

**12TH EURO FED LIPID CONGRESS: OILS, FATS AND LIPIDS:
FROM LIPIDOMICS TO INDUSTRIAL INNOVATION**

Experimental approach versus COSMO-RS assisted solvent screening for predicting the solubility of rapeseed oil

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Received 29 January 2015 – Accepted 25 February 2015

Abstract – Vegetable oils take a large part in industry for food and non-food applications. However the extraction process of oil from oilseeds includes a solvent extraction step using hexane. Despite its various advantages it presents numerous drawbacks; it is sourced from petroleum, it has a high flammability and it appears to be dangerous for health and environment (CMR2). This study presents a theoretical screening using COSMO-RS simulations of the relative solubility of vegetable oil constituents regarding several bio-based solvents as well as an experimental screening of the efficiency of these solvents. The aim is to correlate simulations and experiments and give a preliminary evaluation for the substitution of hexane by bio-based solvents for the extraction of vegetable oils. Differences between theory and practice have been noticed for several solvents such as terpenes that appeared to be good candidates in theory and that were in fact the solvents that gave the lowest extraction yield.

Keywords: Bio-based solvents / COSMO-RS / solvent screening / extraction / rapeseed oil

Résumé – **Évaluation expérimentale et par modélisation assistée par COSMO-RS de différents solvants pour le solubilisation de l'huile de colza.** Les huiles végétales tiennent une place importante dans l'industrie pour des applications alimentaires ou non. Toutefois, le procédé d'extraction d'huile à partir de graines oléagineuses comprend une étape d'extraction par solvant mettant en jeu l'hexane. Malgré ses différents avantages, l'hexane présente de nombreux désavantages; d'origine pétrolière, il présente une grande inflammabilité et apparaît comme étant dangereux pour la santé et l'environnement (CMR2). Cette étude consiste en une procédure de sélection théorique utilisant des outils de prédiction tels que COSMO-RS pour déterminer la solubilité relative des constituants des huiles dans divers agro-solvants. Ces solvants ont été testés expérimentalement afin d'évaluer leur efficacité. L'objectif est d'établir une corrélation entre les prédictions théoriques et les essais expérimentaux et ainsi fournir une première évaluation d'un candidat potentiel à la substitution de l'hexane pour l'extraction des huiles végétales. Des différences ont été constatées entre les résultats théoriques et expérimentaux; des solvants comme les terpènes qui paraissaient être théoriquement de bons candidats pour la substitution sont apparus comme étant ceux qui donnaient les rendements d'extraction les plus faibles.

Mots clés : Agro-solvants / COSMO-RS / sélection de solvants / extraction / huile de colza

1 Introduction

Oilseeds can be considered as very important resources worldwide as their products, such as vegetable oils, are major ingredients in food industry but also in a diversity of industrial applications such as biodiesel production. Vegetable oil pro-

duction has increased continuously over the past decades and is likely to keep growing. The present study focuses on rapeseed oil that represented in 2011 around 15% of vegetable oil production in the world and more than 50% of oil production in Europe which is around 9 million tonnes (CETIOM, 2011; Carré and Pouzet, 2014).

The industrial process for rapeseed oil extraction encompasses several steps including a solvent extraction. Currently,

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the state of the art solvent is hexane, given its numerous advantages such as solubility, selectivity, ease of implementation at industrial scale, relatively low boiling point, ease of removal and recycling, etc. (Johnson, 2008). However, hexane remains sourced from petroleum, a non-renewable resource, and one of the main constituents of industrial hexane, *n*-hexane (Hexane Extraction Grade Europe Data Sheet, 2007), has recently been classified under the REACH Regulation as a category 2 reprotoxic and as a category 2 aquatic chronic toxic (Classifications – CL Inventory, 2008). With considerable amounts processed and the global potential impact on environment and occupational health, finding alternative to solvents like hexane has become a major concern for the industrials that wish to anticipate a possible change in the legislation (Fine *et al.*, 2013). Bio-based solvents mostly produced from agricultural sources seem to be potential candidates for the substitution of petroleum derived solvents.

