

## Changes in chemical composition of catalytically hydrogenated orange oil (*Citrus sinensis*)

Elena E. Stashenko\*, Ramiro Martínez, M. Helena Pinzón, Jesús Ramírez

Chemistry Department, Industrial University of Santander, A.A. 678, Bucaramanga, Colombia

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### Abstract

Orange oil obtained from fresh fruit peels by cold pressing was subjected to hydrogenation at 60, 70 and 80°C and 0.46 MPa (H<sub>2</sub> pressure) over Adam's catalyst (PtO<sub>2</sub> at 0.5 and 0.75%, w/w). The chemical composition of neat and hydrogenated oils was established by high-resolution gas chromatography (HRGC) with flame ionization (FID) and mass spectrometric (MS) detection. The principal components of orange oil were monoterpenes (limonene 94.00%,  $\alpha$ -pinene 0.54%, sabinene 0.74%,  $\beta$ -myrcene 1.18%), followed by oxygenated compounds such as alcohols (linalool 0.89% and  $\alpha$ -terpineol 0.06%) and aldehydes (citral-Z 0.09%, citral-E 0.14%, citronellal 0.07%). HRGC-FID-MS analysis of the hydrogenated mixtures revealed the presence of over twenty components, mainly the products of hydrogenation of limonene, citral, linalool,  $\beta$ -myrcene, sabinene and  $\beta$ -ocimene.  $\alpha$ -Pinene and aliphatic aldehydes did not react under these conditions. The appearance of  $\alpha$ -terpinolene and the increase of  $\gamma$ -terpinene concentration from 0.05% to 0.15% in the modified oils indicated isomerization associated with hydrogenation. Citral (*E*- and *Z*-) was converted into citronellal (0.06–0.12%) and dihydrocitronellal (0.06–0.16%). Linalool was transformed into 3,7-dimethyl-1-octen-3-ol (0.42–0.63%) and 3,7-dimethyloctan-3-ol (0.11–0.32%). Various isomers formed by H<sub>2</sub> addition to the endo and exo double bonds in limonene constituted the main products (up to 95%) in the hydrogenated orange oils. The concentration of hydrogenated products increased from 62.78 to 89.76% when the temperature dropped from 80 to 60°C at a catalyst concentration of 0.5% (w/w). A smaller change was observed with 0.75% (w/w) catalyst.

**Keywords:** *Citrus sinensis*; Orange oil; Fruits; Essential oils; Terpenes

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### 1. Introduction

Orange oil is a relatively inexpensive and abundant raw material with applications in the food and flavor industries. It can also serve as an excellent starting material in the synthesis of fine chemicals and of new fragrances for the cosmetics industry. The industrial processing of essential oils typically

includes a dewatering step to remove unsaturated components which may polymerize and give rise to gums that are detrimental to the quality of the essential oil. We report the use of catalytic hydrogenation as a new tool in the search of new flavor ingredients from natural sources, giving rise to new oils with a greatly reduced content of unsaturated components. The detailed analysis of the chemical transformations that take place in these mixtures of closely related terpenes was possible only through the combined use of high-resolution gas chromatog-

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\*Corresponding author.

raphy (HRGC) with flame ionization (FID) and mass spectrometric (MS) detection.

## 2. Experimental

### 2.1. Plant material

The fruits (*Citrus sinensis*) used in this study were collected at an intermediate stage of maturity (45–75% green) from a plantation located 30 km north of Bucaramanga (Santander, Colombia). The extractions were performed within 2 days of the collection, using peels manually chopped into ca. 4 cm<sup>2</sup> fragments.

### 2.2. Essential oil extraction

A hand cold press was used to extract oil from 5.0 to 5.5 kg of orange peel, as described elsewhere [1,2]. Freshly obtained oils were subjected to chromatographic analysis prior to catalytic hydrogenation over Adam's catalyst (PtO<sub>2</sub>).

### 2.3. Catalyst preparation

The preparation of Adam's catalyst involved the synthesis of ammonium chloroplatinate, (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub>, and its fusion with sodium nitrate according to a method that has been described [3,4]. The cooled mass was washed at least five times with distilled water. The platinum oxide was then dried in a desiccator and stored in a closed container.

