

The Effect of Randomly Interesterified Triacylglycerols and Vegetable Oils on the Autoxidative Stability

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트리아실글리세롤 및 食用油脂의 自動酸化 安定성에
대한 에스테르 交換의 영향

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(Received March 31, 1987)

ABSTRACT

No difference was observed on autoxidative stability of triacylglycerols before and after randomly interesterification. It indicates that randomization of the glyceride composition has no significant effect on the autoxidative stability.

On the other hand, the autoxidation of randomly interesterified vegetable oil was accelerated, caused mainly by decrease of tocopherols during the series of interesterification procedures.

INTRODUCTION

Intesterification is widely used as well as hydrogenation in the field of oil production. The reaction mechanism^{1,2)} technical problems³⁻⁵⁾ alteration in the glyceride composition⁶⁻⁸⁾, and change in physical properties⁹⁻¹²⁾, have been well investigated. However, contradictory results have been reported on the effect of interesterification on the stability of oils against autoxidation¹³⁻¹⁶⁾.

The purpose of this work is to clarify the effect of randomized interesterification of vegetable oils on their autoxidative stability.

MATERIALS and METHODS

1. Materials

Trilaurin (TLa) and Trilinolein (TL), all 99 % pure, were purchased from Sigma Chem. Co.,

Missouri. TL was purified by means of column chromatography with the use of Florisil (100-200 mesh) to eliminate any peroxides¹⁷⁾. Soybean oil was obtained from Nakarai Chem. Ltd., Kyoto. Triglyceride (TG) was prepared from the oil by the method described in the previous paper¹⁸⁾ and was further purified by means of Lobar column (Lchroprp Si, 60~63 μ m, Merck Co.) and then eluted with hexane. TG means the oil purified by the procedure as described above from commercially available parent oil. Sodium methoxide was provided by Katayama Chem. Co., Osaka. *d*- α -Tocopherol (α -Toc), *d*- γ -tocopherol (γ -toc), *d*- δ -tocopherol (δ -toc) were provided by Eisai Co. Ltd., Tokyo, and purified by Sephadex LH-20 column chromatography¹⁹⁾.

2. Interesterification

The procedure of interesterification is schematically described in Fig. 1. One gram of TG of 3g

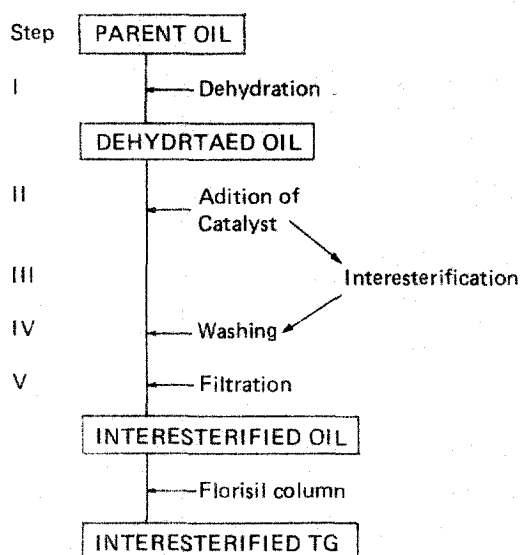


Fig. 1. Procedure of Interesterification.

of vegetable oil (parent oil) was dehydrated by bubbling with nitrogen gas at 140°C for 2 hr (step I), and then a catalyst, sodium methoxide (0.3%, w/w) was added to the oil (step II). The reaction temperature was maintained at 75~80°C with vigorous stirring under nitrogen gas (step III). After the reaction was completed (1 hr), the oil was dissolved in ethyl ether (10 volume of the sample) and washed 4 times with distilled water (10 volume of the sample) to remove the catalyst (step IV). The ether layer was then treated with 0.5 g of Celite and decolorizing carbon to remove

Table 1. Triglyceride Compositions of Interesterified Mixture of TL and TL_a.

	Carbon number			
	C ₃₆	C ₄₂	C ₄₈	C ₅₄ ^a
Parent TG ^b	47	—	—	53
Dehydrated TG	48	—	—	52
Esterified TG				
Reaction time				
2 min	18	39	34	9
10 min	15	43	36	6
60 min	15	43	36	6

a: relative weight percentage

b: TL and TL_a (1:1, w/w) were mixed

of the soaps and colored bodies which formed during the interesterification (step V). After evaporation, oil was kept at -20°C until used in the experiment. Randomized TG was further purified by means of column chromatography as described above before being used in autoxidation experiments.

