils. Thus, for sample PS1, this value was 3.01 and for PS2 it was 2.83 meO_2/kg of oil. Alfawaz, 2004 reported that the peroxide number in pumpkin oil was 0.85±0.46 mg of KOH/g of oil [6d]. Ahmed & Elfaki, 2013 reported that the peroxide number in pumpkin seed oil was 2.30 mg of KOH/g of oil [7c]. The peroxide number in linseed oil was 0.95 meO_2/kg of oil. The peroxide number is also one of the basic indicators of oil quality and directly indicates the presence of primary oxidation products, peroxides and hydroperoxides. Given that hydroperoxides are also precursors to the creation of secondary oxidation products, they are very important indicators of oil quality and sustainability. An increase in the value of the peroxide value with a decrease in the shelf life of the oil is quite natural, since oxidative processes take place on the surface of the oil in contact with oxygen. The intensity of these processes further depends on the diffusion of oxygen into the deeper oil layers.

3.6. Anisidine number

Figure 6. shows the results of determining the anisidine number of selected edible cold pressed oils.

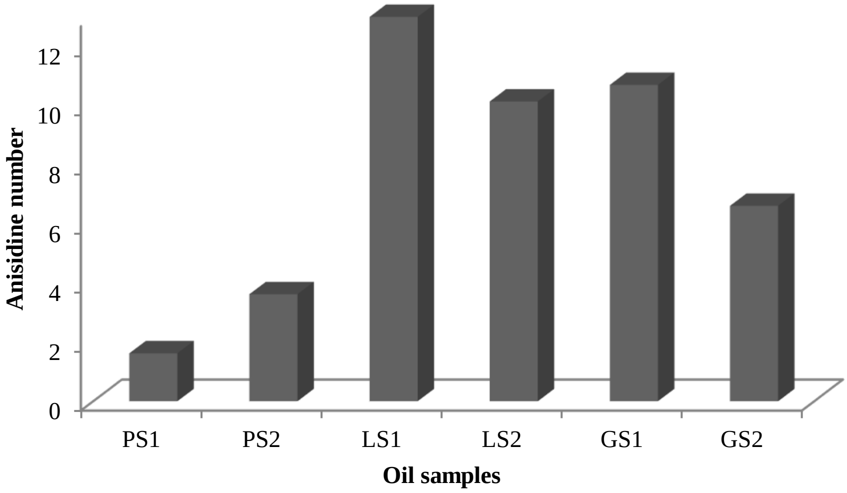

Figure 6. Anisidine number of selected edible cold pressed oils

Based on *Figur 6*., it can be seen that LS1 has the highest anisidine number, while PS1 has the lowest value. It is considered that good quality oils should have a value less than 10, which is the case with all tested samples except for the linseed sample, which shows that in that sample, oxidation of the primary products of oxidation (hydroperoxide) into secondary products (aldehydes) has occurred to a considerable extent, while in the case of pumpkin oil, this value is the lowest, which indicates a very good oxidative stability of this oil. The value of the anisidine number indicates the amount of non-volatile carboxylic compounds that represent secondary oxidation products of vegetable oils (aldehydes) formed by the decomposition of unstable primary oxidation products (hydroperoxides). The sustainability of edible vegetable oils can be estimated from the value of anisidine number, where a higher value of this number indicates a weaker sustainability of the oil.

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3.7. Totox number

Figure 7. shows the results of determining the totox number of selected edible cold pressed oils.

