

# Hydrogenation of (2*E*,4*E*)-hexadienol

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## Abstract

Catalytic hydrogenation of (2*E*,4*E*)-hexadienol over Pt, Pd, Rh, Ru and Ni supported on active carbon and  $\gamma$ -alumina has been studied. In all the reactions, diverse isomers of alkenic hexenols were primarily produced, which further hydrogenated to hexanol. Various hexenals were identified in the reaction mixture as well as hexanal, hexenes and hexane. The composition of the reaction mixture depended foremost upon the type of a catalyst used and was independent on the hydrogen pressure and catalyst weight. A great number of intermediates and products was produced over palladium, platinum and rhodium catalysts. These catalysts were not selective due to desired intermediates' production. Over ruthenium catalyst, (3*E*)-hexenol and (2*E*)-hexenol were produced in higher concentrations compared to the rest of the intermediate products, and the least quantity of hexene and hexane were also produced. Regarding the production of various hexenols, the most selective catalyst was Raney nickel. When Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was used, hexenols were produced in higher concentrations, but the selectivity was not higher than with Raney nickel. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Selective hydrogenation; (2*E*,4*E*)-hexadienol; Leaf alcohols; Sorbic acid

## 1. Introduction

Catalytic hydrogenation of (2*E*,4*E*)-hexadienol can be utilized for preparation of various hexenols [1–3], from which some (so-called leaf alcohols) are important components of fruit and vegetable odors and flavors [4,5]. These are either used by themselves or utilized for carboxylic acid esterification in the perfume industry. Leaf alcohols are *trans*-2-hexenol and *cis*-3-hexenol. The indication 'leaf' is commonly used, since they occur in Nature in the green parts of almost all herbs, especially in their leaves. Of all hexenols, the title leaf alcohol is

used exclusively for these two isomers, due to their specific odors and flavor properties.

Common technological procedures [6] aiming at the synthesis of leaf alcohols are multi-step operations, fastidious of their stereospecificity, often accompanied with low yields. The majority of these technological procedures consist in a preparation of the pertinent hexynol and its subsequent selective partial catalytic hydrogenation, alternatively in its partial chemical reduction. On the other hand, there are well-known procedures, which use the 2,4-hexadienic structural unit of a readily available sorbic acid [6] for the synthesis of leaf alcohols. There exist homogenous catalysts [1–3], which selectively catalyze the 2,4-hexadienic system producing *cis*-3-hexenol. In this work, we were concerned

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with the opportunity to prepare the required hexenols using the selective heterogeneous catalytic hydrogenation of (2*E*,4*E*)-hexadienol. This work is a continuation of the preceding research on this problem [7], where methyl sorbate hydrogenation was studied.

## 2. Experimental

### 2.1. Catalysts

The following catalysts were used for the hydrogenation reactions: Pt/C (Doduco Kat.), Pd/C (Chemopetrol, Litvínov), Rh/C (DOT, ICT Prague), Ru/C (Johnson Matthey), Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Leuna Werke) and the Raney Ni (Engelhard). All the catalysts were applied in a very fine powder form. The catalysts were characterized with their elementary crystallite size (XRD 3000 P diffractometer, Rich. Seifert, Germany) and their specific surface area (BET, Pulse Chemisorb 2700, Micromeritics, USA). The properties of the catalysts used are shown in Table 1.

### 2.2. Chemicals

Sorbic acid, pure (Aroma Prague-import), methanol p.a., sulfuric acid p.a., diethyl ether p.a. and sodium hydroxide p.a. (Penta Prague), lithium aluminium hydride (DOT, ICT), hydro-

gen, grade 3.0 (Linde-Technoplyn Prague), calcium chloride (anhydrous) p.a. (Lachema Brno).

