REICHERT–MEISSL AND POLENSKE VALUES IN WALNUT OIL

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Abstract: During storage, walnut oil is extremely unstable. It is subject to physical and chemical changes with the accumulation on primary and secondary oxidation compounds. The present paper describes the fatty–acid composition of Reichert–Meissl (RM) and Polenske (P) fractions in different walnut oil samples stored at different temperatures in transparent and dark containers. The generally used but highly empirical RM and P values are considered to be a measure of the soluble and insoluble volatile fatty acids respectively, in vegetable oils. Both RM and P values were determined according to the methods of the association of Official Analytical Chemists, adjusted walnut oil at the Department of Food Technology UTM. In this context there are presented Specific Gravity and Refractive index at 25ºC of walnut oil samples.

Key words: walnut oil, Reichert–Meissl Value, Polenske Value

Introduction

Oil oxidation is an undesirable series of chemical reactions involving oxygen that degrades the quality of an oil. Oxidation eventually produces oil rancidity, with accompanying off flavours and smells. The entire oil is in a state of oxidation – you cannot stop it completely – but there are ways to reduce it. Therefore, attempts should be made to reduce oxidation at each stage of oil manufacture. Oxidation is not one single reaction, but a complex series of reactions. When oil oxidises it produces a series of breakdown products in stages, starting with primary oxidation products (peroxides, dienes, free fatty acids), then secondary products (carbonyls, aldehydes, trienes) and finally tertiary products [8].

Reichert Meissl and Polenske values are a measure of the shorter chain of fatty acids which are present in some oils, especially dairy butter, coconut and palm kernel oils. The Reichert Meissl value is a measure of the water–soluble volatile acids, while the Polenske value is a measure of the water–insoluble volatile fatty acids.

The value allows one to distinguish between butter and butter substitutes made from vegetables oils. The hydrolysis of the butter fat gives C4,C6,C8 acids which are volatile in steam, while no acid below C10 is obtained from vegetable oils. Butter has Reichert Meissl number of 17 to 34, while that of cotton seed oil the value is less than 1[9].

Reichert Meissl Number – is the number of milliliters of 0.1 N alkali (such as potassium hydroxide) required to neutralize the volatile water –soluble fatty acids in 5 g. sample of fat. The Reichert Meissl test determines the amount of butyric and caproic acids which are readily soluble in water and the caprylic and capric acids which are slightly soluble.

*Polenske number – i*s the number of milliters of 0.1 N alkali necessary to neutralize the volatile, water –insoluble fatty acids which are present in 5 g sample.

Materials and methods

Materials

Walnuts (Juglans regia L.) from Cogalniceanu variety, harvested in Moldova. Oil extraction was carried out with mechanical press. In one case after extraction oil was filtered, treated with antioxidants sych as ascorbic acid and betacarotebe. After the treatment, oil was stored at different temperatures and then used for experiments. In another case, without being filtered, walnut oil was stored at light and at dark, then were carried the same experiments.

Medods and Reagents

Reagents:

– Glycerine;
– Concentrated sodium hydroxide solution: 50 % (w /w) Dissolve
– Pumice stone grains
– Dilute sulfuric acid solution, 1.0 N;
– Sodium hydroxide solution: 0.1N solution in water;
– Phenolpthalein indicator: Dissolve 0.1 g of phenolpthalein in 100 ml of ethyl alcohol
– Ethyl alcohol: 90% by volume.

Reichert–Meissl Value [6]

Weigh accurately 5±0,1g of filtered oil fat sample into a clean, dry, 300ml distilled flask. Add 20 ml of glycerine and 2 ml of concentrated sodium hydroxide solution and heat with swirling over a flame until completely saponified, as shown by the mixture becoming perfectly clear. Cool the contents slightly and add 90 ml of boiling distilled water, which has been vigorously boiled for about 15 min. After thorough mixing, the solution should remain clear. If the solution is not clear (indicating incomplete saponification) or is darker than light yellow (indicating over–heating), repeat the saponification with a fresh sample of the oil or fat. If the sample is old, the solution may sometimes be dark and not clear.

