NATURAL ANTIOXIDANTS OF RAPESEED OIL

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The utilisation of the synergistic effect between tocopherol /Toc/ and other natural compounds may play an important role in the inhibition of edible fats autoxidation processes. Among other natural compounds phospholipids /Ph/ are of special interest.

The data about antioxidant activity of Toc are results from many investigations performed on various experimental models.

Individual isomers of Toc are not equivalent in their antioxidant activities. Lundberg /1962/ reported the dependence of their action on temperature.

Acording to Bazin /1984/ effect of the antioxidant activity of individual Toc depends on their concentration and reacting system.

The antioxidant effect of Toc can be intensified by addition of synergetic compounds.

Ishikawa /1984/ stated that flavoglaucin isolated from mycelias mats of Eurotium chevalieri is an excelent inhibitor and synergist for oils and fats. During the autoxidation of lard containing Toc /0,04% / the addition of flavoglaucin did not retard the oxidative decomposition of Toc but increased stability of lard. The same authors and others /1984/ proved that in presence of trimethylaminooxide and tri-n-octylamine, which are widely presented in fish, Toc was decomposed and its reducing dimers appeared. In the presence of Ph this process is synergisticly inhibited.

Acording to Rafat Husain /1986/ heated Ph can perform a stabilising effect on fats and oils. This effect depends on brown colour products formed from unsaturated Ph.

During technological processes of extraction and refination of oils the particular operations promote autoxidation of fats. Hence, it was important to investigate how far α-Toc could retard the autoxidation process in the presence of natural Ph isolated from rapeseed oil.

That oil contains about 0,1% Toc, including 27% α-Toc, which is a compound very unstable, readily undergoing autoxidation and even is considered to act as a prooxidant.

It should be pointed out that the inhibiting role of natural compounds of fats, e.g. Ph, is not explained exhaustively and further work is being conducted to provide more detailed information on this problem.

Experimental procedure

The autoxidation process of rafined rapeseed oil containing α-Toc and Ph were investigated.
α-Toc used was a commercial product /Eisai Co, Tokyo, Japan/. Rafined rapeseed oil was supplied by Gdańsk Fats Industry Enterprise with acid value-0,3, peroxide value-5,6 /meq O_2/kg oil/. Fatty acid composition indicates that the oil was a low erucic one /erucic acid-2,9%/and had unsaturated acids: oleinic, linolic and linolenic-84%.
Ph were prepared from low erucic oil and were obtained from commercial lecithin containing 65% Ph, 3,3% moisture and 30,8% rapeseed oil, peroxide value-3,4, acid value--44,0 and acid value of the rapeseed oil-9,2. Removal of the oil from commercial Ph was performed with acetone cooled down to 5°C. Then, to remove nonlipids contamination, Ph were soluted in diethyl ether and precipitated with acetone. The obtained Ph were a yellow powder with peroxide value-8,0, acid value-33,0. Preparative thin-layer chromatography indicated the presence in Ph of the following compounds: phosphatidic acids, PE, PCh, PS, lyso--PCh and lyso-PE. The major fatty acids in Ph are palmitic /13,5%/, oleic /43,6%/ and linoleic /33,8%/.

Autoxidation of rapeseed oil containing Toc and Ph was carried out in 300 cm^3 vessel with a cintered glass plate. Reaction temperature 90°C, oxygen flow 9 - 10 l/hr, sample weight 100g. The process of autoxidation was controled by

determination of peroxide value. The obtained results were presented as kinetic curves. Autoxidations of refined rapeseed oil containing 0,1, 0,05, 0,025 and 0,01% α-Toc were performed. The obtained kinetic curves are shown in Fig. 1. 0,1% and 0,05% solutions of α-Toc in rapeseed oil presented induction periods shorter than those of pure rapeseed oil. For 0,1% α-Toc induction period was 16,0 hr, for 0,05% α-Toc-16,9 hr, for rapeseed oil it was 17,6 hr. At these concentrations α-Toc showed prooxidant properties. Reducing α-Toc content to 0,025% prolonged induction period to 18,7 hr and to 0,01% α-Toc to 18,2 hr. Comparing these results with the induction period of rapeseed oil it should be pointed out that α-Toc at above concentration possessed antioxidant properties. Concentration of 0,025% was more effective than 0,01%. Those results were confirmed by parallel experiments, which were carried out for all four concentrations of α-Toc in rapeseed oil. The influence of Ph on antioxidant properties of α-Toc was investigated on the two samples. Both of them contained 0,025% α-Toc, 0,1% and 0,2% Ph. The above concentration of Ph in rapeseed oil prolonged considerably induction period, which for 0,1% Ph was 20,7 hr and for 0,2% Ph was 22,4 hr. Fig. 2 presents the kinetic curves of rapeseed oil with Toc and Ph.

