

## Article

# Simultaneous Distillation–Extraction of Essential Oils from *Rosmarinus officinalis* L.

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**Abstract:** The present study describes a procedure to isolate essential oils from *Rosmarinus officinalis* L. using simultaneous distillation–extraction (SDE). *Rosmarinus officinalis* L. can be used for medicinal purposes, as well in the cooking and cosmetics industries. SDE technique extraction combines a steam distillation combined with a continuous extraction using a solvent or a co-solvent mixture, providing faster extractions with low extraction solvent volumes. The effect of the solvent nature and the extraction time on the simultaneous distillation–extraction efficiency was evaluated. The best performance was achieved using pentane as a solvent for 1 h of extraction. The essential oils obtained by simultaneous distillation–extraction extracts were analyzed by gas chromatography with flame ionization detection (GC-FID). Extraction efficiencies ranged from 40 to 70% for the majority of the compounds tested, and the precision (measured by the relative standard deviation) varied between 6 and 35%. Among the compounds analyzed the most abundant in the *Rosmarinus officinalis* L. sample were 1,8-cineole, (-)-borneol,  $\alpha$ -pinene, (S)-(-)- $\alpha$ -terpineol, (-)-bornyl acetate, linalool, and 2,2,6-trimethylcyclohexanone. The SDE method proved to be a suitable option for obtaining extracts free from cuticular waxes or chlorophylls.

**Keywords:** simultaneous distillation–extraction; *Rosmarinus officinalis* L.; essential oils; foods; cosmetics; nutraceuticals



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## 1. Introduction

*Rosmarinus officinalis* L. is an aromatic shrub with an intense, pleasant smell belonging to the Lamiaceae family [1–3]. It is indigenous to the Mediterranean region, cultivated mainly in Spain, Morocco, and Tunisia [1], but also China, India, Algerian, North America, Northern Europe, and England [4]. In Portugal, it is an abundant species, mainly in the North East, Centre, and South of the country mainland.

However, in the innermost regions, it is possible to find more abundance.

The flowering season is very long and gradual, from April to August, but often, it flowers all year long. Due to its rusticity, it grows in every soil type, but it prefers a sandy, arid, calcareous, and humus-poor soil [1].

*Rosmarinus officinalis* L. has been used since ancient times for medicinal purposes and is known for its antiseptic, anti-rheumatic, anti-inflammatory, and antispasmodic properties. *R. officinalis* extracts also exhibit hepatoprotective, anti-diabetic, anti-ulcerogenic, and antidepressant effects [5,6]. This plant can be used fresh, dried, or as a tea infusion, for cooking purposes as flavoring agents, in the preservation of foods, and cosmetics [6,7].

Essential oils extracted from *Rosmarinus Officinalis* L. are widely used in the cosmetics and perfumery industry and also aromatherapy, in particular by therapeutic techniques such as massage, inhalation, or bath. They are also used as ingredients in the pharmaceuti-

cal industry to flavor oral forms, to perfume dermo-pharmaceutical preparations, and to ensure the preservation of pharmaceutical forms [8].

Due to their broad antimicrobial activities, the essential oils of *Rosmanirus Officinalis* L. have preservative potential for the food and cosmetic industries [9].

Essential oils have a complex composition, containing a few dozens to several hundred constituents, especially hydrocarbons (terpenes and sesquiterpenes) and oxygenated compounds (alcohols, aldehydes, ketones, acids, phenols, oxides, lactones, acetals, ethers, and esters). Both hydrocarbons and oxygenated compounds are responsible for the characteristic odors and flavors [10]. Many studies have pointed out the variability of the composition and the yield of the essential oil due to intrinsic (genetics, subspecies, and plant age) or extrinsic factors, such as climate and cultivation conditions (geographical origin) or isolation methods [1].

This variation of the composition is usually more quantitative than qualitative, and due to that, essays performed with essential oils should always provide a biological characterization of the plant material and the oil's phytochemical profile, enabling the reproducibility and accuracy of data.

Essential oils can also be microencapsulated for use in cosmetics and personal health-care products. In cosmetic products, essential oils (EOs) play a major role as fragrance ingredients. They can optimize its proprieties and preservation, as well as the marketing image of the final product. Microencapsulation of EOs can protect and prevent the loss of volatile aromatic ingredients and improve the controlled release and stability of these core materials [11–13].

