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Determination of the disproportionation products of limonene used for the catalytic hydrogenation of castor oil

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Abstract

The direct determination by GC–MS analysis of the products from the limonene disproportionation obtained from the catalytic hydrogenation of castor oil is not possible since a transesterification of the oil is required before injection. Therefore, a method for the determination of those products is proposed here: a solid-phase microextraction (SPME) followed by GC–MS. With the optimization of SPME it was possible to isolate a great number of products of the disproportionation of limonene used as hydrogen donor in the catalytic hydrogenation of castor oil by Pd/C. This system also proved to be appropriate to monitor castor oil hydrogenation by following and identifying the limonene disproportionated products.
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1. Introduction

Oil hydrogenation is a very important operation in the industrial process of producing starting components for the cosmetic and chemical industry (lubricants, emulsifier, soaps, creams, pastes, and others).

The hydrogenation of vegetable oil can be performed by a great number of processes [1–6] in homogeneous or heterogeneous catalysis, using molecular hydrogen or solvents as hydrogen donor.

Catalytic transfer hydrogenation (CTH) using several organic liquids as hydrogen donors is of interest because it avoids some of the inconvenient aspects of the conventional hydrogenation procedures with molecular hydrogen, such as high pressure and high temperature. Quantitative reduction of castor oil and other vegetable oils can be achieved in CTH using formic acid [4,7,8], indoline [9], isopropanol [9–11], hydrazine [12], cyclohexene [12], and other hydroaromatic compounds, as hydrogen donor solvents.

Limonene (Fig. 1) is a hydrogen donor solvent used for catalytic hydrogenation with Pd/C [13] for several organic molecules. This solvent is a good source of hydrogen since it is immediately generated when the system is heated to boiling. This monoterpene is low-priced and naturally occurring in essential oils, extracted from orange and lemon peel. The disproportionation of limonene in the presence of palladium has been reported to occur under rather vigorous conditions to give mostly *p*-cymene,

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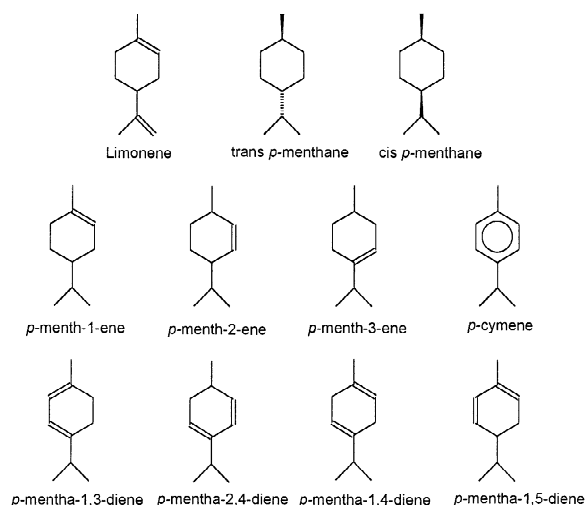*E-mail address:* elina@vortex.ufrgs.br (E.B. Caramão).

Fig. 1. Formula of limonene and of some products of the disproportionation of limonene.

p-menthane and *p*-menthenes (Fig. 1). In this work, hydrogenation of castor oil was promoted by using limonene and Pd/C. To monitor the hydrogenated products formed on the reaction by gas chromatography–mass spectrometry (GC–MS) it is necessary to transesterify a small sample many times during the reaction course. In order to avoid those steps we propose the use of solid-phase microextraction (SPME) to follow the reaction by analyzing the limonene disproportionation products. Thus, the reaction was monitored by the analysis of these disproportionation products by SPME, in a headspace mode or straight from the reaction flask, and GC–MS.