The present study associates a simulation approach with COSMO-RS of the relative solubility of major and minor constituents of rapeseed oil in selected bio-based solvents (*i.e.* 2-methyltetrahydrofuran (MeTHF), cyclopentyl methyl ether (CPME), dimethyl carbonate (DMC), isopropanol (IPA), ethanol (EtOH), ethylacetate (EtOAc), *p*-cymene and *d*-limonene) to an experimental validation with Soxhlet extractions of rapeseed by candidate bio-based-solvents benchmarked against hexane. The aim of the study is to obtain preliminary assessment on the potential of bio-based solvents for the substitution of hexane for the extraction of vegetable oils.

2 Materials and methods

2.1 Materials and reagents

Rapeseed, of the Astrid breeding line (Euralis Semences), were provided by the *Centre Technique Interprofessionnel des Oléagineux et du Chanvre industriel* (CETIOM, Pessac, France). Hexane, MeTHF, DMC, IPA, ethanol, ethylacetate, *p*-cymene and *d*-limonene, all technical grade, were sourced from VWR International (Darmstadt, Germany). CPME was sourced from by Sigma Aldrich. Methanol, sulfuric acid, sodium chloride, chloroform, methyl acetate, acetic acid, diethyl ether, *n*-hexane and potassium chloride were of analytical grade and were sourced from VWR International (Darmstadt, Germany).

2.2 Lipid extraction: conventional Soxhlet procedure

Rapeseed samples were finely ground, for 60 s using a knife mill Microtron MB 550 (Kinematica AG, Luzern, Switzerland) less than 30 min before the extraction. The moisture content (5.89%) of rapeseeds was determined using a MB35 moisture analyzer (Ohaus, Nänikon, Switzerland). This device works by the principle of thermogravimetry; the mass change of a sample is measured as a function of the temperature (set at 110 °C) until a constant mass. Once the stable weight reached, the drying is complete and the displayed result indicates the percentage of moisture present in the matrix. Oils were isolated from rapeseeds by means of Soxhlet

extraction (Soxhlet, 1879) According to ISO standard procedure 659 (AFNOR, 2009), 30 g of coarsely ground rapeseeds were weighed and transferred into a 30 mm × 100 mm cellulose thimble (Macherey-Nagel, Germany), which was plugged with cotton in order to avoid transfer of sample particles to the distillation flask. They were then placed in the extraction chamber of a 125 ml Soxhlet apparatus fitted with a condenser, which was placed on a 500 ml distillation flask containing 300 ml of solvents. Samples were extracted under reflux with the solvents (respectively *n*-hexane, MeTHF, CPME, DMC, IPA, ethanol and ethylacetate) during 4 h (18–22 cycles/h). Thereafter, the cellulose thimble was cooled to room temperature in a desiccator and its content was then ground before being loaded again in the cellulose cartridge. The described procedure was thus repeated twice under the same conditions during 2 h until a total extraction of 8 h (4 h + 2 h + 2 h). Extractions with *p*-cymene and *d*-limonene were performed under reflux during 8 h.

After the extraction with *n*-hexane, MeTHF, CPME, DMC, IPA, ethanol and ethylacetate the content of distillation flask was evaporated under reduced pressure. The flask was then weighted and this operation was repeated until the difference between two consecutive weights was less than 10% (w/w).

The recovery of *p*-cymene and *d*-limonene was carried out according to a different way. Both terpenic compounds have a boiling point around 180 °C, which makes their elimination inachievable by conventional evaporation under reduced pressure with a rotary evaporator. Knowing that terpenes are the primary constituents of essential oils from plants and flowers which are commonly extracted from their matrix using water hetero-azeotropic distillation, the principle of hetero-azeotropic distillation was applied in this case by the addition of 50% (V/V) water in the solvents. The mixture is then commonly evaporated under reduced pressure as described previously.

