Synthesis of a high-grade lubricant from sunflower oil methyl esters

Oléagineux, Corps Gras, Lipides. Volume 10, Numéro 5-6, 370-2, Double 5-6, SEPTEMBRE-OCTOBRE-NOVEMBRE-DÉCEMBRE 2003, UTILISATIONS ET APPLICATIONS DES MATIÈRES PREMIÈRES RENOUVELABLES

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Résumé : Cet article présente la synthèse d'esters méthyliques d'acides gras saturés branchés par codimérisation de l'éthylène sur un composé diénique conjugué issu d'esters méthyliques d'huile de tournesol. Le système catalytique est constitué d'un complexe à base de fer et d'une diimine, traité par un agent réducteur. Les quatre étapes nécessaires à l'obtention de cet ester branché saturé sont développées. Une dernière étape de transestérification utilisant du triméthylolpropane conduit à l'obtention d'une base lubrifiante possédant d'excellentes propriétés physiques et rhéologiques avec notamment un bon comportement à froid, ainsi qu'une bonne résistance à l'oxydation.

Summary : This paper presents the synthesis of saturated branched fatty acid methyl esters by codimerization of ethylene with conjugated linoleic methyl esters from sunflower oil. The catalytic system used is composed of iron, diimine and a reducing agent. This four-step synthesis will be discussed. After a last step of transesterification with TMP (trimethylolpropane) a lubricant with interesting characteristics (in particular a high thermal stability and a good cold behavior) is obtained.

Mots-clés : esters branchés saturés, codimérisation, éthylène, TMP, lubrifiant

Keywords : saturated branched methyl esters, codimerization, ethylene, TMP, lubricant

ARTICLE

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In view to obtain high performance lubricants from vegetable oils, chemical modifications of the fatty hydrocarbon chains have to be made, the aim being the synthesis of saturated branched chains. Saturated chains improve thermal stability of the product, while branched chains improve cold behavior performances by decreasing the pour point. Considering this kind of branched fatty acid

Article disponible sur le site http://www.ocl-journal.org ou http://dx.doi.org/10.1051/ocl.2003.0370

esters, some compounds such as isostearic acids are already produced as byproducts coming from the synthesis of dimer acids [1]. In this paper a new way of synthesis of saturated branched methyl esters from sunflower oil methyl esters (SOME) is described. With this new method, monoethyloleate is selectively synthesized in soft conditions described in the following chapters.

Results and discussion

A logical diagram *(figure 1)* shows the different stages of the production of the lubricant base.
The sunflower methyl esters are isomerized by basic catalysis. Then, the conjugated methyl esters obtained are codimerized with ethylene and totally hydrogenated. A stage of purification by crystallization increases the branched methyl esters content and a final step of transesterification with TMP leads to the lubricant base.

Isomerisation

This operation consists in the conjugation of the double bonds [2] of linoleic acid methyl esters with a basic catalyst. The conjugated form is required to increase the reactivity of double bonds in codimerization reaction. The catalyst used is potassium methoxide in methanol. The reaction is performed at 160 °C. After 2 hours, the yield of the production of isomerized esters is generally higher than 96 %. The product can be used in the following stages without washing steps soaps. Removal is easily performed by centrifugation because of the low solubility of these salts in the esters.

The 9-10 and 10-12 cis-trans isomers account for 95 % of the mixture, weight the remaining 5 % being cis-cis and trans-trans isomers *(figure 2)*.