### 2.3. Analysis

The samples of the reaction mixtures withdrawn during the hydrogenation reactions and the products of the chemical reductions with LiAlH<sub>4</sub> were analyzed using gas chromatograph HP 5890 Series II Plus of the Hewlett-Packard (USA) with a flame ionization detector (FID) and the capillary column VA-WAX (60 m × 0.25 mm × 0.25 μm) of Varian (USA). The analysis was carried out using the temperature program of 80–200°C, the carrier gas pressure of  $p(\text{N}_2) = 80$  kPa, and the split ratio of 1:50. The structure of the main product of the hydrogenation, (2*E*,4*E*)-hexadienol, was verified with <sup>1</sup>H NMR and <sup>13</sup>C NMR using the instrument Bruker AMX-340 (Germany), the structure of the other compounds using GC-MS with the analytical system of Saturn 2000 of Varian.

### 2.4. Apparatus and procedure

The initial substrate for the hydrogenations, (2*E*,4*E*)-hexadienol, was prepared from sorbic acid in two steps. During the first step, sorbic acid was esterified with methanol, producing methyl sorbate. The second step was a reduction of methyl sorbate using LiAlH<sub>4</sub> in Et<sub>2</sub>O. The description of these experiments is given elsewhere [7–9].

The hydrogenations were carried out in a solvent under atmospheric or elevated hydrogen

Table 1  
The properties of the catalysts used

Catalyst	Brand name	Crystallite size [nm]	$S_{\text{BET}}$ [m <sup>2</sup> /g <sub>cat.</sub> ]
5% Pt/C	Secomet 'AN'	15.5	778
3% Pd/C	Cherox 4100Ch	20.2	1161
5% Rh/C	<sup>a</sup>	< 5.0; X-ray amorphous	1201
5% Ru/C	Type 19A	< 1.0; X-ray amorphous	1167
50% Ni/Al <sub>2</sub> O <sub>3</sub>	6524	7.6	179
RaNi	Actimet M	–	75

<sup>a</sup>Carrier: Supersorbon HB-3 (Degussa).

pressures. The hydrogenations under atmospheric pressure were carried out in a glass reactor of volume 30 ml. 0.2 ml of substrate and 14.8 ml of solvent were admitted to the reactor. The quantity of catalyst used ranged from 0.02 to 0.6 g. The reaction temperature was 25°C. Hydrogenations under an increased hydrogen pressure were carried out in an autoclave of the volume 250 or 300 ml. One hundred seventy-five milliliters of methanol was used as a solvent. The substrate quantity was 5 ml and the catalyst weight ranged from 0.02 to 1 g. The reaction temperature was 60–125°C, depending upon the type of catalyst used. The hydrogen pressure was 3 MPa.

### 3. Results and discussion

Methyl sorbate, prepared by esterification of (2*E*,4*E*)-hexadienic (sorbic) acid with methanol [7–9], was reduced using LiAlH<sub>4</sub> in Et<sub>2</sub>O to (2*E*,4*E*)-hexadienol. The methyl sorbate reduction was carried out with 50%—surplus of LiAlH<sub>4</sub> compared to the stoichiometry. The raw reduction product, after two hours under reflux, always contained only the *trans,trans*-isomer of 2,4-hexadienol. During this reaction, there was no occurrence of simultaneous saturation of methyl sorbate C–C double bonds. After the product refining by rectification (79–81°C; 1.2 kPa; 42 theoretical plates; reflux 1:7), (2*E*,4*E*)-hexadienol (99,9%) was acquired as a colorless liquid of the characteristic scent, which rapidly solidified and formed white, imbricate crystals. (2*E*,4*E*)-hexadienol is a white crystalline substance with the melting point 31°C and the boiling point 177°C under standard conditions. After distilling off the solvent and a subsequent product rectification, a reaction yield of 89% was obtained. The product was analyzed using MS, <sup>1</sup>H and <sup>13</sup>C NMR. The position and the *trans*-configuration of the alcoholic double bonds were confirmed by means of these procedures.

Five supported catalysts with a different type of an active component (Pd, Pt, Rh, Ru and Ni), and the Raney nickel catalyst, were tested for the hydrogenations. These catalysts were characterized with the elementary crystallite size and their surface area (see Table 1). Based on X-ray powder diffractometry, the catalysts can be divided to X-ray amorphous ones and catalysts specific with their crystalline structure. Rhodium catalyst, which showed only a mildly increased diffractogram background, belongs to the former group. The other catalysts are characteristic by their specific crystalline structure. The surface area of the catalyst samples remarkably differed, especially in relation to a carrier. The largest area surfaces were observed in the samples supported on an active carbon, while the smallest were the ones with an  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> carrier type. The surface areas of the nickel-catalysts reached a values about 200 and 100 m<sup>2</sup>/g<sub>cat.</sub> for Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and RaNi, respectively.