The weight of the extracted rapeseed oil was determined and then used for calculating the yield of extracted oil. All extractions were performed in triplicate and the mean values were reported. Results were obtained by high performance thin layer chromatographic analysis in order to obtain the lipid yields of extracted oils. The yield of extracts was expressed as a percentage of the total weight of lipids obtained after extraction relative to the weight of dry rapeseeds used for extraction, as described hereinafter,

Yield of extracts (DM)

$$= \frac{\text{Weight of lipids obtained after extraction}}{\text{Weight of rapeseeds (dry materials)}} \times 100.$$

2.3 Chromatographic analysis

2.3.1 Gas chromatography

Fatty acids methyl esters (FAMES) were separated and identified by gas chromatography coupled with flame ionization detector (GC-FID). Samples were prepared from extracted oils using acid-catalyzed trans-methylation (Morrison and Smith, 1964). 1 ml methanolic sulfuric acid (5% v/v) was added to a specific amount (20 mg) of extracted

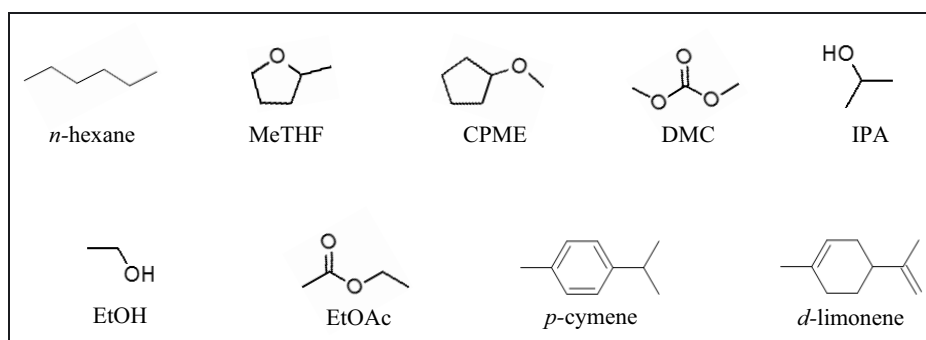


Fig. 1. Selected solvents for COSMO-RS study and experiments.

oils. The mixture was then heated at 85 °C for 90 min and then removed from heater. 1.5 ml of sodium chloride (0.9%) solution and 1 ml of *n*-hexane were added afterwards. The flask was stoppered and shaken vigorously during 30 s before centrifugation at 4000 rpm for 2 min. A small amount of the organic layer was sampled and transferred in a vial before direct injection in a gas chromatography.

Analyses were performed by a 7820A GC system (Agilent technologies, USA) equipped with a FID detector and auto-sampler. Gas chromatography was performed by a BD-EN14103 capillary column (30 m × 0.32 mm × 0.25 μm) using helium as a carrier gas at the velocity of 33 cm/s. 2 μl of various samples were injected in split mode (split ratio: 1:20) a 250 °C. The oven temperature program was operated as follows: initial temperature at 50 °C for one minute, increasing at a rate of 20 °C/min to 180 °C and at a rate of 2 °C/min from 180 °C to 230 °C, held isothermally at 230 °C for 10 min. Data were collected with Agilent EZChrom Elite software. FAMES were identified comparison with purified FAME standards (Sigma Co., USA).

2.3.2 High Performance Thin Layer Chromatography (HP-TLC)

Lipids were detected by charring and quantified using a CAMAG 3 TLC scanning densitometer (CAMAG, Muttenz, Switzerland) with identification of the classes against known polar and neutral lipid standards. Typically, lipid extract was loaded as a spot onto 20 × 10 cm silica gel 60 F254 HP-TLC plates (Merck KGaA, Germany) using an ATS 5 automatic TLC sampler (CAMAG, Switzerland). Plates were then developed in an ADC2 automatic developing chamber (CAMAG, Switzerland) using first a methyl acetate/isopropanol/chloroform/methanol/KCl (0.25% solution) (25:25:25:10:9) mixture running to a height of 5.5 cm from the origin and then a *n*-hexane/diethyl ether/glacial acetic acid mixture (70:30:2) to a height of 8.5 cm from the origin. After drying, the plate was dipped for 6 s in a modified CuSO₄ reagent (20 g CuSO₄, 200 ml methanol, 8 ml H₂SO₄, and 8 ml H₃PO₄) then heated at 141 °C for 30 min on a TLC plate heater and finally scanned using a TLC Scanner 3 with WinCATs software (CAMAG). The densitometry data are reported as values which are expressed as percent of lipid class in total rapeseed lipids.

