



Received on 03 March 2022; received in revised form, 27 March 2022; accepted, 29 March 2022; published 31 March 2022

ANALYSIS OF ESSENTIAL OILS IN COMMERCIAL GERANIUM OIL BY USING GC-MS TECHNIQUE

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Keywords:

Geranium, Essential oils, GC-MS, Quality control

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ABSTRACT: Essential oils are largely employed for their therapeutic properties, and marketed extensively in the pharmaceutical and cosmetic industry. Geranium oil is a floral substitute for rose essential oil with its pungent rose-like odor and is one of the most valuable essential oils. Favorable quality properties make the geranium essential oil exigible for food industry applications. Our study aimed to assess the purity and quality of geranium oil available from various commercial producers. The gas chromatography-mass spectrometry (GC-MS) technique was used to detect and quantify the volatile constituents of geranium essential oil. 40 (fourty) volatile compounds were determined by the GC-MS method. The most abundant compounds were determined as geraniol (27.98%), citronellol (20.71%), isomenthone (6.57%), geranyl formate (6.52%) and linalool (6.38%).

INTRODUCTION: Plants have been used for their aromatic and medicinal purposes for centuries. With the world's development and the appearance of many illnesses in modern civilization, there has been considerable interest in bioactive agents, especially antimicrobial and antioxidant substances from natural sources, mainly in essential oils, also called volatile odoriferous/volatile oils¹⁻⁶. Nowadays, essential oils as alternative therapies have gained worldwide concern, owing to their various biological activities. Considerable attention has been devoted to peppermint oil, which is widely used for its important properties, including antimicrobial, anti-inflammatory, antispasmodic, cytoprotective, hepatoprotective, with strong antioxidant actions.

It is also used for its cooling effect to enhance the dermal penetration of pharmaceuticals. Then, it is a standout amongst the most vital seasoning added substances in the World^{7, 8}. Moreover, essential oils replace synthetic substances in the nutritional, pharmaceutical and agricultural fields due to their reported antiviral, nematocidal, antifungal and insecticidal properties. For medical purposes, they need to comply with national or international Pharmacopoeia⁹⁻¹¹. Essential oils vary in compound composition, properties, odour, flavour, and color. Depending on plant health, growth stage, habitat, and harvest time of starting material, the odoriferous oils are composed of different ratios of lipophilic and highly volatile secondary plant metabolites.

The essential oil of *Pelargonium graveolens* is one of the most expensive essential oils used in perfumery, flavoring, and cosmetics. Geranium oil **Fig. 1** is a commercially important hydro-distilled essential oil obtained from cultivars of *Pelargonium graveolens* L'Her. ex Ait. *P. graveolens* (Geraniaceae) is native to the Western Cape region

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| | DOI: 10.13040/IJPSR.0975-8232.IJP.9(3).62-66 |
| | Article can be accessed online on: www.ijpjournal.com |
| DOI link: http://dx.doi.org/10.13040/IJPSR.0975-8232.IJP.9(3).62-66 | |

of South Africa, however, commercialization has seen cultivation extending to China (which currently is the biggest producer), Egypt, Algeria, Morocco, and Reunion Island. The essential oil of *P. graveolens* is one of the most expensive essential oils used in perfumery, flavoring, and cosmetics¹². Mass spectrometry (MS) techniques have an important role in developing the natural products industry over the five decades. It provided a starting point for the identification or structure determination of the most natural products and the molecular weight¹³. MS techniques can provide a lot of structural information with little expenditure of the studied molecules based on their electron ionization mass spectra¹⁴.



FIG. 1: GERANIUM OIL

Even if essential oils are marketed extensively in the pharmaceutical and cosmetic industry, not all products available to use are properly controlled in terms of the quality of their composition. The analytical methods applied for the analysis of essential oils are numerous and include methods exploiting volatility or their optical activity, along with the IR spectral methods, refractometry and thin layer chromatography¹⁵⁻¹⁷.

