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# Water Soluble Fractions of Caraway (*Carum carvi L.*) Essential Oil

[Fracción de aceite esencial de alcaravea (*Carum carvi L.*) soluble en agua]

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## Abstract

Natural essential oils are used extensively in fragrances, flavorants, and in the food and pharmaceutical industries. During hydrodistillation, a part of the essential oil becomes dissolved in the condensate and lost as this water is discarded. In this study, carvone and limonene content recovered from hydrodistillation waste water of caraway fruit were quantified using two methods for recovering dissolved aromatic molecules from condensate water: extraction through distillation and extraction by means of a solvent. This allows for the conservation of useful molecules which are typically discarded with the waste water produced during the distillation process. The objective of this study was to quantify the carvone and limonene content recoverable from waste water derived from the distillation of caraway essential oil. The well-known Clevenger method and a simpler, more practical technique employing cyclohexane as a solvent were employed to determine the recoverable content of aromatic molecules from the hydrosol. The chemical compositions of the respective recovered extracts were compared with those of the primary oils to analyze the efficacy of these methods. Recovered extract accounted for 10 to 40% of the total oil yield. The limonene and carvone molecules recovered using these methods were quantified through gas chromatography in order to characterize the composition of the secondary extract produced.

**Keywords:** Caraway; carvone; limonene; recovered essential oil; cyclohexane-based method; Clevenger method

## Resumen

Los aceites esenciales naturales se utilizan ampliamente en las fragancias, saborizantes, y en la industria alimentaria y farmacéutica. Durante la hidrodestilación, una parte del aceite esencial se disuelve en el condensado y se pierde como agua de descarga. En este estudio, el contenido de carvona y limoneno recuperados del agua de desecho de la hidrodestilación de la fruta de alcaravea se cuantificaron utilizando dos métodos para recuperar las moléculas aromáticas disueltas en el agua condensada: extracción a través de la destilación y la extracción con un disolvente. Esto permite la conservación de las moléculas útiles que normalmente son desechadas con las aguas residuales producidas durante el proceso de destilación. El objetivo de este estudio fue cuantificar el contenido de carvona y limoneno recuperable de las aguas residuales procedente de la destilación del aceite esencial de alcaravea. El conocido método de Clevenger y una técnica sencilla y práctica que emplea ciclohexano como disolvente fueron utilizadas para determinar el contenido de moléculas aromáticas contenidas en el hidrosol. La composición química de los extractos recuperados fue comparada con los aceites primarios para analizar la eficacia de estos métodos. El extracto recuperado representa del 10 al 40% del contenido total de aceite esencial. Las moléculas de limoneno y carvona recuperadas mediante estos métodos se cuantificaron mediante cromatografía de gases con el fin de caracterizar la composición del extracto secundario.

**Palabras Clave**: Alcaravea; carvona; limoneno; aceite esencial recuperado; método basado en ciclohexano; método Clevenger.

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## INTRODUCTION

Caraway (*Carum carvi* L.) has been used traditionally in medicine as an antispasmodic, a carminative, an emmenagogue, an expectorant, a galactagogue, a stimulant, as a stomachic, and as a tonic (Morton, 1976). The essential oil of caraway is well known for its antibacterial and antifungal properties (Iacobellis et al., 2005; Bouwmeester et al., 1998; Helander et al., 1998; Naigre et al., 1996; Hartmans et al., 1995). In addition, it is used as a flavorant in ice cream, candy, meat, cheese, condiments, soft drinks, and alcoholic beverages (Morton, 1976). Recently, (+)-carvone extracted from caraway seeds has been introduced as an effective sprouting inhibitor for potatoes (Bailer et al., 2001; Sorce et al., 1997; Kerstholt et al., 1997 Oosterhaven et al., 1995 ; Hartmans et al., 1995). Carvone also has medical relevance. Various medical effects have recently been reviewed and discussed by Carvalho et al., 2006. These authors suggested that carvone may lead to the development of better pharmaceuticals and to an effective treatment for candidal infections. It has also been used in stereoselective synthesis of the marine antitumor agent eleutherobin, a potential chemopreventive anticarcinogenic agent.

