Industrial Crops & Products 124 (2018) 870–877

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

Characterization of essential oils from Myrtaceae species using ATR-IR vibrational spectroscopy coupled to chemometrics

Nermeen F. Farag[a], Sherweit H. El-Ahmady[b,*], Enas H. Abdelrahman[a], Annette Naumann[c], Hartwig Schulz[c], Shadia M. Azzam[a], El-Sayeda A. El-Kashoury[a]

[a] Faculty of Pharmacy, Cairo University, Cairo, Egypt
[b] Faculty of Pharmacy, Ain Shams University, Cairo, Egypt
[c] Julius Kuehn Institute (JKI), Institute for Ecological Chemistry, Plant Analysis and Stored Product Protection, Berlin, Germany

ARTICLE INFO

Keywords:
Essential oils
Myrtaceae
ATR-IR
Vibrational spectroscopy
Chemometrics
Quality control

ABSTRACT

The essential oils obtained from plants belonging to various Myrtaceae genera (*Eucalyptus*, *Corymbia, Melaleuca*, *Syzygium*, and *Eugenia*) were analyzed non-destructively by applying Attenuated Total Reflection Infrared (ATR-IR) vibrational spectroscopy. The spectroscopic analysis was based on the key bands of the individual volatile substances using the spectral data of the individual terpenoids, which allowed for the discrimination of different essential oil profiles. The spectroscopic data was compared to Gas Chromatography– Mass Spectroscopy GC–MS) analyses of the oils and results showed high correlation. Additionally, the combination of vibrational spectroscopy and chemometric analyses provided a fast, easy and reliable method for volatilome based classification comparable to that of chromatographic results. These results suggest ATR-IR as a potentially reliable method for identification, classification and quality control purposes of various essential oils.

1. Introduction

Essential oils represent an integral part of several industries including the phytopharmaceutical, cosmetic and food industry. The economic importance of essential oils has led to various strategies for increasing oil yield and production through the development of new plant cultivars in addition to various optimization techniques including variations of agronomy and environment (Haghighi et al., 2017). As a result, the chemical profiling of the oils are usually deviated from standard product quality and consequently this opted for the ongoing development of quality control assessment methods. Among the highly acclaimed essential oil sources are plants of family Myrtaceae, also known as the Myrtle family, with approximately 6000 species belonging to 145 genera of aromatic shrubs and trees (The Plant List, 2017) of the tropical regions. Myrtle, guava, clove, eucalyptus and tea tree are among the significant members of this family and known for their essential oils used medicinally as well as for other commercial purposes (Siddique et al., 2017).

The genus *Eucalyptus* comprises approximately 900 species and subspecies (Brooker and Kleinig, 2004; Gilles et al., 2010). This genus is one of three similar genera that are commonly referred to as 'eucalypts' including also *Corymbia* and *Angophora*. *Eucalyptus* originates from Australia but has spread worldwide and in Egypt, it is represented by 40 species that were mainly introduced by Khedive Ismail in the 1800s (Hamdy et al., 2007). Essential oils and wood are the main products obtained from *Eucalyptus* species. The essential oils extracted from the leaves were found to exhibit antimicrobial, antifungal, anti-inflammatory and expectorant properties (Batish et al., 2008; Ghaffar et al., 2015). In addition, inhalation of *Eucalyptus* derivatives has been used to treat pharyngitis, bronchitis, and sinusitis (Cermelli et al., 2008). The main constituents of *Eucalyptus* leaf oils were reported as *p*-cymene, *α*-pinene, 1,8-cineole, spathulenol, cryptone and *α*-terpineol (Cermelli et al., 2008; Elaissi et al., 2012).

Melaleuca species are best known for the production of the medicinal essential oil known as 'tea tree oil' (*Melaleuca alternifolia*) with reported antibacterial (D'Arrigo et al., 2010), antifungal (Hammer et al., 2004), and antiviral (Garozzo et al., 2011) activities, as well as for treating different respiratory and inflammatory diseases (Caldefie-Chezet et al., 2006). The genus comprises approximately 230 species of worldwide occurrence with 220 species endemic to Australia and Tasmania (Craven and Lepschi, 1999), and was recently introduced to Egypt from Thailand. The main components of the essential oils extracted from most *Melaleuca* species are 1,8-cineole and terpinen-4-ol, whereas methyl eugenol is the predominant component in *M. ericifolia*

* Corresponding author.
E-mail address: selahmady@pharma.asu.edu.eg (S.H. El-Ahmady).

https://doi.org/10.1016/j.indcrop.2018.07.066
Received 2 February 2018; Received in revised form 22 June 2018; Accepted 26 July 2018