As can be seen from Fig. 2 the addition of Ph to solution of α-Toc in rapeseed oil prolonged its induction period from 18,7 hr to 21,6 hr. Similarly, the addition of 0,2 Ph reduced the oxidation rate and the induction period was 23,4 hr /Fig. 3/. To establish the role of Ph it has been studied the synergism of those compounds toward α-Toc in the additional experiments. For this purpose 0,025% of α-Toc in rapeseed oil, 0,025% Ph in rapeseed oil and solution with 0,0125% α-Toc+0,0125% Ph were prepared. The results were shown in Fig. 4. The longest induction period, 20,1 hr, was exhibited by the oil containing α-Toc and Ph against to 18,7 hr for α-Toc solution and 19,2 hr for Ph solution. These induction periods did not vary greatly. So it was especially essential to confirm the obtained results. Further experiments showed a

great repeatibility of the kinetic curves.

It should be pointed out that the conclusions about the synergism of Ph with α-Toc are true in the relation to investigated system. This statement corresponds with investigation of some authors, who established the synergistic role of Ph in relation of some antioxidants. The differences in role of Ph in autoxidation process are due to mechanism of their action, which is not investigated precisely up to now. This confusion may be due to the structural complexity of Ph containing different functional groups and various fatty acid composition. Most likely is the assumption that in every separate case the mechanism is different.

The present study indicates that α-Toc presence in rapeseed oil at investigated concentrations indicated antioxidant properties which are influenced synergisticly by Ph, which resulted in substantial prolongation of the stability of the investigated rapeseed oil.

References

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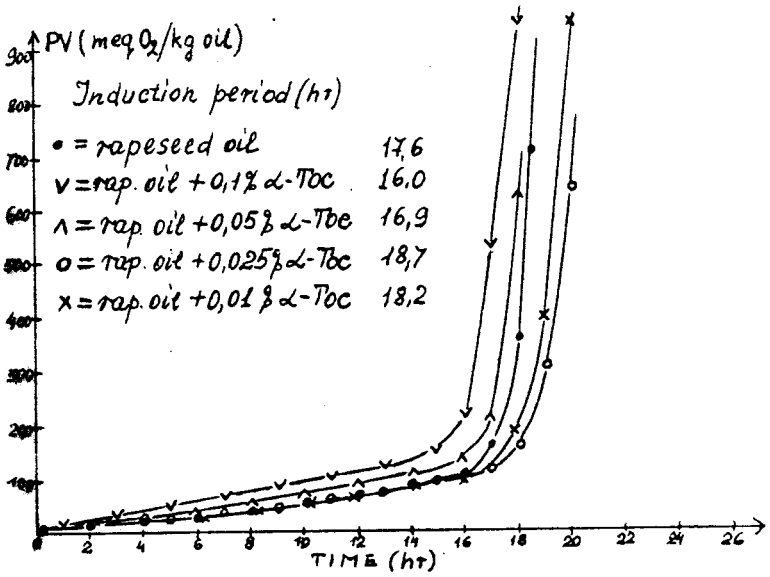

FIG.1. Autoxidation of rapeseed oil with various amount of α-tocopherol (α-Toc).

