CHEMICAL CHARACTERIZATION OF CASTOR MEAL EXTRACTS FROM HIGH-PRESSURE CO_2

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This work reports the chemical characterization of castor meal extracts obtained from high-pressure CO_2. The experiments were performed in a laboratory scale unit in the temperature range of 293 - 323K from 100 to 250bar with a CO_2 mass flow rate constant of $2gmin^{-1}$, employing around 40g of castor meal. The extract chemical analyses were accomplished in a GC/MSD equipped with a capillary column OV-05. Analyses of NMR ^1H and infrared spectroscopy were also conducted for the extracts collected at each 30 min. Results show that though the use of carbon dioxide provides low liquid yields, relevant compounds, not observed in the conventional (commercial) castor oil extraction, are possible to be extracted.

INTRODUCTION

Biotransformation of vegetable oils through the use of enzymes as catalysts in supercritical medium has been a matter of intense investigation nowadays. Among several raw materials available, castor oil, obtained from the growing native castor plant, is one of the most versatile products with applications in food, pharmaceutical and cosmetic industries [1-3].

Besides, the possibility of using biodiesel as an additive to diesel fuel resulting in a less pollutant, sulfur-free, with a higher cetane number from a renewable resource has motivated the biomodification of vegetable oils towards reduction of environment investments and import needs [4,5]. The conventional process of castor oil extraction produces a residue, known as castor meal, still rich in oil, almost 5%. With the aim of recovering the remaining oil and thus incorporate some value to a waste, this work investigates the influence of temperature and pressure (solvent density) on the characteristics of the extracts of castor meal obtained from high-pressure carbon dioxide.

For this purpose, castor meal samples were submitted to high-pressure CO_2 extraction in a laboratory scale unit using the dynamic method in the temperature range of 293 - 323K from 100 to 250bar. The CO_2 mass flow rate was kept constant around $2gmin^{-1}$ in all runs, employing around 40g of castor meal.

The extract chemical analyses were carried out in a GC/MSD (Shimadzu, Model QP 5050A) equipped with a capillary column OV-05. Analyses of NMR ^1H and infrared spectroscopy (HATR/FTIR) were also conducted for the extracts collected at each 30 min.

EXPERIMENTAL

Material. Samples of castor meal obtained from the conventional extraction process (pressing technique) were employed in the extraction experiments at high pressures. Carbon dioxide (99.9% purity) was purchased from White & Martins.

Apparatus and Experimental Procedure. The experiments were performed in a laboratory scale unit, as presented in Figure 1, which consists basically of a CO_2 reservoir, two thermostatic baths, a syringe pump (ISCO 260D), a 0.1dm^3 jacketed extraction vessel, an absolute pressure transducer (Smar, LD301) equipped with a portable programmer (Smar, HT 201) with a precision of $\pm$ 0.12 bar, a collector vessel with a glass tube and a cold trap. Amounts around 40 g of castor meal samples were charged into the extraction vessel. The CO_2 at a constant rate of 2gmin^{-1} was pumped into the bed, which was supported by two 300 mesh wire disks at both ends, and was kept in contact with the herbaceous matrix for at least one hour to allow the system stabilization. Afterwards, the essential oil was collected opening the micrometering valve and the CO_2 mass flow was accounted for by the pump recordings. The experiments were accomplished isothermally, at constant pressure. The experimental range investigated was 293 to 323 K in temperature and from 100 to 250bar in pressure. Triplicate extraction runs were accomplished for all conditions.