### 2.4. Catalytic hydrogenation

The catalytic hydrogenation of neat orange oil was performed in a Parr 3911 shaker-type hydrogenator (Moline, IL, USA) equipped with a borosilicate glass reaction vessel. A 20-ml volume (16.6 g) of neat orange oil and the corresponding catalyst amount (0.5 or 0.75%, w/w) were loaded into the reactor and air was removed by purging with hydrogen (0.38 MPa) four times. The bottle was then pressurized with hydrogen (0.46 MPa) and heated to the desired reaction temperature (60, 70 and 80°C). The shaker was started and the progress of the reaction was followed by monitoring the vessel pressure. The

reaction was considered complete when the pressure did not change for 20 min. The shaker and the heating were stopped and the catalyst was allowed to settle under the hydrogen pressure for 10 min. The pressure was released and the hydrogenated oil was decanted and analyzed by HRGC–FID and HRGC–MS. Control runs were performed identically, but with no catalyst. All runs were performed in triplicate.

### 2.5. Essential oil analysis

HRGC analysis of the samples was performed on a Hewlett-Packard (HP) (Palo Alto, CA, USA) 5890A Series II gas chromatograph equipped with split/splitless injector (250°C, split ratio 1:10) and FID operated at 250°C. Chromatographic data were processed with an HP ChemStation 3365-II. The column used was a DB-5 (J&W Scientific, Folsom, CA, USA) cross-linked fused-silica capillary column (30 m×0.25 mm I.D.), coated with 5% phenyl-polymethylsiloxane (0.25 μm phase thickness). The oven temperature was programmed from 40°C (5 min hold) at 4 C°/min to 250°C. Helium (AGA, 99.995%) was used as a carrier gas (inlet pressure 79 kPa) with linear velocity 35 cm s<sup>-1</sup>. Air, hydrogen and nitrogen (make-up) flow-rates for FID were 300, 28 and 30 ml min<sup>-1</sup>, respectively. The injection volume was 0.5 μl of a 20% (v/v) solution of neat and hydrogenated orange oils in dichloromethane (chromatography grade reagent, Merck). The concentration data reported here are the averages of triplicate hydrogenation runs.

A HP 5890A Series II gas chromatograph interfaced to an HP 5972 mass-selective detector with an HP MS ChemStation data system was used for MS identification of the GC components. The column used was a HP-5MS (Hewlett-Packard) cross-linked fused-silica capillary column (30 m×0.25 mm I.D.) coated with 5% phenyl-polydimethylsiloxane (0.25 μm phase thickness). The oven was programmed as described for HRGC–FID analysis. The helium inlet pressure was 79 kPa, with linear velocity 37.7 cm min<sup>-1</sup> (split 10 ml min<sup>-1</sup>). The injector temperature was kept at 250°C and the volume injected was 1 μl. The temperatures of the ionization chamber and of the transfer line were 180°C and 285°C, respectively.

The electron energy was 70 eV. Mass spectra and reconstructed chromatograms were obtained by automatic scanning in the mass range  $m/z$  40–350 at 2.2 scan  $s^{-1}$ . Chromatographic peaks were checked for homogeneity with the aid of the mass chromatograms for the characteristic fragment ions. NBS75K and WILEY138 data bases were used for automatic identification of GC peaks.

### 3. Results and discussion

Typical chromatographic profiles of (A) neat orange oil and (B) catalytically hydrogenated oil (60°C, 0.5%, w/w, PtO<sub>2</sub>) are shown in Fig. 1. Table 1 gives the compositions found for orange oil and the hydrogenated mixtures obtained under the various conditions of temperature and catalyst used. The

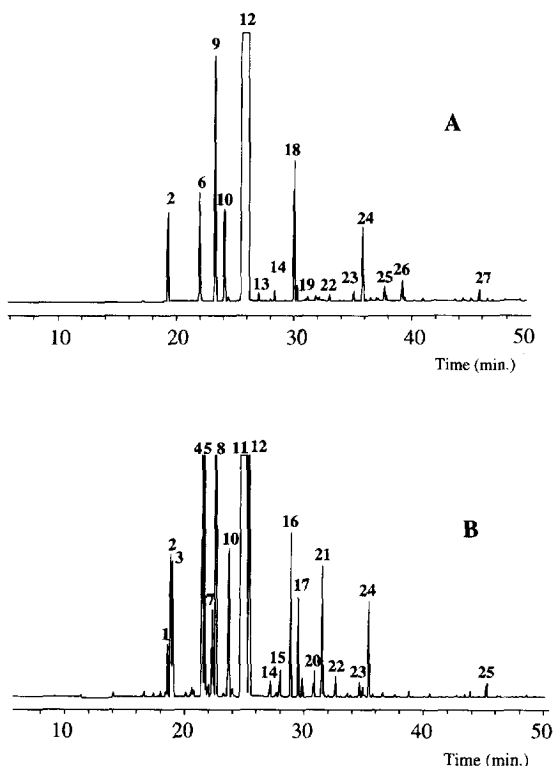


Fig. 1. Gas chromatograms from a sample of (A) orange oil extracted by cold pressing from fruit peels and (B) orange oil hydrogenated at 60°C over 0.5% (w/w) PtO<sub>2</sub>. Column: DB-5 (30 m × 0.25 mm, 0.25  $\mu$ m). Detection: FID. Peak labels correspond to those appearing in the first column of Table 1.