*Rosmarinus officinalis* L (Rosemary) essential oil mainly contains monoterpenes and monoterpene derivatives (95–98%), with sesquiterpenes being the remainder (2–5%) [14]. Monoterpene hydrocarbons present in *Rosmarinus officinalis* L (Rosemary) essential oil include 1,8-cineole, *p*-cymene, linalool,  $\gamma$ -terpinene, thymol,  $\beta$ -pinene,  $\alpha$ -pinene, eucalyptol, (-)-bornyl acetate, camphor, and camphene [5,6,15–19] (Table 1).

**Table 1.** The composition of essential oils (%) for *Rosmarinus officinalis* L.

Compound	CAHD	CAHD	CAHD	SFE
$\alpha$ -Pinene	11.87	10.1	37.22	-
2,2,6-Trimethylcyclohexanone	NS	-	-	-
1,8-Cineole	34.82	35.8	23.76	48–67
Linalool	0.62	0.7	2.93	-
(-)-Borneol	5.09	9.2	0.80	6–15
(S)-(-)- $\alpha$ -Terpineol	4.12	4.4	1.51	-
Citronellol	-	-	0.18	-
(R)-(+)- Pulegone	-	-	-	-
Geraniol	-	-	2.94	-
(-)-Bornyl acetate	1.56	1.6	1.70	1–2
Eugenol	-	-	-	-
Geranyl acetate	-	-	0.22	-
Reference	Badreddine et al., 2015	Yosr et al., 2013	Cassel et al., 2009	Vicente et al., 2013

CAHD—Clevenger Apparatus hydrodistillation; SFE—Supercritical extraction; NS—not studied.

Essential oils of leaves, with approximately the same length, taken at the same zone of the branches and differing by their age, were characterized by a high content of 1,8-cineole (35.8%), camphor (14.5%), and  $\alpha$ -pinene (10.6%). Oils from stems and flowers contain high contents of caryophyllene oxide (11.4%) and  $\beta$ -caryophyllene (16.68%), respectively [5].

Extraction techniques based on compounds solubility involve a direct contact of the sample with the solvent (e.g., supercritical fluid extraction) or with the adsorbent (e.g., solid-phase microextraction in the direct extraction mode), leading to a co-extraction of heavy components which pollutes gas chromatograph injectors.

Volatility-based techniques do not exhibit such a drawback; however, they either yield high water volumes containing a low concentration of the volatiles (hydrodistillation, steam distillation), or they isolate the most volatile fraction. Only a few methods take advantage of both properties [4,20].

Simultaneous distillation–extraction (SDE), introduced in 1964 by Likens and Nickerson, has been successfully applied in the extraction of essential oils, aromatic compounds, and other volatile products from several matrices. This technique has usually been considered superior to classical ones, such as distillation or solvent extraction, once it combines steam distillation with continuous extraction with a solvent or a mixture of solvents [21].

This one-step isolation–concentration technique allows a dramatic time saving over the separated operation and, because of their continuous recycling, a great reduction in treated volumes of liquids [20].

This technique does not require a clean-up step. Moreover, the extracts obtained by SDE are free from non-volatile materials such as cuticular waxes or chlorophylls. The SDE enables high extraction efficiencies associated with high reproducibility. This technique has also been used to analyze volatile compounds in several matrices [21].

## 2. Experimental

### 2.1. Chemicals

Twelve essential oils were investigated,  $\alpha$ -pinene (Sigma-Aldrich 99%); 2,2,6-trimethyl cyclohexanone (Fluka 99%); 1,8-cineole (Sigma-Aldrich 99%), linalool (Sigma-Aldrich 99%); (-)-borneol (Fluka 99.5%), (S)-(-)- $\alpha$ -terpineol (Merck 98%), citronellol (Sigma 95%); (R)-(+)-pulegone (Aldrich 97%), geraniol (Sigma 98%); (-)-bornyl acetate (Fluka 99%), eugenol (Sigma 99%); geranyl acetate (Fluka 99%).

Acetophenone (internal standard) was purchased from Fluka (98%). Ethanol was from Panreac (99.9%). Extraction solvents were *n*-Pentane (Carlo Erba 95%) and Chloroform (Panreac 99.0%).

### 2.2. Sample

The sample analyzed was *Rosmarinus officinalis* L., collected on 10 March 2018, in the Portuguese region of Vila Real.