2.4 Computational method: COSMO-RS calculations

COSMO-RS (Conductor like screening model-realistic solvation) is a powerful method for molecular description and solvent screening based on a quantum-chemical approach. COSMO-RS combines quantum chemical considerations (COSMO) and statistical thermodynamics (RS) to determine and predict thermodynamic properties without experimental data. The model based on the prediction of chemical potential of a substance in the liquid phase (Klamt *et al.*, 2010, 2002). Calculation of the relative solubility of typical triglycerides (TAGs), tocopherols and sterols of rapeseed oil in various solvents was made by implementing this COSMO-RS model in COSMOtherm software (C30 1401, CosmothemX14, COSMOlogic GmbH & Co. KG). The relative solubility x_j of compound j is calculated from the following equation (COSMOlogic GmbH & Co. KG, 2013):

$$\log_{10}(x_j) = \log_{10} \left[\frac{\exp(\mu_j^{\text{pure}} - \mu_j^{\text{solvent}} - \Delta G_{j,\text{fusion}})}{RT} \right]$$

with:

- μ_j^{pure} : chemical potential of pure compound j (J/mol),
- μ_j^{solvent} : chemical potential of j at infinite dilution (J/mol),
- $\Delta G_{j,\text{fusion}}$: free energy of fusion of j (J/mol),
- x_j : solubility of j (g/g solvent),
- R : gas constant,
- T : temperature (K).

Relative solubility is always calculated in infinite dilution. The logarithm of the best solubility is set to 0 and all other solvents are given relatively to the best solvent. A solvent with a $\log_{10}(x_j)$ value of -1.00 yields a solubility which is decreased by a factor 10 compared to the best solvent.

3 Results and discussion

3.1 Prediction study: COSMO-RS calculations

A COSMO-RS simulation was conducted in order to determine the relative solubility, $\log(x_j)$, of the major components of rapeseed oil (currently extracted with hexane) in the various solvents represented in Figure 1. These constituents, presented in Figure 2, include 4 TAGs (TAG 1