components were identified by comparison of their mass spectra with those of standard compounds or MS libraries, or by analysis of their fragmentation patterns. While the native orange oil contained fifteen compounds at concentration >0.03%, the hydrogenated oils presented more than twenty components.

The principal components of neat orange oil were monoterpenes (limonene 94.00%,  $\alpha$ -pinene 0.54%, sabinene 0.74%,  $\beta$ -myrcene 1.18%), followed by oxygenated compounds such as alcohols (linalool 0.89% and  $\alpha$ -terpineol 0.06%) and aldehydes (citral-Z 0.09%, citral-E 0.14%, citronellal 0.07%) and a 1.73% represented by octanal, nonanal, decanal and dodecanal (Table 1). The hydrogenated mixtures contained mainly the products of hydrogenation of limonene, citral, linalool, and some monoterpenes such as sabinene,  $\beta$ -myrcene and  $\beta$ -ocimene.  $\alpha$ -Pinene and aliphatic aldehydes were not altered under these conditions.

The concentration of  $\gamma$ -terpinene increased from 0.05% to 0.11–0.15% both in control and catalytically modified samples thus indicating a thermally activated isomerization. This could be the source of higher  $\gamma$ -terpinene contents in orange oil after prolonged storage [5].  $\alpha$ -Terpinolene is not present in native orange oil and is possibly formed from a carbocation intermediate during hydrogenation of limonene and related terpenes.

Various isomers, generated by the hydrogen addition to the endo- and exo-double bonds in limonene, constituted the main products (up to 95%) in the hydrogenated oils (Fig. 2). 1-Methyl-4-(1-methyl-ethyl) cyclohexane, the principal product of limonene hydrogenation, was found at levels from 55.86 to 80.89% in the modified oil mixtures.

Linalool was transformed into 3,7-dimethyl-1-octen-3-ol (dihydrolinalool, 0.42–0.63%) and 3,7-dimethyloctan-3-ol (tetrahydrolinalool, 0.11–0.32%) (Fig. 3). No linalool was detected in the hydrogenated oils. The concentration of hydrogenated products from limonene (dihydro- and tetrahydro-limonenes) decreased when catalyst amount and hydrogenation temperature were increased (Fig. 4). A similar trend was observed with the concentration of dihydro- and tetrahydrolinalools (Table 1).

Citral (Z- and E-isomers, 0.23%) was converted into citronellal and dihydrocitronellal (0.06–0.12%;