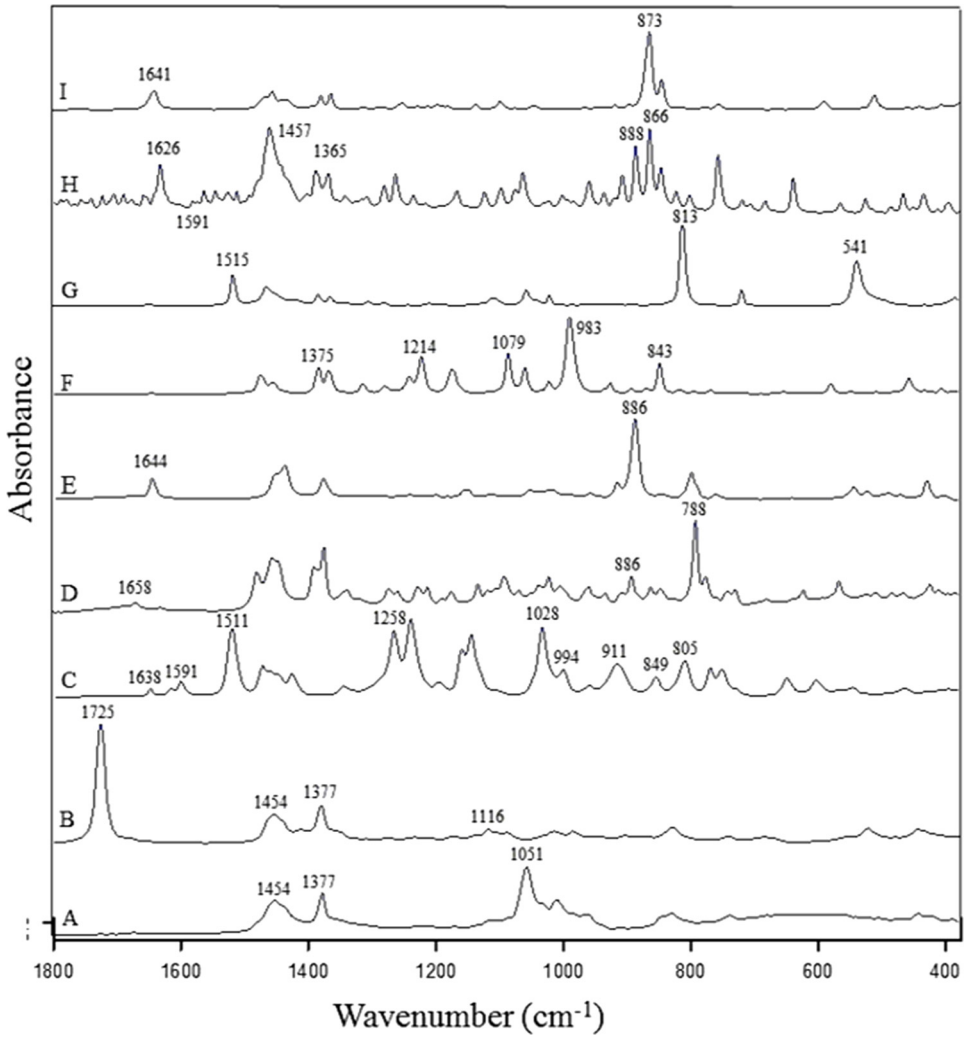

Fig. 1. ATR-IR spectra of major constituents of the investigated oils. Citronellol (A), citronellal (B), methyl eugenol (C), *α*-pinene (D), limonene (E), 1,8-cineole (F), *p*-cymene (G), caryophyllene oxide (H) and *β*-pinene (I).

oil. Caryophyllene oxide and spathulenol are the main constituents of *M. styphelioides* cultivated in Egypt (Farag et al., 2004).

Eugenia is the largest genus of the Myrtaceae family with more than 1000 species distributed worldwide especially in tropical and subtropical regions (The Plant List, 2017). The genus is common in North and South America (800 species), Africa (60 species), Malaysia (60 species), New Caledonia (50 species) and was recently introduced to Egypt from Thailand. *Eugenia* species were reported to have cytotoxic, anti-inflammatory and antimicrobial properties (Han and Parker, 2017; Ogunwande et al., 2005; Santos et al., 2012). The essential oils of *Eugenia* species show characteristic chemical diversity. In general, there is a predominance of cyclic sesquiterpenes, along with monoterpenes as a minor fraction (Apel et al., 2004). The monoterpene *α*-pinene and the sesquiterpene *β*-caryophyllene are the most abundant compounds of the oils (Setzer et al., 2006; Stefanello et al., 2008).

The *Syzygium* genus constitutes more than 1000 species distributed in tropical and subtropical regions of South-East Asia, Australia and Africa (The Plant List, 2017). The essential oil of *Syzygium samarangense* has been shown to inhibit *Escherichia coli* growth by reducing its extracellular protease (Adesegun et al., 2013; Reddy and Jose, 2011). It contains *α*-pinene, γ-terpinene, *β*-caryophyllene and caryophyllene oxide as major components (Gao et al., 2012; Lee et al., 2016).

Gas chromatography coupled to flame ionization (GC-FID) or mass spectrometry (GC—MS) is commonly the tool of choice used for the analysis of essential oils and unveiling their chemical composition. During the last decade, several vibrational spectroscopic methods using Raman and infrared spectroscopy have been described as efficient tools in this context (Baranska et al., 2005, 2006; Schulz et al., 2004, 2005; Schulz and Baranska, 2007 Wang and Sung, 2011). In addition, applying chemometric analyses to spectral data sets proved to be an effective way to visualize the specific differences among plant chemotypes (Baranska et al., 2005; Schulz et al., 2004; Schulz and Baranska, 2007). In this study, 15 samples of laboratory-distilled essential oils of different myrtaceous plants leaves collected in Egypt were analyzed using Attenuated Total Reflection Infrared (ATR-IR) spectroscopy and compared to their GC—MS analyses. ATR-IR is introduced as an effective, rapid, reliable and non-destructive tool for the identification of essential oil chemical profiles. Chemometric analyses were applied to the results obtained from both techniques based on the oils composition in an effort to establish a model for efficient essential oil classification