

SYNTHESIS OF NEW DERIVATIVES FROM VEGETABLE SUNFLOWER OIL METHYL ESTERS VIA EPOXIDATION AND OXIRANE OPENING

Xavier PAGES, Carine ALFOS, ITERG

ITERG, French Institute for fats and Oils, rue Monge, ZI - 33 600 PESSAC

Fax : + 33 5 56 36 57 60 – e.mail : xavier-xatart-pages@wanadoo.fr

SUMMARY

Recently, epoxides have received increased attention because they are of interest both as end-products and as chemical intermediates ; epoxidized oils, mainly High Oleic Sunflower Oil, and their ester derivatives have thus found important applications as plasticizers and additives for polyvinyl chloride (PVC).

Epoxidized esters have been produced classically from High Oleic Sunflower Methyl Esters (HOSME) using H₂O₂ and formic acid. The epoxidation reaches 90% on pilot scale (5 kg). Epoxidized esters produced from HOSME have respectively hydroxyl values of 0, oxirane values of 5.2 / 4.5 and iodine values of 1.7 / 1.5.

Cleavage trials of the oxirane group of the epoxidized esters with different reactants have been undertaken in order to produce on pilot scale new derivatives to be characterized and tested in different fields of application (lubrication, detergency and as chemical intermediates).

Reaction of Epoxy-HOSME with an **excess of oleic acid** was conducted under atmospheric pressure without any catalyst and solvent. The oxirane opening leads to complete estolide formation : after neutralization, analytical controls (chemical values, GC and HPLC analysis) indicate that the estolides are composed of a mixture of C36 (oleate of methyl hydroxystearate) and C54 (di-oleate of methyl dihydroxystearate).

Oxirane opening **with alcohols (ethanol and octanol)** was preferentially performed by acid catalysis at 100 °C under atmospheric pressure. Analytical controls show the formation of different etheralcohols and secondary products resulting from dehydration, transesterification and dimerization side-reactions.

Cleavage reaction of Epoxy-HOSME **with a primary amine (butylamine)** was conducted under pressure, at high temperature (180/200 °C). Both transesterification and opening of the oxirane group occur under these conditions. Reaction products are composed of amides formed by transesterification and a mixture of fatty amines/imines obtained by ring opening as established by analytical determinations.

INTRODUCTION

The preparation and characterization of epoxides were described, as early as 1861, by the chemists Berthelot, Wurtz and Reboul (Ashland, 1967) (1)

More recently, epoxides have received increased attention because of their interest, both as end-products and as chemical intermediates ; so epoxidized oils -mainly soybean oil- and their ester derivatives have found important applications as plasticizers and additives for polyvinyl chloride (PVC) (Gan, 1992) (2).

The high reactivity of the oxirane group undergoes a wide variety of ring-opening reactions with a broad range of electrophile and nucleophile agents (Zoebelein, 1992) (3). Therefore, new routes toward an interesting range of functional groups are provided.

In our present work, cleavages of the oxirane group of epoxidized HOSME were studied according to the following routes:

- acid opening by reaction with fatty acids from High Oleic Sunflower Oil,
- alcoholysis by reaction with ethanol and octanol (acid and base catalysis),
- reaction with butylamine

MATERIAL AND METHODS

Preparation of epoxidized esters (1, 2, 3, 4, 7, 12, 13)

Material

Commercial high oleic sunflower methyl esters (HOSME) were from industrial sources and provided by NOVANCE Cy (Compiègne, France). The main characteristics of these raw materials are reported in the table 1.

Table 1: Characteristics of methyl esters used for epoxidation-Fatty acid composition by GC *

Fatty acids (%)	HOSME ^b	Determination	HOSME
C16:0	3.7	Acid value (mg KOH / g) NF ISO 660	0.3
C18:0	3.9		
C18:1	80.5	Iodine value (g I ₂ / 100g) NF ISO 3961	84
C18:2	9.0		
C18:3	0.1	Saponification value (mg KOH / g) NF ISO 3657	190
C20:0	0.3		
C20:1	0.3		
C22:0	0.9		
C22:1	0.1		
C24:0	0.3		
C24:1	0.1		
N.I. ^c	0.8		

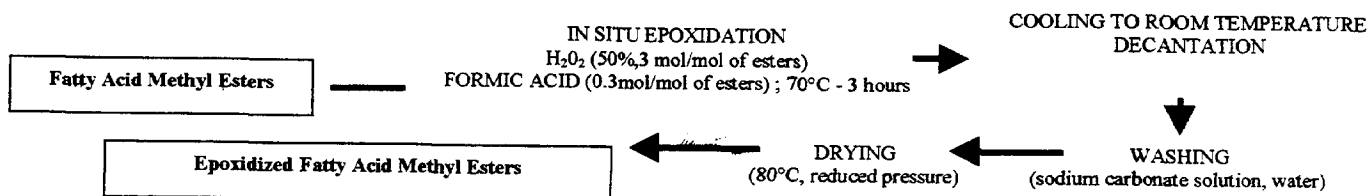
*Gas chromatography (GC) method: NF ISO 5508/5509 - ^bHOSME: High Oleic Sunflower Methyl Esters - ^cN.I: not identified

Epoxidation was conducted with analytical grade formic acid (99 %, Merck) and hydrogen peroxide (50 %, Prolabo).