Table 1  
The chemical composition of neat and hydrogenated orange oils

Peak No.	Compound	$M_r$	GC peak area ( $\pm$ S.D.), %											
			Neat orange oil				70°C				80°C			
			Catalyst (PtO <sub>2</sub> ) (% w/w)											
			0.00	0.50	0.75	0.00	0.50	0.75	0.00	0.50	0.75	0.00	0.50	0.75
1	1-Methyl-4-(1-methylethylidene)-cyclohexane	138	-	0.22 $\pm$ 1.10 <sup>-2</sup>	0.31 $\pm$ 2.10 <sup>-2</sup>	0.51 $\pm$ 3.10 <sup>-2</sup>	0.25 $\pm$ 1.10 <sup>-2</sup>	0.32 $\pm$ 2.10 <sup>-2</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.25 $\pm$ 1.10 <sup>-2</sup>	0.32 $\pm$ 2.10 <sup>-2</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.25 $\pm$ 1.10 <sup>-2</sup>	0.32 $\pm$ 2.10 <sup>-2</sup>
2	$\alpha$ -Pinene	136	0.54	0.51 $\pm$ 2.10 <sup>-2</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.52 $\pm$ 1.10 <sup>-3</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.51 $\pm$ 4.10 <sup>-2</sup>	0.51 $\pm$ 3.10 <sup>-2</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.51 $\pm$ 4.10 <sup>-2</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.52 $\pm$ 3.10 <sup>-2</sup>	0.52 $\pm$ 9.10 <sup>-3</sup>
3	<i>trans</i> -1-Methyl-4-(1-methylethyl)-cyclohexane	138	-	0.01 $\pm$ 4.10 <sup>-3</sup>	0.82 $\pm$ 4.10 <sup>-2</sup>	1.00 $\pm$ 7.10 <sup>-2</sup>	0.81 $\pm$ 2.10 <sup>-2</sup>	0.89 $\pm$ 1.10 <sup>-2</sup>	0.81 $\pm$ 1.10 <sup>-3</sup>	0.89 $\pm$ 1.10 <sup>-2</sup>	0.89 $\pm$ 1.10 <sup>-2</sup>	0.89 $\pm$ 1.10 <sup>-2</sup>	0.73 $\pm$ 1.10 <sup>-2</sup>	0.85 $\pm$ 2.10 <sup>-2</sup>
4	2,6-Dimethyloctane	142	-	1.13 $\pm$ 1.10 <sup>-1</sup>	1.11 $\pm$ 8.10 <sup>-2</sup>	1.11 $\pm$ 8.10 <sup>-2</sup>	1.09 $\pm$ 6.10 <sup>-2</sup>	1.07 $\pm$ 1.10 <sup>-2</sup>	1.02 $\pm$ 2.10 <sup>-3</sup>	1.09 $\pm$ 6.10 <sup>-2</sup>	1.07 $\pm$ 1.10 <sup>-2</sup>	1.01 $\pm$ 4.10 <sup>-2</sup>	1.01 $\pm$ 4.10 <sup>-2</sup>	0.97 $\pm$ 3.10 <sup>-2</sup>
5	<i>trans</i> -1-Methyl-4-(1-methylethyl)-cyclohexane	140	-	2.62 $\pm$ 2.10 <sup>-1</sup>	2.33 $\pm$ 1.10 <sup>-1</sup>	2.33 $\pm$ 1.10 <sup>-1</sup>	2.62 $\pm$ 2.10 <sup>-3</sup>	2.04 $\pm$ 9.10 <sup>-2</sup>	0.02 $\pm$ 1.10 <sup>-3</sup>	2.04 $\pm$ 9.10 <sup>-2</sup>	1.86 $\pm$ 3.10 <sup>-2</sup>	1.54 $\pm$ 1.10 <sup>-2</sup>	1.54 $\pm$ 1.10 <sup>-2</sup>	1.37 $\pm$ 2.10 <sup>-2</sup>
6	Sabinene	136	0.74	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 1.10 <sup>-3</sup>
7	<i>cis</i> -1-Methyl-4-(1-methylethyl)-cyclohexane	138	-	0.01 $\pm$ 1.10 <sup>-3</sup>	0.46 $\pm$ 2.10 <sup>-2</sup>	0.47 $\pm$ 3.10 <sup>-2</sup>	0.43 $\pm$ 1.10 <sup>-2</sup>	0.45 $\pm$ 2.10 <sup>-2</sup>	0.02 $\pm$ 3.10 <sup>-3</sup>	0.43 $\pm$ 1.10 <sup>-2</sup>	0.45 $\pm$ 2.10 <sup>-2</sup>	0.40 $\pm$ 2.10 <sup>-2</sup>	0.40 $\pm$ 2.10 <sup>-2</sup>	0.44 $\pm$ 3.10 <sup>-2</sup>
8	<i>cis</i> -1-Methyl-4-(1-methylethyl)-cyclohexane	140	-	0.03 $\pm$ 2.10 <sup>-3</sup>	2.41 $\pm$ 3.10 <sup>-2</sup>	2.14 $\pm$ 2.10 <sup>-2</sup>	2.04 $\pm$ 4.10 <sup>-2</sup>	1.86 $\pm$ 3.10 <sup>-2</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	2.04 $\pm$ 4.10 <sup>-2</sup>	1.86 $\pm$ 3.10 <sup>-2</sup>	1.54 $\pm$ 1.10 <sup>-2</sup>	1.54 $\pm$ 1.10 <sup>-2</sup>	1.37 $\pm$ 9.10 <sup>-3</sup>