3. Autoxidation

Oil or TG (100 or 300 mg) in the glass vial (1 cm diameter) was autoxidized by incubating it at 60°C in the dark. Peroxide value was measured after intervals of time according to the method of Asakawa and Matsushita²⁰⁾

4. Analysis of TG molecular species

Molecular species of TGs were determined by means of GLC which was carried out on a Shinadzu GC-7A. The column was a glass tube (0.5 m x 3 mm) packed with 3% Dexsil on Chromosorb W, 60-80 mesh. Nitrogen gas was used at 60 ml/min. The temperature of the oven was set at 280 to 340°C (5°C/min).

5. Determination of tocopherols

The oil used for determination was saponified and tocopherols in saponifiable matter were determined by means of GLC²¹⁾ or GC-MS analysis²²⁾ of their trimethylsilyl derivatives.

RESULTS

1. Autoxidation of interesterified TG

Table 1 shows the change of TG composition of the mixture of TL consisting of the linoleoyl group alone and TL_a consisting of lauryl group alone after interesterification. The reaction was completed within 10 min. Resulting in the formation of a new TG species, C₄₂ TG, consisting of two lauryl groups and one linoleoyl group, and C₄₈ TG, consisting of one lauryl group and two linoleoyl groups. The weight ratio of four TG molecular species indicate that each group in TL and TL_a were exchanged at random by the procedure described in Materials and Methods.

The autoxidative stability of TGs before and after interesterification is shown in Fig. 2. The degree of oxidation was determined by peroxide value at intervals of elapsed time. No oxidized difference was observed before and after interesterification of TL and TL_a. It indicates that change in the molecular species of TG does not affect the autoxidation rate.

2. Autoxidation of interesterified soybean oil

Fig. 3 shows the difference in the autoxidative stability of soybean oil before and after interesterification. Interesterified soybean oil was autoxidized more rapidly than the parent oil. This is supposed to be due to the loss of tocopherols by the interesterification procedures. Thus, tocopherol contents in interesterified and parent soybean oils were determined by means of GLC as shown in Table 2. Tocopherols decreased through the interesterification procedure. Contents of γ -toc and δ -toc were decreased to 12 % and 39 % of the parent oil levels and α -toc disappeared completely. Same tendency was observed in the mixture of soybean oil and olive oil (not shown here).

To confirm the effect of tocopherol content on the autoxidation before and after interesterification, the stability of soybean oil TG and interesterified soybean oil TG was compared at three different tocopherol levels (added tocopherol contents are based on the analysis of tocopherol content before and after interesterification, from Table 2). Fig. 4 shows the results when tocopherol was added to the soybean oil TG which can be compared with the parent and interesterified soybean oil shown in Fig. 3. A significant difference in autoxidative stability was observed

Table 2. Tocopherol Contents in Parent and Interesterified Soybean Oils

oil	α -Toc	γ -toc ($\mu\text{g}/1\text{ g of oil}$)	δ -toc
Parent oil	129	889	269
Interesterified oil	n.d.	107	105

Contents were determined by GLC. n.d. : not detected

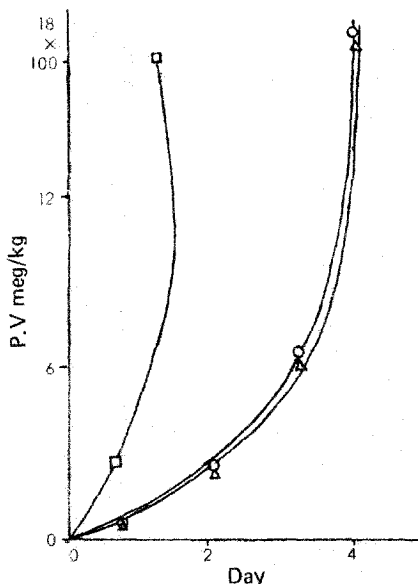


Fig. 2. Effect of interesterification against autoxidative stability of TL and TL_a mixtures.

□ : TL; ○ : TL and TL_a mixture; △ : interesterified TL and TL_a mixtures.

TG (100 mg) was autoxidized in the dark at 60°C. Autoxidative extent was determined by measuring Peroxide Value after intervals of time.

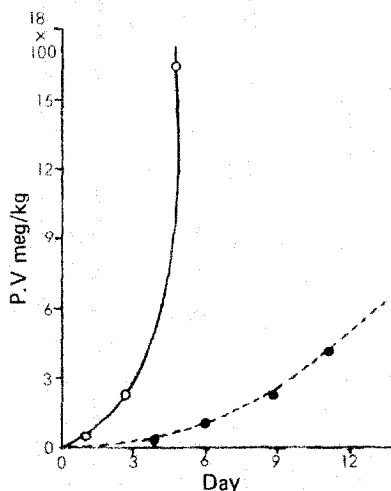


Fig. 3. Effect of interesterification against autoxidative stability of soybean oil. Each oil (300 mg) was autoxidized in the dark at 60°C.