Method of epoxidation

In this work, in situ epoxidation with formic acid was performed following the usual process conditions described in figure 2.

Figure 1 : Epoxidation process of Fatty Acid Methyl Esters



Cleavage of epoxidized esters (5, 6, 8, 9, 10, 11, 13, 14)

Materials

Fatty acids were produced from HOSME on pilote scale (1kg) by saponification and acid splitting. Fatty acid composition is reported in table 1. The alcohols were analytical grade: Ethanol (99.8%, Carlo Erba), octanol (99%, Fluka). Para-toluene sulfonic acid (PTSA) was also analytical grade. Butylamine (98 %) was provided by Fluka.

Analytical methods

The analytical methods for the characterization of raw materials and reaction products are given in table 2.

Table 2: Main analytical methods used for starting and final products characterization

Determination	Method
Saponification value	NF ISO 3657
Iodine value	NF ISO 3961
Acid value	NF ISO 660
Oxirane value	AOCS Cd 9-57
Hydroxyl value	AFNOR NF T60-213
Fatty acid composition by GC	NF ISO 5508/5509
Polymer content	IUPAC 2508
Composition of epoxidized esters	GC ITERG's method ^a
Composition of N-derivatives (Amines, amides)	GC ITERG's method ^b
Total amine value	and Infrared Spectroscopy AOCS Tf 1b-64

^aOn column injector, detection: FID, Cap. Col., L=7.5m, Ø=0.25mm, Phase SE 52/54, film thickness 0.15 µm, oven temp.: 60 to 340°C, 10°C/min; P_{H2}: 0.7bar; transesterification with trimethylammonium hydroxide. - ^bChromatographic cond: same as ^a; oven temp. 60 to 250 °C, silylated derivatives (BSTFA/TMCS).

RESULTS AND DISCUSSION

Epoxidation

Fatty acid compositions and the chemical characteristics of epoxidized methyl esters determined by GC are given in table 3.

Table 3: Characteristics of epoxidized methyl esters-Fatty acid composition by GC^a

Fatty acids	Epoxidized HOSME ^b	Determination	Epoxidized HOSME ^b
C16:0	5	Iodine value	1.6
C18:0	5	Saponification value	182
C18:1 + C18:2 + C18:3	<0.1	Acid value	0.4
C20:0	0.4	Hydroxyl value	<0.1
C20:1	<0.1	Oxirane value	4.8
C22:0	1		
C22:1	<0.1		
C24:0	0.4		
C18:0 1OX ^c	79.8		
C18:0 2OX ^d	7.3		
C18:0 3OX ^c	<0.1		
C20:0 1OX	0.3		
N.I.	0.7		

^aGC special conditions: injector on column; detector FID; cap.Col., Phase SE 52/54, L = 7.5 m, Ø = 0.25 mm; film thickness 0.15 µm; oven temperature: 60 to 340°C; 10°C/min; P_{H2}: 0.7 b; transesterification with trimethylammonium hydroxide. - ^bHOSME: High Oleic Sunflower Methyl Esters - ^{c,d} Epoxidized oleic acid: respectively 1,2 and 3 oxirane groups

Cleavage of epoxidized esters

Reactions of epoxidized esters with High Oleic Sunflower Fatty Acids (HOSFA)

The reaction of epoxidized HOSME with HOSFA can be performed through an easy, environmentally friendly route. We found that no catalyst and solvent are needed.

The reactions were carried out under atmospheric pressure. The reaction produces mainly estolides but also small quantities of dimers and polymers as side products.

HPLC analysis of the reaction mixture, before and after saponification followed by acid splitting, allows to determine the estolide content, because dimer and polymer fractions are not saponifiable. This analysis was performed according to the IUPAC method 2508 (Column PL gel 5 μm , 100 Å , L=300mm, diam.: 7mm ; detector: differential refractor; solvent :THF).

The results of a pilot trial are reported in the table 4.

After neutralization of the oleic acid excess with caustic soda, the total estolide content reaches 100 %. The high hydroxyl value (174) is due to the ring opening resulting also in the formation of alcohol functions. The main estolide (80% of the reaction products) is a C36 diester, namely the oleate of methyl-hydroxystearate. The characteristics of this product are interesting and allow to face its using in the field of lubricants.