9	$\beta$ -Myrcene	136	1.18	1.78 $\pm$ 8.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.75 $\pm$ 7.10 <sup>-3</sup>	1.46 $\pm$ 9.10 <sup>-2</sup>	1.46 $\pm$ 9.10 <sup>-2</sup>	1.37 $\pm$ 9.10 <sup>-2</sup>
10	Octanal	128	1.10	1.11 $\pm$ 3.10 <sup>-3</sup>	1.10 $\pm$ 5.10 <sup>-3</sup>	0.99 $\pm$ 2.10 <sup>-3</sup>	0.98 $\pm$ 5.10 <sup>-3</sup>	0.97 $\pm$ 5.10 <sup>-3</sup>	1.11 $\pm$ 4.10 <sup>-3</sup>	0.98 $\pm$ 5.10 <sup>-3</sup>	0.97 $\pm$ 5.10 <sup>-3</sup>	1.10 $\pm$ 4.10 <sup>-3</sup>	0.97 $\pm$ 6.10 <sup>-3</sup>	0.98 $\pm$ 7.10 <sup>-3</sup>
11	1-Methyl-4-(1-methylethyl)-cyclohexene	138	-	0.20 $\pm$ 1.10 <sup>-2</sup>	80.89 $\pm$ 1.10 <sup>-1</sup>	78.66 $\pm$ 2.10 <sup>-1</sup>	80.89 $\pm$ 1.10 <sup>-1</sup>	64.2 $\pm$ 3.10 <sup>-2</sup>	0.30 $\pm$ 2.10 <sup>-2</sup>	71.59 $\pm$ 3.10 <sup>-2</sup>	64.2 $\pm$ 3.10 <sup>-2</sup>	1.11 $\pm$ 8.10 <sup>-2</sup>	56.3 $\pm$ 4.10 <sup>-2</sup>	55.86 $\pm$ 7.10 <sup>-2</sup>
12	Limonene	136	94.00	93.7 $\pm$ 3.10 <sup>-3</sup>	7.86 $\pm$ 9.10 <sup>-2</sup>	9.79 $\pm$ 8.10 <sup>-2</sup>	18.01 $\pm$ 1.10 <sup>-2</sup>	25.23 $\pm$ 5.10 <sup>-2</sup>	93.64 $\pm$ 7.10 <sup>-3</sup>	18.01 $\pm$ 1.10 <sup>-2</sup>	25.23 $\pm$ 5.10 <sup>-2</sup>	92.45 $\pm$ 9.10 <sup>-2</sup>	33.6 $\pm$ 5.10 <sup>-2</sup>	32.23 $\pm$ 8.10 <sup>-2</sup>
13	$\beta$ -Ocimene	136	0.04	0.03 $\pm$ 9.10 <sup>-4</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>	0.03 $\pm$ 1.10 <sup>-3</sup>
14	2,6-Dimethyl-5,7-octadiene	138	-	0.01 $\pm$ 1.10 <sup>-4</sup>	0.05 $\pm$ 9.10 <sup>-3</sup>	0.06 $\pm$ 8.10 <sup>-3</sup>	0.04 $\pm$ 9.10 <sup>-3</sup>	0.05 $\pm$ 7.10 <sup>-3</sup>	0.01 $\pm$ 2.10 <sup>-4</sup>	0.04 $\pm$ 9.10 <sup>-3</sup>	0.05 $\pm$ 7.10 <sup>-3</sup>	0.01 $\pm$ 3.10 <sup>-3</sup>	0.02 $\pm$ 8.10 <sup>-3</sup>	0.02 $\pm$ 7.10 <sup>-3</sup>
15	$\gamma$ -Terpinene	136	0.05	0.15 $\pm$ 3.10 <sup>-3</sup>	0.10 $\pm$ 7.10 <sup>-3</sup>	0.13 $\pm$ 6.10 <sup>-3</sup>	0.11 $\pm$ 7.10 <sup>-3</sup>	0.12 $\pm$ 8.10 <sup>-3</sup>	0.12 $\pm$ 9.10 <sup>-3</sup>	0.11 $\pm$ 7.10 <sup>-3</sup>	0.12 $\pm$ 8.10 <sup>-3</sup>	0.10 $\pm$ 1.10 <sup>-2</sup>	0.10 $\pm$ 9.10 <sup>-3</sup>	0.11 $\pm$ 8.10 <sup>-3</sup>
16	$\alpha$ -Terpinolene	136	-	0.53 $\pm$ 1.10 <sup>-3</sup>	0.61 $\pm$ 2.10 <sup>-3</sup>	0.61 $\pm$ 2.10 <sup>-3</sup>	0.54 $\pm$ 1.10 <sup>-3</sup>	0.73 $\pm$ 2.10 <sup>-3</sup>	0.53 $\pm$ 1.10 <sup>-3</sup>	0.61 $\pm$ 2.10 <sup>-3</sup>	0.73 $\pm$ 2.10 <sup>-3</sup>	0.62 $\pm$ 2.10 <sup>-3</sup>	0.62 $\pm$ 2.10 <sup>-3</sup>	0.77 $\pm$ 3.10 <sup>-3</sup>
17	3,7-Dimethyl-3-octanol	158	-	0.32 $\pm$ 3.10 <sup>-3</sup>	0.30 $\pm$ 1.10 <sup>-3</sup>	0.30 $\pm$ 1.10 <sup>-3</sup>	0.23 $\pm$ 2.10 <sup>-3</sup>	0.14 $\pm$ 1.10 <sup>-3</sup>	0.32 $\pm$ 3.10 <sup>-3</sup>	0.23 $\pm$ 2.10 <sup>-3</sup>	0.14 $\pm$ 1.10 <sup>-3</sup>	0.15 $\pm$ 3.10 <sup>-3</sup>	0.15 $\pm$ 3.10 <sup>-3</sup>	0.11 $\pm$ 4.10 <sup>-3</sup>
18	Linalool	154	0.89	0.78 $\pm$ 1.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.76 $\pm$ 2.10 <sup>-2</sup>	0.75 $\pm$ 2.10 <sup>-2</sup>	0.75 $\pm$ 2.10 <sup>-2</sup>	0.75 $\pm$ 2.10 <sup>-2</sup>