The use of SPME has introduced additional important advantages in the efficiency of the analysis of volatile organic compounds in many different samples: it produces rapid extraction and allows direct introduction in the analytical equipment; it does not disturb the living system equilibrium and provides better analytical performance in lesser time; it is easily automated and solvent-free [14–23]. The sampling and the extraction are made in a single step due to the diffusion of the analyte through the headspace to the SPME film, promoting the concentration of the substances of interest.

The purpose of this work is to study the best conditions for the analysis of all organic volatile compounds produced by the disproportionation of

limonene as a method to monitor the products of the hydrogenation of castor oil.

2. Experimental

2.1. Reagents

All the solvents were analytical-reagent grade. Pd/C (10%) was purchased from Merck and used without any pre-treatment. Commercial limonene was obtained from Dierberger Óleos Essenciais, Brazil; refined castor oil was donated by Cleveland Química do Brasil.

2.2. Equipment

The chromatographic analysis was performed in a gas chromatograph with a mass spectrometer detector from Shimadzu, Model GC-MS-QP5050A, in the electronic impact ionization mode at 70 eV. A HP-5 (polymethylsiloxane with 5% of phenyl groups) fused-silica open tubular column was used, of 60 m×0.25 mm I.D., 0.25 μm film thickness. The temperature program was started at 50 °C, heated at 1.3 °C/min to 100 °C, and heated to 170 °C at 10 °C/min, remaining at this temperature for 2 min. The split/splitless injector, in the splitless mode, was kept at 270 °C and the interface was kept at 300 °C. Helium was used as carrier gas at a flow-rate of 1.0 ml/min. A special liner was used, of 0.75 mm I.D., to SPME, from Supelco.

In the first part of this study—optimization of the conditions—the equipment was operated in the scan mode, and in the second part selected ion monitoring (SIM) was used to improve the efficiency, monitoring the ions 55, 68, 81, 93, 95, 97, 119, 134, 136, 138 and 140.

2.3. Procedures for headspace SPME

The fiber was conditioned at 270 °C for 60 min prior to use and a blank desorption was performed with the fiber exposed in the injection port.

A 100-μl volume of the sample, after the hydrogenation, was placed in vials of 20 ml, with screw caps containing PTFE-lined septa. Due to the complexity of the sample and the relatively high con-

centration of the compounds, SPME was used in the headspace mode with a 100 μm polydimethylsiloxane (PDMS) fiber, supplied by Supelco.

After the adsorption time, which was optimized in the range of 4 s until 10 min, with eventual manual stirring, the fiber was retracted into the protective sheath and removed from the vial and it was transferred, without delay, to the injection port of the gas chromatograph. The thermal desorption was made at 270 °C by 20 min, that is, during the entire chromatographic analysis. This time was chosen to guarantee the complete cleaning of the fiber, allowing its use immediately after the analysis.

2.3.1. Hydrogenation procedure

The hydrogenation reaction was performed in a 50-ml two-necked round-bottomed flask with a thermometer and a reflux condenser for 1 h at 178 °C. Hexane was added to the flask, immediately followed by centrifugation.

The extract was hot filtered, for the separation of Pd/C, and the hydrogenated product was precipitated by freezing. The liquid phase was separated and stored at 4 °C and the hydrogenated product was dried and also stored.

3. Results and discussion

Preliminary studies were conducted to establish the optimum conditions for extraction, desorption, and GC analysis of the compounds using SPME.