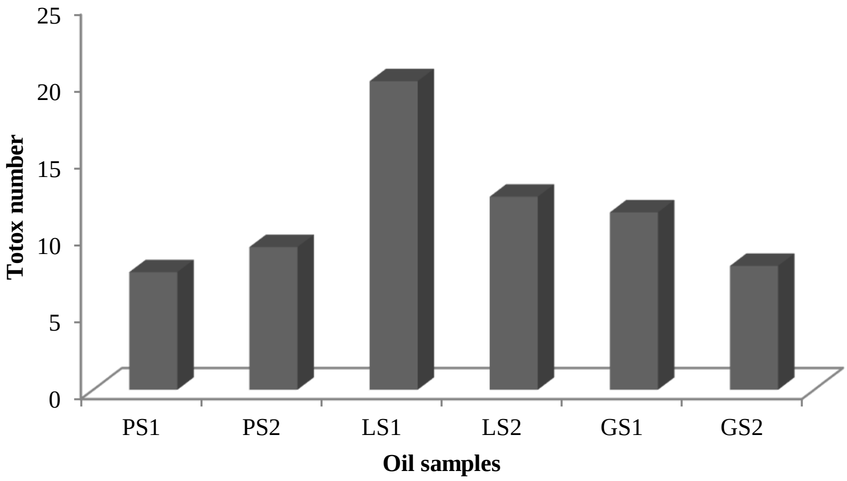

Figure 7. Totox number of selected edible cold pressed oils

The Totox number along with the peroxide (Pn) and anisidine number (An) gives an insight into the total oxidation value of vegetable oils. The equation for calculating totox number is *Totox number = 2Pn + An* and from this equation it is noticeable that the higher the peroxide and ansidine number, the higher the totox number. This number is considered a significant indicator of quality and oxidation stability, because the anisidine number provides information about the oxidation history, and the peroxide number provides information about the current oxidation state of the oil. From *Figure 7.* it follows that linseed oil of a more recent production date has a higher totox number, i.e. the lowest oxidation stability and quality, while pumpkin oil proved to be the most stable.

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3.8. Density

Figure 8. shows the results of determining the density of selected edible cold pressed oils.

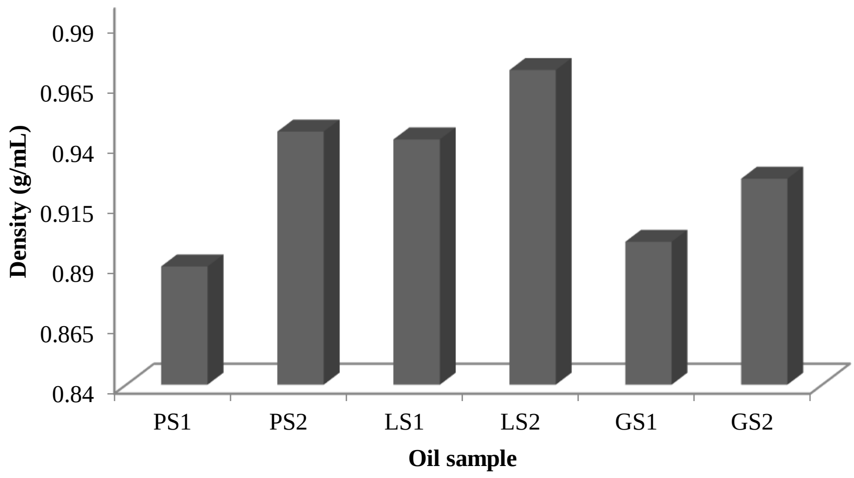

Figure 8. Density of selected edible cold pressed oils

The density of all edible cold-pressed oils had approximate values, however, the LS2 sample had the highest value and this value was 0.970 g/mL. The lowest density value was recorded at PS1 and was 0.889 g/mL.

3.9. Unsaponifiable matter

Figure 9. shows the results of determining the unsaponifiable matter of selected edible cold pressed oils.