19	Nonanal	142	0.18	0.18 $\pm$ 9.10 <sup>-3</sup>	0.17 $\pm$ 1.10 <sup>-2</sup>	0.17 $\pm$ 1.10 <sup>-2</sup>	0.18 $\pm$ 1.10 <sup>-2</sup>	0.17 $\pm$ 1.10 <sup>-2</sup>	0.17 $\pm$ 1.10 <sup>-2</sup>	0.18 $\pm$ 1.10 <sup>-2</sup>	0.17 $\pm$ 1.10 <sup>-2</sup>	0.16 $\pm$ 2.10 <sup>-2</sup>	0.16 $\pm$ 1.10 <sup>-2</sup>	0.17 $\pm$ 1.10 <sup>-2</sup>
20	Dihydrocitronellal	156	-	0.01 $\pm$ 7.10 <sup>-3</sup>	0.14 $\pm$ 8.10 <sup>-3</sup>	0.14 $\pm$ 8.10 <sup>-3</sup>	0.14 $\pm$ 8.10 <sup>-3</sup>	0.07 $\pm$ 9.10 <sup>-3</sup>	0.02 $\pm$ 9.10 <sup>-3</sup>	0.14 $\pm$ 8.10 <sup>-3</sup>	0.07 $\pm$ 9.10 <sup>-3</sup>	0.01 $\pm$ 8.10 <sup>-3</sup>	0.11 $\pm$ 2.10 <sup>-2</sup>	0.06 $\pm$ 6.10 <sup>-3</sup>
21	3,7-Dimethyl-1-octen-3-ol	156	-	0.01 $\pm$ 9.10 <sup>-4</sup>	0.44 $\pm$ 3.10 <sup>-3</sup>	0.44 $\pm$ 3.10 <sup>-3</sup>	0.52 $\pm$ 1.10 <sup>-3</sup>	0.55 $\pm$ 4.10 <sup>-4</sup>	0.02 $\pm$ 1.10 <sup>-3</sup>	0.52 $\pm$ 1.10 <sup>-3</sup>	0.55 $\pm$ 4.10 <sup>-4</sup>	0.08 $\pm$ 1.10 <sup>-4</sup>	0.60 $\pm$ 2.10 <sup>-2</sup>	0.63 $\pm$ 3.10 <sup>-3</sup>
22	Citronellal	154	0.07	0.02 $\pm$ 7.10 <sup>-3</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.07 $\pm$ 2.10 <sup>-2</sup>	0.08 $\pm$ 2.10 <sup>-2</sup>	0.11 $\pm$ 2.10 <sup>-2</sup>	0.03 $\pm$ 8.10 <sup>-3</sup>	0.08 $\pm$ 2.10 <sup>-2</sup>	0.11 $\pm$ 2.10 <sup>-2</sup>	0.02 $\pm$ 8.10 <sup>-3</sup>	0.09 $\pm$ 9.10 <sup>-3</sup>	0.12 $\pm$ 1.10 <sup>-2</sup>
23	$\alpha$ -Terpineol	154	0.06	0.05 $\pm$ 9.10 <sup>-3</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.05 $\pm$ 1.10 <sup>-2</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.07 $\pm$ 9.10 <sup>-3</sup>	0.05 $\pm$ 1.10 <sup>-2</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.07 $\pm$ 9.10 <sup>-3</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.06 $\pm$ 9.10 <sup>-3</sup>	0.06 $\pm$ 9.10 <sup>-3</sup>
24	Decanal	156	0.39	0.40 $\pm$ 3.10 <sup>-2</sup>	0.36 $\pm$ 3.10 <sup>-2</sup>	0.35 $\pm$ 6.10 <sup>-2</sup>	0.37 $\pm$ 6.10 <sup>-2</sup>	0.36 $\pm$ 4.10 <sup>-2</sup>	0.39 $\pm$ 4.10 <sup>-2</sup>	0.37 $\pm$ 6.10 <sup>-2</sup>	0.36 $\pm$ 4.10 <sup>-2</sup>	0.38 $\pm$ 4.10 <sup>-2</sup>	0.35 $\pm$ 3.10 <sup>-2</sup>	0.36 $\pm$ 6.10 <sup>-2</sup>
25	Citral-Z	152	0.09	0.09 $\pm$ 1.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 2.10 <sup>-2</sup>	0.09 $\pm$ 1.10 <sup>-2</sup>	0.09 $\pm$ 1.10 <sup>-2</sup>	0.09 $\pm$ 1.10 <sup>-2</sup>
26	Citral-E	152	0.14	0.13 $\pm$ 9.10 <sup>-3</sup>	0.13 $\pm$ 8.10 <sup>-3</sup>	0.13 $\pm$ 8.10 <sup>-3</sup>	0.13 $\pm$ 8.10 <sup>-3</sup>	0.14 $\pm$ 7.10 <sup>-3</sup>	0.13 $\pm$ 8.10 <sup>-3</sup>	0.13 $\pm$ 8.10 <sup>-3</sup>	0.14 $\pm$ 7.10 <sup>-3</sup>	0.14 $\pm$ 7.10 <sup>-3</sup>	0.14 $\pm$ 7.10 <sup>-3</sup>	0.14 $\pm$ 7.10 <sup>-3</sup>
27	Dodecanal	184	0.06	0.06 $\pm$ 9.10 <sup>-3</sup>	0.05 $\pm$ 8.10 <sup>-3</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.06 $\pm$ 9.10 <sup>-3</sup>	0.07 $\pm$ 1.10 <sup>-2</sup>	0.06 $\pm$ 1.10 <sup>-2</sup>	0.06 $\pm$ 9.10 <sup>-3</sup>	0.07 $\pm$ 1.10 <sup>-2</sup>	0.05 $\pm$ 9.10 <sup>-3</sup>	0.06 $\pm$ 9.10 <sup>-3</sup>	0.05 $\pm$ 1.10 <sup>-2</sup>

