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ROSEMARY EXTRACT CAN BE USED AS A NATURAL PROTECTIVE AGENT AGAINST DECOMPOSITION OF FREE FATTY ACIDS

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Abstract

Rosemary extract usage as a natural material to prevent the decomposition of free fatty acids (pure oleic acid) was investigated in this study. Free fatty acids in general are an important composition of edible oils and other food stuff. Monitoring of fatty acids direct in edible oils is impossible mission because they are in low level in real samples and interferences from other components with similar structure are too high. Pure oleic acid was used as model compound to further understand its decomposition under thermal treatment at boiling point into aldehydes and other components and to show the effect of rosemary oil. Density and iodine value were analyzed for all samples followed by FTIR-spectroscopy. Pure oleic acid, oleic acid with stainless steel Cr-Ni as a catalytic presence and third samples contain oleic acid, stainless steel and rosemary oil 1 % as an antioxidant component were analyzed. Density and iodine value decrease which is an indication of structural changes of oleic acid. FTIR spectroscopy on the other hand shows clearly the structural changes and furthermore confirms that presence of rosemary oil on oleic acid with stainless steel Cr-Ni plays the role of a natural protective agent against decomposition of oleic acid.

Keywords*: oleic acid, rosemary oil, FTIR-spectroscopy, natural antioxidant.*

Introduction

The chemistry of lipid oxidation under air and high temperature heating such as frying is highly complex degradation process because the parallel reaction of thermal and oxidative simultaneously happened [1]. Otherwise free fatty acids are minor component of oils and other foods and also they are product of degradation from normal lipids, from this point of view their continue of degradation involve their decarboxylation and b-oxidation in corresponding ketones or aldehydes [2,3].

In general, stainless steel metal component as catalyst increase conversion level of oleic acid to corresponding aldehydes [4] but their conversion in presence of natural antioxidant as a protective agent is still unknown.

Recent years Reported for antioxidant activity of Rosemary extract as natural and better antioxidant activity which is attributed to high content of total phenolic components [5,6] compare with synthetic antioxidant such as butylatedhydroxyanisole (BHA) and butylated hydroxytoluene (BHT). Rosemary extract confirms high antioxidant effect for lipid oxidation for different type of vegetable oils moreover rosemary can elevate vitamin E in meat and other food products and reduce lipid oxidation [7,8].

Several methods were applied for monitor product degradation from lipid oxidation such as GCMS, GC-FTIR but limited reports about possibility to use FTIR Spectroscopy and

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physico-chemical properties which is completely green, sensitive, fast and inexpensive method of analysis [9-11].

Really it is very clear effect of rosemary as a natural antioxidant for lipids and other ingredients in edible oils but we do not have any official report about their possibility role as a protective effect for pure fatty acids and especially under catalytic thermal degradation of fatty acids.

The aim of this study is to increase knowledge about thermal degradation of oleic acid in presence of extract of Rosemary as a natural antioxidant with and without metal catalytic oxidation using FTIR Spectroscopy in correlation with some of the physicochemical parameters.

Material and Methods

Reagent and Chemicals

Oleic acid 99%, Rosemary oil (<=100 %), Stainless steel (Cr-Ni), Iodobromine (IBr) (98 %), Sodium thiosulphate (99 %) All reagents are purchased from Sigma Aldrich.

Sample Treatment

We compare thermal treated samples of pure oleic acid, oleic acid with stainless steel Cr-Ni as a catalytic presence and third samples contain oleic acid, stainless steel and rosemary oil as a antioxidant component 1 % and oleic acid mixed with Rosemary 1 %. All treated samples were analyzed by FTIR Spectroscopy, Density and Iodine value.

Density Measurements

Densities of treated samples were measured by an R.D bottle with a capacity of 10 mL.