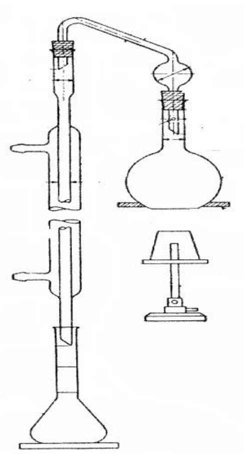

Fig.1. Reichert–Meissl Distilation Apparatus

Add about 0.6–0.7gm of pumice stone grains and 50 ml of dilute sulfuric acid solution. Immediately connect the flask to the distillation apparatus. Place the flask on asbestos board so that it fits snugly into the aperture. This will prevent the flame from impinging on the surface of the flask above the level of the liquid and avoid super heating. Heat very gently until the liberated fatty acids melt and separate. Then set flame so that 110 ml of distillate shall be collected within 19 to 21 min. The beginning of the distillation is to be taken as the moment when the first drop of the distillate falls from the condenser in the receiving flask. Keep the water in the condenser flowing at a sufficient speed to maintain the temperature of the outgoing water from the condenser between 15 and 20^oC. Collect the distillate in a graduated flask.

When the distillate exactly reaches the 110 ml mark on the flask, remove the flame and quickly replace the flask by a 25 ml measuring cylinder. Stopper the graduated flask and without mixing place it in a water bath maintained at 15^oC for 10 min so that the 110 ml graduation mark is 1 cm below the water level in the bath. Swirl round the contents of the flask from time to time. Remove the graduated flask from the cold water bath, dry the outside and mix the content gently by inverting the flask 4 to 5 times without shaking. Avoid wetting the stopper with the insoluble acids. Filter the liquid through a dry, 9 cm Whatman No.4 filter paper. Reject the first 2–3 ml of the filterate and collect the rest in a dry flask. The filtrate should be clear. Pipette 100ml of the filtrate and add 5 drops of the hydroxide solution.

$$\text{Reichert} - \text{Meissl Value} = (\text{A} - \text{B}) \times \text{N} \times 11, \qquad (1)$$

where:

A – volume in ml of standard sodium hydroxide solution required for the test;
B – volume in ml in standard sodium hydroxide solution required for the blank;
N – normality of standard sodium hydroxide solution.

Polenske Value [6]

After titrating the soluble volatile acids, detach the head and rinse the condenser with three successive 15ml portions of cold distilled water passing each washing separately through the measuring cylinder, 110 graduated flask and the filter paper and allow all of it to pass through. Discard all the washings. Place the funnel on a clean conical flask. Dissolve the insoluble fatty acids by three similar washings of the condenser, the measuring cylinder, the 110ml flask with stopper, and the filter paper with 15ml portions of ethyl alcohol. Combine the alcoholic washings in a clean flask, add 5 drops of phenolphthalein indicator solution, and titrate with standard (0.1N) sodium hydroxide solution.

$$\text{Polenske Value} = 10 \times \text{V} \times \text{N}, \qquad (2)$$

where:

V – volume in ml of standard sodium hydroxide solution required for the test;
N – normality of standard sodium hydroxide solution.

Results and discussion

Walnut oil is a product of an exceptionally high nutritional value with high content of biologically active substances, including essential unsaturated Ω–3 and Ω–6 fatty acids. During storage, walnut oil is extremely unstable, subject to physical and chemical changes with the accumulation on primary and secondary oxidation compounds (figure 1).

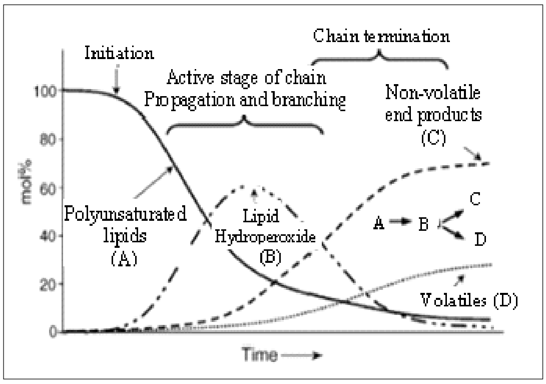

Fig.1. Schematic representation of the time course of Fatty acids autoxidation [2]

In the last stage of autoxidation oils are volatile and non volatile form. In this context, it was set the objective of determining volatiles in walnut oil, evaluating indicators Reichert–Meissl and Polenske. The Reichert–Meissl number, thus, measures the quantity of short chain fatty acids (up to C 10 inclusive) in the fat molecule.

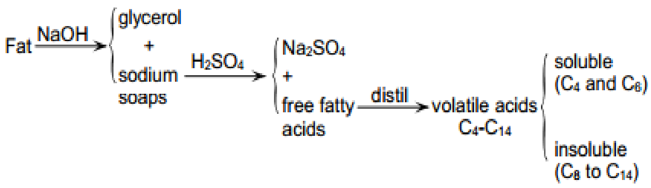

Fig.2. Summary of Reichert – Meissl, Polenske and Kirschner value determination

Conducted bibliographical study shows that these indicators are included in the indices of quality of both fat and vegetable oils [2, 3]. To be mentioned that data Reichert–Meissl and Polenske values in walnut oil not found. Only in the study [10] stated that Reichert–Meissl value 0.2–1.0; Polenske value 0.2–0.7.

