

# The Synthesis of Allyl-3-Cyclohexylpropionate

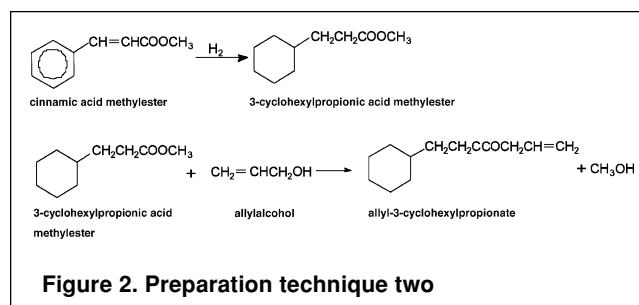
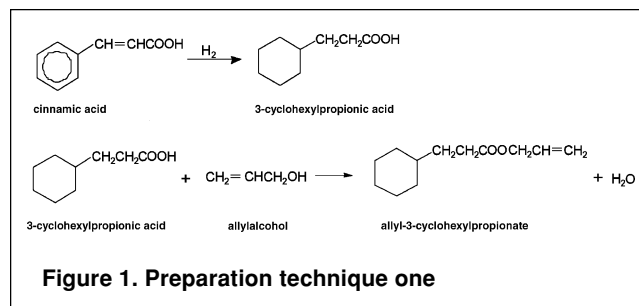
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This article discusses the synthesis of allyl-3-cyclohexylpropionate, which includes cinnamic acid, its ester and/or its methylester, hydrogenation and esterification, transesterification, of hydrogenation products. The hydrogenation kinetics of both initial substances using platinum (Pt/C), palladium (Pd/C), and ruthenium on active carbon as catalysts (Ru/C) were studied. Consequently, 3-cyclohexylpropionic acid was esterified using p-toluenesulfonic acid as the catalyst. The reaction equilibrium was shifted with the elimination of the resulting water in a hexane-water azeotrope form (formation, mold). Next, 3-cyclohexylpropionic acid methylester was transesterified with allyl alcohol and catalyzed with carbonate calcium. The reaction equilibrium was shifted with the elimination of the resulting methanol in a cyclohexane-methanol azeotrope form. Based on the previous experiments, a procedure for preparation of allyl-3-cyclohexylpropionate was chosen, which included cinnamic acid methylester hydrogenation and 3-cyclohexylpropionic acid methylester transesterification with allyl alcohol.

## Theoretical

Allyl-3-cyclohexylpropionate is an important compound for preparation of perfume compositions and taste complexes of the pineapple type. This ester<sup>1</sup> cannot be found in nature. It has a strong fruity fragrance and sweet fruity taste resembling pineapple. It is used as a major carrier of a fruity essence in pineapple imitations and interesting modifier in strawberry, raspberry and other imitations.

For the preparation of allyl-3-cyclohexylpropionate, 3-cyclohexylpropionic acid, allyl alcohol or allylchloride are usually used as the starting material. One of the less-frequently described preparation techniques of 3-cyclohexylpropionate is the reaction of allyl alcohol with the aqueous solution of either the sodium or calcium salt of a pertinent acid in the presence of sodium iodide and  $\text{Et}_3\text{N}(\text{CH}_2\text{Ph})\text{Cl}$  as the phase-transfer catalyst. Another



preparation technique<sup>3</sup> of allyl-3-cyclohexylpropionate is the reaction of 4-vinyl-1-cyclohexene with carbon dioxide in methanol in the presence of  $(\text{CO})_5\text{CO}_2$ -pyridine complex, followed with hydrogenation and re-esterification with allyl alcohol of the attained methyl-3-cyclohexylpropionate. Literature provides preparation techniques of the mentioned ester initiated with metacrylate<sup>3</sup> and benzaldehyde<sup>3</sup>.

The objective of this work was to assess two preparation methods of allyl-3-cyclohexylpropionate (Figure 1 and Figure 2).

In the first technique (Figure 1), cinnamic acid was hydrogenated, producing 3-cyclohexylpropionic acid. The product was consequently esterified with allyl alcohol. In the second technique (Figure 2), cinnamic acid methylester was hydrogenated, producing 3-cyclohexylpropionic

acid methylester, which was transesterified with allyl alcohol. The literature pertaining to this matter is very poor. The described hydrogenations of cinnamic acid were carried out in various solvents using catalysts with the bases of Ni, Ir, Pt, Pd and Pd-Rh. Hydrogenation of aromatic carboxylic acids using polycarboxylic acid-Pt or Rh catalytic systems is also described.<sup>10</sup> In the literature, there is no similar description to our methods of complete allyl-3-cyclohexylpropionate synthesis, which we studied.