Iodine Value

Iodine value is chemical parameter to measure the number of double bonds in fat and oils. Experiments was done by mixing sample with iodobromine (IBr) dissolved in glacial acetic acid. Unreacted iodobromine will be converted in iodine after reaction with potassium iodide. Iodine then is determined by titration using standard solution of sodium thiosulphate.

FTIR Meauserements

Monitored samples were measured by FTIR IRaffinity-1 Shimadzu after each cycle of thermal treatment by depositing sample between two CaF_2 windows. Resolution of FTIR spectra was 4 cm^{-1} and recorded from 1000-4000 cm^{-1}. The IR Spectrum of samples shown clear changes in frequency and intensity of the selected bands. The analytical evaluation and their vibrations are shown in Table 1 [12, 13].

Table 1. FTIR absorbance bands and their characteristic functional groups

Wavenumbers cm^{-1}	Characteristic group and mode of vibration
3008	=C-H Stretching (cis)
2925	−CH(CH_2) Asymmetric stretching
2854	−CH(CH_2) Symmetric stretching
1745	−C=O (ester group in triglycerides) Stretching
1700	−C=O carbonyl group of free fatty acid
1730-1740	−C=O carbonyl group of aldehydes
1653	−C=O (ester) Stretching
1463	−C−H (CH_2 and CH_3) Bending
1377	−C−H (CH_3) Symmetric bending
1237	Stretching vibration of the C−O ester groups
1163	Stretching vibration of the −C−O ester groups
1099	−C−O Stretching

Results and Discussion

Iodine value measure the degree of unsaturation but does not indicate the position of double bonds in oils or fat samples. At all sample was measured density and iodine value and they are decreased after thermal treatment. This can be indicator of structural changes in sample of oleic acid.

Table 2. Results of sample`s density and iodine value

Sample	Density (g/cm^{-1})	Iodine Value (g)
Pure oleic acid before treatment	0.9	90
Oleic acid and stainless steel	0.82	79
Oleic acid and stainless steel and Rosemary	0.88	86
Oleic acid and Rosemary	0.86	85

Measurements of FTIR Spectroscopy shows clear changes in band vibrations shown in Figure 1 where in sample of pure oleic acid was clear band in position 2936 cm^{-1} and after treatment of oleic acid only with presence of stainless steel has disappear this band and appear two other band 2912 cm^{-1} and 2939 cm^{-1} but this was not happened and in sample where also it is present stainless steel together with presence of rosemary where Rosemary play role of a protective agents and in this sample still is present band 2926 cm^{-1}. This changes in one sample can be from aliphatic long chain in methyl or methylene group converts oleic acids in other compounds compare with pure or protected oleic acids where changes in band positions are mistake.

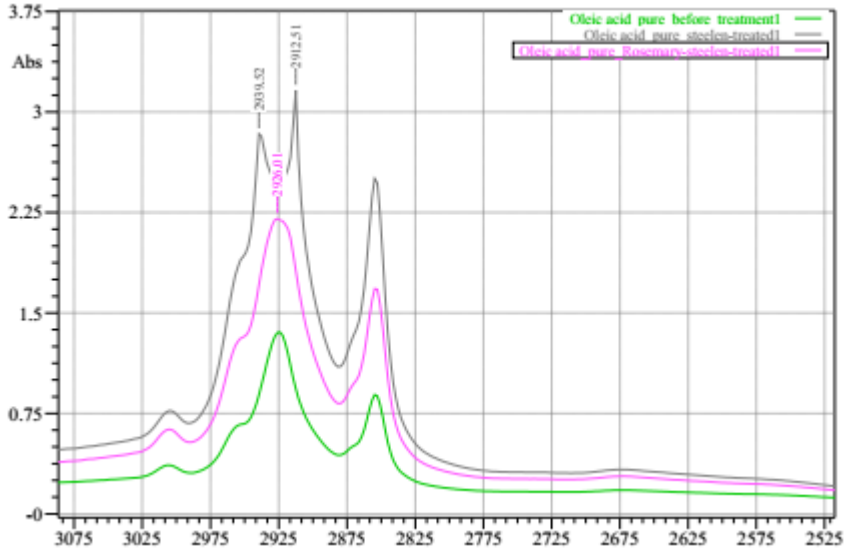

Fig. 1. FTIR Spectra of measured samples; red line oleic acid before treatment, pink line is for oleic acid mixed with Rosemary and stainless steel (Cr-Ni), black line oleic acid with stainless steel (Cr-Ni)