Fig. 1 shows the typical development of product concentrations with time during the hydrogenation of (2*E*,4*E*)-hexadienol using the Raney nickel catalyst. The intermediates and products of concentration lower than 5% were

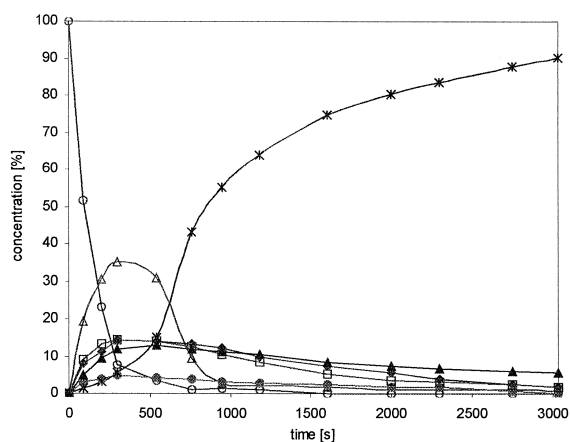


Fig. 1. The course of the (2*E*,4*E*)-hexadienol hydrogenation using Ra-Ni: ○—(2*E*,4*E*)-hexadienol, △—(2*E*)-hexenol, ◆—(3*E*)-hexenol, ●—(3*Z*)-hexenol, □—(4*E*)-hexenol, ▲—hexanal, \*—hexanol.

not included in this figure. (2*E*,4*E*)-hexadienol rapidly hydrogenated producing a great amount of intermediate products, in particular, diverse hexenol isomers. Various hexenals were identified in the reaction mixture as well as hexanal, hexenes and hexane. Unsaturated hexenols further hydrogenated to the common product hexanol. Based on these facts, a general reaction scheme of (2*E*,4*E*)-hexadienol hydrogenation (Fig. 2), containing even the produced intermediates as well as the products in low concentration, was designed.

The composition of the reaction mixture primarily depended upon a catalyst type. Besides hexenols, varied isomeric hexenals and hexenes, which further hydrogenated to hexanal and hexane, were produced in the majority of the reactions. The product of hexenol's hydrogenation was 1-hexanol. Hexanal was in particular the product of hexenols' isomerization; hexane originated from the subsequent hydrogenation of hexenes, which were formed by dehydration, isomerization and the partial hydrogenation of hexenols. (2*E*)-Hexenol (B) was produced by a

simple hydrogenation of the double bonds in the 4-position. (3*E*)-hexenol (C) was produced by isomerization reactions. (3*Z*)-hexenol (D), which was present in lower concentrations in the reaction mixture, could have been produced in a like manner. Relating to the *trans*-isomer, it could have in the same way arisen from the isomerization reactions or from the concurrent interactions of both of the double bonds with the catalyst surface, after the 1,4-addition of hydrogen to the hexadienol dienic system [10]. (4*E*)-hexenol (E) was formed either by the double bonds hydrogenation in the 2-position or arisen from the isomerization reactions occurring among intermediate products.

The composition of the reaction mixture was independent on the hydrogen pressure and the catalyst weight. In the first place, the advantage of the hydrogenation carried out under a higher hydrogen pressure consisted in the smaller catalyst weights compared to the great volume of the substrate. Introductory experiments showed that with increasing the temperature, selectivity decreases. The variation of reaction conditions