### 2.3. Apparatus and Material

Gas chromatography was performed using a Bruker 430-GC gas chromatograph (GC) equipped with a Flame Ionization Detector (FID). A BR-1MS column from Bruker was used (15 m length, 0.25 mm internal diameter, 0.25  $\mu$ m film thickness). The GC oven was programmed (50 °C for 1 min, raised a rate of 50 °C/min until 280 °C and then maintained for 1 min). Injections were performed in split mode (1:10 ratio) using a 0.5  $\mu$ L syringe (SGE), and the injection volume was 0.2  $\mu$ L. Helium was used as carrier gas at a constant flow of 1 mL/min.

Extractions were performed in a Simultaneous Distillation Extraction (SDE) using a Likens–Nickerson apparatus.

### 2.4. Extraction

For the extraction of samples, 25 g of fresh plant grinded into a fine paste using a mortar and pestle were placed in the aqueous flask together with 250 mL of distilled water, using a method adapted from [21].

The preparation of the organic phase included 50 mL of solvent (either *n*-Pentane or Chloroform) was introduced. The time of extraction was optimized from 30 to 120 min. The solvent was removed in a rotating evaporator (Buchi Rotavapor E-210 rotary evaporator) at room temperature. The extract was washed with 4 portions of 1 mL of ethanol and transferred to a vial. Ethanol was then evaporated under a gentle stream of nitrogen (approximately 1 L/min) and the extract was reconstituted with 1 mL of ethanol.

### 3. Method Optimization and Validation

Individual compounds were identified by the retention time using the injection of individual standards.

The calibration curves for all the essential oils were obtained by the internal standard method, using acetophenone as the internal standard, at a constant concentration of 39 mg/L. For each oil, seven concentration level standards were prepared in ethanol. The prepared samples were injected in triplicate, as well as the respective calibration standards. The injections in the GC were performed manually.

### 4. Results and Discussion

After identifying chromatographic peaks (Figure 1), calibration was performed. The results of the retention times, the concentration range, and the correlation coefficient are presented in Table 2.