Other changes are in region near 1700 cm^{-1} Figure 2 where only in sample with presence of same stainless steel (Cr-Ni) with catalytic activity has clear increasing intensity in band 1734 cm^{-1} which is carbonyl group of aldehyde this band is in low level in three other treated samples.

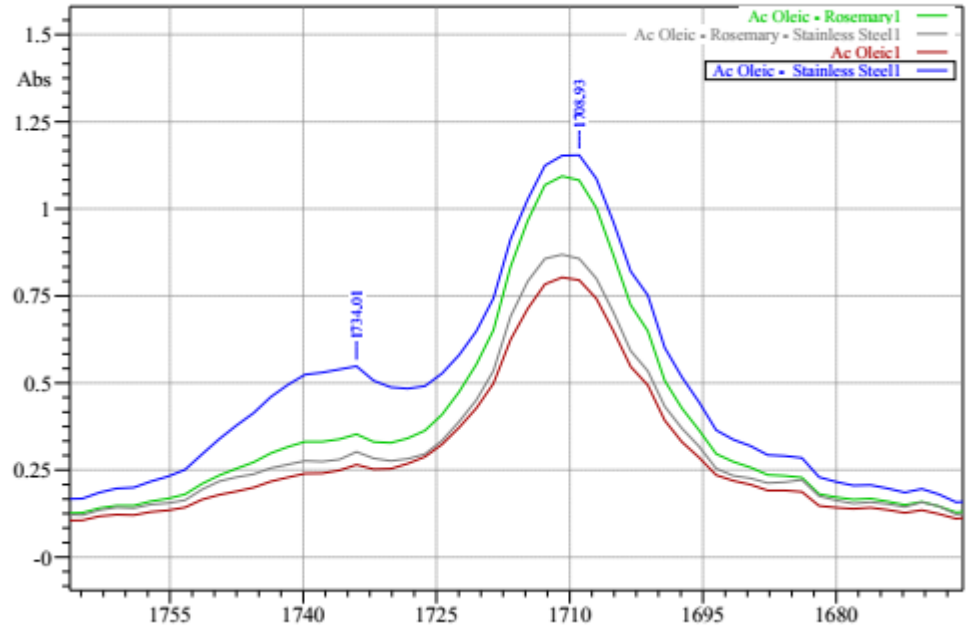

Fig. 2. FTIR Spectra of measured samples

Changes starts from double bonds this is confirms also and from decreasing of iodine value and their cleavage which mean aldehyde groups can be formed in this functional group or in carboxyl group of oleic acid. In general we have two mayor point of reaction changes in aliphatic group and aldehyde compounds synthetized which are not happened and in pure oleic acid and also in the presence of Rosemary as a natural protective agents.

This can confirm all changes what happened in samples where oleic acids can be in interaction with metal without rosemary reagent will have catalytic cleavage of oleic acid and will be synthetized aldehydes with complex chemical structure based on significant change on aliphatic and aldehyde vibrations of basic functional group. But presence of rosemary this reaction will be prevented and catalytic conversion of oleic acid is reduced.

But final product can be more complex and clear identify all products of reaction need more investigation and including and other powerful methods of analysis.

Conclusion

FTIR can be considered as an alternatively method for fast and suitable method of oleic acid analysis in different chemical condition. Otherwise this research can initiate research about complex reaction for small molecules of fatty acids and their rapid decomposition under metal catalytic activity and frying temperature, identifying their mayor chemical conversion and understanding rosemary effect as a protective substance.

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