Table 4 : Cleavage of epoxidized HOSME^a with HOSFA^b-Results of a pilot plant trial (1 kg)

Starting materials	Cleavage conditions	Neutralization conditions
Epoxidized HOSME (841 g) Oleic acid from HOSFA (760 g)	No catalyst, 175°C, 17h	Caustic soda (10.6 g), 70°C, 30 min.
	Characteristics of reaction products after cleavage	Characteristics of reaction products after neutralisation
Weight	-	1265 g
Oxirane value	<0.1	<0.1
Acid value	9.2	0.25
Hydroxyl value	-	174
Iodine value	-	45 g ₂ /100g
Saponification value	-	195 gKOH/100g
Total estolide content (%)	90.7	100
Gardner color	-	6/7
Sight	-	clear
Dynamic viscosity at 40°C	-	48.7 mm ² /s
Dynamic viscosity at 100°C	-	8.02 mm ² /s
Viscosity index	-	136
Flash point	-	220°C
Flow point	-	-1°C
Cloud point	-	+7.2°C

^aHOSME: High Oleic Sunflower Methyl Esters ^bHOSFA: High Oleic Sunflower Fatty Acids

Reaction of epoxidized esters with alcohols - Alcoholysis of epoxidized HOSME with ethanol and octanol

Alcoholysis study of epoxidized HOSME with ethanol and octanol was conducted in order to determine the best cleavage conditions of the oxirane group: acid catalysts (zinc chloride, para-toluene sulfonic acid) and basic catalyst (sodium methylate) were tested. As expected, no cleavage of the oxirane group occurs when no, or basic catalyst is used at temperatures below 100 °C.

With ethanol, the best results were obtained with PTSA.

The oxirane ring cleavage is complete at 80 °C, after 12 hours, under 1 bar. Ether formation is confirmed by different determinations and particularly the saponification value and GC analysis of the reaction products. The main component of the reaction mixture is the methyl

ethoxyhydroxystearate (>50%, by GC). Secondary products are also formed during the reaction. The characteristics of the reaction products are reported on table 5. The low flow point value and iodine value (best resistance to oxidation) allow to face its using in the field of lubrication.

Table 5: Cleavage of epoxidized HOSME by alcoholysis^b with ethanol -Characteristics of reaction product

Reactant	Acid value	Iodine value	Flow point	Saponification value	Main compounds(GC) ^b
Ethanol	0.4	19	-13°C	167	Methyl ethoxyhydroxystearate < 50% + Ethyl ethoxyhydroxystearate

^aalcoholysis conditions: 1% PTSA, 100°C, 12h, 1 bar ^bGC conditions: same as reported in table 7

With octanol as reactant, the best results were obtained with PTSA (0.5% w/w) under the following conditions: 100 °C during 17 hours, with a molar esters/ alcohol ratio of 1/3 for a conversion rate close to 100 %. The characteristics of the reaction products are reported on table 6.

Table 6: Cleavage of epoxidized HOSME^a by alcoholysis^b with octanol-Chemical characteristics of reaction products

Oxirane value	Iodine value	Hydroxyl value	Saponification value	Acid value
0	49	174	160	0.2

^aHOSME: High Oleic Sunflower Methyl Esters - ^bPilot scale production (1kg), PTSA 0.5%, 100°C, 17h, 1 bar

As indicated by the oxirane value after reaction (0), the ring opening is complete under these conditions. Other chemical values reported as well as GC analysis of the reaction products confirm the formation of etheralcohols and side products. The main final compound obtained (more than 60% of the final mixture) is the methyl octoxy-hydroxystearate. Secondary products are also formed during the reaction. The physical characteristics of the final products are reported in table 7.

Table 7: Cleavage of epoxidized HOSME^a by alcoholysis^b with octanol-Physical characteristics of reaction products

	Gardner colour	Viscosity 40°C mm ² /s	Viscosity index	Flow point(°C)	Cloud Point(°C)	Flash Point(°C)
Reaction products	6/7	22.3	100	-4	-0.5	170
HOSME	4	4.6/5.2	-	-6	+3.7	158

^aHOSME: High Oleic Sunflower Methyl Esters

^bPilot scale production (1kg), PTSA 0.5%, 100°C, 17h, 1 bar

For comparison we also indicated the corresponding values for the methyl esters of high oleic sunflower oil. It appears that the viscosity of octylic ethers is higher; the cold performances are similar but the oxidation stability is better due to the very low unsaturation.