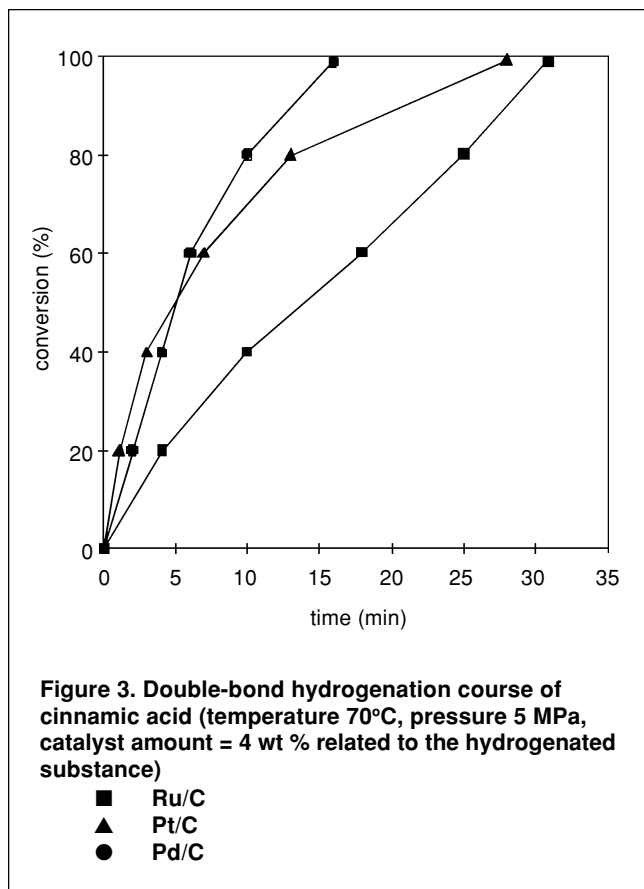
### Experiment

The following chemicals were used in our research: cinnamic acid, cinnamic acid methylester (from the reserves of the Institute of Organic Technology), 3-cyclohexylpropionic acid (Chemische Werke Hüls AG), allyl alcohol, methanol, p-toluensulphonic acid, sodium carbonate, calcium carbonate (Lachema Brno), hexane, cyclohexane (Penta Chrudim), dekane (Aldrich), and hydrogen (Linde, Technoplyn). The following catalysts were also employed: 4% Pd/C (Sala), 5% Ru/C (Johnson & Matthey), and 5% Pt/C (Doducco Kat. GmbH).

**Operating procedure:** The hydrogenation of cinnamic acid and cinnamic acid methylester, respectively, was carried out in an autoclave with a volume of 250 ml. The appropriate catalyst (0.6 g) and the solution of acid (15.0g/100ml) or methylester were inserted into a clean dry autoclave. The autoclave was closed and purged with hydrogen. The pressure of 2MPa was set and the autoclave was heated to the required temperature (70, 160°C). After reaching this temperature, the hydrogen pressure was raised to the chosen value (5, 8 MPa). The hydrogenation was initiated with the start of stirring. The reaction course was monitored through the time dependence of the hydrogen consumption. The temperature was kept at a constant value ( $\pm 2^\circ$  C). The reaction was terminated when the reaction rate significantly decreased. Then the reaction mixture was cooled, the catalyst was separated by filtration and, after the elimination of methanol, the mixture was processed with vacuum distillation.

