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Formation of conjugated double bonds in soybean oil with iodine as a catalyst

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Abstract: A method for the iodine-catalyzed formation of conjugated double bonds in soybean oil was developed, and the conjugated product was analyzed by UV, IR and ^{1}H-NMR. The results indicated that the optimal conditions for the isomerisation included a temperature of 180 °C, a catalyst loading of 0.5 mass % and a reaction time of 3 h. Under these conditions, the concentration of conjugated linoleum acid was 1.51 mol L^{-1} and the CLNA concentration reached 0.225 mol L^{-1} with a conversion rate of 99.9 %. The reaction predominantly produced *trans–trans*, *trans–cis* and *cis–trans* isomers. It was also revealed that the isomerisation of linolenic acid was much faster than that of linoleic acid. The method possessed the advantages of a short procedure, a high conversion rate, and no conversion into methyl esters of the raw material and it is an environmentally friendly technology that does not require the use solvents.

Keywords: soybean oil; conjugation; iodine; linoleic acid; linolenic acid.

INTRODUCTION

For a long time, petroleum has been used as a raw material of chemicals. However, due to the exhaustion of petroleum resources, alternative feedstocks must be found. Agricultural-based chemicals, as one of the most attractive alternatives, have gained much attention during the last few years. Vegetable oils are easily utilized because of their unsaturated double bonds and are sustainable environmentally friendly chemical feedstocks.

Conjugated vegetable oils have found their way into many industrial applications because of their improved drying property.[1–5] In recent years, the physiological functions of the conjugated linoleic acid (CLA) were identified, and studies on the formation of conjugated double bonds in oils or fatty acids have become a major focus of the international chemistry community. Over the past

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few decades, there have been numerous reports on the preparation of conjugated fatty acids and oils.[6–16] Dejarlais *et al.* found that the isomerisation of methyl esters affording conjugated double bonds were much faster than those of glycosides using the sodium salt of dimethyl sulfoxide as the catalyst.[15] Larock *et al.* prepared conjugated oils and fatty acids with homogeneous transition metals as catalysts.[9] Basu and Kasar described an isomerization method of safflower oil and methyl linoleate using cationic rhodium complexes as catalysts.[12] Radlove *et al.* performed a nickel–carbon catalyst method that could reach yields of 30–45 % in 3–6 h at 170 °C.[16] They also mentioned that some investigators found that sulfur dioxide could be used as an isomerisation catalyst for linseed and soybean oils under certain conditions. Simakova *et al.* primarily focused on the development of heterogeneous catalytic approaches.[17] Many of these methods have drawbacks, including being difficult to scale-up and having poor product yields, unwanted side reactions, high catalyst costs, the requirement of pressure, and long reaction times.

Iodine is inexpensive and non-toxic. In recent years, iodine has been used as a catalyst for various organic reactions, including isomerization.[18–22] There have also been reports concerning oil isomerization affording conjugated double bonds with iodine as the catalyst. Gangidi[22] prepared CLA isomers from soybean oil by photo-isomerization of linoleic acid with the help of iodine within the temperature range 35–40 °C under irradiation from a mercury lamp for 120 h. Jain and Proctor[23,24] obtained CLA-rich soybean oil also by a photochemical reaction with iodine as the catalyst, maintaining the oil temperature between 22 and 25 °C. However, photochemical methods have common shortcomings of low reaction rates, long reaction times and low yields. They are also not easy to scale-up to an industrial level.

For these reasons, the main purpose of this work was to develop an efficient procedure for oil isomerization affording conjugated double bonds using iodine as the catalyst. The new method has a high conversion rate, short reaction time, and is easy to operate under industrial conditions. Additionally, it is an environmentally sensitive technology that does not require the use of organic solvents.

MATERIALS AND METHODS

Materials and equipment

Transgenic soybean oil was purchased from the Cofco Corporation. The mass fractions of linoleic acid (LA) and linolenic acid (LNA) determined by GC were 50.88 and 6.86 %, respectively. Analytical grade iodine was purchased from Tianjin Zhongxing Chemical Reagent Factory. Analytical grade hexane was purchased from Sinopharm Chemical Reagent Co., Ltd. The standard products of CLA were purchased from Nu-Chek-Prep Inc. Nitrogen (99.99 % purity) was obtained from Guangzhou Chun Jiang Industrial Gas Co., Ltd. All other chemical reagents were analytical grade.