Cleavage with butylamine

Oxirane ring opening of epoxidized HOSME with amines and particularly with butylamine is more difficult than with the former reactants. The difficult point is that the opening of the oxirane group competes with the transamidation reaction. The figure 2 describes the competition between these reactions.

We actually observed that transamidation always joins amination. On the first trial, reaction with different catalysts under «soft conditions», for instance at 80°C which is the boiling point of butylamine, were not successful. The final optimized operating conditions need to work under pressure (3 bar) at 140/200°C without catalyst, with a molar ratio 1/36 (epoxidized HOSME/butylamine) during 3 hours. The reaction temperature appears to be a key parameter (details below in table 8).

The reaction products were then washed with distilled water and dried under reduced pressure. The compounds from routes A (1-butylamido epoxidized oleic methyl esters) and B (1-butylamido 10-hydroxy-9-butylamino oleic methyl esters) mentioned in figure 2 are found in the final reaction products at levels depending on the operating parameters. The table 8 reports the different concentrations obtained for A and B, as a function of the reaction temperature.

Figure 2 : Cleavage of Epoxidized High Oleic Sunflower Methyl Esters with Butylamine-Main reactions

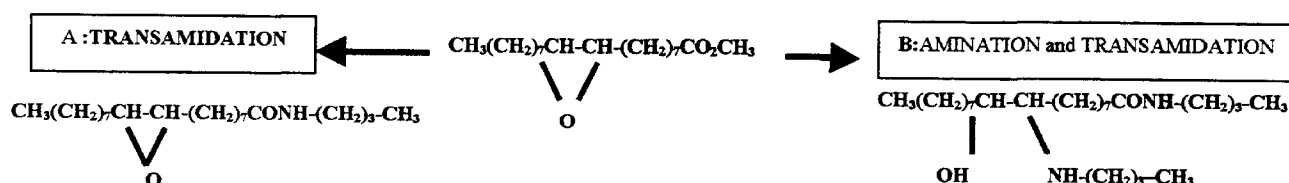


Table 8 : Cleavage of epoxidized HOSME^a with butylamine^b-Composition and characteristics of the reaction products at different temperatures

Reaction temperature(°C)	80	100	120	140	180	200
%A ^c /%B ^d (GC)	47/2	44/2	49/12	25/24	5/54	0/80
Total amine value	3.2	9.8	44	82	162	172
Polymer content (GC)	20	-	-	23	36	38

^aHOSME: High Oleic Sunflower Methyl Esters - ^bOperating conditions: 3h, 3 bar, no catalyst, molar ratio epoxidized product/amine 1/36; analytical methods: GC, LC, IR and chemical indexes) - ^cA compound: 1-butylamido epoxidized oleic methyl ester ^dB compound: 1-butylamido-10 hydroxy-9-butylamino oleic methyl ester

The characterization of the final reaction products is a delicate issue. As said previously, classical hydroxyl and oxirane determinations are not suitable because of analytical interferences. Different chromatographic methods have been developed in order to determine nitrogen derivatives content and side reaction products. From the analytical results, complete transamidation and amination can only be achieved with high temperature (180/200°C). Infrared spectroscopy clearly detected that, under the reported operating conditions, imine and polycondensation products -obtained by dehydration- are also formed during the reaction. The presence of dimers formed by dimerization of non epoxidized transaminated methyl esters, is also characterized, probably in very small quantity .

CONCLUSIONS

- Epoxidation of high oleic sunflower methyl esters (HOSME) was successfully performed following the classical in situ formic acid process with a high conversion rate and satisfactory characteristics. The conversion yield is about 85 - 90 % and the low hydroxyl

- values indicate that negligible oxirane cleavage occurs, allowing to conclude that the diol side formation is minimized.
- Cleavage trials of these epoxidized methyl esters with different reactants, both on laboratory and pilot scale (up to 5 kg), demonstrate their potential interest as starting materials to produce, under "soft" conditions:
 - - hydroxy esters or estolides by cleavage with fatty acids from high oleic sunflower oil with a conversion rate of 90 %,
 - ether alcohols with monoalcohols as reactants.

For these last reactions, acid catalysis gives better conversion rate than basic catalysis which promotes transesterification and side products formation.

With Epoxidized High Oleic Sunflower Methyl Esters and octanol as reactant (100°C, 17 h), the conversion rate is close to 100% to produce mainly (60%) the methyl-octoxy-hydroxystearate. The final products obtained on pilot scale contain also side products and are currently tested to determine their potential applications in the field of lubrication and as chemical intermediates for detergency.

- Using more drastic conditions (pressure and temperature) with butylamine as reactant, it is possible to obtain hydroxy-butylamine derivatives. Under the reported conditions, transamidation is the inevitable co-reaction of amination, and side products such as imine and polycondensation products have been identified .

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