APPLICATION OF γ-CYCLODEXTRIN FOR THE STABILIZATION AND/OR DISPERSION OF VEGETABLE OILS CONTAINING TRIGLYCERIDES OF POLYUNSATURATED ACIDS

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ABSTRACT

To improve the storage stability of instable vegetable oils with a high content of polyunsaturated fatty acid triglycerides, these essential compounds can be complexed with native cyclodextrins. Only with γ-CD a nearly complete complexation of the oils was achieved as shown by complexation kinetics measurements. Storage trials of the insoluble CD-complexes followed by the determination of the peroxide value of the oils indicated that the best stabilization against autoxidation is obtained with γ-CD. An additional benefit of the complexation of triglycerides of polyunsaturated fatty acids with γ-cyclodextrin is the formation of stable dispersions of these oils in aqueous media.

1. INTRODUCTION

Liquid vegetable oils with a high content of polyunsaturated fatty acid triglycerides, like evening primrose, borage or blackcurrant oil are valuable substances, which are used for cosmetic applications, most of all for skin care to enhance elasticity and to decrease transepidermal loss of moisture [1]. In addition they are very important in the food sector for the supply with essential fatty acids.

Table 1. Typical fatty acid profile of the vegetable oils

fatty acid	double bonds	evening primrose oil	borage oil	blackcurrant oil
palmitic acid	0	6 - 10 %	9 - 13 %	6 %
stearic acid	0	1.5 - 3.5 %	3 - 5 %	1 %
oleic acid	1	6 - 12 %	15 - 17 %	10 - 12 %
linoleic acid	2	74.2%	40.4%	48 %
linolenic acid	3	8 - 12 %	19 - 25 %	30 %

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The unfavorable property of these oils that prevents their broader application in cosmetics, pharmaceuticals and food is their low stability against atmospheric oxygen, especially in combination with the exposure to heat and daylight. The primary formation of toxic hydroperoxides by autoxidation induces further degradation to aldehydes, ketones and polymeric species, which account for a bad, rancid smell and for discolorization. The amount of peroxides is expressed by the peroxide value (POV). It is known from the literature that unsaturated fatty acids and the corresponding triglycerides can be complexed by α– and β–cyclodextrin [2,3,4]

2. MATERIALS AND METHODS

α-, β- and γ-cyclodextrin are products of Wacker-Chemie GmbH, Munich.
The vegetable oils used in this study were a gift of Görlich-Handels GmbH, Wasserburg or purchased in a pharmacie.
The complexes were prepared in suspension or in concentrated cyclodextrin solution or by kneading with the exclusion of light and oxygene. Kinetic measurements were carried out by determining the amount of the water soluble fraction of the reaction mixture. peroxide values (POV [meq/kg]) of the oils after storage of the complexes were measured by decomplexation in a methanol/hexane mixture at room temperature. and potentiometric thiosulfate titration after addition of iodid to the oils.

3. RESULTS AND DISCUSSION

3.1. Complexation

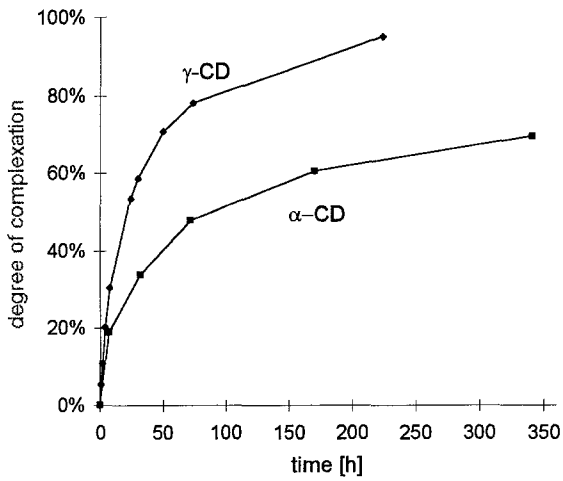

Fig.1 Kinetics of complexation in suspension at 25°C with excess of wheat germ oil

All three types of native CDs are forming insoluble complexes with vegetable oils. The degree of complexation can be easily determined by measuring the water soluble fraction of the reaction mixture, because uncomplexed oil and cyclodextrin complex have an extremely low solubility in water. The kinetics of the complexation with α- and γ-CD were studied.

