

# Synthesis of Methyl, Propyl, Butyl, Isobutyl, Hexyl, Cyclohexyl, Octyl, and 2-Ethylhexyl Esters of Epoxyoleic Acid

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## Abstract

A series of esters of 12,13-epoxyoleic acid were prepared by means of alcoholysis of triepoxyolein (trivernolin). The procedure for the alcoholysis, and isolation and purification of the esters are described. Analytical characteristics of the esters are reported.

## Introduction

PREVIOUS WORK from this laboratory (1) has shown that the methyl ester of epoxyoleic acid can be prepared in pure form and without significant destruction of oxirane through methanolysis of triglycerides containing this acid.

The present paper may be considered an extension of this work to prepare through alcoholysis a series of pure higher molecular weight esters of epoxyoleic acid, which were needed in investigation of their comparative plasticizer-stabilizer values for poly (vinyl chloride) and for other potential uses. The preparation and purification of these esters are described and some of their analytical constants and properties are listed.

## Experimental

The various alcohols employed were purified by distillation through an efficient column, the principal fractions being analyzed by gas-liquid chromatography (GLC). The most effective means for purification of n-hexanol, however, was by crystallization from low boiling (30–60C) petroleum ether 3:1 v/wt at –80 to –90C followed by distillation. All of the alcohols were 99+% pure.

Triglycerides of epoxyoleic acid obtained by crystallization of oil from seed of *Vernonia anthelmintica* (2) served as starting material for the preparation of the series of esters, and contained about 96% 12,13-epoxyoleic acid principally as triepoxyolein. The remaining 4% consisted of normal fatty acids, such as oleic, linoleic and palmitic acids, present as mixed triglycerides, e.g., linoleo-diepoxyolein.

## Alcoholysis

The following general procedure was satisfactory for the alcoholysis reaction for preparation of the methyl, propyl, butyl, isobutyl, and hexyl esters of epoxyoleic acid: to 300 ml of the corresponding pure dry alcohol, small pieces of freshly cut bright sodium or potassium were added in amounts required to make about 0.1 M solution of the alkoxide. This solution was added to 200 g of triepoxyolein contained in a glass-stoppered flask. After flushing with nitrogen and warming to 40C the flask was stoppered and shaken mechanically for 3½ hr in a cabinet or room regulated at this temperature. An alternative procedure of stirring the mixture by means of a slow

stream of nitrogen for 3½ hr in a bath at 40C was equally satisfactory.

Since sodium or potassium reacted very slowly with 2-ethyl hexanol and cyclohexanol, it was found satisfactory to add solid sodium or potassium methylate as the catalyst to these alcohols in amounts required to make a 0.1 M solution. The alcoholysis reaction was then carried out as described.

## Recovery and Purification of Esters

The alcoholysis reaction mixture was cooled to about 20C and neutralized by adding only the calculated amount of 0.5N HCl solution slowly with stirring, transferred to a 3-liter separatory funnel with 500 ml of redistilled petroleum ether (30–60C), and washed thoroughly (6 times) with equal volumes of water. The petroleum ether solution was dried over sodium sulfate and filtered. When the alcohol employed was water soluble, i.e., methyl or propyl alcohol, the excess was removed by the washing, and the dry petroleum ether solution was subjected directly to low temperature crystallization. The solution was held overnight at –75 to –80C and the precipitate filtered on a Büchner funnel cooled to the same temperature within the freezer cabinet. This precipitate was recrystallized from petroleum ether under the same conditions. When the alcohol employed was water insoluble (butyl, hexyl, etc.), the washed and dried petroleum ether solution of reaction product was first subjected to rotary vacuum treatment to remove the solvent; then the ester product with the excess alcohol remaining was transferred to a deodorization-type apparatus (3) and the alcohol removed under high vacuum (about 2 mm measured at top of deodorization flask). Nitrogen, in place of steam, was introduced through the material by means of a fine capillary to provide vigorous agitation and inert atmosphere. The first cold trap of the apparatus was modified to accommodate a flask at the bottom of the trap which received most of the alcohol. The temperature of the first cold trap was maintained at about –10 to –12C (with salt-ice) whereas the attached receiver flask was maintained at near –70C with a dry ice bath to decrease volatilization of the alcohol into the second cold trap which was maintained at near –70C also with dry ice. The higher temperature was maintained in the first cold trap in order to keep the higher alcohols from solidifying but yet cold enough to effectively condense the vapor. (In one preparation, the 2-ethyl hexyl ester, the excess of 2-ethyl hexanol was removed satisfactorily by distillation in a cyclic molecular still.) Following the removal of the excess alcohol, the crude ester was crystallized from low boiling petroleum ether in a low temperature cabinet at –75 to –85C as described earlier. Some difficulty was experienced in obtaining filterable crystals in the crystallization of isobutyl, 2-ethylhexyl and cyclohexyl esters. It

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was helpful in these instances to carry out the crystallization on smaller batches of about 50 g of product using a dry ice bath and slow rate of cooling and stirring. The yields of recrystallized products, 98 to 99% pure, varied from 65 to 85% of theory depending on the difficulties encountered in the crystallizations.

#### Analysis

A combination of methods and techniques were employed to serve as criteria of purity. Thin-layer chromatography, using a solvent system of Skellysolve F, ethyl ether and acetic acid, 80:20:1, v/v/v, was used to detect unreacted trivernolin and other impurities in the reaction products and in the recrystallized esters.  $R_f$  values of the esters were not determined. In addition, GLC and chemical methods such as iodine numbers (Wijs) and oxirane oxygen (Durbetaki) were used. In general, the conditions used in the GLC work were the same as those previously described (4). However, in order to elute the higher molecular weight esters in a reasonable time, the temperature was increased. Table I summarizes

TABLE I  
Analytical Characteristics of Esters of Epoxyoleic Acid

Ester	Iodine value		Oxirane oxygen		$\eta_D^{20}$	mp °C
	Found	Theory	Found	Theory		
Methyl	81.4	81.7	5.14	5.15	1.4583	+ 1.9
Propyl	75.3	75.0	4.65	4.73	1.4567	+ 0.5
Butyl	72.1	72.0	4.53	4.54	1.4569	+ 0.3
Isobutyl	72.3	72.0	4.44	4.54	1.4556	-12.3
Hexyl	66.9	66.8	4.14	4.21	1.4578	+ 5.9
Octyl	62.0	62.2	3.84	3.92	1.4588	+14.3
2-Ethylhexyl	63.0	62.2	3.83	3.92	1.4596	- 4.5
Cyclohexyl	66.7	67.1	4.11	4.23	1.4596	-18.0

the analytical data obtained on the series of esters. None had any measurable optical rotation.

A study of the separation of these esters by GLC is being prepared for publication.

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