Codimerization

The codimerization of ethylene and butadiene 1,3 is well known [3-5]. An industrial process used rhodium and cobalt based catalysts. Other catalytic systems using nickel, palladium or titanium have been described. The first experiment with linoleic methyl esters and ethylene has been reported in 1990 [6]. The catalytic system used was a rhodium complex. Then, IFP has been working with rhodium [7], then with nickel and cobalt [8] complexes using nitrogenous ligands. Several isomers can be obtained according to the catalyst system used. For instance, with a catalyst also able to isomerize the conjugated double bonds, a second or third addition of ethylene is made possible as shown in *figure 3*.
With cobalt-based catalyst the selectivity leads to mono-addition products while the nickel catalytic system produces di-addition products and oligomerization of ethylene.
Recently, a new catalytic system [9] has been developed containing a soluble iron salt such as acetylacetonate, octoate or oleate salt, a nitrogen ligand and a reducing agent. Nitrogen ligands are compounds of the family of the diimine. Their general formula is reported in *figure 4*.
With these diimines a total or a partial substitution is obtained with methyl, isopropyl or butyl radicals *(figure 4)*. The 2,3 bis [2,6-dimethylphenyl(imino)butane] is an example of diimine which gives good results. The reducing agent used is the TEA (triethylaluminium).
As an example, the typical molar ratio Fe/Ligand/TEA is respectively 1/1.1/15 and the molar ratio of Fe/Conj-SOME is 1/630. The catalytic complex (Fe/diimine) can be prepared in solution in the conjugated SOME.

At 80 °C under 3 MPa of ethylene the conversion yields in branched methyl esters are respectively 80 % (wt) after 1 hr and 97 % (wt) after 2 hrs. The selectivity in mono-addition products is higher than 95 % (wt). With this catalytic system ethylene does not polymerize.

Hydrogenation

Total hydrogenation is required to improve thermal stability of mixture of methyl esters. This stage can be operated without eliminating the catalyst of codimerization. After codimerization and depressurization a commercial fat-hydrogenation catalyst (25 % by weight of nickel divided particles in stearine) is added.

The hydrogen pressure in the reactor is maintained at 1 MPa during the first hour to limit the heat generation and then increased to 3 MPa. The hydrogenation is completed after 5 hours at a temperature of 200 °C. The composition of the product is reported in *table I*.

Table I. *Composition of the synthesized products.*

Fatty acids methyl esters	**Sunflower methyl esters**	**Conjugated methyl esters**	**Branched methyl estes**	**After hydrogenation**
palmitic	6.3	6.3	6.1	6.1
stearic	3.7	3.7	3.5	32.9
oleic	29	29	28.6	
linoleic	61	0.6	0.6	
S conjugated isomers		60.4		
mono-addition			59.1 (insaturated)	59 (saturated)
di-addition			1	2

Elimination of catalysts

In the mixture containing both catalysts of codimerization and hydrogenation (iron and nickel) the nickel particles are first eliminated by filtration then the soluble iron complex has to be treated by an aqueous solution of sulfuric acid to convert iron, aluminum and eventually soaps of nickel in sulfate salts soluble in the aqueous phase. The recovered product is then washed with fresh water and vacuum-dried. At the end of this stage, the mixture is composed of linear saturated and branched saturated methyl esters.

Crystallization stages

The difference between the melting points of linear and branched methyl esters allows their separation by crystallization. In order to get a good cold behaviour of the product, the concentration of linear methyl esters must be reduced to a value lower than 5 % (wt). This requires to perform the crystallization in two steps, i.e. one at 5 °C and the second at – 30 °C. These operations are performed in an ethanol phase. After the second filtration at – 30 °C, ethanol is removed by distillation.
The composition of filtrates after 1 and 2 stages of crystallization is reported in *table II*. The global yield of conversion of SOME into ethylstearate methyl esters is about 57-58 % (wt).

Table II. *Saturated methyl esters distribution after 1 and 2 stages of crystallization.*

Fatty acids methyl esters	**Hydrogenated product**	**Crystallization – 5 °C**	**Crystallization – 30 °C**
palmitic	6.1	3.2	2
stearic	32.9	13.7	0.8
total branched products	61	83.1	97.2

Trimethylolpropane esters

TMP is a well-known neopentylpolyol used in lubrication fields [10].
Conventional homogeneous catalysts like tin salts, alcoholates of alkalis, on tetra isopropyl titanium may be selected. Tin dibutyl oxide at a concentration of 0.05 % (wt) is used as a catalyst in the reactional mixture.
The conditions of the reaction are the following :
– Branched methyl esters/TMP-ratio : 3.1/1
– Temperature : 200-220 °C
– Reaction time : 5 hrs
A two-step reaction is performed :
– The first at atmospheric pressure at 200 °C, and the second under vacuum (10 mbar) up to 220 °C.
The methanol is continuously recovered in a condenser. The catalyst (tin salts) are removed by an ion-exchanger treatment. Conversion yields in triesters of TMP are higher than 98.95 % (wt) and the remaining branched methyl esters are less than 1.05 %. Hydroxyl and acidic index are respectively lower than 2 and 0.2. This new product is compared with some other TMP esters *(table III)*.