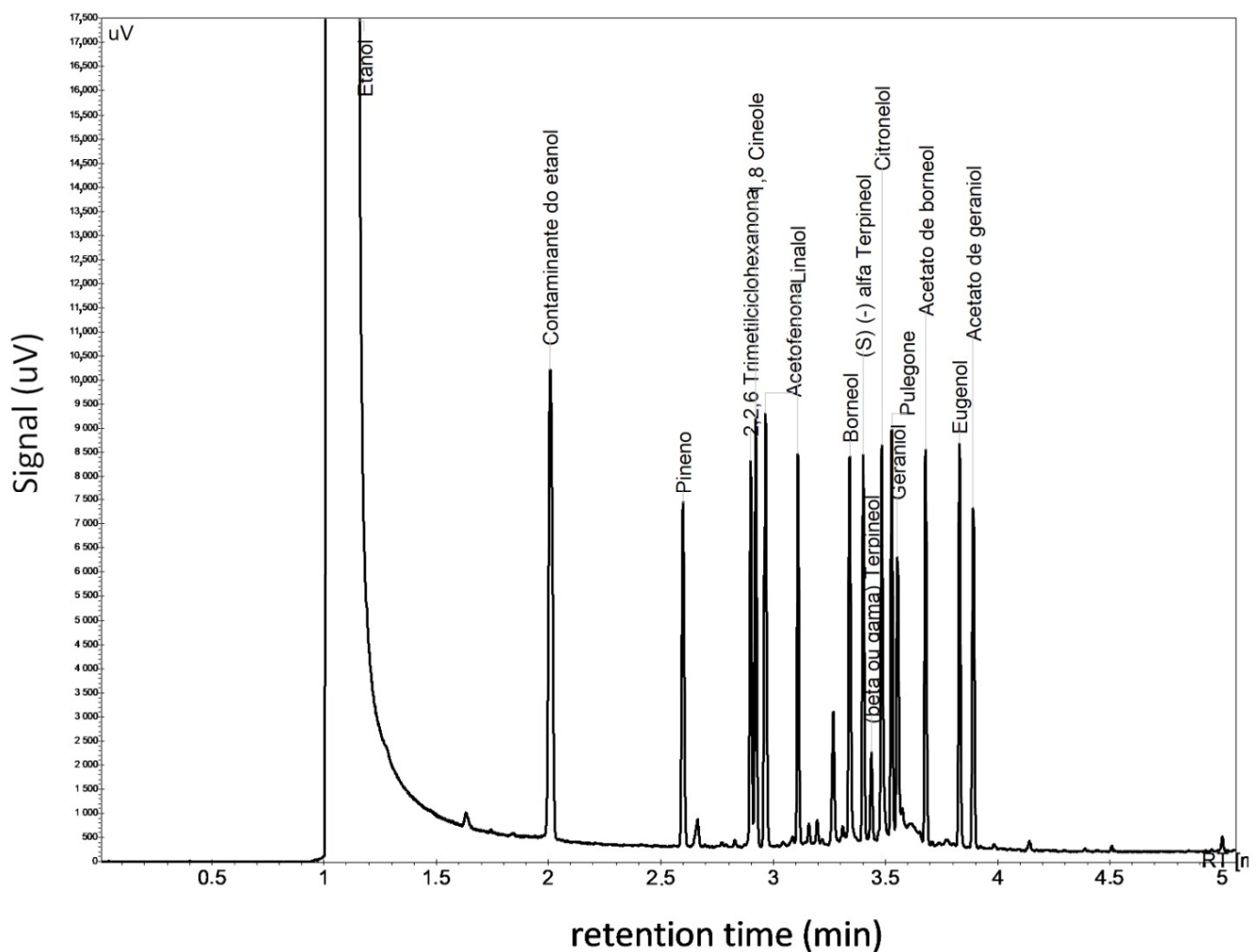


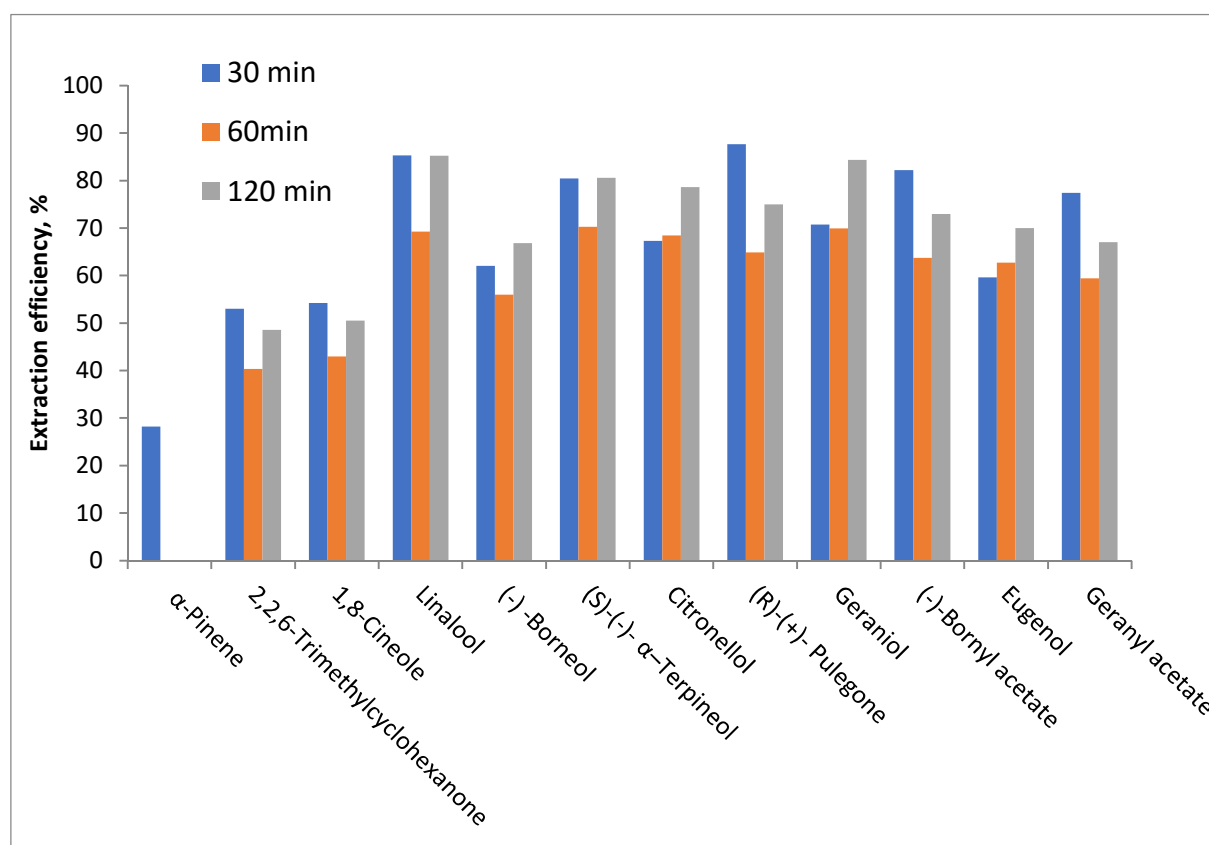
Figure 1. Chromatogram of an essential oils standard mix analyzed by GC-FID.

