

Comparative analysis of chemical components of essential oils from different samples of *Rhododendron* with the help of chemometrics methods

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Abstract

Essential oils from four samples of *Rhododendron* were extracted by water distillation and analyzed by gas chromatography–mass spectrometry with the help of retention indices and chemometrics resolution method named subwindow factor analysis (SFA). A total of 128 volatile components were identified reliably and fleetly. A temperature-programmed retention index (I_u^T) dataset including these components has been constructed on a slightly polar capillary column (HP-5MS) at the given GC operating condition in which the standard GC parameter $S=r_{TM}/\beta=0.0087$. The present work proved the usefulness of chemometrics and retention indices in complicated systems analysis and the I_u^T 's obtained can be used in other essential oil identification. The major components of the analyzed samples showed that essential oils from different genus or even different parts of azaleas are different from each other in chemical components.

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1. Introduction

Rhododendron, or azalea, belongs to *Rhododendron* and grows originally in China. The genus of *Rhododendron* comprises more than 900 species in the world, 600 of which growing in south to north of China [1]. So China is called “a *Rhododendron* emperor country”. *Rhododendron* is not only of high value in view but also a good medicinal plant because of the essential oil involved in its twigs, leaves, and flowers can be used as high grade spices and cosmetics, especially of many efficacies such as detoxification, relieving a cough and calming asthma, dispelling phlegm, diminishing inflammation and acesodyne, and depressing blood pressure and etc. [2–4]. The essential oils from it are good in curing chronic tracheitis

[5]. In Tibet and west part of China, it is widely used to cure pulmonary disease, laryngitis, urethritis, indigestion, gastroptosis, gastrectasis gastric cancer, hepatoma and dropsy [6]. The essential oils of some species of *Rhododendron* were studied in the last decades [6–8]. But to our knowledge, the volatile constituents of the following three species of *Rhododendron* as *Rhododendron simii* planch., *Rhododendron mucronatum* G. Don and *Rhododendron naamkwanense* Merr., growing in Yuelu mountain located in central south of China, were not characterized so far.

Gas chromatography–mass spectrometry (GC–MS) has contributed greatly to the analysis of various mixtures of organic compounds. It is certainly a useful and powerful tool in the essential oil analysis. However, it is common that in many cases co-elution of two or more different compounds is possible under given conditions, and whether this occurs or not cannot be determined by GC alone for unknown samples. On the other hand, many plant essential oil samples are difficult to identify just by mass spectra alone, since two or

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more GC peaks have very similar or even identical mass spectra although they have different retention times and different chemical natures. Secondly, some compounds existing in plant essential oils couldn't be found in mass spectrum libraries. Thus, compound identification by GC–MS often requires the assistance or confirmation of GC retention indices. Retention times and mass spectra are complementary to each other.

Retention index [9] system is a measure of relative retention times referenced to the homologous series of organic compounds. Hayes and Pitzer [10,11] demonstrated the usefulness of determining of retention indices for identifying compounds in complex mixtures. Many GC and GC–MS analyses were carried out under isothermal conditions in the past, but now more and more complicated samples, such as plant essential oils whose boiling point range varies widely, need temperature-programmed analysis in order to improve the separation.

The calculation of isothermal retention indices is usually performed according to the linear equation put forward by Kovats [9]. While Van den Dool and Krutz [12] thought a quasi-linear relationship exists for a non-isothermal GC analysis with a linear temperature program, that is, $I_u^T = 100 \left(\frac{t_u - t_n}{t_{n+1} - t_n} + n \right)$, where I_u^T is the temperature-programmed retention index of the interest; t_n , t_{n+1} , and t_u are the retention times (in minute) of the two standard n -alkanes containing n and $n+1$ carbons and the interest, respectively. Thus the temperature-programmed retention indices can be calculated through the quasi-linear equation.

R. Richmond and co-workers [13–15] thought that I_u^T could be highly reproducible on a given capillary column, whose stationary phase is fixed, if working variables, such as carrier flow-rate, film thickness and linear temperature programming rate, were standardized. He has done much work in I_u^T standardization. Another parameter $S = r_T t_M / \beta$ was proposed by Sun et al. [16], who pointed out that when one wanted to use some reported I_u^T data in the case of a certain kind of stationary phase, only if the parameter S equaled to each other. That is to say, if S is constant, retention index datasets can be used by others who work in the same laboratory or other laboratories. So it should be meaningful to construct I_u^T datasets for future analysis of other plant essential oils.

The aim of this paper is to obtain first the chemical compositions of 4 essential oil samples extracted from the leaves and flowers of *Rhododendron* and then to compare their sameness and differences. In order to deal with overlapped peaks in the sample chromatograms, a chemometrics resolution method, named subwindow factor analysis (SFA) [17,18], was introduced to get the pure chromatography peaks at the given GC operating condition. A total of 128 compounds were identified and the major components of the analyzed samples showed that essential oils from different genus or even different parts of azaleas are different from each other in chemical components. At the same time a temperature-programmed retention index (I_u^T) dataset including these components was also constructed on a slightly polar

capillary column (HP-5MS) in the condition of parameter $S = r_T t_M / \beta = 0.0087$, which might be used in other essential oil identification.

2. Experimental

2.1. Plant materials and n -alkane standard solution

The leaves and flowers of *Rhododendron* were collected at flowering stage, in April 2004, from Yuelu mountain, located in central south part of China. Sample 1 to 4 are essential oils which were extracted from flowers of *Rhododendron mucronatum* G. Don, flowers and leaves of *Rhododendron simii* planch., and leaves of *Rhododendron naamkwanense* Merr., respectively. The Voucher specimens were made by Prof. Fang Hong-zhuang and identified by Professor Liu Juan working at Department of Chinese Herbal Medicine, Jamusi University, P. R. China.

n -Alkane standard solutions of C_8 – C_{20} (mixture No. 04070) and C_{21} – C_{40} (mixture No. 04071) were purchased from Fluka Chemika.

2.2. Extraction of essential oils

Essential oil samples were extracted by water distillation for 12 h from green materials, using a set of standard apparatus, according to the procedure described in the Chinese Pharmacopoeia [19]. The essential oils obtained were stored in the dark prior to analysis. The average yields of the essential oil samples of *Rhododendron* were 0.01 to 0.1% (v/w) in fresh materials, respectively.

2.3. Gas chromatography–mass spectrometry

Analyses were carried out in a Hewlett-Packard 6890 gas chromatograph fitted with a HP-5MS fused silica column (5% phenyl methyl polysiloxane 30 m × 0.25 mm i.d., film thickness 0.25 μm), interfaced with a Hewlett-Packard mass selective detector 5973N (Agilent Technologies, USA) operated by HP Enhanced ChemStation software, G1701DA MSD ChemStation Rev. D.00.00.38. Oven temperature program: 80 to 300 °C, at 4 °C/min; injector temperature: 280 °C; carrier gas: helium, adjusted to a column velocity of flow 1.0 mL/min; splitting ratio 50:1; interface temperature: 280 °C; standard electronic impact (EI) MS source temperature: 230 °C; MS quadrupole temperature: 150 °C; mass scan range: 30–500 amu; scan velocity: 3.12 scans/s.

2.4. Qualitative and quantitative analysis

Most of the component identification can be performed by G1701DA MSD ChemStation Rev. D.00.00.38. But many overlapped peaks, which couldn't be identified by GC–MS, should be resolved into pure spectra by using chemometrics resolution method (see later for more details). Retention indices of some structures eluted before eicosane ($C_{20}H_{42}$) were measured with simultaneous injection of n -alkanes

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