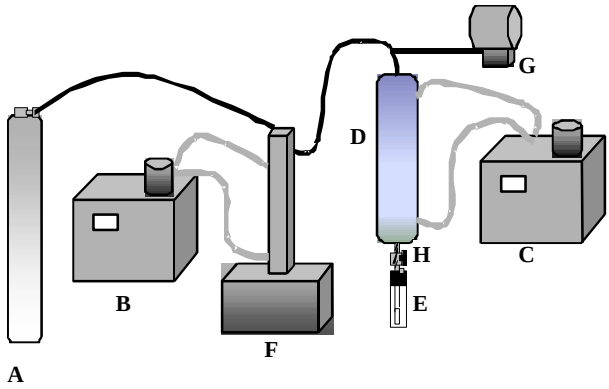

Figure 1: Schematic diagram of the high-pressure extraction apparatus. A - CO_2 reservoir; B, C - thermostatic baths; D - extraction vessel; E - collector vessel with a glass tube; F - high pressure pump; G - absolute pressure transducer; H - electrical heater.

Extract Characterization. The extract chemical analyses were carried out in a GC/MSD (Shimadzu, Model QP 5050A) equipped with a capillary column OV-05 (30m X 0,25mm X 0,25μm). NMR ^{1}H and infrared spectroscopy (HATR/FTIR) analyzes were also conducted for the extracts collected at each 30 min.

RESULTS AND DISCUSSION

Table 1 presents the extraction yields and the experimental conditions employed in this work. As one could expect, low yields were obtained since the conventional extraction technique (raw material pressing) of castor oil from seeds is very efficient [6] and also due to differences in asymmetry (size) and chemical nature between solvent and components present in the oil. Thus, it seems that the highest extraction yield was achieved due mainly to static pressure than solubility effects.

Table 1: Extraction yield and characteristic parameters for castor meal samples.

Run	T (K)	P (bar)	Extraction yield (mg extract /100g castor meal)
1	293	100	306.7
2	293	250	716.6
3	303	175	361.0
4	323	100	73.2
5	323	250	561.7

Quantitative evaluation of the extracts was performed at each 30 min of extraction by infrared spectroscopy (HATR/FTIR), ^{1}H NMR and then using GC/MSD. For the case of GC/MSD analysis, the extracts were previously submitted to silica gel column fractionation. In Figure 2, one can observe the chromatograms relative to run 2 after fractionation in n-hexane (F1), n-hexane/benzene (F2), dichloromethane (F3), ethyl acetate (F4) and methanol (F5). It is surprising to note that caffeine appears in the diluted fraction F5.

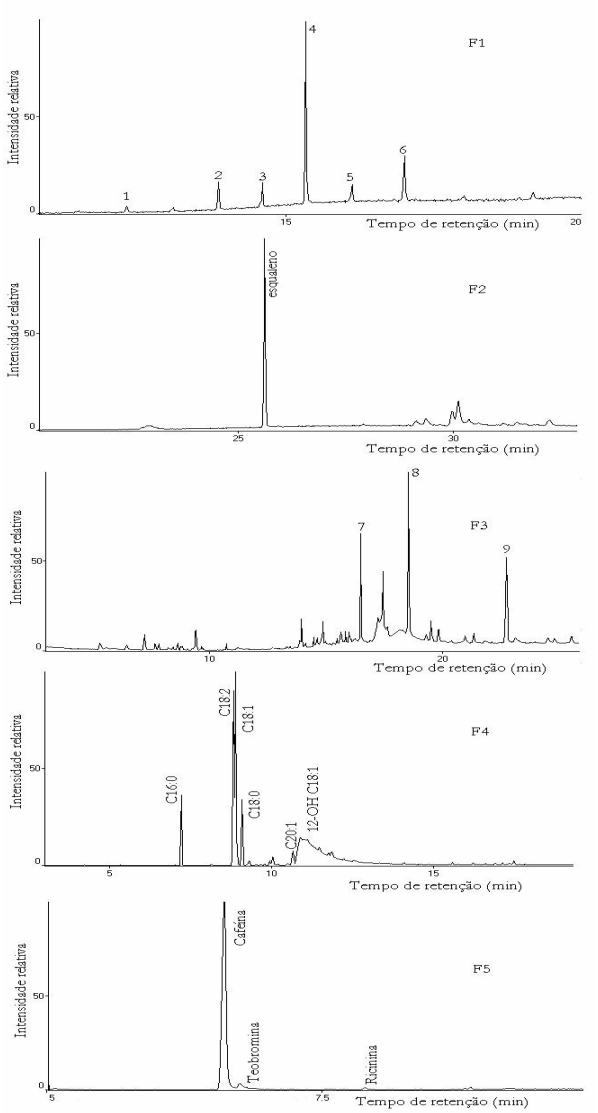

Figure 2: Total ion chromatogram (TIC) of the fractions obtained from high pressure CO_2 extraction of castor meal (run 2).