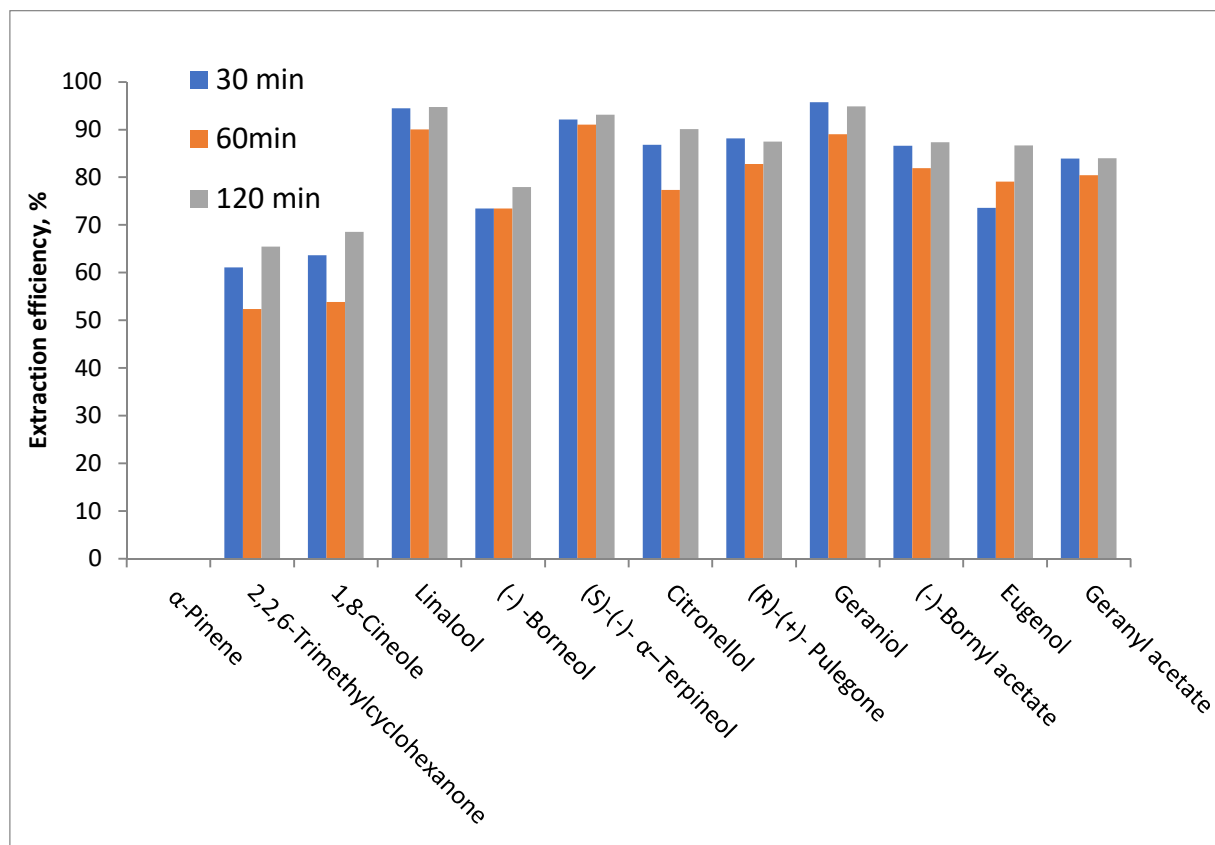
**Table 2.** Retention time, linearity concentration range, and correlation coefficients of the studied compounds with SDE/GC-FID.

