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НАУКОВИЙ КОМІТЕТ

ЧЛЕНИ КОМІТЕТУ

СЕКРЕТАР

2. DETERMINATION OF SUNFLOWER OIL OXIDATION PRODUCTS BY NMR 1H SPECTROSCOPY

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Sunflower lipids are very susceptible to oxidative processes owing to their degree of unsaturation, giving rise to the development of off-flavour and a decrease of nutritional quality and safety. Autoxidation is based on the spontaneous reaction of atmospheric oxygen with lipids under mild conditions via a radical chain reaction. One of the express and non-destructive methods for determination of oxidation products is NMR ^{1}H spectroscopy providing a straightforward approach to quantitative analysis of oils and fats and enabling a simultaneous detection of different oxidation products in one single analysis. Up to now, NMR is not widely used in food control and in food industry. The aim of work was to study autoxidative processes in sunflower oil, stored in opened receptacles at room temperature for a long period, using NMR ^{1}H spectroscopy.

Samples of sunflower oil containing oleic and linoleic ester groups, extracted from different varieties of sunflower seeds, NMR spectroscopy, deuterated chloroform.

Within the course of the autoxidation process of lipids, hydroperoxides are formed as primary products that are easily decomposed to secondary products such as aldehydes, ketones, alcohols and acids. The presence of secondary lipid oxidation products influences the overall quality of a lipid.

From consideration of higher field NMR spectra in the literature various other resonances can be assigned to specific chemical groups (see Table 1).

Table 1. Chemical shifts of protons in NMR spectra

Signal	Functional group	Chemical shift (ppm) of protons in oleic and linoleic esters of glycerin
1	$-CH_3$	0.96 – 0.82 (dd)
2	$-CH_2-$	1.43 – 1.16 (m)
3	$-CH_2-C-CO_2$	1.70 – 1.51 (m)
4	$-CH_2-CO_2-$	2.11 – 1.91 (m)
5	$-C-CH_2-C=C-$	3.38 – 2.21 (m)
6	$-C=C-CH_2-C=C-$	2.83 – 2.73 (t)
7	$-C-CH_2-O-CO-C$	4.21 – 4.08 (dd)
8	$-C-CH_2-O-CO-C$	4.36 – 4.22 (dd)
9	$-CH(-C-O-CO-C-)_2$ $+C-HC=CH-C$	5.43 – 5.13 (m)

Signal multiplicity: s, single; d, doublet; t, triplet; m, multiplet

The set of peaks at δ5.2 ppm arises largely from the ^{1}H nuclei attached to carbons involved in a double bond, usually referred to as olefinic. Signals at δ2.7 ppm arise from bis-allylic protons from the $-CH_2-$ group located between pairs of unsaturated bonds.

The susceptibility of fatty acids to autoxidation strongly depends on the strength of the CH-bonds. The dissociation energy of allylic hydrogens is approximately 50 kJ/mol greater

than the dissociation energy of bis-allylic hydrogens and 90 kJ/mol smaller than the dissociation energy of hydrogens of saturated fatty acids. These differences explain the divergent oxidation rates of monounsaturated and polyunsaturated fatty acids at room temperature. In comparison to oleate, linoleate is 40 times more reactive being attributed to greater resonance stabilization of the pentadienyl radical intermediate.

The results of the monitoring fatty acid composition by NMR ^{1}H spectroscopy indicate a progressive decrease in the contribution of linoleic acid throughout the store period. Finally, the ratios of relative intensities between olefinic protons (9) to aliphatic protons (1-5) decreased as result of the oxidative processes. Peaks of diallylmethylene protons (6) almost disappeared.

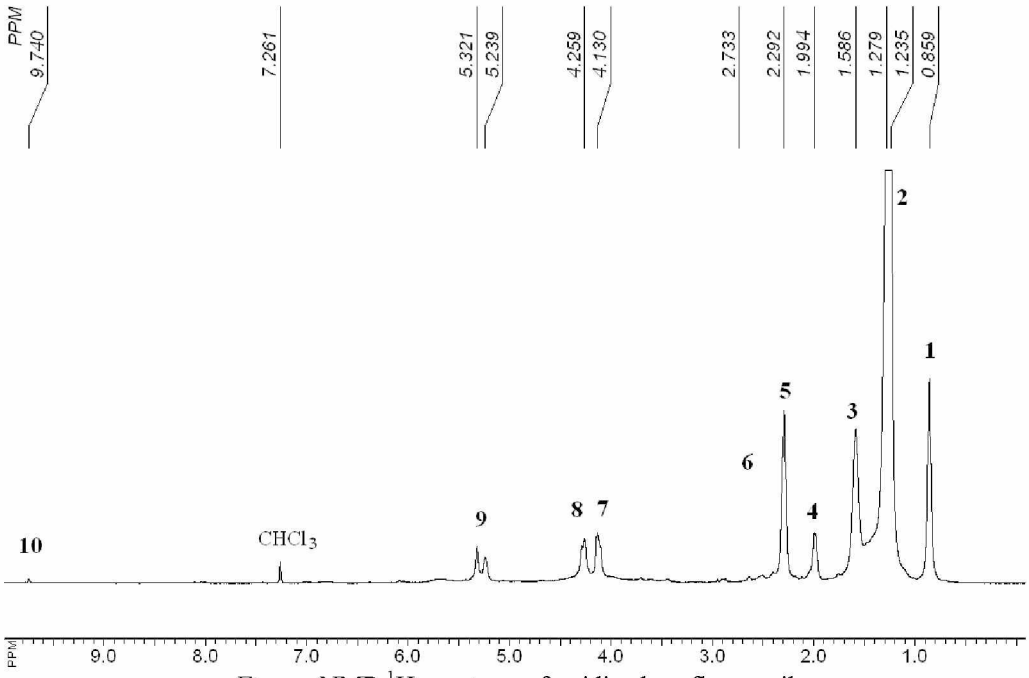

Figure. NMR ^{1}H spectrum of oxidized sunflower oil

With increasing storage time, the process becomes more and more complicated since primary oxidative products undergo further reactions forming volatile and non-volatile secondary products. Thus, the very small peak (10) of aldehyde group is observed at δ9.74 ppm that is in according to literature (see Fig).

Sunflower oil containing a high level of linoleate reacts with oxidative agents much faster than oil with a high content of oleic acid. NMR ^{1}H spectroscopy may be used as express and non-destructive method of estimation of sunflower oil quality.

References.

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