



Short communication

## Gas chromatographic retention indices of trimethylsilyl derivatives of terpene alcohols

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### ABSTRACT

This paper presents the experimentally determined retention indices ( $RI_{TMS}$ ) for a set of 75 silylated terpenols (33 monoterpenols and 42 sesquiterpenols). The attempt was made to assess the dependence of  $RI_{TMS}$  on  $RI$  (for non-silylated terpenols) and on  $RI_{Ac}$  (for acetylated terpenols). Satisfactory linear regression parameters ( $RI_{TMS} = b_0 + b_1 RI$ ) were observed for tertiary substituted monoterpenols and primary or secondary substituted sesquiterpenols. The mass spectra of silylated terpenols that were not found in the available literature are in [Supplementary information](#).

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### 1. Introduction

Terpene alcohols are widespread in nature, particularly in plants. Together with monoterpenes  $C_{10}H_{16}$  and sesquiterpenes  $C_{15}H_{24}$ , they make the major part of essential oils and plant tissue exudates. As constituents of plant material, they appear in different products, both food and others, such as raw and processed vegetables and fruits, beverages, cosmetics and medicines. Their wide application comes also from the well-documented antimicrobial action.

Usually, the GC/MS identification of terpenols in samples like essential oils does not show any major difficulties, since for many of them literature provides important analytical characteristics, such as electron impact mass spectra and gas chromatographic retention indices for phases of different polarities. However, terpene alcohols may also constitute a part of more complex mixtures containing multifunctional substances, such as polyols, phenol carboxylic acids, flavonoids and chalcones. Plant tissue extracts, plant exudates and propolis belong to these mixtures. Essential oil from birch buds is a rich source of caryophyllene-type alcohols (betulenols) [1–3]. During analysis of such mixtures, the single injection method is preferred [4]. This is possible only under the condition of derivatization of polar compounds, for instance their silylation. However, available literature provides mass

spectra of TMS derivatives of terpene alcohols and their chromatographic retention indices only for a few substances of this class. It significantly limits the possibility of terpenols identification.

The purpose of this work is to present both gas chromatographic retention indices and mass spectra for a collection of silylated terpenols with different types of substitution (primary, secondary, tertiary, *endo*-, *exo*-cyclic –OH groups). There were used both commercially available terpene alcohols, as well as ones separated for this purpose from plants and commercial essential oils.

### 2. Experimental

#### 2.1. Chemicals

Commercial sabinene hydrate, nerol, geraniol, linalool, (Z)-verbenol, (E)-verbenol, menthol, isomenthol, isopulegol, (E)-pinocarveol, myrtanol, terpineols (mixture of  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers, 1- and 4-terpineols), (E)-nerolidol, (Z,E)-farnesol, (E,E)-farnesol,  $\alpha$ -bisabolol,  $\beta$ -eudesmol, (–)-globulol and (+)-cedrol were purchased from Sigma-Aldrich, Fluka and Roth (Poznań, Poland). Part of commercial preparation of monoterpene alcohols was obtained from Chemistry of Natural Products Division of Institute of Chemistry, University of Białystok (Białystok, Poland). Commercial essential oils from *Amyris balsamifera*, *Aniba roseodora*, *Malaleuca alternifolia* (tea tree oil), *Juniperus virginiana* (cedar oil), sandal-wood oil and ylang-ylang oil were purchased from AVICENA-OIL (Wrocław, Poland). Pyridine, *n*-hexane and bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing

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1% trimethylchlorosilane were purchased from Sigma–Aldrich (Poznań, Poland). Ethyl acetate and diethyl ether were purchased from POCH SA (Gliwice, Poland).

## 2.2. Isolation of terpenols from plant materials

Some of not commercially available terpenols were isolated from essential oils or ether extracts from plant material of different origins. Essential oils from leaves of Scots pine (*Pinus sylvestris*) and thuya (*Thuja occidentalis*), as well as from black poplar (*Populus nigra*) buds, were extracted by hydrodistillation in a Clevenger-type apparatus [5] and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . These preparations as well as commercial essential oils were fractionated by column chromatography on a silica column. Pure *n*-hexane was used to elute the mixtures of non-polar and slightly polar compounds (terpene hydrocarbons, carbonyls, ethers and esters). Next, gradient elution (*n*-hexane/ethyl acetate) was used to isolate fractions containing terpene alcohols. Some of these fractions were rechromatographed to provide a fraction enriched in terpene alcohols of interests. There was no attempt to isolate a pure single compound and the only task of column chromatography was to obtain fractions containing a few (two to four) compounds which could be well separated (without overlapping of peaks) on the GC capillary column. All these fractions were analyzed by GC/MS and the terpenol identification was performed using both mass spectral data and calculated retention indices which were compared with the ones reported by Adams [6].

Because there were not enough birch buds to isolate the essential oil by hydrodistillation, the buds of two species of birch (*Betula pubescens* and *Betula litwinowii*) were extracted by diethyl ether. Dried at 40 °C, buds (5 g) were crushed and while constantly stirred, three portions of ether 25 mL each were applied. The joint extracts were filtered through a paper filter and the solvent was removed to a volume of ca. 1 mL on a rotor evaporator. These concentrated extracts were subjected to column chromatography (as above) and all the fractions were analyzed by GC/MS. The automatic system of processing data of GC/MS is supplied by NIST (US National Institute of Standards and Technology) and Wiley mass spectra libraries which do not contain the mass spectra of betulenols. Hence, the registered spectra of these alcohols were compared with published in the literature [1,2].