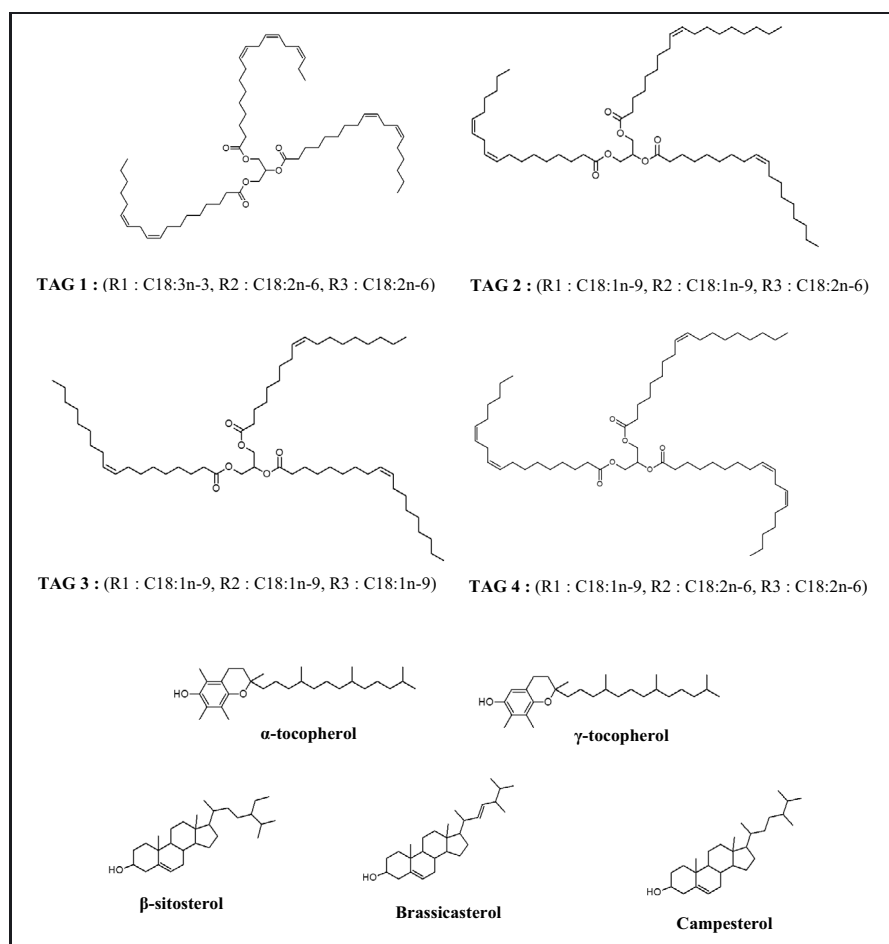


Fig. 2. Major components found in rapeseed oil.

Table 1. COSMO-RS prediction results regarding the solubility of the major components of rapeseed oil in several solvents.

	TAG 1	TAG 2	TAG 3	TAG 4	α -tocopherol	γ -tocopherol	Brassica sterol	β -sito sterol	Campe sterol
<i>n</i> -Hexane	-0.6390	0	0	0	-0.1356	-0.2974	-0.8087	-0.8017	-0.7582
MeTHF	0	0	0	0	0	0	0	0	0
CPME	0	0	0	0	0	0	0	0	0
DMC	-0.3153	-1.4228	-1.4633	-1.6227	-0.6462	-0.6102	-0.8877	-1.0366	-1.0650
Isopropanol	-1.1684	-1.5552	-1.5248	-1.7726	-0.4937	-0.4291	-0.2366	-0.2687	-0.3015
Ethanol	-1.8570	-2.4547	-2.4428	-2.7206	-0.9490	-0.8650	-0.5313	-0.5797	-0.6308
Ethyl Acetate	0	0	0	0	0	0	0	-0.0866	-0.0967
<i>p</i> -cymene	0	0	0	0	-0.0928	-0.2018	-0.7401	-0.7829	-0.7714
<i>d</i> -limonene	0	0	0	0	-0.0150	-0.1324	-0.6732	-0.6992	-0.6767

Reference or equivalent
Better than reference
Lesser than reference

TAG 1 ((R1: C18:3n-3, R2: C18:2n-6, R3: C18:2n-6), TAG 2 ((R1: C18:3n-3, R2: C18:2n-6, R3: C18:2n-6), TAG 3 (R1: C18:1n-9, R2: C18:1n-9, R3: C18:1n-9), TAG 4 (R1: C18:1n-9, R2: C18:2n-6, R3: C18:2n-6), 2 tocopherols (α -tocopherol and γ -tocopherol) and 3 sterols (campesterol, brassicasterol and β -sitosterol). Results of the COSMO-RS simulation are presented in Table 1. As the logarithm of the best solubility is set to 0 and all other solvents are given relatively to the best solvent, it can be noticed that at 50 °C, which is close to the

temperature of extraction under industrial conditions, $\log(x_j)$ for TAG2, TAG3 and TAG4 with *n*-hexane (taken as the reference) is equal to 0. It means that it has the best solubility compared to other tested solvents. Nevertheless, $\log(x_j)$ for the other components is below zero; *n*-hexane is found not to be the best solvent for extraction of these compounds among all the candidate solvents. Considering the TAGs, $\log(x_j)$ with MeTHF, CPME, ethylacetate, *p*-cymene and *d*-limonene are computed at 0 which means that in terms of relative solubility

these five solvents are equivalent to *n*-hexane (and even found better for TAG1). These five solvents are also found better than *n*-hexane regarding the solubility of tocopherols. It can be noticed that MeTHF, CPME and ethylacetate are computed optimal as their $\log(x_j)$ is null; then come *d*-limonene and *p*-cymene. The other solvents, DMC, IPA and ethanol, are theoretically not good substitute to *n*-hexane for the extraction of TAGs and tocopherols as $\log(x_j)$ for these constituents are found lower than with *n*-hexane. Nevertheless, regarding the results for the sterols, only DMC appears to be worse than *n*-hexane. MeTHF and CPME are also the best for these constituents as $\log(x_{\text{solub}}) = 0$. Considering their relative solubility towards sterols, the other solvents can be classified as follows: ethylacetate > IPA > ethanol > *d*-limonene > *p*-cymene.