Of course, this interesting result claims for a more detailed investigation concerning the presence of alkaloid compounds in the castor plant if we take into account that the central nervous system is very sensitive to stimulating substances, like caffeine. From F1, F2 and F3 fractions of runs 1 to 5, several components were observed with clear evidence to squalene in F2. The F4 fractions of all samples were constituted mainly of triglycerides formed by palmitic, oleic, linoleic, stearic and ricinoleic acids. We can also observe in F4 fraction the occurrence of eicosenoic acid (C20:1) and with 95% similarity the following esters (Figure 3): azelaic (10), pentadecanoic (12), and heptadecanoic (15). The myristic (11) and palmitoleic (13) acids were identified by comparison with their respective standards. It was also possible to identify the fatty acids C16:0, C18:0, C18:1, C18:2 and 12-OH 9-C18:1.

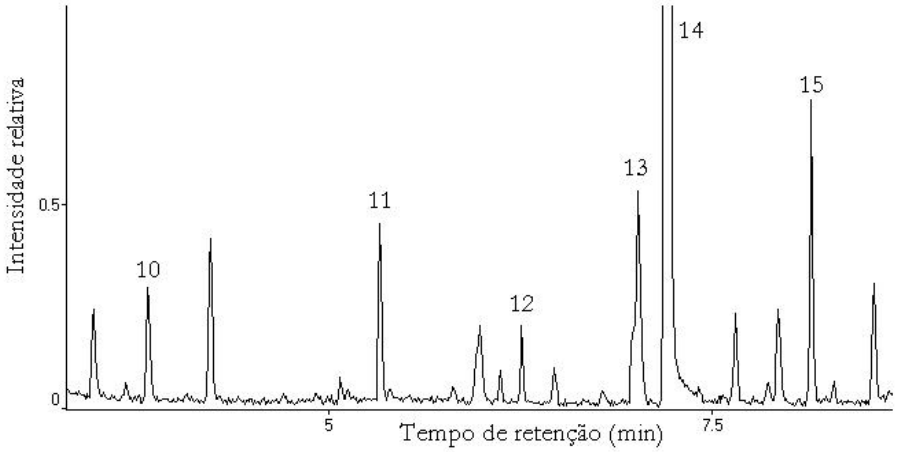

Figure 3: Amplified view of TIC of the extract from run 4.

Infrared spectroscopy. The different fractions obtained from all runs exhibit a similar spectrum of castor oil, showing that there is no discrimination among experimental extraction conditions concerning this analysis.

Nuclear Magnetic Resonance of ^{1}H. As depicted in Figure 4, some other compounds were identified in the extracts, corroborating the presence of caffeine observed previously by GC/MSD. Then, the methyl hydrogen (3, 2 and 4) was verified in 3.4 ppm, 3.6 ppm and 4 ppm, respectively. The singlete, of methyl hydrogen (1) appeared close to 7.5 ppm.