Other techniques, inexpensive, remain a fast alternative, although there are limitations in terms of specificity and sensitivity. But, GC-MS is the elected technique for analyzing. To date, no GC-MS method is accounted for till date for assurance of essential oils by GC-MS in commercial geranium oil in Turkey. Therefore, the present study aims to investigate the use of GC-MS in the identification of the chemical composition of geranium oil and to elucidate the molecular

structure of the main essential oil constituents based on their electron ionization mass spectra.

MATERIALS AND METHODS:

Chemicals and Reagents: Geraniol, citronellol, isomenthone, β -bourbonene, geranyl formate, geraniol butyrate, geranyl isovalerate, linalool, and different synthetic compounds were acquired from Sigma-Aldrich (St. Louis, MO, USA). Geranium oil was purchased at a local herbalist. It was labeled as 100% natural product.

GC-MS System: GC-MS investigations were completed on an Agilent 7820A gas chromatography system equipped with 7673 series autosampler chemstation and 5977 series mass selective detector. HP-5 MS segment with 0.25 μ m film thickness (30 m \times 0.25 mm I.D., USA) was utilized for separation. The temperatures of the inlet and transfer line were 250 and 300 $^{\circ}$ C, respectively.

GC-MS Conditions: Different temperature programs were researched for the technique. The finish of this examination, GC broiler temperature was at 60 $^{\circ}$ C for 10 min and afterward was customized to 220 $^{\circ}$ C at a rate of 4 $^{\circ}$ C/min and kept in this temperature for 10 min. The stove temperature was at long last modified to 240 $^{\circ}$ C at a rate of 1 $^{\circ}$ C/min with the last hold time of 80 min. The split proportion was 40:1.

Identification of Components: The range of the obscure segment was contrasted, and the range of the part put away in the National Institute of Standards and Technology Library Version (2005), Software, Turbomass 5.2. The parts were distinguished by contrasting direct Kovats maintenance list and mass spectra with those obtained from the MS library. Understanding on mass range GC-MS was directed by utilizing the National Institute Standard and Technology database having in excess of 62,000 examples. The relative rate measure of every part was determined by contrasting its normal pinnacle region with the complete areas. The name, atomic weight and structure of the segments of the test materials were discovered.

RESULTS AND DISCUSSIONS:

Method Development and Optimization: The strategy advancement for examining phyto-

components depended on their synthetic properties. In this investigation, the fine segment covered with 5% phenyl and 95% dimethyl-polysiloxane is a decent decision to partition these analytes since they elute as symmetrical tops at a wide scope of focuses. Distinctive temperature programs were explored for GC oven. To finish this examination, the best temperature program was chosen for good detachment. The GC broiler's temperature projects were as follows: beginning temperature of 60 °C, held for 1. min, expanded to 220 °C at a rate of 4

°C/min held for 10 min. The oven temperature was at long last modified to 240 °C at a rate of 1 °C/min with the last hold time of 80 min. Mass spectra were taken at 70 eV, and the mass range was from m/z 35 to 450.

GC-MS Analysis: GC-MS is a standout amongst the best procedures to distinguish the constituents of unstable issues, long-chain, stretched chain hydrocarbons, alcohols, amines, esters, ketones, heterocycles, and terpenes.