Regarding the global results of the computation and considering all the constituents and candidate solvents, MeTHF and CPME appear to theoretically be the most promising alternative solvents to hexane among all other tested solvents for the extraction of the 7 major constituents found in rapeseed oil. These solvents were then experimentally tested for the actual extraction of rapeseed oil in order to correlate the results of the actual extraction to those computed using COSMO-RS.

3.2 Experimental study: Soxhlet extractions of rapeseed oil

For these experiments rapeseed samples were very finely ground in a knife mill for 60 s just before the extractions in order to focus on solubility and at least avoid as much as possible the effect of diffusivity of the solvents inside the matrix. After 8 h Soxhlet extraction, relative composition were determined by GC-FID after transmethylation of fatty acids, lipid classes and total lipid yield of the extracts were determined by HP-TLC (High Performance Thin Layer Chromatography). Hexane is taken as reference for the comparison of the efficiency of candidates solvents.

3.2.1 Qualitative and quantitative comparison of the extracts

As shown in Table 2, lipid profile of oils obtained with MeTHF, CPME, DMC, IPA, ethanol, and ethylacetate are comparable to the one obtained with hexane. No important differences of selectivity between hexane and these solvents has been noticed as the composition in fatty acids remains the same; the main fatty acids in extracted oils are oleic (C18:1), linoleic (C18:2), linolenic (C18:3) and palmitic (C16:0) which represent more than 90% of the total fatty acids in extracted oil. Moreover, a HP-TLC analysis allows to confirm that more than 80% of the constituents extracted with these solvents are triglycerides (TAG) as shown in Table 3. Other constituents found in oils extracted with MeTHF, CPME, IPA and ethanol, are phospholipids and were presents in variable amounts in extracts. The presence of phospholipids is due to the higher polarity of these solvents compared to *n*-hexane; the more polar the solvent the higher the amount of phospholipids. In practice, crude oils obtained by solvent extraction with hexane are

rich in phospholipids compared to oils obtained by pressing, as described by Nash and Frankel (Clark and Snyder, 1991; Nash and Frankel, 1986).

Regarding the extracts obtained with *p*-cymene and *d*-limonene, more than 90% of total fatty acids in extracts are also oleic (C18:1), linoleic (C18:2), linolenic (C18:3) and palmitic (C16:0). However, a slight difference in the composition can be noticed as these solvents allow for the extraction of acid γ -linolenic, C18:3n-6 (1.61% and 0.50% respectively). The HPTLC analysis shows that lipids extracted with these solvents are also TAGs. The relatively low percentage obtained with *d*-limonene as well as remaining percentages that are not lipids in the other samples can be explained by the amount of solvent left after the evaporation step.

It can be noticed that all tested solvents allow for an extraction of rapeseed oil with relatively good yields. The lipid yields given in Table 3 show that all tested solvents allow for an extraction of rapeseed oil with relatively good yield; hexane enables the extraction of around 47 g lipids/100 g dry matter as well as MeTHF and ethanol. IPA gives a yield of at least 45 g lipids/100 g dry matter, but this is mainly due to a higher extraction of phospholipids (as well as for ethanol) that are usually of poor desirability in vegetable oils. Ethylacetate and DMC considering the high standard deviation of the yields are comparable to hexane. The last three solvents, CPME, *p*-cymene and *d*-limonene, give slightly lower yields than the other tested ones but allow at least an extraction of 37 g lipids/g dry matter which represent around 80% of the amount extracted with *n*-hexane. An ANOVA (ANalysis Of Variance) oneway analysis with a Student test showed that MeTHF, ethanol, IPA, Ethylacetate, DMC and CPME are not significantly different from hexane ($p > 0.05$) regarding the extraction yield of rapeseed oil. However *p*-cymene and *d*-limonene significantly give a lower yield than hexane ($p = 0.0255$ and $p = 0.0047$, respectively). The statistical study showed that MeTHF ($p = 0.8556$) and ethanol ($p = 0.9600$) are the solvents that give the results the closest to those obtained with hexane.