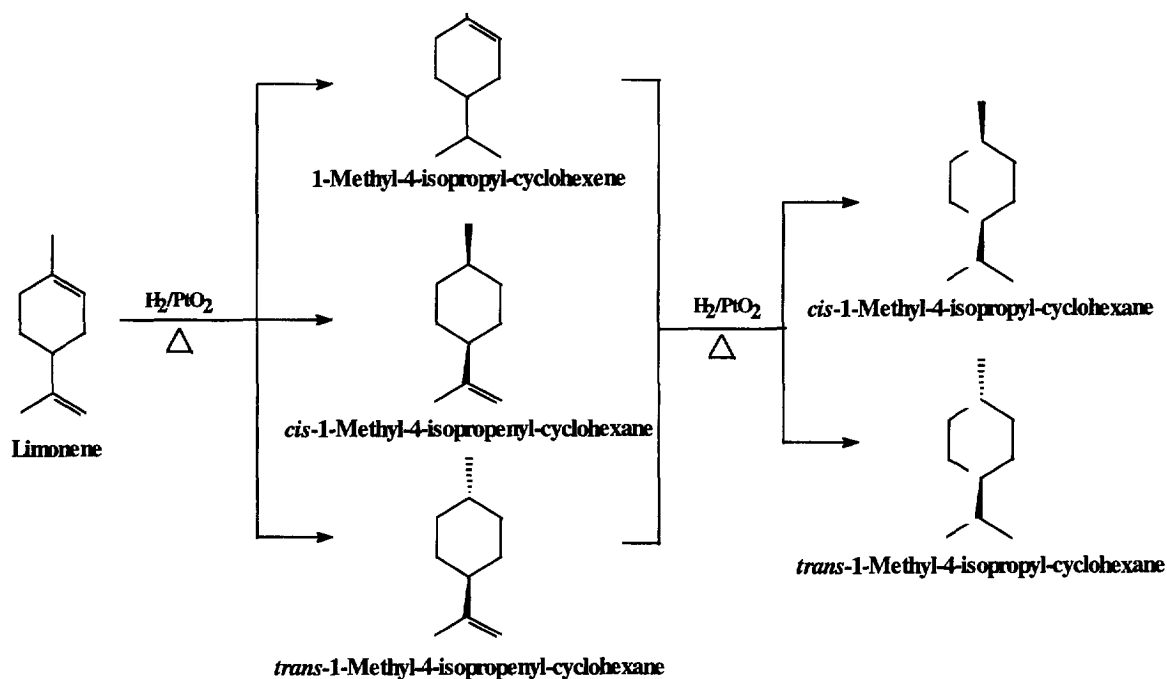


Fig. 2. Hydrogenation products of limonene formed in the catalytically modified orange oil.

