The Preparation of Alkyl Esters from Highly Unsaturated Triglycerides. II

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Abstract

A previously described procedure for the base-catalyzed alcoholysis of fish-oil triglycerides with alcohols of low molecular weight has been applied to the preparation of alkyl esters using high molecular weight, aromatic, and terminally unsaturated alcohols. Some monoethers of ethylene- and diethylene glycol have also been used in this work. Thin-layer chromatography was used to follow the course of the reaction and determine optimum reaction times and yields of products.

Introduction

A NUMBER OF PAPERS have appeared in the literature on the upgrading or modification of a drying oil via an ester-ester interchange (1–5). Most of these papers have been concerned with the use of low molecular weight alcohols and have generally involved prolonged reaction times and elevated reaction temperatures. In addition, the oils used were those of vegetable origin; consequently, they did not contain the large amounts of polyunsaturated moieties present in fish oils.

As was shown in a previous paper (6), fish oils can be used in a base-catalyzed alcoholysis reaction with low molecular weight alcohols. This reaction may be carried out at moderate temperatures and short contact times and gives good yields of alkyl esters with a minimal change or loss of the polyenoic structures. The present paper is a continuation of that work using higher molecular weight normal alcohols, a terminally unsaturated alcohol, and monoethers of ethylene and diethylene glycol.

Experimental

Materials and Equipment

Menhaden oil triglycerides (I.V. 172.1; sap eq 297.9) free of unsaponifiable matter were obtained by molecular distillation of light cold-pressed menhaden oil (7). These distilled triglycerides were used for all of the preliminary reaction studies. Large scale reactions were carried out using commercial light cold-pressed menhaden oil and commercial herring oil.

All of the alcohols used were of commercial or industrial grade and were dried by conventional methods only where necessary.

Glass plates (20 × 20 cm), for thin-layer chromatography (TLC), were coated with thin layers (250–275 μ) of either silica gel G or aluminum oxide G according to the method of Stahl (8).

Preparation of Alkyl-Esters

The general procedure used for the synthesis of alkyl esters from menhaden oil triglycerides may be illustrated by the reaction with allyl alcohol. All of the other esters were prepared by the same general method except for increased reaction temperatures in some cases. The alcohols used, reaction conditions, TLC adsorbents, TLC solvent systems, and yields obtained in the synthesis of the various esters are summarized in Table I.

The alcoholysis reaction was carried out in a round-bottom reaction flask equipped with mechanical stirrer, condenser, thermometer, and gas-bubbling tube. The reaction vessel was charged with 44.69 g (0.05 mole) of molecularly distilled menhaden oil triglycerides and 13.42 g (0.231 mole) of allyl alcohol. The reaction vessel was then placed in a constant temperature bath at 60.0 ± 0.1C and vigorously stirred under an atmosphere of purified (99.99%) nitrogen. When the contents of the flask reached 60C, a solution of 0.13 g (0.0057 mole) of sodium in 4.0 g (0.0689 mole) of allyl alcohol was rapidly added to the reaction mixture. Small samples of the reaction mixture were withdrawn from the reaction vessel at regular timed intervals after the addition of the catalyst. These samples were immediately dropped into cold water to quench the reaction. The samples were extracted with petroleum ether (bp 30–60C) and washed with water several times to remove the base and the unreacted excess allyl alcohol. After drying the petroleum ether, extracts over anhydrous sodium sulfate, the solvent was removed under vacuum on a steam bath.

The extent of conversion of the triglycerides to allyl esters was estimated by means of TLC using a

TABLE I

Reaction Conditions and Results of the Alcoholysis of Menhaden Oil by Various Alcohols