In order to optimize the SPME procedure for the analysis, several adsorption times (4 s, 30 s, 60 s and 10 min) were tested. The best result, in terms of reproducibility and sensitivity, was obtained at response time of 4 s. These results are shown in Fig. 2. In this figure it is possible to observe several products obtained from the limonene disproportionation during catalytic reaction for the hydrogenation of castor oil using a Pd/C system. Most of those products are identified and listed in Table 1. Some of
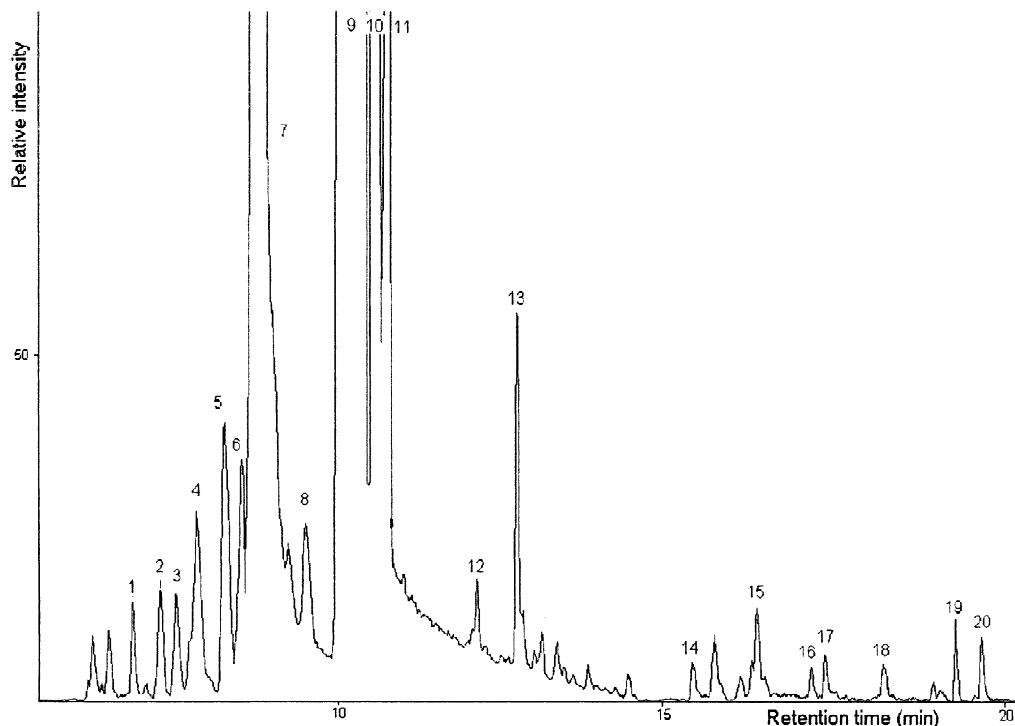

Fig. 2. Total ion chromatogram using SPME—in the headspace mode—of the sample after the hydrogenation. Chromatographic and SPME conditions are described in the text.

Table 1
Volatile compounds identified by SPME–GC–MS

	Compound	Formula	M_r	Relative content (%)[a]			
				Limonene de partida	Limonene after reaction with 2% Pd/C (178 °C)[c]	Limonene after reaction with 0.5% Pd/C and oil (178 °C)[c]	Limonene after reaction with 2% Pd/C and oil (178 °C)[c]
1	α-Pinene	$C_{10}H_{16}$	136	0.20	0.12	0.14	0.07
2	Camphene	$C_{10}H_{16}$	136	0.10	0.09	0.10	n.d
3	2-Ethyl-oct-2-ene	$C_{10}H_{20}$	140	0.12	0.05	0.12	0.11
4	2,6-Dimethyl-oct-2-ene	$C_{10}H_{20}$	140	0.06	0.05	0.20	0.29
5	cis-p-Menthane	$C_{10}H_{20}$	140	0.51	24.01	0.17	0.32
6	p-Menth-2-ene	$C_{10}H_{18}$	138	0.16	0.11	0.13	0.21
7	p-Menth-3-ene	$C_{10}H_{18}$	138	0.50	1.20	5.46	12.37
8	p-Menth-4(8)-ene	$C_{10}H_{18}$	138	n.d.	1.42	1.20	1.60
9	p-Cymene	$C_{10}H_{14}$	134	0.20	67.13	22.48	73.44
10	p-Menth-1-ene	$C_{10}H_{18}$	138	n.d.	2.00	2.82	7.13
11	Limonene	$C_{10}H_{16}$	136	97.32	3.04	62.97	4.12
12	p-Menthadiene	$C_{10}H_{16}$	136	n.d.	n.d.	0.30	n.d.
13	p-Cymenyl	$C_{10}H_{12}$	132	0.40	0.30	1.36	0.14
14	Menthone	$C_{10}H_{18}O$	154	0.04	0.10	0.36	n.d.
15	Methyl-acetophenone	$C_9H_{10}O$	134	0.13	n.d.	n.d.	n.d.
16	cis-Dihydrocarvone[a]	$C_{10}H_{16}O$	152	0.02	0.03	0.41	n.d.
17	Carvomenthone[a]	$C_{10}H_{18}O$	154	0.02	0.04	0.35	n.d.
18	Carvone	$C_{10}H_{14}O$	150	0.02	0.03	n.d.	n.d.
19	Carvenone[a]	$C_{10}H_{16}O$	152	0.08	0.10	n.d.	n.d.
20	Carveol	$C_{10}H_{16}O$	152	0.03	0.05	0.45	n.d.
	Σ			99.91	99.87	99.02	99.80
	Not identified			0.09	0.13	0.98	0.20
	Hydrogenation grade (%)[b]	–	–	–	–	49.9	78.2