Essential oils can be isolated using various techniques, the most commonly used of which are steam distillation and hydrodistillation. Other methods have been developed for molecular extraction, such as solvent extraction and supercritical fluid extraction, as well as the use of superheated, subcritical water, and combination methods, utilizing the above mentioned techniques in conjunction with others such as ultrasound and microwave-assisted processes (Roldán-Gutiérrez et al., 2008; Wang and Weller, 2006; Chemat et al., 2005; Kaufmann and Christen, 2002).

None of these processes is universal; in effect, each process presents specific advantages and disadvantages when used for a particular material. Nevertheless, hydrodistillation and steam extraction are the most widely used in industry, and the oldest. Not only do they produce high quality essential oil, they are straightforward and easy to employ.

In the hydrodistillation method, an aromatic biomass is loaded into a distillation tank with an aqueous solution heated to boiling temperature. The essential oil present in the biomass vaporizes, and subsequently passes through a condenser. The condensate (mixture of water and essential oil) is collected in a receptacle. The resulting essential oil is decanted and its moisture is removed; this essential oil is referred to as “primary” or “decanted” essential oil. During the process of distillation, a portion of the essential oil becomes dissolved in the condensate water (hydrosol). The hydrosol is typically discarded, leading to the loss of viable, dissolved essential oil. The discarding of this dissolved oil not only reduces the overall yield, but produces considerable economic loss. Losses of up to 25% of total essential oil volume were reported in Israel (Fleisher and Fleisher, 1985). This phenomenon has been observed in many other aromatic plants, and attempts have been made to recover the dissolved oil from the hydrosol. The extract thus recovered is often referred to as “secondary” or “recovered”. The method employed to recover aromatic oils from hydrosol has typically been cohobation (Bohra et al., 1994). Nevertheless, this is not the most efficient method for the extraction of secondary extract. A considerable loss of volatile molecules is produced due to the constant heating of hydrosol utilized in cohobation. In this study, the Clevenger method as well as an alternative method utilizing cychlohexane as a solvent were used to extract and quantify the carvone and limonene content derived from waste water used for the hydrodistillation of caraway. The chemical compositions of the respective recovered oils were compared with those of the primary oils to analyze the efficacy of these methods.

## 2. Materials and Methods

### 2.1 Materials

The caraway fruits used as raw material were obtained from the French wholesaler Alp’Erbo S.A. The hydrosol was colleted and removed from the Tournaire distiller apparatus in the facilities of the *Laboratoire de Chimie Agro-Industrielle, Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques, Institut National Polytechnique de Toulouse.* The experiment was carried out during research on new methods of essential oil extraction from caraway fruit on a pilot scale.

### 2.2 Methods

The dried fruits were weighed and directly introduced in the hydrodistillation unit following an isolation process. The primary decanted essential oil was

separated and measured. The distillation water, mixed with cyclohexane in 10:1 proportion, was vigorously shaken for 15 minutes and the cyclohexane saturated with carvone and limonene molecules was separated from the hydrosol. Subsequently, the cyclohexane was distilled to yield a secondary extract in a rotary evaporator. Secondary extract yield was calculated in order to evaluate the efficiency of cyclohexane-based extraction. There were carried out three batches of distillation, each with three replicates, 22500 g, 15000 g and 7500 g of caraway fruits to obtain the yield of primary and secondary essential oil.

The same hydrodistillation procedure used for primary extraction was followed in applying the Clevenger method to the hydrosol, and the secondary extract yield was calculated and characterized.