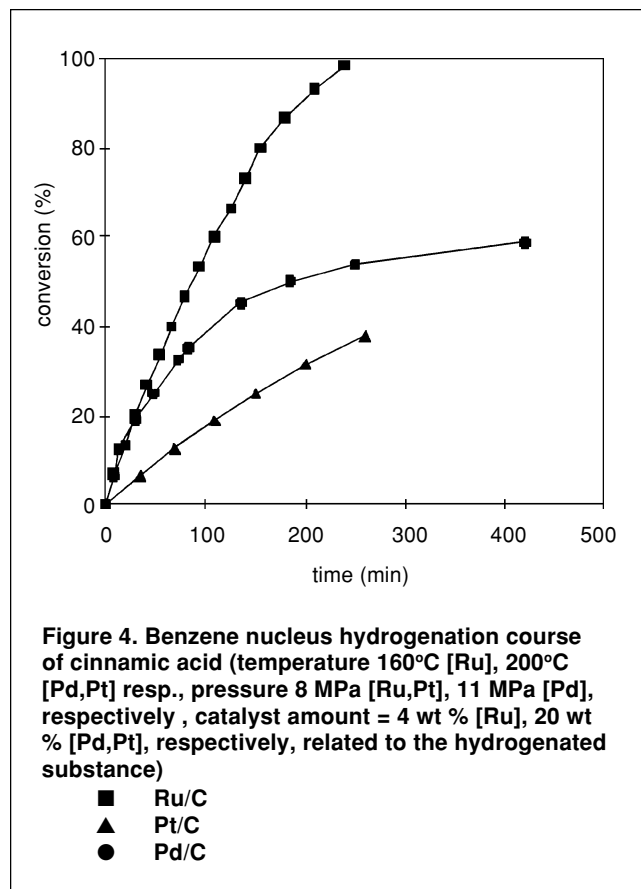
The esterification of 3-cyclohexylpropionic acid was carried out in a three-necked flask equipped with a thermometer, a needle for sample withdrawals and attachment for azeotropic distillation. 3-(cyclohexylpropionic) acid (10 g), allyl alcohol in 5-molar excess (18.6 g), p-toluensulfonic acid (catalyst, 0.3 g), decane (internal standard for GLC, 3.0 g), and hexane (15.0 g) were inserted into the flask. The reaction mixture samples were withdrawn at appropriate time intervals, then, after being analyzed with chromatography, cooled. After the reaction termination, the reaction mixture was cooled, extracted once with water and twice with a sodium carbonate solution. The organic layer was dried using sodium carbonate and, after the drying agent was separated with filtration, it was processed first with atmospheric later with vacuum distillation.

The 3-cyclohexylpropionic acid methylester transes-



terification with allyl alcohol was carried out in a three-necked flask equipped with a thermometer, a needle for sample withdrawals and a 20-cm-long packed column. Methyl ester (10 g), allyl alcohol in 5-molar excess (17.1 g), decane (internal standard for GLC, 2.0g), and cyclohexane (10.0 g) were inserted into the flask. The mixture was heated up to its boiling point (82-88° C) and calcium carbonate was added (catalyst, 1.0 g). The samples were withdrawn at appropriate time intervals and, after being cooled, analyzed with chromatography. After the reaction termination, the catalyst was separated using filtration. The mixture was processed first with atmospheric and vacuum distillation.

**Analytical methods:** The chromatographic analysis of the substances contained in the reaction mixture during the hydrogenation was carried out by a Hewlett Packard 5890 Series II Plus chromatograph with flame-ionization detector and a Data Monitor II chromatographic integrating data station. For the individual substance identification, a HP-20M capillary column (50 m x 0.32 mm x 0.30 mm). The chromatographic analysis of the substances contained in the reaction mixture during the esterification, were carried out in a Chrom 5 chromatograph with flame-ionization detector. A Shimadzu C- R3A Integrator was attached to the device. A glass column with the length 2.5 m with an internal diameter of 2.5mm filled with 15% SE 31 in Chromaton NAW-DMCS was used for the identifica-



tion of the individual substances. The chromatograms were, in the case of the quantity analysis, evaluated using the internal standard method.

## Results and Discussion

### *The hydrogenation of cinnamic acid and its methyl ester:*

During the hydrogenation of cinnamic acid, a double-bond hydrogenation occurs; this occurs later in the benzene nucleus. Three catalysts were tested: 5% Ru/C, 5% Pt/C and 4% Pd/C. The individual hydrogenation courses are depicted in Figure 3 and Figure 4. The double-bond and benzene-nucleus hydrogenations were carried out under different conditions because the hydrogenation of the benzene nucleus was taking too slow a course and the total reaction time would have been too long. On the contrary, the double-bond hydrogenation would happen so fast that it would not be possible to record it. For the same reasons, none of the cases was carried out under constant conditions.

It was found that the palladium catalyst was, for the double-bond hydrogenation, the most active, while the more difficult benzene-nucleus hydrogenation happened to occur most easily when using the ruthenium catalyst.