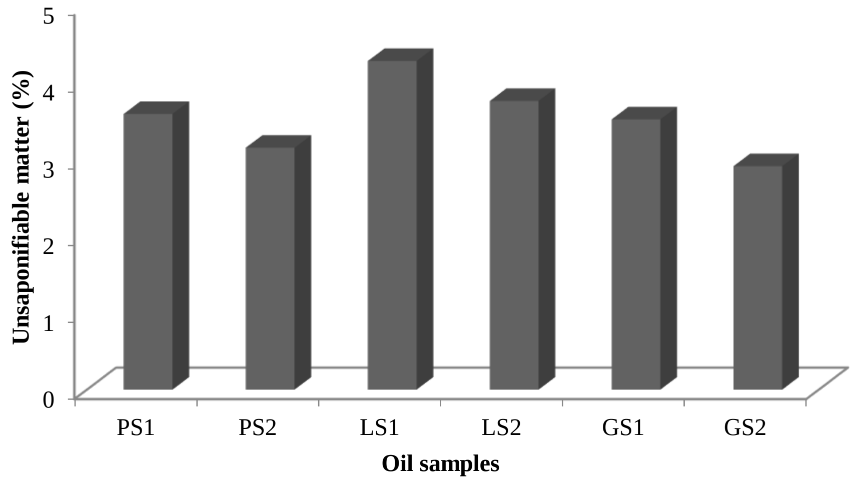

Figure 9. Unsaponifiable matter of selected edible cold pressed oils

Apart from triacylglycerol, fats and oils also contain small amounts of substances that dissolve together with fats in organic solvents that include higher alcohols, higher hydrocarbons, lipochromes, sterols and fat-soluble vitamins. These ingredients after saponification of the fat remain as an unsaponified fraction and in this research of such fractions the most contained in linseed oil, LS1 and that value was 4.28%. The lowest value of unsaponifiable matter was in grape seed oil and this value was 2.91%. The results of the determination of unsaponifiable matter for all oils show the same: more unsaponifiable matter (higher alcohols, hydrocarbons, fat-soluble vitamins, lipochromes, sterols) are contained in oils with a longer shelf life. Those ingredients dissolved in organic solvents after saponification of the fat remain as an unsaponifiable fraction, and this shows that with time, there is a loss of those ingredients such as vitamins, sterols, higher alcohols. Pumpkin and linseed oil have more of these ingredients, while grape seed oil contains a slightly smaller amount of them.

3.10. Thiobarbituric acid (TBA*)*

Figure 10. shows the results of determining the thiobarbituric acid (TBA*)* of selected edible cold pressed oils**.**

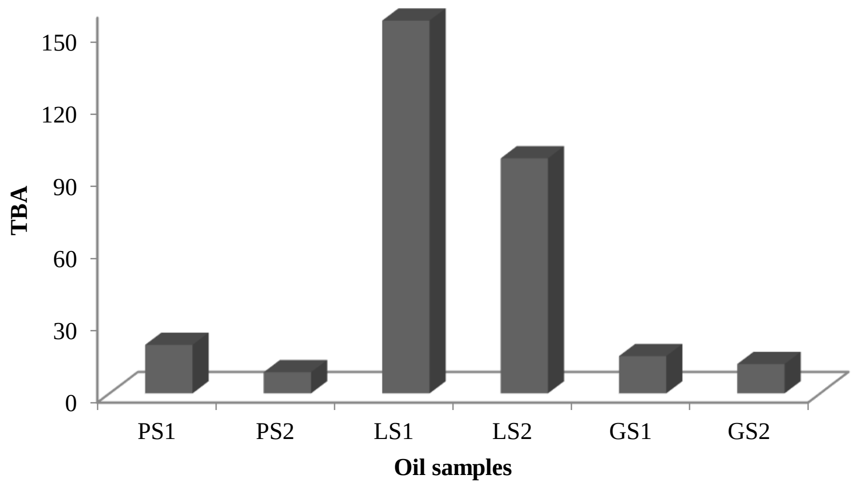

Figure 10. Thiobarbituric acid (TBA) of selected edible cold pressed oils

The results from *Figure 10.* clearly show that the sample of linseed oil of a recent production date (LS1) has the highest thiobarbiturate number, i.e. that sample is in an advanced stage of oxidation, which was to be expected because that sample gave a bright red color in the reaction during the analysis with thiobarbituric acid. In the case of a sample of linseed oil with an older production date (LS2), a weaker red coloration occurred, but that sample also gave a very high absorbance value and therefore the value of the TBA number. The other samples showed very little coloration or the coloration was completely absent, which means that they were only in the first stages of oxidation.

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3.11. Total phenols

Figure 11. shows the results of determining the total phenols of selected edible cold pressed oils.