3.2.2 Relation with the theory

The COSMO-RS calculations indicate that MeTHF and CPME were theoretically the best alternatives to *n*-hexane. Nevertheless the actual experiments show that among both solvents only MeTHF was as good as hexane qualitatively and quantitatively, taking into account global yield and lipid composition. CPME gives a lower yield than nearly all the other tested solvents but remains statistically comparable to the reference. Ethanol and IPA experimentally give rather good lipid yields, but this appears to be due to the extraction of phospholipids. Despite the high standard deviation obtained on actual tests for Ethylacetate and DMC the statistic study showed that they are comparable to hexane regarding rapeseed oil extraction which was theoretically not the case for DMC that was part of one of the worst candidates. Surprisingly *p*-cymene and *d*-limonene that theoretically looked better than hexane for the extractions of most of the components of rapeseed oil are experimentally the worst ones.

Table 2. Fatty acid composition of rapeseed oil extracted with various solvents.

Fatty Acids	Extracted Amounts of fatty acids (%)									
	<i>n</i> -hexane	MeTHF	CPME	DMC	IPA	EtOH	EtOAc	<i>p</i> -cymene	<i>d</i> -limonene	
C16	4.46 ± 0.22	4.80 ± 0.06	4.82 ± 0.01	4.79 ± 0.03	4.91 ± 0.09	4.98 ± 0.02	4.99 ± 0.04	4.72 ± 0.05	5.01 ± 0.06	
C16: 1 <i>n</i> -7	0.21 ± 0.03	0.25 ± 0.00	0.26 ± 0.01	0.27 ± 0.02	0.27 ± 0.01	0.28 ± 0.01	0.27 ± 0.01	0.25 ± 0.00	0.46 ± 0.03	
C18	1.42 ± 0.11	1.42 ± 0.03	1.47 ± 0.01	1.34 ± 0.08	1.47 ± 0.04	1.47 ± 0.01	1.50 ± 0.01	1.54 ± 0.06	1.48 ± 0.04	
C18: 1 <i>n</i> -9	54.58 ± 0.01	53.62 ± 0.03	53.75 ± 0.11	53.53 ± 0.48	53.43 ± 0.05	53.23 ± 0.29	54.34 ± 0.90	52.97 ± 0.47	52.62 ± 0.19	
C18: 1 <i>n</i> -7	3.28 ± 0.03	3.36 ± 0.05	3.31 ± 0.01	3.23 ± 0.07	3.17 ± 0.06	3.28 ± 0.11	3.27 ± 0.07	3.46 ± 0.06	3.45 ± 0.04	
C18: 2 <i>n</i> -6	22.34 ± 0.38	22.65 ± 0.11	22.34 ± 0.11	22.27 ± 0.01	22.55 ± 0.27	22.58 ± 0.08	22.77 ± 0.55	21.12 ± 0.43	22.02 ± 0.15	
C18: 3 <i>n</i> -6	–	–	–	–	–	–	–	1.61 ± 0.31	0.50 ± 0.04	
C18: 3 <i>n</i> -3	9.11 ± 0.25	9.41 ± 0.07	9.32 ± 0.01	9.48 ± 0.05	9.39 ± 0.09	9.33 ± 0.03	9.01 ± 0.23	8.98 ± 0.01	9.00 ± 0.12	
C20	0.46 ± 0.05	0.49 ± 0.02	0.48 ± 0.01	0.50 ± 0.02	0.45 ± 0.01	0.44 ± 0.00	0.47 ± 0.01	0.46 ± 0.02	0.47 ± 0.01	
C20: 1 <i>n</i> -9	1.71 ± 0.07	1.74 ± 0.01	1.83 ± 0.09	1.87 ± 0.08	1.75 ± 0.08	1.74 ± 0.00	1.71 ± 0.02	1.72 ± 0.01	1.64 ± 0.01	
C20: 4 <i>n</i> -6	0.58 ± 0.10	0.55 ± 0.02	0.48 ± 0.06	0.57 ± 0.03	0.75 ± 0.09	0.87 ± 0.10	0.97 ± 0.14	1.42 ± 0.05	1.58 ± 0.08	
C20: 5 <i>n</i> -3	0.37 ± 0.04	0.24 ± 0.01	0.24 ± 0.02	0.30 ± 0.05	0.28 ± 0.04	0.33 ± 0.04	0.33 ± 0.01	0.33 ± 0.01	0.33 ± 0.05	
C22: 1 <i>n</i> -9	1.48 ± 0.07	1.47 ± 0.12	1.71 ± 0.21	1.73 ± 0.23	1.57 ± 0.17	1.46 ± 0.03	1.37 ± 0.00	1.42 ± 0.04	1.43 ± 0.06	
∑SFAs	6.34	6.71	6.77	6.63	6.83	6.89	6.96	6.72	6.95	
∑MUFAs	61.26	60.44	60.86	60.63	60.19	59.99	60.96	59.82	59.60	
∑PUFAs	32.40	32.85	32.38	32.62	32.97	33.11	33.08	33.46	33.43	