## 2.3. Sample preparation and analysis

TMS derivatives of commercial preparations and terpene alcohols isolated from plant materials were synthesized according to the unified procedure. 1–2 mg of the materials were put into a vial of 2 mL in volume and dissolved in 200–250  $\mu\text{L}$  of pyridine, after that, 50–80  $\mu\text{L}$  of BSTFA was added. The reaction mixtures were heated at 70 °C for 0.5 h. The terpenols and their TMS derivatives were analyzed on an Agilent 6890 Gas Chromatograph with Mass Selective Detector 5973 and Autosampler 7683, electronic pressure control and split/splitless injector. Separation was performed on the HP-5ms (30 m  $\times$  0.25 mm I.D.; 0.25  $\mu\text{m}$  film thickness) fused silica column. Helium flow rate through the column was 1 mL/min. The injector worked in split (1:50) mode; injector temperature 250 °C. The EIMS spectra were obtained for ionization energy of 70 eV, at the source temperature 230 °C and quadrupole one 150 °C. The MSD was set to scan 41–600 a.m.u. Chromatograms were registered in a linear temperature programmed regime from 50 °C to 220 °C at the rate of 3 °C/min.

Hexane solution of  $\text{C}_{10}$ – $\text{C}_{22}$  *n*-alkanes was chromatographed under above conditions. Linear temperature programmed retention indices (RI) were calculated from the results for this mixture, and for solutions of terpene alcohols and their TMS derivatives.

## 3. Results and discussion

The success of the GC/MS identification in the routine analysis depends entirely on the availability of such analytical parameters as mass spectra and chromatographic retention indices of analytes [7]. In case of TMS derivatives of terpene alcohols, an access to such data is very limited. In the most comprehensive of available databases [8], there are presented the mass spectra for only five TMS derivatives of  $\text{C}_{10}\text{H}_{18}\text{O}$  monoterpenols and four  $\text{C}_{15}\text{H}_{26}\text{O}$  sesquiterpenols. Because of this, in some papers, the authors are limited to the identification on the group level (and not the particular substances) in case of finding terpenols in samples. For example, in the study [9], 13 sesquiterpenols were registered in the form of TMS derivatives, but only two substances were positively identified ((*E*)-nerolidol and bisabolol) and one (guaiol) – presumably.

The identification of terpenol TMS derivatives gets complicated also by a small informative value of their mass spectra. In many cases, after silylation, mass spectra of alcohols get significantly simpler and contain only a few intensive peaks, what is the case for e.g.  $\alpha$ -eudesmol and its TMS derivative, as shown in Fig. 1(A) and (B). However, even when a researcher possesses standard mass spectra of TMS derivatives, correct identification of terpenols is not always guaranteed due to high similarity between the spectra of these substances. In Fig. 1(C) and (D) there are presented the mass spectra of derivatives of two sesquiterpenols with completely different structures. It can be seen that the set of fragment ions is identical in both cases, and the usual distortions of the mass spectra do not give a choice possibility in favor of one of the two alcohols on the basis of peaks intensity differences (for the  $m/z$  161, 204, 105, and 189). In such a situation, the role of chromatographic retention indices as reference analytical parameters is rising. Besides, aforementioned database [8] contains retention indices of TMS derivatives of only one  $\text{C}_{10}\text{H}_{16}\text{O}$  alcohol, five  $\text{C}_{10}\text{H}_{18}\text{O}$  monoterpenols and five  $\text{C}_{15}\text{H}_{26}\text{O}$  sesquiterpenols. There are no mass spectra, nor retention indices, for  $\text{C}_{15}\text{H}_{24}\text{O}$  TMS sesquiterpenols derivatives in the available literature.

Table 1 presents experimental values of retention indices for 75 terpenols (33 mono- and 42 sesquiterpenols). Measured retention indices for terpene alcohols are in good accordance (usually in range  $\pm 3$  i.u.) with ones presented by Adams [6], and their mass spectra – with ones contained in the libraries of the used GC/MS apparatus software. Mass spectra of terpenol TMS derivatives (absent in [8]) are presented in Supplementary information.

Since the limited number of commercial and plant-isolated terpene alcohols was available, it was interesting to calculate the retention indices of terpenol TMS derivatives not included in our data. One may assume that the retention indices of silylated terpenols can be calculated from the relationship between  $\text{RI}_{\text{TMS}}$  and RI or between  $\text{RI}_{\text{TMS}}$  and  $\text{RI}_{\text{Ac}}$  (for this purpose the values of  $\text{RI}_{\text{Ac}}$  – the retention indices for acetylated terpenols from [6] were gathered in Table 1). After initial data analysis, it was found that the fact if a given terpenol is tertiary substituted (or not) has a significant influence on relationships between  $\text{RI}_{\text{TMS}}$  and RI or between  $\text{RI}_{\text{TMS}}$  and  $\text{RI}_{\text{Ac}}$ . The regression equation (model) parameters for different subgroups (all, tertiary, non-tertiary substituted) are presented in Table 2. It was assumed that regression parameters should meet the following conditions: (1)  $n > 10$ , (2)  $\text{SE} < 15$  u.i., (3) regression parameters statistically significant at the level of 5% ( $P < 0.05$ ). Only two models ( $\text{RI}_{\text{TMS}}$ –RI relationships) fulfilled these conditions: for tertiary monoterpenols, and for non-tertiary sesquiterpenols. It is a surprise, that  $\text{RI}_{\text{TMS}}$ – $\text{RI}_{\text{Ac}}$  relationships do not satisfy these conditions. Perhaps larger set of data  $\text{RI}_{\text{Ac}}$  would change this situation. It is believed that greater possibilities of  $\text{RI}_{\text{TMS}}$  prediction will be achieved with the application of the chemometric approach with the use of molecular descriptors. The better opportunities are

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