Table III. *Physical characteristics of the different lubricant bases.*

Products	**Cloud point (°C)**	**Pour point (°C)**	**TGA § (°C)**	**Viscosity 40 °C (mm^2/s)**	**Viscosity 100 °C (mm^2/s)**	**V.I.***

Methyl ethyl-stearate ***new synthesis***	– 11	– 33	205	6.8	2.2	140
Trioleate of TMP *from oleic sunflower oil*	– 5	– 15	305	48.5	10.8	221
Triethylstearate of TMP ***new synthesis***	– 35	< 53	340	92.7	14	155
Triisostearate of TMP *from commercial isostearic acid methyl esters*	– 33	– 33	290	103	13.5	130

[§]TGA : thermogravimetry under argon ; [*] V.I. : Viscosity Index

This lubricant base coming from ethyl stearate methyl esters and TMP has very interesting physical and rheological characteristics with a viscosity index higher than 150 and noteworthy properties of thermal stability and cold behaviors often higher than the commercial products.

Conclusion

This new synthesis of branched fatty acids methyl esters from vegetable oils has been largely optimized and good conversion yields have been achieved. The chemical structures of the synthesis product made up of a limited number of isomers are well-known. After transesterification with TMP this product behaves as an excellent lubricant. This could be a new way of developing vegetable oils which are renewable feedstocks.

When compared with isostearic acids whose production is totally dependent upon dimer acids manufacturing, the possibility to synthesize a lubricant base according to lubricant request without any constraint presents an advantage. Other fields of applications can be considered, in particular detergency where the soaps of branched fatty acids have noteworthy foaming, antistatic and emulsifying properties. The cosmetic industry can be also considered.