Compound	Retention Time (min)	Concentration Range (mg/L)	Correlation Coefficient—(R <sup>2</sup> )
$\alpha$ -Pinene	2.602	3.5–139.5	0.9993
2,2,6-Trimethylcyclohexanone	2.899	0.9–36.8	0.9997
1,8-Cineole	2.925	1.0–38.3	0.9996
Acetophenone	2.968	39.3	Internal standard
Linalool	3.110	0.9–36.6	0.9998
(-)-Borneol	3.345	0.9–36.1	0.9998
(S)-(-)- $\alpha$ -Terpineol	3.405	0.9–35.7	0.9998
Citronellol	3.479	1.0–39.0	0.9995
(R)-(+)-Pulegone	3.523	0.9–37.8	0.9997
Geraniol	3.553	0.8–33.0	0.9996
(-)-Bornyl acetate	3.683	0.9–35.9	0.9999
Eugenol	3.834	1.0–40.2	0.9992
Geranyl acetate	3.892	0.9–36.1	0.9986

Two extraction solvents were tested: *n*-Pentane and Chloroform. For these two solvents, three different times of extraction were tested: 30, 60, and 120 min. Extraction efficiency was evaluated by extracting 100  $\mu$ L of a highly concentrated oil mixture. Extraction efficiency was calculated as the ratio between the concentration determined by the analysis of the spiked extract and the amount of compound spiked to the water. The concentration of each compound was calculated by the ratio between the amount of compound quantified in the extract divided by the extraction efficiency for that compound and divided by the weight of the sample extracted.

Extraction efficiency results are presented in Figures 2 and 3.

**Figure 2.** Extraction time optimization results using *n*-pentane as the extraction solvent.



**Figure 3.** Extraction time optimization results using chloroform as the extraction solvent.

Less extraction was observed for  $\alpha$ -pinene as the time of extraction increased. This should be caused by the losses by evaporation due to the volatility of this compound, once it is the one with the lowest boiling point and due to the fact that the boiling point of chloroform is superior to *n*-pentane and as such, evaporation occurs at higher temperatures. Furthermore,  $\alpha$ -pinene also has a lower solubility in chloroform than in *n*-pentane.

Since extraction efficiencies were similar for both solvents, *n*-pentane was chosen due to the environmental impact of chloroform. The time of extraction chosen was 30 min once  $\alpha$ -pinene was detected with this extraction time, and extraction efficiency did not increase with time for the other compounds.