n.d., Not detected.

[a] Relative content (%) related to the area, considering the total addition of the compounds area as 100%.

[b] Calculated by ^{1}H nuclear magnetic resonance (NMR) [24].

[c] The sample was transferred from the reaction flask to a headspace vial, where the SPME was exposed for 4 s, at 3 cm from the liquid surface and at 25 °C.

them also appear on a limonene sample before hydrogenation reaction as compounds 1, 2, 3, 4, 14, 15, 16, 17, 18, 19 and 20 from Table 1.

Although there are many compounds identified in this sample not all of them are of interest since the intermediate compounds mechanism involved in the reaction are p-menthanes, p-menthenes, p-cymene and p-menthadienes, shown in Fig. 1.

In continuing the optimization of SPME, the adsorption temperature (25 and 65 °C) and the distance between the fiber and the liquid surface in the headspace vial (1 and 3 cm) were tested. The results obtained showed that no important difference was achieved with these modifications, meaning that it is possible to collect a sample at room temperature

(25 °C) and at 3 cm of distance between the fiber and liquid surface.

Once the SPME conditions were established and the products of limonene disproportionation were identified, by GC–MS (Fig. 3), the settings used to obtain the chromatogram in Fig. 2 were optimized by SIM. The results are shown in Fig. 4, where the headspace mode was used to collect the sample by SPME at 25 °C during 4 s, at 3 cm between the fiber and liquid surface. Those compounds are the main intermediates, in CTH using limonene as solvent donor.