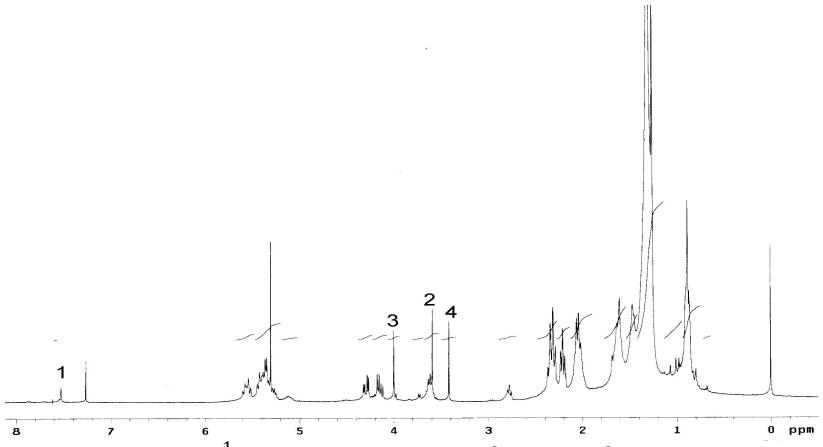

Figure 4: ^{1}H NMR spectrum of extract from run 2.

We have also observed from the spectra the presence of a singlete in 5.2 ppm, which refers to the protons 1 to 6 of squalene in accordance with Figure 5. The methyl groups spread out the squalene molecules can be found between 1.5 and 2 ppm. The importance of squalene is due to its well-known metabolic precursor properties.

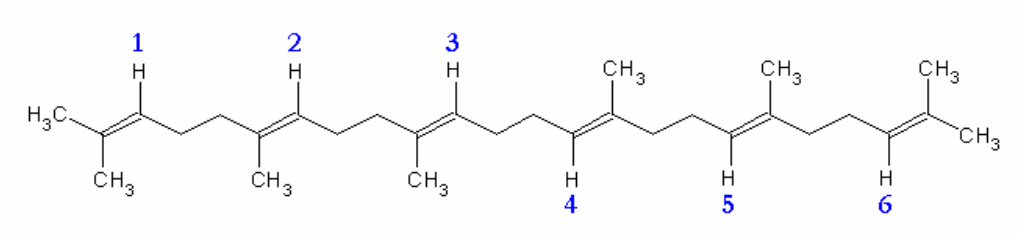

Figure 5: Plane structural formula of squalene.

From proper calculations of double bounds per mol, it was possible to quantify the number of insaturations of the glycerides present in the oil and also to confirm that the extracts are enriched with the acids C18:0, C18:1, C18:2 and C18:3. One can notice from Table 2 a greater content of polyunsaturated compounds with regard to the oil, as also verified by the GC/MSD.

Table 2: Number of insaturations and hydroxyls of the glycerides in the extracts obtained from high pressure CO_2 extraction.

Extracts	Insaturations (double bonds/mol)	Hydroxyls (OH/mol)	Polyunsaturated (CH_2 between double bonds/mol)
1	4.1	-	0.2
2	4.0	-	0.4
3	4.6	2.6	0.8
4	4.3	2.3	0.7
5	3.5	2.3	0.4
6	4.5	3.1	0.6
7	4.0	2.3	0.4
8	4.0	2.2	0.8
9	3.4	2.0	0.4
10	3.6	2.1	0.4
11	4.2	2.1	0.4
12	4.2	2.1	0.3
13	3.8	2.2	0.4
14	3.5	1.9	0.5
15	3.6	2.2	0.9
castor oil	3.2	2.7	0.0*

*Negligible signal observed from the ^{1}H NMR.

In general and more intensively in run 2, there is a superposing of the hydrogen resonance's in approximately 5.3 and 3.6 ppm. Despite this result, one notes for all experiments an enhancement of insaturations and diminution of hydroxyls compared to the results found for the oil. This indicates a lower solubility of triricinolein in CO_2 at high pressures than in the acyl glycerides, which contain the acid groups identified by GC/MSD.

CONCLUSION

Extractions of castor meal samples with carbon dioxide at high pressures provided very low liquid yields but with the presence of relevant compounds not observed in the conventional extraction method of castor oil. Chemical analyses performed show that the distribution of chemical components in the extracts depended on the pressure and extraction temperature. Components found in the extracts, like caffeine and squalene for example, emphasizes the need of a more detailed investigation concerning the composition of castor meals samples obtained in the industrial environment in a attempt to incorporate some value to a waste commonly used as fertilizer.

Acknowledgements

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