Reichert–Meissl number of coconut and palm oil varies between 5 and 8, for linseed oil is 1, for castor oil it is 1–4, for olive oil it is 0.6–1.5, butter fat between 17–35. This high value makes possible the detection of any foreign fats which are, sometimes, adulterated in the manufacture of butter [7].

Table 1. Analytical values for some oils [3]

Fat/Oil	Saponification number (mgKOH/g)	Iodine value, (g $I_2$100g)	Rechert–Meissl Number	Acetyl number	Acid value (mgKOHg)
Plant fats					
Castor oil	175–187	80–90	1.4	146–150	0.2–4
Corn oil	187–195	104–128	–	–	1.0–2
Linseed oil	188–195	170–195	1.0	4.0	1.0–4
Olive oil	190–195	89–90	0.6–1.5	10–11	0.2–3
Coconut oil	254–262	7–10	0.6–7.5	2.0	2.5–6

Table 2. Chemical characteristics of karela seed oil [2]

Caracteristics	Goj karela	Guti karela	Majhari karela
Iodine value (Wijs)	131.06	125.21	128.39
Saponification value	184.08	187.01	186.15
Acid value	304.76	1.73	301.36
Free fatty acids (%) as oleic	1.12	0.86	1.10
Peroxide value (mEq/kg)	8.50	6.13	7.56
Reichert–Meissl value	1.98	2.13	2.02
Polenske number	0.61	0.63	0.57

This study shows Chemical and Physical characteristics of walnut oil stored at different temperatures: Reichert–Meissl and Polenske values, Specific Gravity and Refractive index at 25°C (table 3).

Table 3.Chemical and Physical characteristics of walnut oil

Type of oils	Storage time, days	Reichert–Meissl Value	Polenske Value	Specific Gravity at 25°C	Refractive index at 25°C
Walnut oil, stored at 20 °C	control	0.374	0.18	919.0	1.4745
	3	0.165	0.26	922.0	1.4766
	7	0.638	0.22	920.0	1.4768
	10	0.671	0.18	920.0	1.4771
	14	0.572	0.36	921.5	1.4784
Walnut oil, stored at 40ºC	control	0.374	0.18	919.0	1.4745
	3	0.511	0.16	919.0	1.4768
	7	0.475	0.14	918.0	1.4767
	10	0.616	0.22	919.0	1.4771
	14	0.429	0.22	921.0	1.4786
Walnut oil, stored at 60ºC	control	0.308	0.34	916,0	1.4760
	2	0.264	0.20	916,0	1.4766
	4	0.352	0.22	916,0	1.4780
	8	0.220	0.13	916,0	1.4785
	10	0.396	0.12	920,0	1.4805
	12	0.352	0.19	925,0	1.4816
	15	0.330	0.20	920,0	1.4820
Walnut oil, stored at light,	Control	0.380	1.76	921,0	1.4763
	2	0.396	0.11	921,0	1.4773
	4	0.440	0.17	919,0	1.4770
	6	0.451	0.12	920,0	1.4690

Walnut oil, stored at dark	Control	0.380	1.76	921,0	1.4763
	2	0.561	0.19	921,0	1.4772
	4	0.682	0.18	921,0	1.4771
	6	0.429	0.14	919,0	1.4763

In the conducted bibliographic study data were found for the values of Reichert–Meissl and Polenske in walnut oil. Reichert–Meissl estimated in samples of cold–pressed walnut oil was 0.31, 0.37 and 0.38. Thus obtained Reichert–Meissl show a low content of volatile soluble fatty acids and this value is also in agreement with the low value of the saponification obtained. Number Polenske (0.18, 0.34 and 1.76) estimated in this study were similar to the values determined by the size of the number of Reichert–Meissl. They also assessed the influence of light and darkness and the content of volatile soluble substances and non–soluble samples of walnut oil, calculating Reichert–Meissl and Polenske indicators.

We have obtained quite different results indicators Reichert–Meissl and Polenske values. Perhaps this is due to the physicochemical and biochemical changes that occur in walnut oil storage, which can be treated differently. The autoxidation rate of reaction of the oil is different according to the storage parameters.

Conclusion

During storage walnut oil is extremely unstable, subject to physical and chemical changes with the accumulation on primary and secondary oxidation compounds.

We studied volatile soluble and insoluble substances in nut oil kept in different conditions by determining Reichert–Meissl and Polenske values.

Currently, we are concerned with the study of these indicators and correlation tooth Peroxide walnut oil produced and stored under different conditions.

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