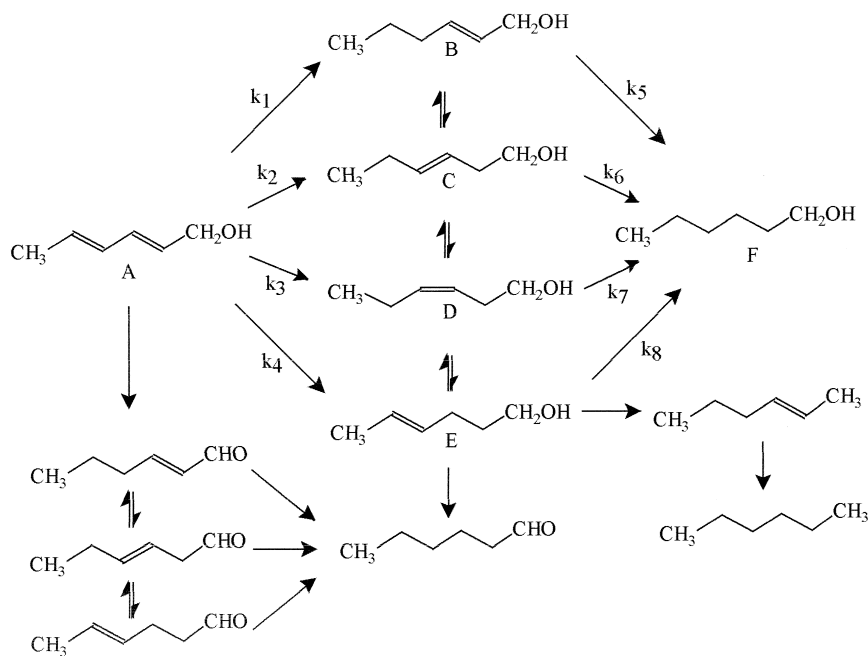


Fig. 2. The general reaction scheme of the (2*E*,4*E*)-hexadienol hydrogenation.

does not provide sufficient area for improvements in selectivity. One of the possible ways is to study the effect of the reaction solvent [11].

All the reactions were carried out with a total conversion of the initial substance. Production of the maximal number of intermediate products occurred during those hydrogenation reactions, in which palladium and platinum catalysts were used, while (3*E*)-hexenol, (2*E*)-hexenol and (4*E*)-hexenol have reached approximately identical concentrations. (3*E*)-hexenol together with (4*E*)-hexenol were primarily produced on palladium catalyst and their maximum attained concentration was about 25%. Beside hexenols, a great number of products and undesired intermediate products were produced on the palladium catalyst: Hexane (as much as 19%), mixture of hexenes (1-, (2*E*)-, (3*E*)- and (3*Z*)-hexene; altogether as much as 14%) and hexanal, which reached a concentration as high as 17%. (2*E*)-hexenal occurred to be produced in the beginning of the reactions (maximum of up to 10%), which though instantly further hydrogenated to hexanal. A similar situation was observed when the rhodium catalyst was used. Besides the mentioned intermediate products, a presence of hexanaldimethylacetal (up to 6%) was observed. It was probably produced by the hexanal having reacted with the solvent, methanol. Simultaneously, the highest concentrations of hexenes (as much as 25%) and hexane (as much as 50% in the final product) were obtained with this catalyst.

Using ruthenium catalyst, (3*E*)-hexenol and (2*E*)-hexenol, compared to the rest of the intermediate products, were produced in higher concentrations. The rest of the intermediate products were contained in the reaction mixture only in lower concentrations (up to 10%). When hydrogenations were carried out using this catalyst, the least quantity of hexene and hexane occurred to be produced, namely within concentrations of up to 1.5%. Regarding the production of varied hexenols (Fig. 1), the most selective catalyst was Raney nickel. In this case, (2*E*)-hexenol reached its peak in a concentration of

around 35%. The other intermediate products reached a concentration of up to 15%. When Raney nickel was used, only a minimum quantity of hexenes was reached. When Ni/Al<sub>2</sub>O<sub>3</sub> catalyst was used, (2*E*)-hexenol (28%), (4*E*)-hexenol (25%) and (3*E*)-hexenol (20%) were produced in higher concentrations. The other intermediate products reached a concentration of up to 5%. Similar to the case of Raney nickel, only a minimum amount of hexenes had been produced.