The following instruments were used in this study: a UV spectrophotometer (2550, Shimadzu, Japan), a Fourier transform infrared spectrometer (Spectrum 100, PerkinElmer, Inc., USA), a magnetic agitator with heat collection and temperature control (DF-101S, Gongyi Yingyu Instrument Factory, China), and a superconducting NMR spectrometer (Avance AV400, Bruker, Germany).

Isomerisation reaction

For the isomerisation reaction, 100 g of soybean oil and a specified amount of iodine (in solid form) were added to a 250 mL three-necked round-bottom flask fitted with a thermometer, a reflux condenser, and a high purity nitrogen gas delivery tube. The mixture was purged with nitrogen for ≈10 min to remove the oxygen, and the flask was lowered into a silicone oil bath, heated and stirred magnetically under the protection of nitrogen. The reactor vessel was covered with protective foil. The reaction products were then cooled to room temperature and washed 3 times with 10–15 mL of 0.2 M sodium thiosulfate and of distilled water. The sample was obtained after drying with anhydrous sodium sulfate.

Determination of the CLA and the conjugated linolenic acid (CLNA) concentrations

Standard CLA was dissolved in *n*-hexane to prepare a series of standard solutions that ranged from 4 to 14 mg L^{-1} in concentration. Using *n*-hexane as a reference solvent, the maximum absorbance at 234 nm was measured to obtain a standard curve. According to the curve, an equation was determined: $A = 0.1047c - 0.046$, $R^2 = 0.9992$, where A is the absorbance and c is the concentration of CLA in mg L^{-1}. The product was diluted with *n*-hexane, and the absorbance was measured at 234 nm. If the absorbance was greater than 1.0, the sample was diluted further. The raw material was also diluted and determined to be the product. The difference of the two absorbencies was used to calculate the CLA concentrations according to the regression equation. The CLNA concentrations were determined according to the IUPAC method.[25] The percentage conversion was also estimated from the ^{1}H-NMR spectra using the glycerol backbone peaks at chemical shifts of 4.15 and 4.30 ppm, according to the literature.[26]

Removal of I_2

Sodium thiosulfate,[27] granulated charcoal and starch[26] are reported to remove iodine in the presence of hexane. Sodium thiosulfate was adopted in this study, owing to its capability to remove iodine quickly.[27] Titrimetry was adopted to determine the optimal sodium thiosulfate concentration in the eluate. Thus, the residual iodine in the oil could be estimated. The results showed that the residual iodine in oil was not more than 0.2 % after washing three times with ≈10 mL 0.1 M sodium thiosulfate. Another method to remove iodine, which utilized the volatility of iodine, was performed at 180 °C under reduced pressure for 1 h. Condensate iodine remained in the flask mouth. However, the dark color of the oil manifested the poor effect. The third method was to wash with a potassium iodide–water solution, due to its high iodine solubility. Determination of the eluate showed that no iodine was removed from the oil after washing three times with ≈10 mL 0.1 mol L^{-1} potassium iodide–water solution. To remove iodine as much as possible, 0.2 M sodium thiosulfate was used. A slightly yellow oil was obtained by washing three times with 10–15 mL.

Spectroscopy analysis

The structures of the products were characterized by UV–Vis, FTIR and NMR analyses. For the UV analysis, approximately 0.1 g of the raw material and the product were diluted with *n*-hexane by a factor of approximately 5000. The samples were scanned from 210–300 nm, using *n*-hexane as the reference. For the FTIR analysis, the raw material and product were spread onto potassium bromide tablets. The samples were scanned from 4000–400 cm^{-1}. For the nuclear magnetic resonance spectroscopy analysis, a superconducting pulse Fourier transform NMR spectrometer was utilized. $CDCl_3$ was used as the solvent, the magnet was 400 MHz, the temperature was 45 °C, and the chemical shift of chloroform, $\delta = 7.27$ ppm, was used as the reference.

RESULTS AND DISCUSSION

Effect of the single factors on the isomerisation reaction

The effect of the catalyst loading on the concentration of the conjugated oil is shown in Fig. 1. Thus, the concentration of the conjugated oil first increased with increasing catalyst loading concentrations up to 0.5 mass %. At a catalyst usage of 0.5 mass %, the concentrations of CLA and CLNA were 1.05 and 0.167 mol L^{-1}, respectively. These values did not increase appreciably at higher catalyst loadings. The product yield increased due to the higher collision probability between the catalyst and the reactant as the catalyst dosage was increased. However, larger amounts of catalyst would lead to higher costs, and the color of the product was deeper at increased iodine usage.