● : parent oil; ○ : interesterified oil.

Table 3. Residual Tocopherol Contents at the Interesterification Steps of Soybean Oil

Procedure	α -toc	γ -toc (relative %)	δ -toc	A
Parent oil	100	100	100	10.
I	94	99	98	9.6
IV	90	98	98	9
V	n.d.	8	25	4.5
IV + V	n.d.	7	24	4
I + II + III + IV	84	96	88	6
I + II + IV + V	n.d.	2	15	1
I + II + III + IV + V	n.d.	1	6	0.5

A : days taken to reach 100 meq/kg of PV. n.d. : not detected.

The description of procedure is described in Figure 1.

between the two additions. However, in every case, the TG and interesterified TG show a similar autoxidation rate at the same level.

This consequently confirmed that the loss in tocopherols during the interesterification procedure is largely responsible for the decrease in stability after interesterification. The Table 3 shows the residual tocopherol contents at each step in the procedure. Tocopherol decreased significantly by treating with Celite and decolorizing carbon for removal of the by-products and the stability of each oil decreased in accordance with the changes of tocopherol contents.

DISCUSSION

The autoxidative stability of edible oils depends on numerous factors, such as temperature, oxygen gas pressure, contaminated peroxidants and antioxidants. It is well known that fatty acid compositions have a significant effect on the stability of oil against oxidation. However, the relationship between the oxidative stability and TG compositions has not been clear, although edible oil consists of various TG molecular species. Raghuvver and Hammound¹²⁾ reported that randomized interesterification towered the autoxidation rate of TG mixtures and suggested that the concentration of unsaturated fatty acids in 2-position of glycerol stabilizes oil toward autoxidation. However,

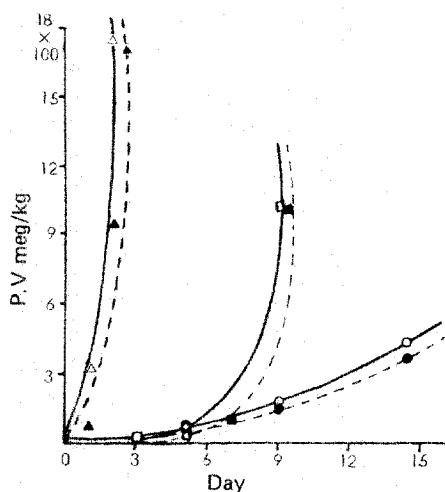


Fig. 4. Influence of tocopherols on the autoxidation of TG prepared from soybean oil. The amounts of tocopherols were adjusted so as to be equivalent to the parent and interesterified oils as shown in Table 2.

△ : parent TG (which was prepared from the parent oil) ; ▲ : interesterified TG (which was prepared from interesterified oil) ; □ : parent TG to which tocopherols were added (γ -toc=106 μ g/g; δ -toc= 105 μ g/g); ■ : interesterified TG to which tocopherols were added at the equivalent weight to □ ; ○ : parent TG to which tocopherols were added (α -toc=129 μ g/g; γ -toc=889 μ g/g; δ -toc= 269 μ g/g); ● : interesterified TG to which tocopherols were added at the equivalent weight to ○.

Zalewski and Gadiss¹⁵⁾ disagreed with Raghuvver and Hammound, and they suggested that rando-

mization of glyceride structure had no effect on the autoxidative stability of lard. List et al.¹⁴⁾ also indicated that glyceride rearrangement by randomization of lard did not affect its resistance to autoxidation. However, the possibility that randomization decreases the stability of soybean oil was recently proposed by Wada et al.¹⁶⁾ The results shown in this study clearly support the idea that randomization of glycerol composition has no effect on the autoxidative stability (Fig. 2 and 4).

On the other hand, the autoxidation of interesterified soybean oil was accelerated, caused mainly by the tocopherols during the series of interesterification procedures. It was shown that the tocopherols in this vegetable oil were only slightly decomposed by the interesterification reaction, but that they were completely removed from the oil by a further purification procedure to remove the soaps and colored bodies formed during their interesterification. When interesterification is applied to vegetable oils, the behavior of tocopherol during the processes should be noted for the preservation of vegetable oils.

This work clearly support that the effect of interesterification of TGs or vegetable oils on their autoxidative stability dose not depend on random distribution of fatty acids in glycerides, but rather on the decrease of tocopherols during the interesterification.

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