Alcohol	Temp, C	Reaction time, min	TLC adsorbent	Solvent system [a]	% Conversion
2-Methoxy ethyl	60.0 ± 0.1	4	Aluminum oxide G	1	85
2-Ethoxy ethyl	60.0 ± 0.1	8	Aluminum oxide G	1	85
2-Butoxy ethyl	60.0 ± 0.1	16	Aluminum oxide G	1	85
2-Phenoxy ethyl	60.0 ± 0.1	16	Aluminum oxide G	1	80
2-(2-Methoxyethoxy) ethyl	60.0 ± 0.1	4	Silica gel G	1	90
2-(2-Ethoxyethoxy) ethyl	60.0 ± 0.1	4	Silica gel G	1	80
2-(2-Butoxyethoxy) ethyl	60.0 ± 0.1	4	Silica gel G	1	80
2-(2-Phenoxyethoxy) ethyl	60.0 ± 0.1	4	Silica gel G	1	80
Allyl	60.0 ± 0.1	2	Silica gel G	2	80
Benzyl	60.0 ± 0.1	8	Silica gel G	2	80
2-Ethyl-1-hexyl	60.0 ± 0.1	360	Silica gel G	2	98
2-Ethyl-1-hexyl	100.0 ± 0.1	4	Silica gel G	2	98
n-Octyl	100.0 ± 0.1	16	Silica gel G	2	85
n-Decyl	100.0 ± 0.1	60	Silica gel G	2	85
n-Dodecyl	100.0 ± 0.1	60	Silica gel G	2	80
n-Octadecyl	100.0 ± 0.1	60	Silica gel G	2	80
n-Eicosyl	100.0 ± 0.1	60	Silica gel G	2	75
n-Docosyl	100.0 ± 0.1	60	Silica gel G	2	75

[a] 1 Petroleum ether (bp 30–60C)/Ethyl Ether/Formic acid 90:10:1.
2 Petroleum ether (bp 30–60C)/Ethyl Ether 92:8.

silica gel G plate and a solvent system of petroleum ether (bp 30–60C)/diethyl ether/formic acid (90/10/1) and iodine vapor stain. It was observed from the thin-layer plate that a yield of about 80% allyl esters was obtained in 2 min and that it was not appreciably increased by longer reaction times.

Kilogram quantities of the allyl esters were prepared from both light cold-pressed menhaden oil and from herring oil. Mole ratios of the reactants were the same as in the initial work described above, and comparable yields were obtained in the same reaction time.

In those reactions involving water insoluble alcohols, no effort was made to remove the unreacted excess alcohol since it did not interfere with the estimation of yields by TLC. All TLC evaluations were compared with authentic standards on the same plate. The excess alcohol can be removed by vacuum distillation or column chromatography, however, to yield a purified ester.

It was advantageous to use sodium methoxide as the catalyst for the reactions involving the 10–22 carbon normal alcohols. These alcohols react so slowly with metallic sodium that it was impracticable to make the individual alkoxides. The small amount of methyl esters present, due to the use of sodium methoxide, was of no consequence in the evaluation of the results.

Discussion

It was desired that the alcoholysis reaction be carried out under as mild conditions as possible in order to keep to a minimum any change or loss of the polyenoic structures present in the fish oil fatty acids. However, the reaction temperatures should be high enough to insure an homogenous reaction mixture and, therefore, good contact with the base catalyst.

As was found in our previous work (6), 60C was a satisfactory reaction temperature in most cases. It can be noted from Table I that good yields were obtained in reasonably short contact times for those reactions run at 60C. It was necessary to raise the temperature to 100C in the reactions with 2-ethyl-1-hexanol and the higher molecular weight normal alcohols in order to decrease the reaction times, which would otherwise be too lengthy.

It will be noted that an increase in bulk of the terminal group in the monoethers of ethylene glycol resulted in an increase in reaction time. In the analogous series of monoethers of diethylene glycol, the change in the terminal group had no apparent effect and maximum yields were obtained in the same length of time for all cases. It would then be within reason to expect monoethers of polyethylene glycol to react just as readily in the alcoholysis reaction as the monoethers of diethylene glycol.

A crude extrapolation of the observed reaction time for n-octyl alcohol was in general agreement with what would be expected based on the previous paper (6). The alcohols having 10–22 carbon chain lengths showed no noticeable increase in reaction times and it would appear that an increase in chain length beyond 10 carbon atoms is no longer a rate determining factor in this reaction.

There have been some objections to the amount of saturates present in fish oils because of the incompatibility of the saturates in certain applications. Since there is no practical method of satisfactorily reducing the relative amount of saturated fatty acid moieties in the triglycerides per se, the other alternative would be to add unsaturation. The alcoholysis of fish oil triglycerides with allyl alcohol gives an ester with a terminal double bond in the alcohol portion. The addition of this reactive site to the saturated fatty acids may serve to increase their acceptability for various uses. The addition of this double bond also increases the overall iodine value quite substantially.

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[Received December 7, 1965]