On this mechanism of reaction [25], both hydrogen, from the solvent donor, and olefin, from the oil, were adsorbed onto the catalyst surface. The hy-
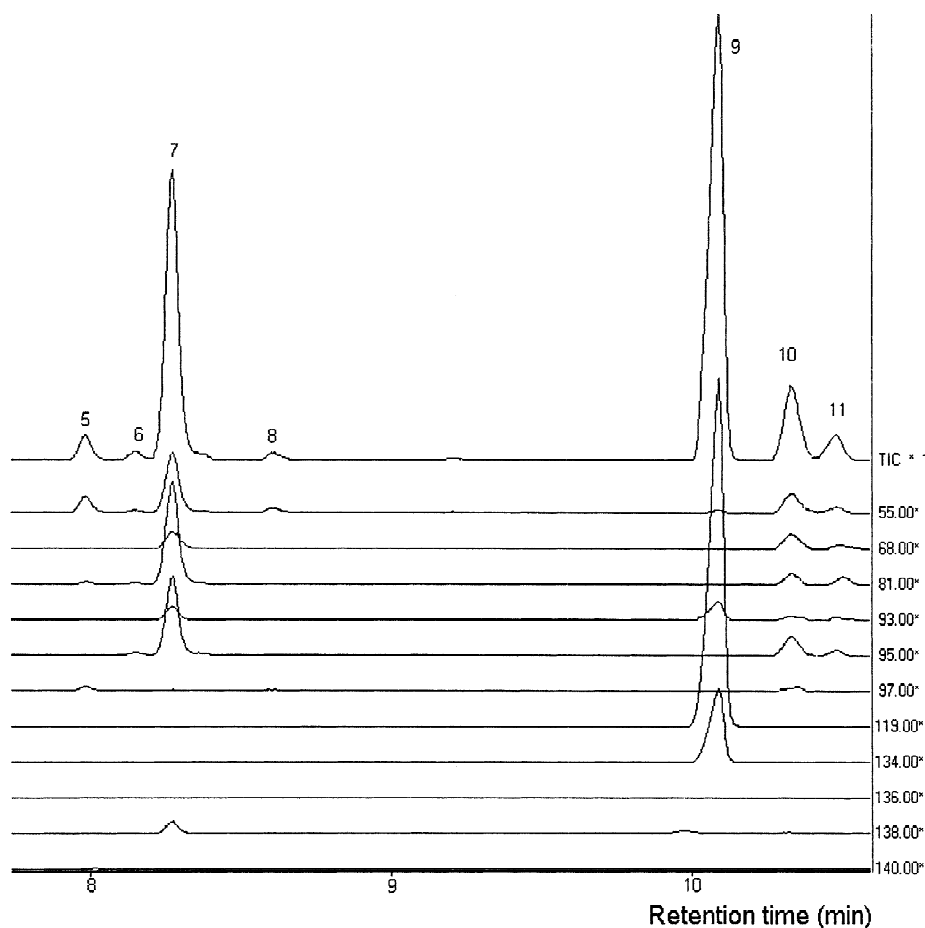
Fig. 3. Selected ion monitoring chromatogram of the SPME—in the headspace mode—of the disproportionation products of limonene. Chromatographic and SPME conditions are described in the text.

drides on the surface were used to reduce the carbon–carbon double bond on the triglyceride, giving partially or fully saturated products and the compounds obtained by the limonene disproportionation.

On the sample of limonene used as starting material, limonene appears in 97% of the relative content. On heating limonene with 2% of Pd/C, at 178 °C for 1 h, limonene was reduced to 3% and its disproportionation products: *p*-cymene (9), *cis*-*p*-menthane (5), *p*-menth-1-ene (10) showed up at 67, 24 and 2% of the relative concentration of those products, respectively. The attempt to explain the high concentration of *cis*-*p*-menthane is that the catalyst is saturated with hydrogen from the

limonene and there is no means to turn into *p*-cymene since there no substrate to be hydrogenated (oil in this case).

By adding castor oil to a similar system and heating it at 178 °C for 1 h, the products extracted by SPME were identified as: *p*-cymene (9)—73.44%, *p*-menth-3-ene (7)—12%, *p*-menth-1-ene (10)—7.13% and limonene at ca. 4%. This data showed that limonene was not totally consumed as a hydrogen donor maybe due to the lack of catalyst (2%) saturation of the catalytic sites, or because the reaction time was not long enough to reach completion. The absence of *cis*-*p*-menthane (5) may show that Castor oil is being hydrogenated.