Surprisingly a complete complexation of the vegetable oils was only achieved with γ-CD, although it was recognized before [2] that for free fatty acids α-CD is more suitable than β-CD. Through the exclusion of light and oxygene during the complexation procedure the peroxid values of the oils were nearly unchanged. Optimal temperature for the complexation was found to be between 40 - 50 °C.

Stirring mixtures of γ-CD and vegetable oils with higher oil to CD ratio in water resulted in very stable o/w emulsions which can be used in cosmetics.

3.2. Stability tests

The rapid autocatalytic oxidation of uncomplexed evening primrose oil is clearly seen in Fig.2 . It could be demonstrated that high peroxide values of the oils are coincident with discolorization and rancid smell. It was also found that the oxidation was enhanced by exposure to daylight.

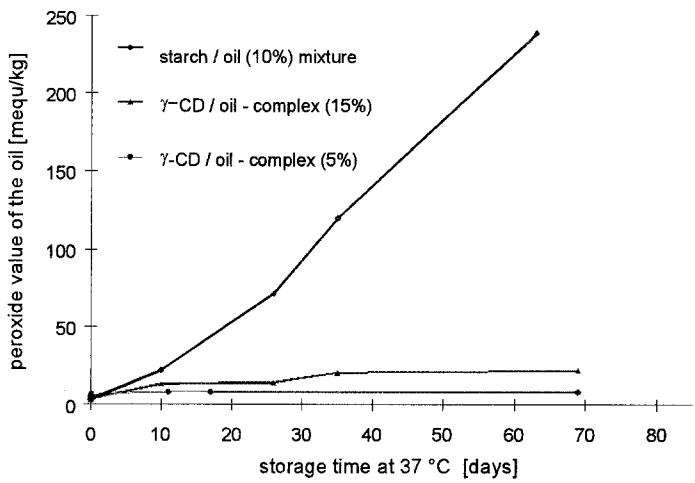

Fig. 2 Storage trials of evening primrose oil / γ-CD complexes in comparison to uncomplexed oil

A very good stability of the oil as its γ-CD complex was proved by a slight increase of the POV over a period of 2 month at elevated temperature. Complexes with higher content of γ-CD seem to be even more stable. Similar results were found with borage and wheat germ oil.

The stabilization of evening primrose oil by complexation with α-, β- and γ-CD was examined in a comparing storage trial at room temperature and daylight exposure over a period of 38 days. Under these conditions γ-CD proved to have the best stabilizing effect of the native cyclodextrins. After 15 days the POV of the α-CD-complexed oil was clearly higher than with γ-CD, while no significant stabilization was found with β-CD. In combination with the complexation kinetics this result indicates that the large cavity of γ-CD is most suitable for the inclusion of long chain triglycerides.

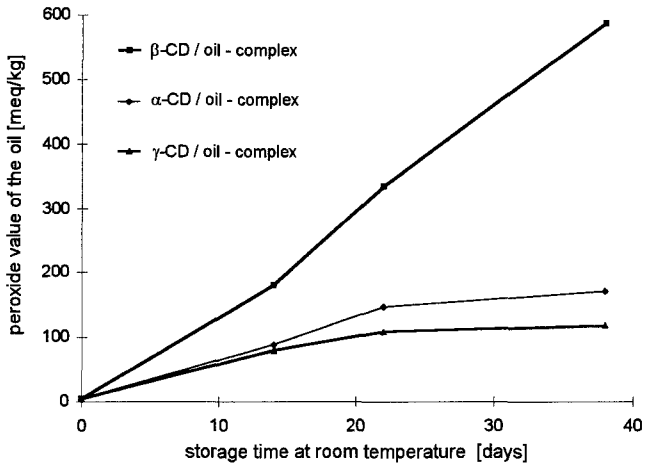

Fig. 3 Storage trials at daylight exposure of evening primrose oil complexes

4. CONCLUSION

As shown by complexation kinetics and stability tests γ-CD is the favorable CD to complex and to stabilize triglycerides of polyunsaturated fatty acids. With γ-CD also stable dispersions of these oils in aqueous systems were obtained.

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