TABLE 1: CHEMICAL COMPOSITION OF THE ESSENTIAL CONSTITUENTS OF GERANIUM OIL

| S. no. | Retention time(min) | Name | % Ratio |
|--------|---------------------|-----------------------------|---------|
| 1 | 3.54 | α -pinene | 0.65 |
| 2 | 3.55 | D-limonene | 0.30 |
| 3 | 3.75 | β -ocimene | 0.18 |
| 4 | 4.88 | Linalool | 6.38 |
| 5 | 7.68 | α -terpineol | 0.40 |
| 6 | 9.42 | Geraniol | 27.98 |
| 7 | 11.10 | Geranyl formate | 6.52 |
| 8 | 11.45 | β -myrcene | 0.24 |
| 9 | 12.22 | α -phellandrene | 0.06 |
| 10 | 13.46 | α -copaene | 0.53 |
| 11 | 13.57 | p-cymene | 0.07 |
| 12 | 13.77 | β -bourbonene | 2.10 |
| 13 | 14.87 | Caryophyllene | 1.35 |
| 14 | 15.33 | β -copaene | 0.05 |
| 15 | 15.74 | Guaia-6,9-diene | 4.44 |
| 16 | 16.05 | α -humulene | 0.39 |
| 17 | 16.35 | Linalool oxide | 0.24 |
| 18 | 16.85 | Germacrene | 1.31 |
| 19 | 17.01 | Isoterpinolene | 0.02 |
| 20 | 17.39 | γ -muurolene | 0.88 |
| 21 | 17.48 | α -bisabolene | 0.02 |
| 22 | 17.74 | Neryl propionate | 0.86 |
| 23 | 17.96 | γ -cadinene | 0.23 |
| 24 | 18.22 | δ -cadinene | 2.02 |
| 25 | 19.23 | Geraniol butyrate | 1.93 |
| 26 | 20.07 | Caryophyllene oxide | 0.05 |
| 27 | 20.41 | L-menthane | 1.38 |
| 28 | 21.13 | Isomenthone | 6.57 |
| 29 | 21.94 | Levomenthol | 0.13 |
| 30 | 24.81 | Citronellol | 20.71 |
| 31 | 28.12 | α -cubebene | 0.12 |
| 32 | 30.16 | α -gurjunene | 0.08 |
| 33 | 32.88 | Allo aroma dendrene | 0.53 |
| 34 | 33.24 | α -muurolene | 0.33 |
| 35 | 34.30 | Trans-sesquisabinen hydrate | 0.26 |
| 36 | 36.25 | Geranyl isovalerate | 0.88 |
| 37 | 36.94 | Epicubenol | 0.28 |
| 38 | 37.81 | Nerolidol | 0.34 |
| 39 | 38.14 | Citronellyl tiglate | 1.70 |
| 40 | 39.25 | Geranyl tiglate | 2.50 |
| Total | | | 95.01 |

GC-MS examination uncovered the nearness of 40 mixes in oil of geranium oil. Pinnacle number,

maintenance time and compound name are expressed in **Table 1**. The structural determination

of the main constituents based on their electron ionization mass spectra has been investigated. The MS of these compounds is absolutely identical in mass values of peaks of fragment ions, where their relative intensities have minor differences. The geranium essential oil has considerable economic and industrial importance. Favorable flavor of geranium essential oil and health-beneficial properties such as antibacterial, antifungal, anti-inflammatory, spasmolytic and antidiabetic effects makes the geranium essential oil appealing for food industry applications.

This research investigated the chemical fingerprinting properties of geranium essential oil using vibrational spectroscopy and gas chromatography mass-spectrometry. Quite limited studies were performed to reveal the chemical characterization of geranium essential oil. Additionally, GC-MS technique was used to detect and quantify the volatile constituents of geranium essential oil.

The substance's 40 basic constituents were recognized dependent on GC-MS in geranium oil provided from the MS library. The significant parts of the geranium oil were geraniol (27.98%), citronellol (20.71%), isomenthone (6.57%), geranyl formate (6.52%) and linalool (6.38%).

CONCLUSION: This investigation recommends that GC-MS is the viable technique for the examination of the fundamental oils. By applying the proposed system, a sum of 40 segments was distinguished for the geranium oil. These parts represent 95.01% of the all-out relative substance of the geranium basic oil. This examination likewise exhibited that the geranium basic oil is rich in geraniol (27.98%), citronellol (20.71%) and could be a decent hotspot for this compound.

Chemical characterization of geranium essential oil will shed light to the researchers and industrial applicators to develop new commercial products in the sectors such as cosmetics, food and beverage, alternative medicine, aromatherapy and cleaning and home. Additionally, the effects of geraniol and citronellol can be investigated in the future.

ACKNOWLEDGEMENT: Nil

CONFLICT OF INTEREST: Nil

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How to cite this article:

Yilmaz B: A review on natural remedies used for the treatment of respiratory analysis of essential oils in commercial geraniumoil by using GC-MS technique. Int J Pharmacognosy 2022; 9(3): 62-66. doi link: [http://dx.doi.org/10.13040/IJPSR.0975-8232.IJP.9\(3\).62-66](http://dx.doi.org/10.13040/IJPSR.0975-8232.IJP.9(3).62-66).

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