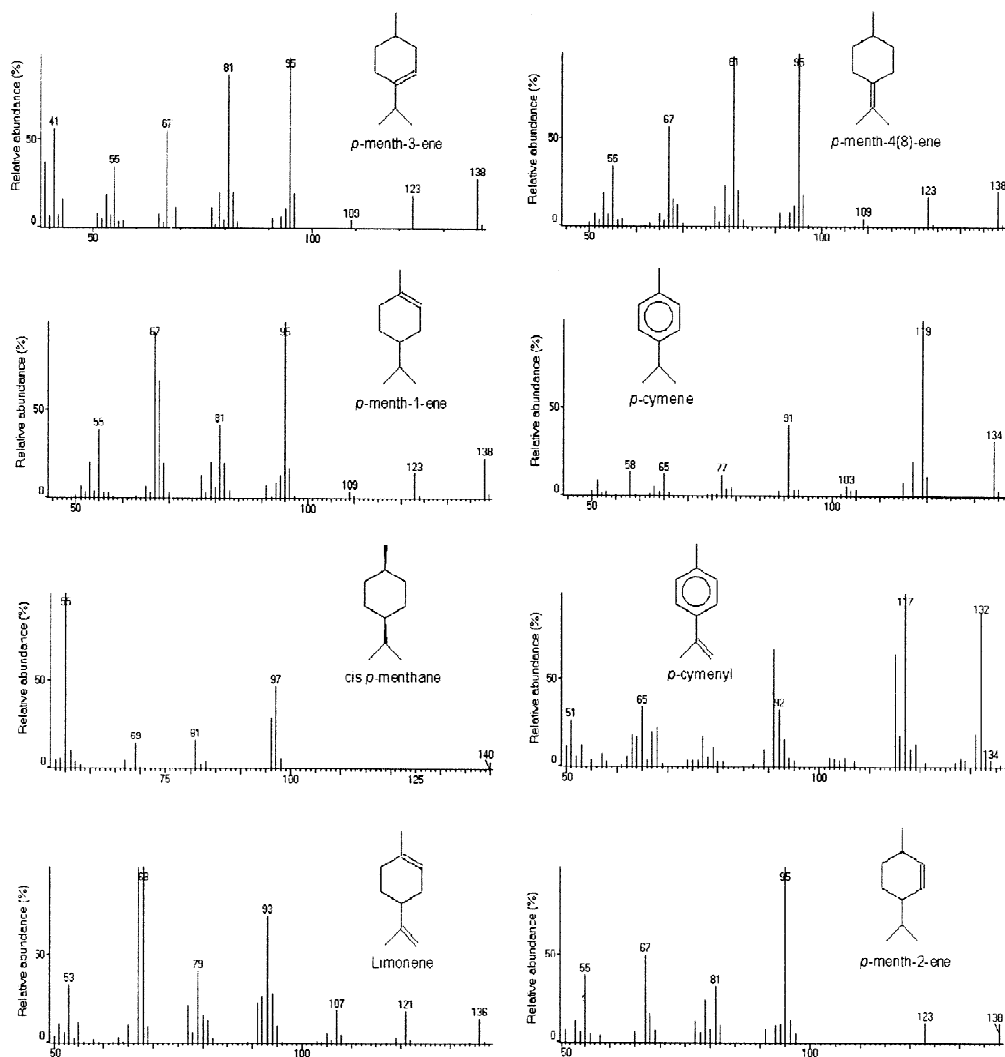The results of the trial where the amount of Pd/C

Fig. 4. Mass spectra of the main products of the disproportionation of limonene.

was reduced to 0.5% showed that, at this concentration, there is not enough catalyst for the reaction. High concentrations of limonene (11), *p*-menth-3-ene (7) and *p*-cymene (10) are observed. The latter product is the final product of disproportionation of limonene together with *p*-cymenyl (13).

Those results were reproduced when the SPME was exposed directly in the atmosphere of the reaction vessel. Similar concentrations of hydro-

genated compounds were found by following the esterification products of castor oil.

4. Conclusion

SPME–GC–MS is a simple and sensible method for the evaluation of the volatile compounds formed

on the disproportionation of limonene during the hydrogenation of castor oil.

The SPME–GC–MS procedure proved to be a good method to follow the intermediate products of disproportionation of limonene as an indicator of the hydrogenation of the starting material (Castor oil).

Acknowledgements

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