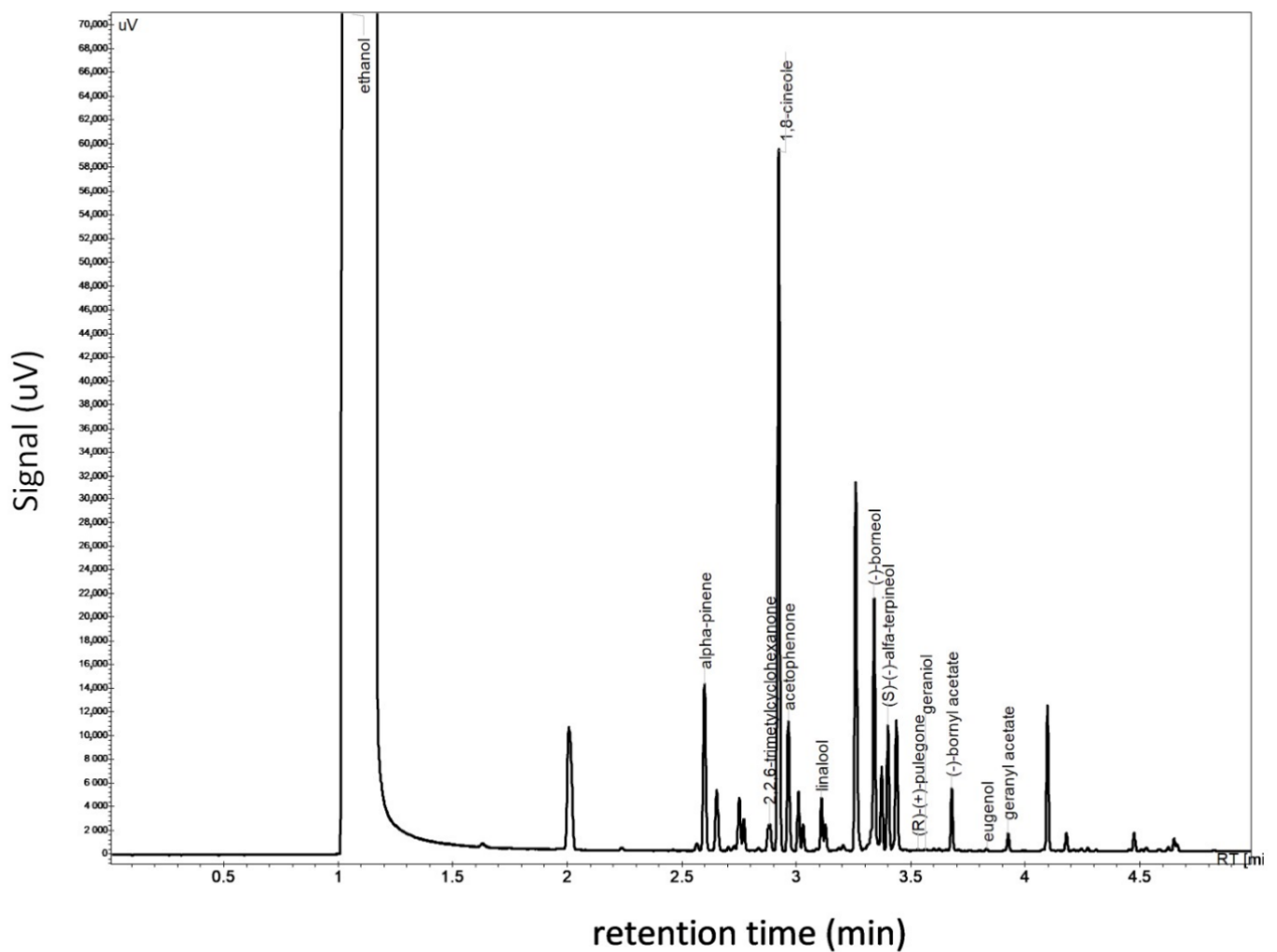
Extraction efficiency was tested using *n*-Pentane as the extraction solvent and with 30 min of extraction time. Extraction efficiency results are presented in Table 3 and show very good accuracy, being the relative standard deviation (RSD (%)) lower than 35% for all compounds. Excluding  $\alpha$ -pinene, extraction efficiencies were high, on average from 53 to 88%.

**Table 3.** Extraction efficiency results for *n*-pentane in four different days.

Compound	Extraction Efficiency Using <i>n</i> -Pentane (%)					RSD (%)
	Day 1	Day 2	Day 3	Day 4	Average	
$\alpha$ -Pinene	23	24	38	ND	28	29
2,2,6-Trimethylcyclohexanone	52	52	60	48	53	9
1,8-Cineole	52	53	62	50	54	10
Linalool	93	95	88	65	85	16
(-)-Borneol	66	71	67	44	62	20
(S)-(-)- $\alpha$ -Terpineol	91	92	85	54	80	22
Citronellol	67	79	73	50	67	18
(R)-(+)-Pulegone	85	103	80	82	88	12
Geraniol	73	85	78	47	71	23
(-)-Bornyl acetate	85	87	79	78	82	6
Eugenol	75	70	66	28	60	35
Geranyl acetate	83	83	75	68	77	9

RSD—Relative Standard Deviation; ND—Not detected.

*Rosmarinus officinalis* L. was then analyzed (Figure 4), and the results are presented in Table 4.