Table 3. Lipid yield and lipid classes in total extracts.

Lipid class composition	Amount in total extracts (%)									
	<i>n</i> -hexane	MeTHF	CPME	DMC	IPA	EtOH	EtOAc	<i>p</i> -cymene	<i>d</i> -limonene	
Neutral lipids										
TAG	99.12 ± 0.11	92.83 ± 0.17	88.60 ± 2.25	89.31 ± 7.63	80.19 ± 1.82	96.71 ± 2.27	87.11 ± 7.23	82.03 ± 5.02	51.31 ± 5.16	
Polar lipids										
PE	–	–	–	–	0.70 ± 0.03	0.38 ± 0.14	–	–	–	
PI	–	–	–	–	1.21 ± 0.03	1.02 ± 0.24	–	–	–	
PC	–	0.59 ± 0.01	0.38 ± 0.11	–	6.34 ± 0.15	1.26 ± 0.00	–	–	–	
LPC	–	–	–	–	0.01 ± 0.00	0.01 ± 0.00	–	–	–	
Total (g/g DM)	46.71 ± 0.75	47.19 ± 0.44	41.53 ± 0.26	42.77 ± 2.33	44.97 ± 1.07	46.57 ± 0.42	42.83 ± 3.34	39.71 ± 3.03	36.94 ± 0.82	

4 Conclusion

The present study illustrates that bio-based solvent could be potential alternatives to hexane even if there are differences between simulations and actual experiments. Theoretical simulations can be seen as a powerful screening tool, but are not yet accurate enough to predict what would be the best solvent experimentally. Differences can be explained not only by the compositions of oils but also by the phys-chem properties of the solvents such as viscosity, density, volatility, specific heat, surface tension. . . Actually, diffusivity of the solvent inside the matrix is an important factor to take into account. It would also be interesting to take into account polar compounds such as phospholipids in the theoretical study as they influence the global lipid yield. Moreover the choice of a solvent for a substitution has to consider other parameters than solubility that are not taken into account in theoretical simulations. Indeed the technical properties of the solvent have a significant importance for the solvation of components of interest but also for the implementation of the process at different scales.

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Cite this article as: Anne-Gaëlle Sicaire, Maryline Abert Vian, Frédéric Fine, Patrick Carré, Sylvain Tostain, Farid Chemat. Experimental approach *versus* COSMO-RS assisted solvent screening for predicting the solubility of rapeseed oil. *OCL* 2015, 22(4) D404.