As with the cinnamic acid, during the hydrogenation of the methyl ester, the double-bond hydrogenation took place before the hydrogenation of the benzene nucleus. The time dependence of the hydrogen consumption which, plotted onto a graph (Figure 5 and Figure 6), was moni-

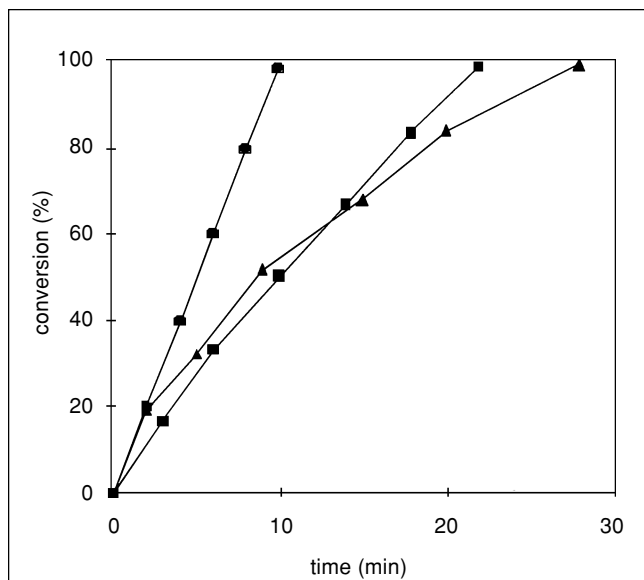


Figure 5. Double-bond hydrogenation course of cinnamic acid methylester (temperature 70°C, pressure 5 MPa, catalyst amount = 4 wt % related to the hydrogenated substance)

■ Ru/C  
▲ Pt/C  
● Pd/C

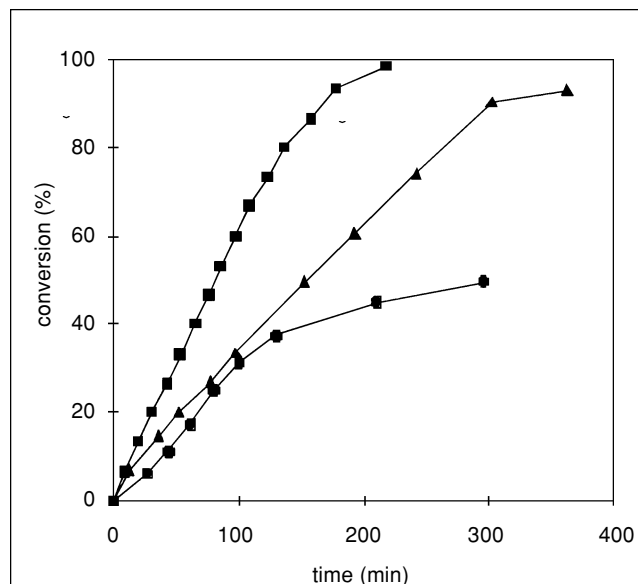


Figure 6. Benzene nucleus hydrogenation course of cinnamic acid methylester (temperature 70°C [Ru,Pt], 200°C [Pd], respectively, pressure 5 MPa [Ru,Pt], 11 MPa [Pd], respectively, catalyst amount = 4 wt % [Ru,Pt], respectively, 20 wt % [Pd] related to the hydrogenated substance)

■ Ru/C  
▲ Pt/C  
● Pd/C

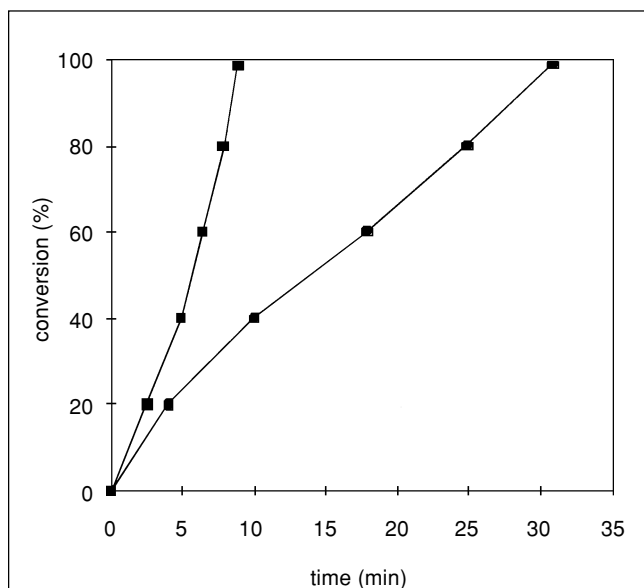


Figure 7. The comparison of cinnamic acid methylester and cinnamic acid double-bond hydrogenation (cinnamic acid - 70°C, 8 MPa, 4 wt % of catalyst related to the hydrogenated substance [Ru/C]) (cinnamic acid methylester - 70°C, 8 MPa, 4 wt % of catalyst related to the hydrogenated substance [Ru/C])