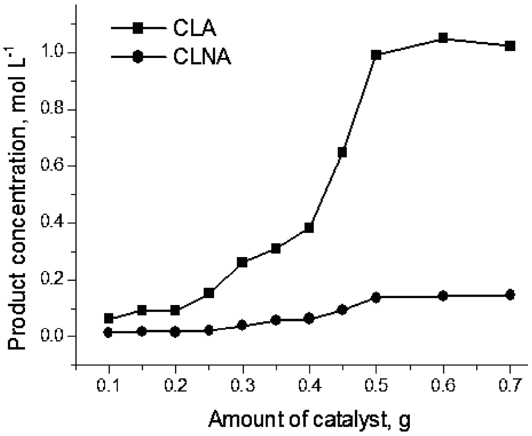

Fig. 1. Effect of catalyst loading on conjugation reaction (at 16 °C for 3 h).

The effect of temperature on concentration of the conjugated oils is shown in Fig. 2. As can be seen, the concentration of the conjugated oils was very low when the temperature was 80 °C, but the product yield increased at higher temperatures. The concentration of CLA increased to its maximum of 1.42 mol L^{-1} at a temperature of 180 °C. The concentration of CLNA reached 0.225 mol L^{-1} when the temperature was 130 °C, corresponding to a conversion of 99.9 %, and then decreased at higher temperatures. Theoretically, at higher temperatures, the number of activated molecules per unit volume increased, the viscosity of the system decreased, and the collision opportunities between the catalyst and reactant increased, all of which served to accelerate the reaction.

The effect of the reaction time on the conjugation reaction is shown in Fig. 3, from which it can be seen that the concentration of CLA and CLNA first increased and then decreased with increasing reaction time. The concentration of CLA first increased remarkably with increasing time, but the product yield began to decrease at reaction times greater than 3 h; therefore, it is important to control the reaction time strictly according to the conjugated products required. However, the concentration of CLNA reached a maximum 0.204 mol L^{-1} at 1.5 h. It should be noted that the mass fraction of LNA in the raw material was only 6.88 %, which was much lower than that of LA at 50.88 %. Therefore, to obtain the same conversion ratio, the former reaction time was relatively shorter than the latter one.

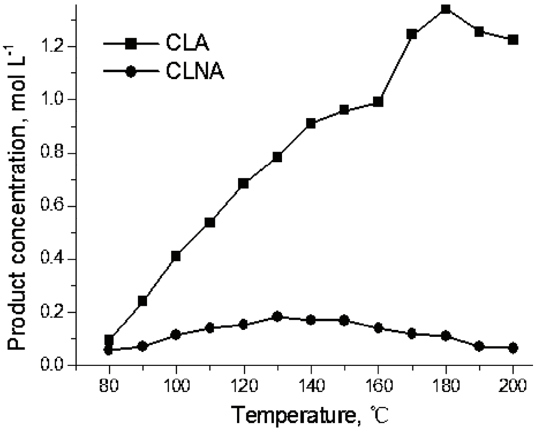

Fig. 2. Effect of temperature on conjugation reaction (with a catalyst usage 0.5 % for 3 h).

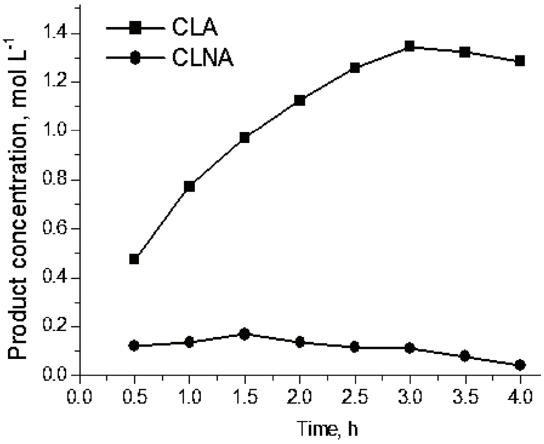

Fig. 3. Effect of reaction time on conjugation reaction (with a catalyst usage 0.5 % at 180 °C).