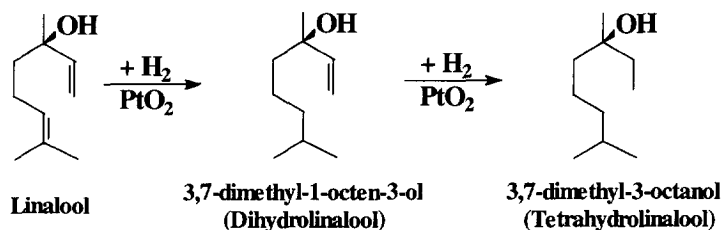


Fig. 3. Hydrogenation products of linalool formed in the catalytically modified orange oil.

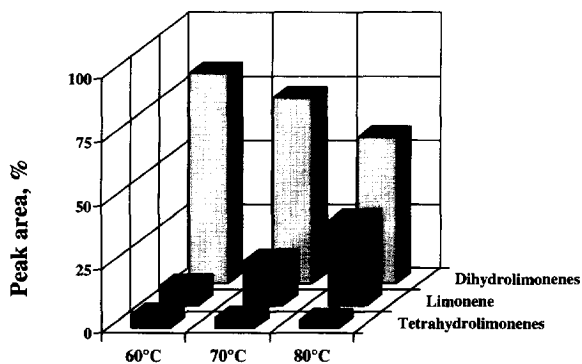


Fig. 4. Concentration of limonene and its hydrogenation products in orange oil heated over 0.5% (w/w)  $\text{PtO}_2$  under 0.46 MPa hydrogen.

0.06–0.16%) (Fig. 5). Just as in the case of limonene and linalool the amount of hydrogenated products (citronellal+dihydrocitronellal) increased with a decrease in the catalyst concentration. Conversely, the amount of citronellal increased when the temperature and amount of catalyst were increased (Table 1).

The efficiency of the hydrogenation process can be estimated from the change in concentration of hydrogenated components. The highest yield was observed at 60°C and 0.5% (w/w)  $\text{PtO}_2$ . Under these conditions, an uptake of 1.4 g of hydrogen per 100 grams of oil caused a decrease in the concentration of unsaturated components from 97.15% to under 9%. The transformed oil contained 89.76% of hydro-

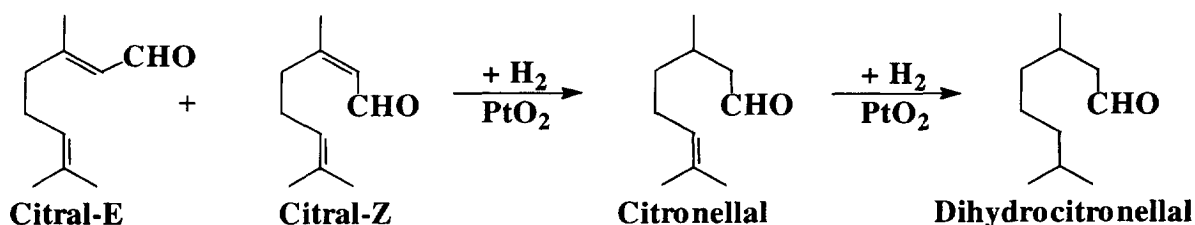


Fig. 5. Hydrogenation products of citral (*E*- and *Z*-isomers) formed in the catalytically modified orange oil.

generated components and some new constituents that resulted from isomerization without hydrogenation (Table 1). In comparison with the freshly extracted oil, the hydrogenated orange oils exhibited lower viscosity and a softer, sweeter, tenuous fragrance [5].

#### 4. Conclusions

The catalytic hydrogenation of orange oil under mild conditions affords a completely new oil with markedly different composition and organoleptic properties which does not require deterpenation. Several schemes to explain the transformation of individual components were constructed with the information from HRGC and HRGC–MS, which proved to be very effective analytical tools to map the chemical transformations and for guidance in the optimization of reaction conditions.

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