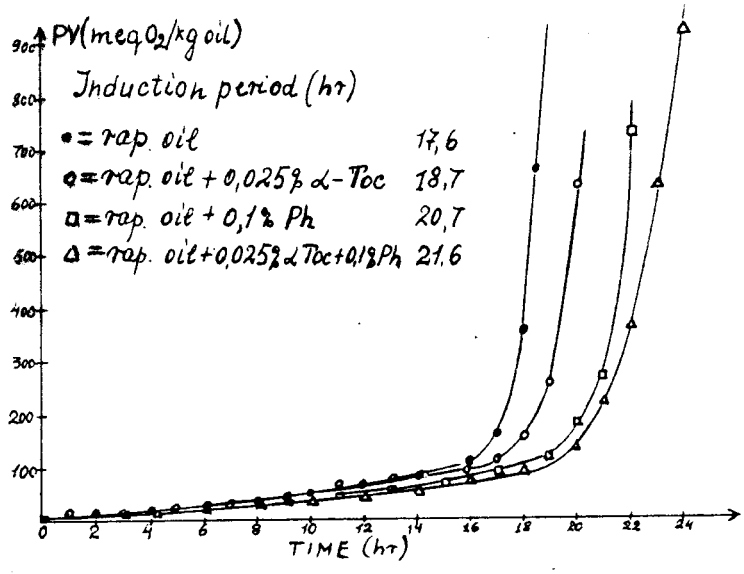

FIG.2. Autoxidation of rapeseed oil containing 0,025% α-tocopherol (α-Toc) and 0,1% phospholipids (Ph).

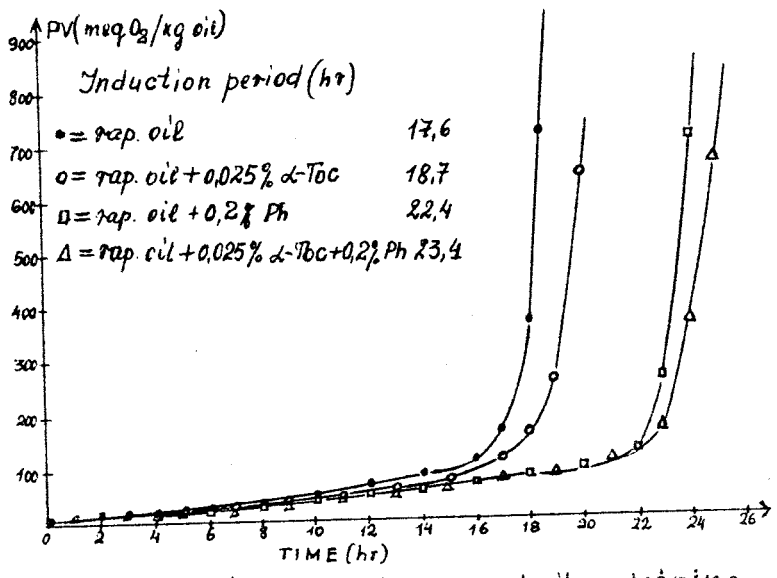

FIG. 3. Autoxidation of rapeseed oil containing 0,025% α-tocopherol (α-Toc) and 0,2% phospholipids (Ph)

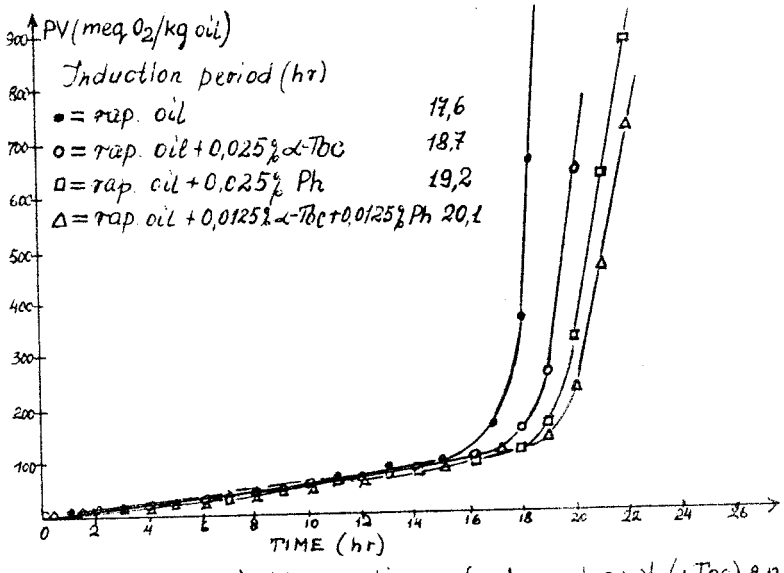

FIG. 4. Synergistic action of α-tocopherol (α-Toc) and phospholipids (Ph) during autoxidation of rapeseed oil.