Some intermediate products were neglected in the reaction course description, because during the hydrogenation course, the production of hexenols was significantly higher compared to the other intermediate products. The following intermediate products were selected for the reaction scheme: (2*E*)-hexenol, (3*E*)-hexenol, (3*Z*)-hexenol and (4*E*)-hexenol, which further hydrogenated to their common product, hexanol. The equilibrium isomerization steps were not included in the kinetic model provided also in the reaction scheme (Fig. 2). Based on these simplified assumptions, the reaction course was expressed using a type of the Langmuir–Hinshelwood equation. The applied reaction rate model of the Langmuir–Hinshelwood type was derived based on assumptions that reactant molecules bond on a single active center, the slowest process is the surface reaction and the total amount of the active centers is included in the reaction rate constant. The adsorption term, included in the denominator of the reaction rate equations  $(1 + K_A c_A + K_B c_B + \dots + K_i c_i + \dots K_r c_r)$  can be reduced to the form  $(1 + K_A c_A + K_B c_B + \dots + K_i c_i)$ , if the relation  $(1 + K_A c_A + K_B c_B + \dots + K_i c_i) \gg (K_r c_r)$  applies, i.e., if the solvent adsorptivity is in comparison to the reactants' negligible. Alternatively, assuming a total surface coverage by the reactants in the equilibrium state  $((K_A c_A + K_B c_B + \dots + K_i c_i) \gg (1 + K_r c_r))$ , it can be reduced to the form  $(K_A c_A + K_B c_B + \dots + K_i c_i)$ . These equations were adjusted by dividing the denominator and the numerator with the adsorption coefficient of the substrate, (2*E*,4*E*)-hexadienol.

This way, the so-called relative adsorption coefficients of the components were introduced into the equations. Since the reactions proceeded in the kinetic region, the concentration of hydrogen dissolved in a liquid phase was constant. Therefore, it was under these conditions possible to include the hydrogen concentration and its adsorption coefficient into the kinetic constants of the hydrogenation steps included in the 'adsorption model'. A series of separate calculations demonstrated that all the presented adjustments markedly improved a convergence of regression methods and led to an increase of reliability of the computed parameter values [12]. Based on these adjustments, a reaction rate model was derived from Langmuir–Hinshelwood relations, expressed with the following differential equations ((1)–(7)).

$$(V/W)dc_A/dt = -k_1K_Ac_A - k_2K_Ac_A - k_3K_Ac_A - k_4K_Ac_A/\theta \quad (1)$$

$$(V/W)dc_B/dt = k_1K_Ac_A - k_5K_Bc_B/\theta \quad (2)$$

$$(V/W)dc_C/dt = k_2K_Ac_A - k_6K_Cc_C/\theta \quad (3)$$

$$(V/W)dc_D/dt = k_3K_Ac_A - k_7K_Dc_D/\theta \quad (4)$$

$$(V/W)dc_E/dt = k_4K_Ac_A - k_8K_Ec_E/\theta \quad (5)$$

$$(V/W)dc_F/dt = k_5K_Bc_B + k_6K_Cc_C + k_7K_Dc_D + k_8K_Ec_E/\theta \quad (6)$$

$$\theta = (K_Ac_A + K_Bc_B + K_Cc_C + K_Dc_D + K_Ec_E + K_Fc_F) \quad (7)$$

The model was determined using the marginal conditions:  $t = t_0$ ,  $c_{A0} = 1$ ,  $c_{B0} = c_{C0} = c_{D0} = c_{E0} = c_{F0} = 0$ . The actual initial concentration was  $c_{A0} = 0.118 \text{ mol l}^{-1}$ . The quotient  $V/W$  represents the ratio of the volume of the reaction mixture (ml) to the catalyst amount (g). The kinetic parameters of the model were acquired with the Random Walk's method [12].