Orthogonal experiment

Based on the single factor experiments described above, an orthogonal test was adopted to determine the optimal conditions, using the concentration of CLA as the index. As shown in Table I, under the tested conditions of the experiments, the most important factor was the reaction temperature. The optimal conditions were a temperature of 180 °C, a catalyst loading of 0.5 mass % and a reaction time of 3 h. Reproducible tests under the optimal conditions showed that the product concentration was 1.51 mol L^{-1}, with a conversion rate of approximately 92 %.

TABLE I. Results of orthogonal experiments

Serial No.	Catalyst amount, %	Temperature, °C	Time, h	Product concentration, mol L^{-1}
1	0.55	170	2.5	1.225
2	0.55	180	3	1.497
3	0.55	190	3.5	0.945
4	0.50	170	3	1.318
5	0.50	180	3.5	1.399
6	0.50	190	2.5	1.127
7	0.45	170	3.5	1.321
8	0.45	180	2.5	1.290
9	0.45	190	3	1.176
k_1	1.222	1.288	1.214	
k_2	1.281	1.395	1.330	
k_3	1.262	1.082	1.222	
R	0.059	0.313	0.116	

A photochemical method for obtaining CLA-rich soybean oil in the presence of iodine as a sensitizer, as reported in literature,[22–24] has the advantages of using a temperature of no more than 40 °C and an iodine loading of less than 0.25 %. However, the reaction rate is very slow. Irradiating soybean oil for 240 h with 0.25 % iodine gave a 54 % conversion of LA to CLA.[23] Other reports indicated that using a similar approach, soybean oil conjugation could be performed rapidly with a 500 W projector lamp,[26] and a pilot-scale apparatus capable of yielding 20 % CLA in 12 h.[28] However, this method is difficult to scale up to an industrial level. Moreover, some methods require large quantities of an organic solvent[26] or a complicated pre-treatment, such as conversion into methyl esters.[29] Compared with a photochemical method, in view of industrialization, the method performed in the present study seems to be more favorable, resulting in a conversion of more than 90 % in 3 hours.

Comparison of isomerisation of LA and LNA

The conjugation of LA and LNA was assumed to be completed in one-step and described by a first-order reaction. The data in Fig. 3 prior to 90 min was used to study the kinetics of the reaction. Thus, the rate curve and equation $\ln (c_0/c) = kt$ were obtained from these data, where c is the concentration of LA or LNA at any time t, c_0 is the initial concentration and k is the rate constant. As shown in Fig. 4, the rate constant of LNA conjugation was much larger than that of LA; the conjugation of LNA was clearly faster than that of LA. In addition, the concentration of LNA was low in the raw material and therefore, it was quickly consumed in the reaction. According to Figs. 1–3, in its conjugation, LNA was completely consumed within 3 h at 130 °C using 0.5 mass % iodine and a reaction time of 3 h. Under these conditions, the CLA yield was not high. Figure 4 also shows that the original hypothesis of the LA conjugation was correct as illustrated by its perfect fitting curve. However, the fitting curve for LNA isomerisation was not appropriate. It was not clear that the three double bonds of LNA were to form a di- or triene conjugation in the first step. Furthermore, when the reaction continued after exhaustion of LNA, as shown in Figs. 1–3, the concentration of CLNA in the system was gradually reduced. Further study on this phenomenon and its mechanism of isomerisation is required.

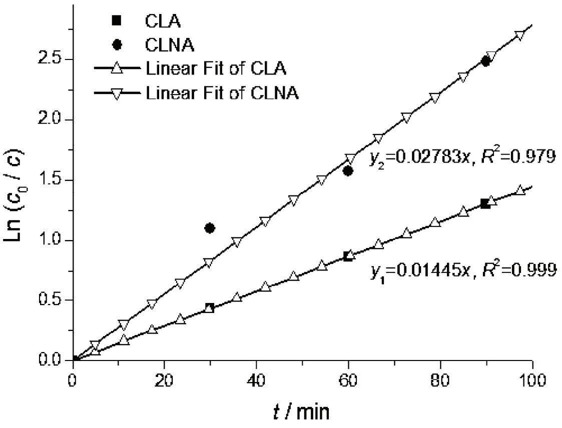

Fig. 4 Curve of ln (c_0/c) as function of time.