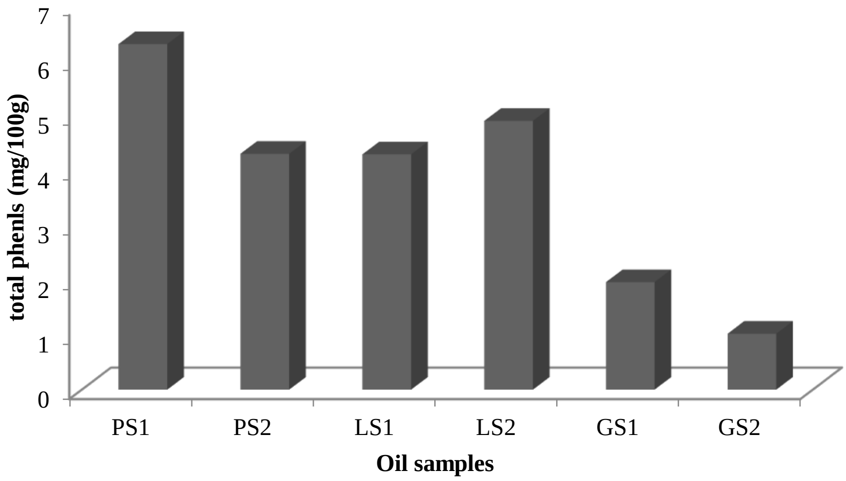

Figure 11. Total phenols of selected edible cold pressed oils

Determination of the content of polyphenolic compounds is based on the oxidation of phenolic compounds by the Folin–Ciocalte reagent, is fast and easy to perform [11]. From *Figure 11*., it is evident that the highest content of polyphenolic compounds has the sample PS1 and this value was 6.30 mg/100g of the sample. Both samples of linseed oil had similar values of polyphenolic compounds, while grape seed oil in both samples had a significantly lower value of polyphenolic compounds, and the lowest value was recorded in GS2 and this value was 1.02 mg/100g of sample. The content of polyphenolic compounds in grape seed oil was the lowest, and the reason for this could be that the tested oil was not obtained exclusively from seeds, but probably also from by-products in the production of wine or other grape products. Matthäus, 2008 reported that the value of total phenols that pass into oil from grape seeds is very small and this value was 0.01 mg/g [12]. Pardo et all. 2009 reported that drying grape seeds with hot air before extraction gave higher physicochemical quality, total phenolic content and stability, and lower wax content in comparison to air-drying of seeds [13]. Oil, as a foodstuff, does not contain a significant amount of polyphenolic compounds, as is the case with fruits or vegetables. However, in this work, a certain amount of these compounds that contribute to the color, strength, taste, smell and oxidative stability of the oil has been proven. The antioxidant activity of polyphenols is manifested in the ability to remove reactive oxygen and nitrogen species, but also in the inhibition of enzymes that increase oxidative stress, i.e. the induction of "antioxidant" enzymes.

3.12. Kreiss reaction

Table 2. Kreiss reaction of selected edible cold pressed oils.

Table 2. Kreiss reaction

Sample	Undiluted sample	Diluted sample
PS1	Negative reaction	
PS2	Negative reaction	
LS1	Positive reaction	Negative reaction
LS2	Negative reaction	
GS1	Negative reaction	
GS2	Negative reaction	

The results obtained by the Kreiss reaction show that the five samples are not in the stage of rancidity because the reaction was negative (although it happens that the fat is rancid and the Kreiss reaction is negative.) The reason for this is that the fat is either in the initial phase in in which epihydrinaldehyde did not form or the fat rancid so much that the epihydrinaldehyde moved to a higher stage of oxidation, while only one sample has a positive reaction and that sample is in the second stage of rancidity.

4. CONCLUSION

Based on the physico-chemical analysis, pumpkin oil proved to be the most stable, while linseed oil is the most susceptible to oxidative changes. Grape seed oil has also shown quite good sustainability. The process of autoxidation of vegetable oils is inevitable and will occur more slowly or faster depending on the composition of the oil, storage conditions and the presence of ingredients that speed up or slow down this reaction. Products created by the autooxidation process (aldehydes, ketones) in small quantities give oils an unpleasant smell and taste, and impair their sensorial properties. For these reasons, determining the oxidative status of the oil is of primary importance.

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