The calculated kinetic data of (2*E*,4*E*)-hexadienol hydrogenation for individual catalysts under atmospheric pressure are provided in Table 2. Contributions of individual rate constants  $k_1$ – $k_4$  and values  $S(B)$ ,  $S(C)$ ,  $S(D)$  and  $S(E)$ , presented in the table, represent reaction selectivities related to individual intermediate products **B**, **C**, **D** and **E**. The quantity Sum (intermed.) represents the maximal acquired concentration of hexenols in the course of the reaction in the reaction mixture using individual catalysts. The relative activities of the catalysts ( $k_1 + k_2 + k_3 + k_4$ ) related to the catalyst with the lowest activity decrease in order: Pd/C (147) > Ni/Al<sub>2</sub>O<sub>3</sub> (27) > Rh/C (8) > Raney nickel (7) > Pt/C (5) > Ru/C (1). The highest selectivity values, expressed with the ratio of rate constants related to (2*E*)-hexenol, were acquired with the Raney nickel catalyst. The highest acquired reaction selectivity values calculated from the relative quotients of the substances in the reaction mixture in their maximum concentration instant, related to leaf alcohols, (2*E*)-hexenol and (3*Z*)-hexenol, were acquired using Raney nickel catalyst as well.

Table 2  
The selectivity values related to individual hexenols

Catalyst	Pd/C	Pt/C	Rh/C	Ru/C	RaNi	Ni/ Al <sub>2</sub> O <sub>3</sub>
$k_1 / (k_2 + k_3 + k_4)$	0.398	0.413	0.924	0.472	1.237	0.663
$k_2 / (k_1 + k_3 + k_4)$	0.325	0.279	0.354	0.702	0.240	0.333
$k_3 / (k_1 + k_2 + k_4)$	0.294	0.084	0.037	0.081	0.071	0.051
$k_4 / (k_1 + k_2 + k_3)$	0.320	0.702	0.286	0.238	0.230	0.435
$S(B)$	0.288	0.175	0.105	0.235	0.399	0.327
$S(C)$	0.286	0.168	0.199	0.315	0.190	0.229
$S(D)$	0.030	0.037	0.025	0.044	0.070	0.041
$S(E)$	0.333	0.219	0.164	0.130	0.215	0.271
Sum (intermed.)	0.699	0.477	0.426	0.625	0.817	0.773

$$S(B) = \%B / (\%B + \%C + \%D + \%E + \%F)_{\max}, \quad S(C) = \%C / (\%B + \%C + \%D + \%E + \%F)_{\max}$$

$$S(D) = \%D / (\%B + \%C + \%D + \%E + \%F)_{\max}, \quad S(E) = \%E / (\%B + \%C + \%D + \%E + \%F)_{\max}$$

## 4. Conclusion

The preparation of various hexenols from sorbic acid was studied. This work was focused on (2*E*,4*E*)-hexadienol preparation by a reduction of methyl ester of sorbic acid and its subsequent hydrogenation to hexenols. First, the esterification of sorbic acid to methyl sorbate, which was subsequently reduced to (2*E*,4*E*)-hexadienol, was carried out. Reduction was effected using  $\text{LiAlH}_4$  and its yield was 89%. Varied metallic catalysts were used for the research on (2*E*,4*E*)-hexadienol hydrogenations. The composition of the reaction mixture depended primarily upon a type of the catalyst used. A great quantity of intermediate products was produced in all the reactions, especially due to isomerization reactions in the course of the hydrogenations. In comparison with the procedure [7], in which first, the catalytic hydrogenation of methyl ester of sorbic acid to methyl esters of hexenic acids, and then their subsequent reduction to pertinent hexenols was effected, the procedure appears as less advantageous, since when applied, a great quantity of intermediate products is produced, among which are the valuable leaf alcohols, (3*Z*)-hexenol and (2*E*)-hexenol, are produced in low concentration.

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## Appendix A

The acquired MS and NMR spectra of (2*E*,4*E*)-hexadienol: MS ( $m/z$ , %): 39(100), 41(66), 43(37), 53(26), 55(81), 69(28), 79(23), 80(37), 81(32), 83(38), 98(12);  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ , TMS, 25°C): 1.72 br.d (3H, 6.6 Hz), 2.11 br.s (1H), 4.04 d (2H, 5.9 Hz), 5.61 m (2H), 6.01 dd (1H, 10.3, 14.7 Hz), 6.15 dd (1H, 15.1, 10.3 Hz);  $^{13}\text{C}$  NMR (100.61 MHz,  $\text{CDCl}_3$ , TMS, 25°C): 18.1 q (C-6), 63.3 t (C-1), 130.0 d (C-2), 130.6 d (C-3), 132.3 d (C-4), 132.5 d (C-5).

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