Structural characterization of the product

Ultraviolet absorbance analysis. The UV absorption spectra of the raw soybean oil (A) and the products formed at different temperatures (B, C and D) are shown in Fig. 5. The absorption peaks at 234 and 268 nm correspond to the maximum of the absorption peaks for CLA and CLNA, respectively. As seen from the plots, the spectrum of soybean oil did not contain any absorption peaks between 220–300 nm. Therefore, soybean oil does not contain a conjugated structure. The spectra B, C and D indicated that conjugation has been formed. In addition, as the temperature was increased from 100 to 180°C, the absorbance of the product at 234 nm increased, corresponding to the increase in the CLA yield. However, the absorbance at 268 nm first increased and then decreased, indicating that the concentration of CLNA also first increased but then decreased with increasing temperature. This result was consistent with the phenomenon described above.

Infrared spectrum analysis. The infrared absorption spectra of the raw material (A) and the products (B) are shown in Fig. 6. As shown in the spectra, the raw oil did not produce any characteristic absorption peak from 900–1000 cm^{-1}, while the reaction product produced very significant peaks at 986, 967 and 948 cm^{-1}. The peak at 986 cm^{-1} revealed the presence of *trans–trans* dienes,[30] the 986 and 948 cm^{-1} peaks revealed *cis–trans* or *trans–cis* dienes,[11] and the 967 cm^{-1} peak corresponded to *trans* monoenes.[30]

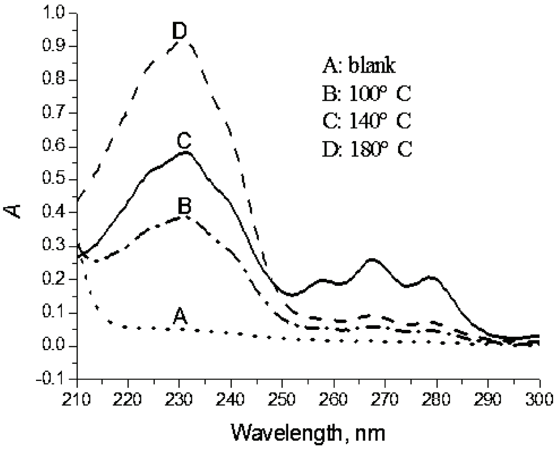

Fig. 5. UV absorption spectrum of raw soybean oil (A) and reaction products (B, C, D).

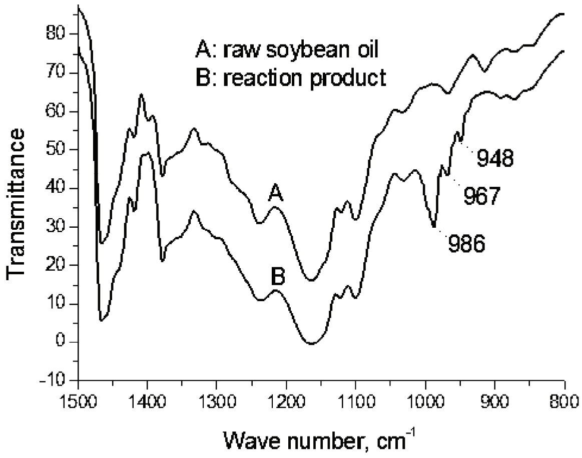

Fig. 6. IR absorption spectra of the raw soybean oil (A) and the reaction products (B).

Proton nuclear magnetic resonance analysis. The ^{1}H-NMR spectra of raw soybean oil and the reaction products after formation of conjugation are shown in Fig. 7a and b, respectively. The degree of unsaturation and information regarding the *cis–trans* isomers of the conjugated oil were determined according to the chemical shifts and coupling constants of the protons from the spectra.[31] Peaks at approximately 5.30 ppm reveal non-conjugated vinylic protons, and they shift to

5.30–6.29 ppm after conjugation.[9] The chemical shifts of interest in spectrum a included $\delta = 5.31$ ppm, –CH=CH–; $\delta = 2.72$ ppm, =CH–CH_2–CH= and $\delta = 2.08$ ppm, =CH–CH_2–, and spectrum b included $\delta = 6.24$ ppm, *Z*-=CH–C*H*=CH; $\delta =$ = 5.92 ppm, *E*-=CH–CH=CH; $\delta = 5.63$ ppm, *E*-=CH–CH=CH; $\delta = 5.52$ ppm, *E*-=CH–CH=CH and $\delta = 5.33$ ppm, *Z*-=CH–C*H*=CH. From the integration of these peaks, the percent conjugation could be estimated. It was evident that iodine-catalyzed isomerization affording conjugated double bonds had occurred. The main composition of the conjugated oil included *trans–trans, trans–cis* and *cis–trans* isomers.