■ cinnamic acid methylester  
▲ cinnamic acid

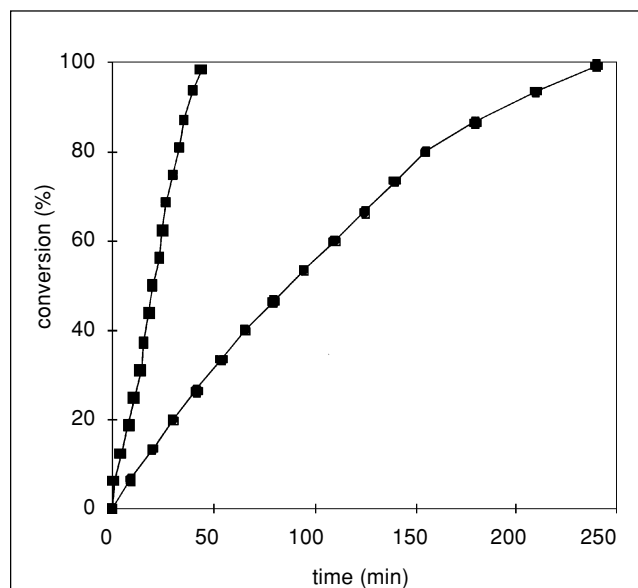


Figure 8. The comparison of cinnamic acid methylester and cinnamic acid benzene nucleus hydrogenation (cinnamic acid - 160°C, 8 MPa, 4 wt % of catalyst related to the hydrogenated substance [Ru/C]) (cinnamic acid methylester - 70°C, 8 MPa, 4 wt % of catalyst related to the hydrogenated substance [Ru/C])

■ cinnamic acid methylester  
▲ cinnamic acid

tored as well. The results concluded that the hydrogenation of cinnamic acid methylester was similar to the conclusions reached in the case of hydrogenation of cinnamic acid.

The hydrogenations of both initial substances are compared in Figure 7 and Figure 8. It is apparent that both the double-bond and the benzene-nucleus hydrogenation take place with a faster reaction rate in the case of cinnamic acid methylester than in the case of cinnamic acid.

During the hydrogenation of cinnamic acid in methanol a simultaneous esterification of the resulting 3-cyclohexylpropionic acid with methanol occurred. Thus, the final reaction mixture contained both 3-cyclohexylpropionic acid and its methylester. For further treatment, it would have been useful to separate these substances and continue with an acidic catalyzed acid esterification and a basic catalyzed acid transesterification of its methylester using allyl alcohol, respectively. Doubtless, the synthesis of allyl-3-cyclohexylpropionate initiated with cinnamic acid methylester appears to be more convenient.

***Esterification of 3-cyclohexylpropionic acid and transesterification of its methylester with allyl alcohol:***

Esterification is a typical equilibrium reaction, thus it is necessary to effectively shift its equilibrium in favor of the ester in order to achieve 100% conversion of the initial acid. Therefore, five molar excess of allyl alcohol were used. Then the reaction water was eliminated in an azeotrope form. In the beginning, the fact that water and allyl alcohol create an azeotrope was utilized. It appeared though, that an insufficient phase separation occurred and water was partially returning to the reaction mixture. For this reason hexane was used as an azeotropic agent, which showed up as acceptable. *p*-Toluensulphonic acid was used as a catalyst and the reaction was carried out at a temperature of 69-74°C.

Under the previously mentioned reaction arrangement, and given conditions, it is possible to achieve 100% conversion of the initial 3-cyclohexylpropionic acid and obtain very pure allyl-3-cyclohexylpropionate after separation.

Both the esterification and the transesterification are equilibrium reactions. For the equilibrium shift favoring the creation of allylester, 5-molar allyl alcohol excess related to molar amount of 3-cyclohexylpropionic acid methylester were used with a simultaneous strip off of the resulting methanol from the reaction mixture. Methanol was being stripped off in an azeotrope form with cyclohexane. However, when working in a larger scale, methanol could be distilled from the reaction mixture individually. The reaction course concluded with 100% conversion of the initial methylester. Calcium carbonate was used as the catalyst.

**Conclusion**

Our objective was to find the production procedure of allyl-3-cyclohexylpropionate as an important medium product for preparations of perfume compositions and taste com-

plexes of the pineapple type. From the two studied methods, the catalytic hydrogenation of cinnamic acid methylester with usage of the ruthenium catalyst, which produced 3-cyclohexylpropionic acid, showed up as more suitable. Alternatively, the transesterification with allyl alcohol could, as a further step, produce allyl-3-cyclohexylpropionate in a high conversion.

**References**

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