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Illustrations

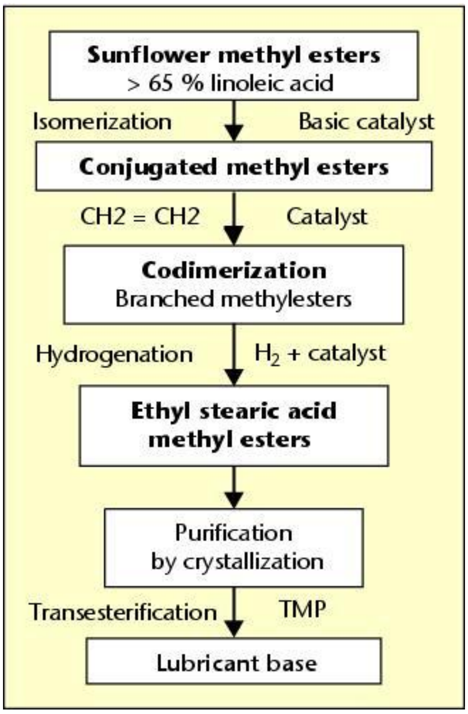

Figure 1. *Logical diagram of different stages.*

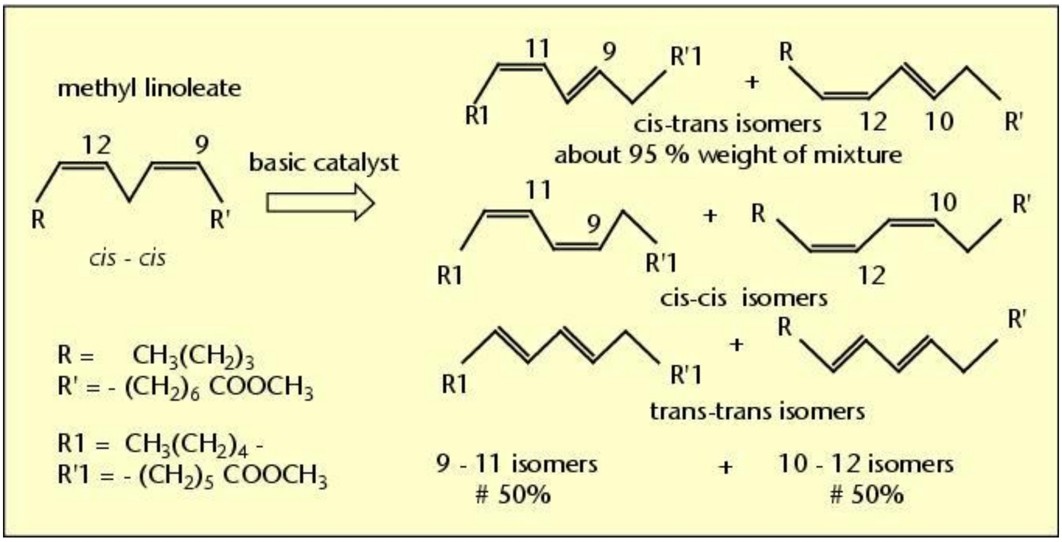

Figure 2. *Conjugated products-different isomers.*

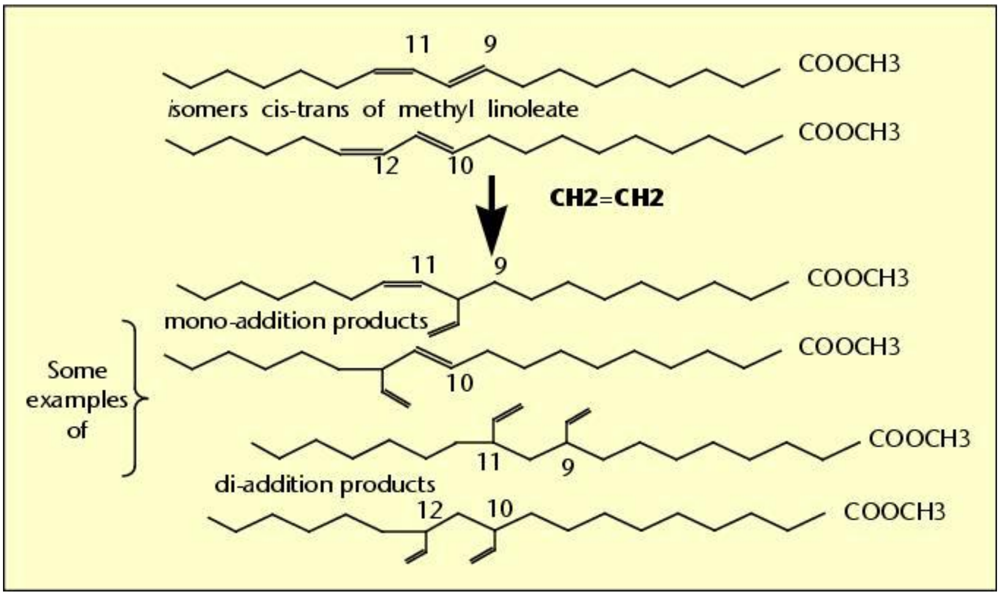

Figure 3. *Products of the codimerization reaction.*

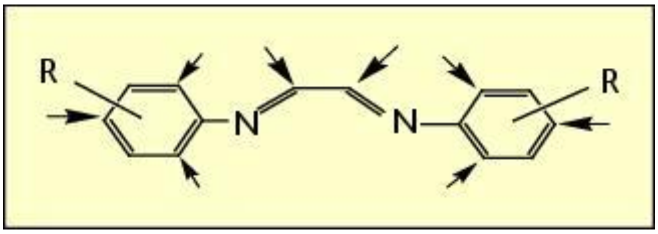

Figure 4. *Formula of nitrogen ligand.*