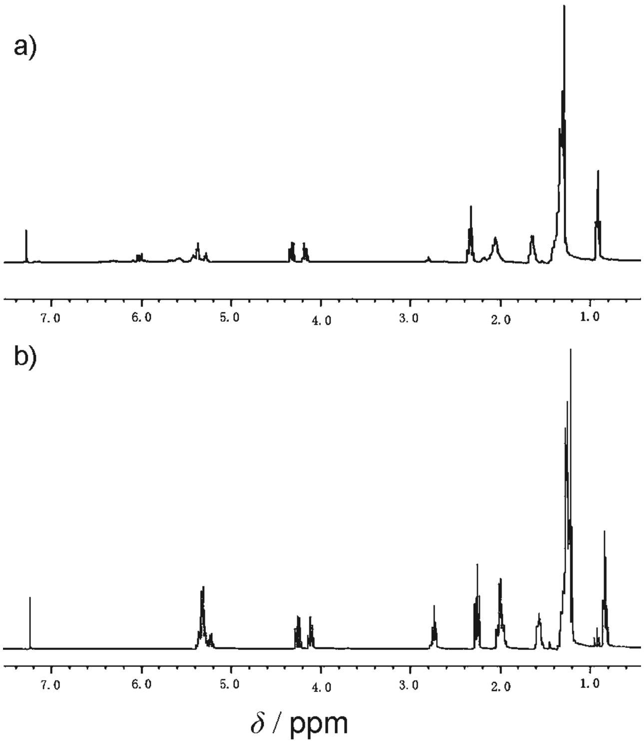

Fig. 7. ^{1}H-NMR spectra of raw soybean oil (a) and reaction products (b).

CONCLUSIONS

The iodine-catalyzed soybean oil isomerization affording conjugated double bonds possesses the advantages of a short procedure, a high conversion rate, no conversion into methyl esters, and easy transition to industrialization. Additionally, it is an environmentally friendly technology not requiring solvents. The optimal conditions included a temperature of 180 °C, a catalyst loading of 0.5 mass %, and a reaction time of 3 h. Under these conditions, the concentration of CLA and percent conversion were 1.51 mol L^{-1} and 92 %, respectively. CLNA reached 0.225 mol L^{-1} with a conversion of 99.9 % when the temperature was 130 °C, at a catalyst loading of 0.5 wt. %.

The main configurations of CLA and CLNA in the final products included *trans–trans, trans–cis* and *cis–trans* isomers, based on UV, IR and ^{1}H-NMR analysis. However, the reaction mechanism, especially the decrease in the concentration of CLNA, requires further study.

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ИЗВОД

ГРАЂЕЊЕ КОНЈУГОВАНИХ ДВОСТРУКИХ ВЕЗА У СОЈИНОМ УЉУ У ПРИСУСТВУ ЈОДА КАО КАТАЛИЗАТОРА

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Развијен је поступак изомеризације сојиног уља у присуству јода као катализатора, а добијени конјуговани производ је анализиран методама UV, IR и ^{1}H-NMR. Оптимални услови за изомеризацију су били следећи: температура 180 °C, почетна концентрација катализатора 0,5 мас. % и реакционо време 3 h. Под тим условима је концентрација конјуговане линолне киселине била 1,51 mol L^{-1}, уз 92 % конверзије. CLNA је достигла концентрацију од 0,225 mol L^{-1} при температури од 130 °C, 0,5 мас. % катализатора и 3 h реакције, а степен конверзије је био 99,9 %. Током реакције су претежно настали *trans–trans*, *trans–cis* и *cis–trans* изомери, али је при истој температури растао удео *trans–trans* изомера са временом реакције. Такође, брзина изомеризације линолеинске киселине је била знатно већа него линолне. Предност описаног поступка је у кратком времену трајања, високом степену конверзије, одсуству превођења у метил естре полазног материјала и у еколошкој чистоћи, пошто се не користе растварачи.

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