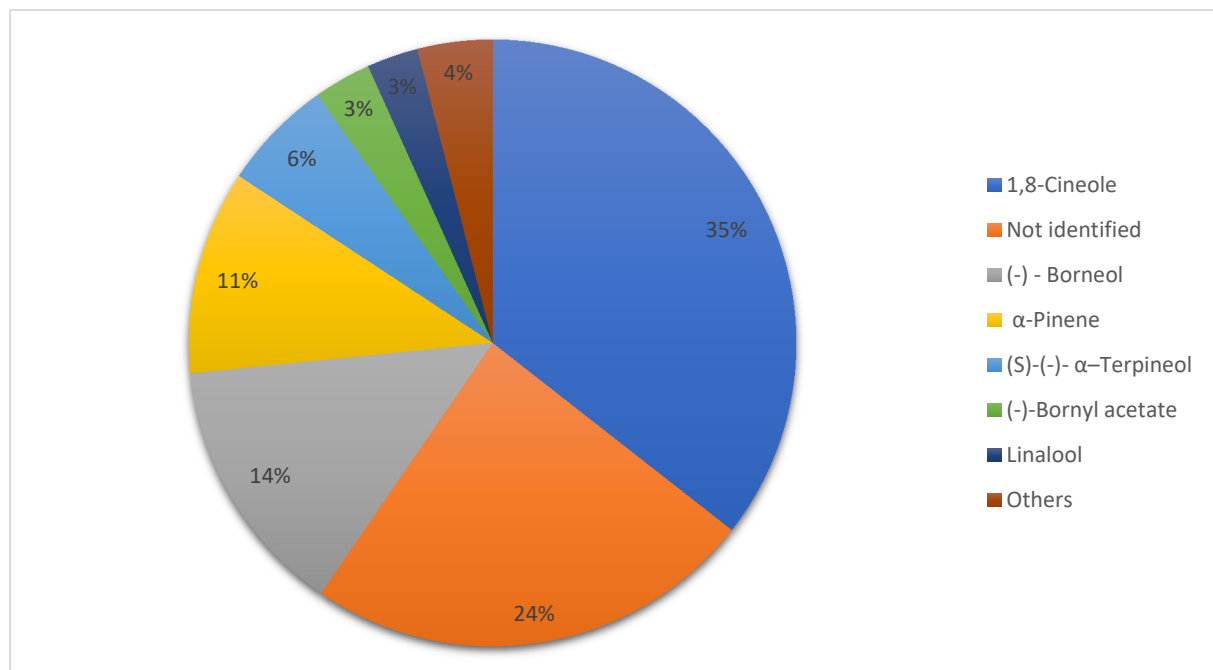
**Figure 4.** Chromatogram of *Rosmarinus officinalis* L. extract analyzed by GC-FID.

**Table 4.** Results for the analysis of analysis *Rosmarinus officinalis* L. fresh plant.

Compound	Concentration (mg/kg)
$\alpha$ -Pinene	3463.3
2,2,6-Trimethylcyclohexanone	114.0
1,8-Cineole	1615.0
Linalool	90.9
(-)-Borneol	531.8
(S)-(-)- $\alpha$ -Terpineol	195.5
Citronellol	ND
(R)-(+)- Pulegone	3.7
Geraniol	8.4
(-)-Bornyl acetate	100.6
Eugenol	7.0
Geranyl acetate	38.7

ND—Not detected.

The oils mostly extracted were mostly 1,8-cineole, (-)-borneol,  $\alpha$ -pinene, (S)-(-)-  $\alpha$ -terpineol, (-)-bornyl acetate, linalool and 2,2,6-trimethylcyclohexanone (Figure 5).



**Figure 5.** Relative composition of the compounds expressed as percentages obtained by peak-area normalization, considering the same response factor for all peaks.

The results are very similar to those obtained by other authors, using other techniques [5,6,12–15].

This technique congregates the advantages of solvent-based and hydrodistillation extractions. A particularly high concentration factor and low solvent volume were used. Acceptable reproducibility and high extraction efficiencies were obtained.

## 5. Conclusions

A method of analysis of essential oils from *Rosmarinus officinalis* L., using simultaneous distillation–extraction followed by analysis by gas chromatography, was validated.

Extraction efficiencies for most compounds tested ranged from 40 to 70%. Extraction efficiencies were fairly reproducible (RSD between 6 and 35%).



The highest concentrations obtained in *Rosmarinus officinalis* L. oils were 1,8-cineole, (-)-borneol,  $\alpha$ -pinene, (S)-(-)- $\alpha$ -terpineol, (-)-bornyl acetate, linalool and 2,2,6-trimethyl cyclohexanone.

Analysis by SDE-GC/FID enhances high extraction efficiencies and reasonable reproducibility with low solvent volume used. Extracts free from cuticular waxes or chlorophylls allow a good chromatographic separation.

**Author Contributions:** Conceptualization—L.S.; Methodology—L.S. and J.L.M.; Software—not applicable; Validation—L.S., J.L.M., and B.S.R.; Formal Analysis—B.S.R., M.d.F.F., and J.L.M.; Investigation—All; Resources—L.S.; Data Curation—All; Writing Original Draft Preparation—L.S., J.L.M., and B.S.R.; Writing—Review and Editing—L.S. and J.L.M.; Visualization—All; Supervision—J.L.M. and L.S.; Project Administration—L.S.; Funding Acquisition—L.S. All authors have read and agreed to the published version of the manuscript.

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