### 2.3 Gas Chromatography

GC analysis was carried out using a Hewlett Packard gas chromatograph HP 5890 II equipped with ionization flame detector and HP 6890 autoinjector. The separation was made on vf5 Varian capillary columns with a column length of 30 m, an inner diameter of 0.25 mm, and a film thickness of 0.25 mm. The oven was programmed to start at 90°C and to continue heating at a rate of 2°C/min to 210°C. The injector and detector temperatures were 200 and 230°C, respectively. The carrier gas, helium, was adjusted to a flow rate of 1.3 mL/min. The extracts were diluted 10 times and 0.5 □L of diluted solution was injected into the GC with same split ratio of 1:100. During the experiment, the calibration factors for limonene and carvone were determined from the external standard method with two independent samples containing 100 and 200 ppm each of these compounds dissolved in cyclohexane.

## 3. Results and Discussion

### 3.1 Comparison of Clevenger and Cyclohexane-based Extraction

The cyclohexane-based extraction method was observed to produce higher carvone and limonene yields in comparison with Clevenger distillation (Table 1).

**Table 1**

**Comparison of Clevenger and cyclohexane extraction methods for carvone and limonene recovery from caraway.**

| Batch | Essential Oil recovery in Clevenger method (g/100 g) | Extract recovery in cyclohexane extraction (g/100 g) | Efficiency of cyclohexane-based method in comparison with Clevenger method (%) |
|---|---|---|---|
| A | 0.25 | 0.31 | 80 |
| B | 0.35 | 0.44 | 81 |
| C | 0.72 | 0.87 | 82 |
| D | 0.23 | 0.29 | 80 |
| E | 0.29 | 0.35 | 83 |
| F | 0.25 | 0.33 | 78 |
| G | 0.25 | 0.30 | 81 |
| H | 0.50 | 0.61 | 82 |
| I | 0.63 | 0.80 | 79 |

**A, D, G: three replications for 22500 g of distilled biomass; B, E, H: three replications for 15000 g of distilled biomass; C, F, I: three replications for 7500 g amount of distilled biomass.**

The lower recoveries in the Clevenger distillations can be attributed to loss due to the high solubility of essential oil in condensate or distillation water, or alternatively loss due to the thermosensitivity of carvone and limonene. Although this method does allow for the recovery of some of the essential oil dissolved in the condensate, a significant portion of essential oil yield remains in the hydrosol or waste water. Specifically, 10 to 40 grams of dissolved extract per 100 g of caraway fruit remain in the hydrosol.

The efficiency of cyclohexane for trapping the dissolved essential oil was demonstrated in this study. This method allows for the recovery of up to 40% of total essential oil yield, as shown in Table 2. Cyclohexane-based extraction prevents the loss of volatile thermo-sensitive molecules seen in the Clevenger method, due to the fact that extraction takes place at ambient temperature. As a result, cyclohexane-based extraction efficiency was up to 83% greater than Clevenger distillation. Additionally, the recoveries recorded using cyclohexanes were higher than those reported in similar studies using synthetic polymer adsorbents (Machale et al., 1997).

### 3.2 Primary Essential Oil and Secondary Extract Yields

Hydrodistillation of biomass produced between 60 and 90% of the total essential oil yield (Table 2).

**Table 2**

**Details of primary essential oil and secondary extract yields of caraway and their recovery percentages in relation to total essential oil yield**

| Batch | Amount of biomass distilled (g) | Humidity of the biomass (%) | Amount of primary essential oil obtained (g) | Amount of secondary extract recovered (g) | Total extract (g) | Recovery (%) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Primary | Secondary |
| A | 22500 | 6.69 | 393.32 | 65.00 | 458.32 | 85.82 | 14.18 |
| B | 15000 | 6.59 | 253.08 | 61.27 | 314.35 | 80.51 | 19.49 |
| C | 7500 | 7.53 | 92.70 | 60.52 | 153.22 | 60.50 | 39.50 |
| D | 22500 | 6.94 | 444.26 | 61.25 | 505.51 | 87.88 | 12.12 |
| E | 15000 | 6.75 | 283.97 | 48.45 | 332.42 | 85.43 | 14.57 |
| F | 7500 | 6.75 | 114.73 | 22.76 | 137.49 | 83.45 | 16.55 |
| G | 22500 | 7.43 | 493.81 | 63.11 | 556.92 | 88.67 | 11.33 |
| H | 15000 | 6.75 | 281.34 | 85.67 | 367.01 | 76.66 | 23.34 |
| I | 7500 | 7.17 | 125.47 | 55.54 | 181.01 | 69.31 | 30.69 |

Cyclohexane treatment of the distillation water yielded 10 to 40% of the total extract yield. Unless recovered, the secondary extract dissolved in distillation water is lost. The loss of essential oil in distillation water for caraway is comparable to the loss reported for other aromatics (Rao et al., 2005; Fleisher, 1991; Fleisher and Fleisher, 1985). Differences between batches were most likely due to variation in the ratio of extractant solutions to caraway fruit. As can be seen in Table 2, the water soluble fractions of the essential oils remaining in the waste water after use of the hydrodistillation method were shown to be most efficiently extracted with cyclohexane.

### 3.3 Essential Oil Composition

The presence of limonene and carvone in primary essential oils and secondary extracts was quantified.

These two main components of caraway constitute 90 - 97% of the essential oil. The variation in the chemical profiles of the primary and the secondary extract are shown in Table 3. Primary essential oil was found to contain 20 – 40% limonene and 60 – 80% carvone, whereas the secondary extract contained 12 to 0.15% limonene and 70 – 98% carvone. The relative abundance of hydrocarbons in the primary essential oil is due to the low solubility of this molecule in distillation water. Hydrophilic molecule yield has been found to be dependant on solvent polarity (Durling et al., 2007). Oxygenated particles have a high solubility, attributable to their polar nature. Consequently, an abundance of carvone molecules was observed in oxygenated compounds. Oxygenated components contribute to the richness and fullness of the organoleptic profile of an essential oil (Fleisher, 1991). An increase in the recovered or secondary extract, which is richer in oxygenated particles, could make the commercial extraction of caraway oil more efficient and thus more financially viable in an industrial context.

**Table 3**

**Chemical composition of primary essential oil and secondary extract of caraway (*Carum carvi* L.)**

| Batch | Compound | Primary essential oil (%) | Secondary extract (%) |
|---|---|---|---|
| A | Limonene | 20.42 | 0.17 |
| | Carvone | 72.59 | 78.12 |
| B | Limonene | 21.44 | 0.16 |
| | Carvone | 71.25 | 79.37 |
| C | Limonene | 19.02 | 0.33 |
| | Carvone | 72.78 | 80.13 |
| D | Limonene | 29.90 | 12.60 |
| | Carvone | 61.61 | 70.13 |
| E | Limonene | 30.29 | 0.15 |
| | Carvone | 61.08 | 80 |
| F | Limonene | 29.16 | 0.16 |
| | Carvone | 63.17 | 77.80 |
| G | Limonene | 34.29 | 1.13 |
| | Carvone | 60.22 | 79.16 |
| H | Limonene | 39.21 | 8.22 |
| | Carvone | 53.67 | 72.71 |
| I | Limonene | 34.38 | 1.67 |
| | Carvone | 57.83 | 98 |

**Conclusions**

Hydrodistillation is not a complete method for efficient extraction of essential oils from aromatic plants. During hydrodistillation, a significant percentage of essential oil is dissolved in the hydrosol and typically discarded. In this study, two methods were employed for the recovery of dissolved essential oil from distillation waste water. A method employing cyclohexane as a solvent was employed for the recovery of dissolved essential oil from distillation waste water. Through this method, 10 to 40% of the total essential oil yield can be recovered from distillation water. The recovered extract is rich in carvone, the main constituent of caraway (*Carum*

*carvi* L.). The results of this study in regards to the quantity and composition of hydrosol justify the pursuit of industrial treatment of this waste product in the agroindustry sector.

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