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Short communication

## Group identification of essential oils components using partition coefficients in a hexane–acetonitrile system

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### Abstract

Partition coefficients  $K_p$  in a hexane–acetonitrile heterogeneous system for 70 components usually encountered in essential oils of plants are reported. It is shown that the application of these values in the group identification stage greatly increases its reliability. The database for  $K_p$  values can be extended by calculations on the basis of the solubility–structure or retention–structure relationships. © 1998 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The problem of identification reliability has not yet lost its importance, although informative methods for the analysis of complex mixtures of organic compounds such as capillary gas chromatography in combination with mass spectral or Fourier transform infrared detector (FTIR) have been developing very rapidly. This problem is especially topical for the investigation of mixtures consisting of numerous components belonging to different classes of organic compounds. In particular, considerable difficulties are encountered in the so-called ‘prospective’ analyses of air, water or soil pollutants in which the a priori information on sample composition often does not exist [1]. The same can be said of analysis of essential oils.

Gas chromatographic (GC) identification is mainly

based on using retention indices ( $I$ ). In recent years a considerable improvement in the reproducibility of characteristics of GC columns with different polarities has been observed. Therefore, the reproducibility of retention parameters reported by different authors has also improved. However,  $I$  values are one-dimensional analytical parameters, and their use often leads to ambiguous identification results. Identification precision can be increased by applying additional characteristics, such as the difference in  $I$  values for columns with different polarity [2]. The coefficients of partition of the analytes between two immiscible liquids,  $K_p = C_1/C_2$ , have also long been recommended as such parameters. The approach based on extra column phase equilibrium (its theory has been considered in a monograph [3]) has been used successfully for the analysis of pesticides [4–7]. Nevertheless, it has not been widely used so far. This is caused to a considerable extent by the absence of representative databases for  $K_p$  values. However, it

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has recently been shown that the combination of  $I$  and  $K_p$  values ensures the efficiency of group identification, which is actually not inferior to that attained by using the differences in  $I$  values on columns with different polarities [8].

This work reports on the results of  $K_p$  determinations for a large number of terpene compounds in a hexane–acetonitrile system in the analysis of essential oils for ten species of plants. It is shown that  $K_p$  values can be predicted on the basis of retention–structure relationships.

## 2. Experimental

### 2.1. Materials

Essential oils of ylang-ylang, lavender, bergamot, lemon, and tangerine of Misitano & Stracuzzi (Italy) were used. Essential oils of pine (*Pinus sylvestris*), spruce (*Picea abies*), larch (*Larix europeae*), juniper (*Juniperus communis*), and thuja (*Thuja occidentalis*) were obtained in the laboratory of the Institute of Chemistry of Warsaw University (Bialystok Branch) by hydrodistillation from plants growing in the Bialystok region. Moreover, to determine  $K_p$  values, the preparations of borneole, isoborneole, linaloole,  $\alpha$ -terpineole, fenchone, citral (isomers mixture), and  $\alpha$ -terpenyl acetate from the collection of the Institute of Chemistry of St. Petersburg University (Russia) were used. Samples of andrane ( $\alpha$ -cedrene epoxide), piconia (isolongifolanone), bisabolone, bisabolol,  $\alpha,\beta$ -santalols, farnesol, nerolidol and cedranoxyde were obtained from a factory of aromatic substances (Grodzisk Mazowiecki, Poland).

Acetonitrile (HPLC grade, Merck),  $n$ -hexane, and toluene were used without additional purification or drying.

### 2.2. Sample preparation and analysis

Samples were prepared for analysis at room temperature. A 3-ml flask was charged through a pipette with 0.5 ml of  $n$ -hexane and 0.5 ml of acetonitrile and 30  $\mu$ l of essential oil (or hexane solution of a terpenoid from the collection), 1  $\mu$ l of

toluene and 5  $\mu$ l of  $C_8$ – $C_{14}$  or  $C_8$ – $C_{18}$   $n$ -alkanes were added. Subsequently the flask was shaken for 30 s, and after phase separation each phase was subjected to GC analysis. Components were separated with flow splitting (1:30) on a GC DANI 86.10 HT chromatograph (Instrumentazione Analitica, Monza, Italy) with a flame ionisation detection (FID) system on fused-silica columns (30 m $\times$ 0.25 mm, film thickness, 0.25  $\mu$ m) with DB-1 or DB-5 phases (J&W Scientific, USA) at a carrier gas flow-rate of 1 ml/min. The column was charged with 1–2  $\mu$ l of the liquid, and the analysis was carried out with temperature programming from 50 to 250°C at a rate of 3°C/min. The chromatograms were recorded with a computer system data processing.

The values of retention times were used to calculate linear  $I$  values from Eq. (1):

$$I = \frac{(t_x - t_n)}{t_{n+1} - t_n} \cdot 100 + 100n \quad (1)$$

Partition coefficients were calculated from the ratio of peak areas of the components by using Eq. (2):

$$K_p = \frac{S_h^x}{S_a^x} \cdot \frac{S_a^t}{S_h^t} \quad (2)$$

where  $S_h^x$  and  $S_a^x$  are the peak areas of the component  $x$  being determined in hexane and acetonitrile and  $S_h^t$  and  $S_a^t$  are the peak areas of toluene on the chromatograms of the hexane and the acetonitrile phases, respectively.

To control the correctness of component identification, essential oils were also subjected to GC–MS analysis on an LKB-2091 instrument (Stockholm, Sweden). Separation was carried out on a capillary column with DB-5 stationary phase. Separation conditions were the same as in GC analysis with FID. The temperature of the mass spectrometer separator was 200°C and that of the ion source was 250°C. Ionisation was carried out by electrons with energy of 70 eV. The cathode current was 25  $\mu$ A and the accelerating voltage was 3.5 kV.

The prediction of partition coefficients based on physicochemical properties and the measured retention indices was made by the least-squares method.

### 3. Results and discussion

The chromatograms in Fig. 1. illustrate the partition of essential oil components between hexane and acetonitrile phase. Table 1 gives the results of *I* determination on a DB-5 column [9] and those of

partition coefficients for 70 substances, 63 of which belong to terpene compounds.

Table 2 gives the results of statistical processing of partition coefficients for different groups of structurally related compounds. The values for DB-5 and DB-1 stationary phases virtually coincide, al-

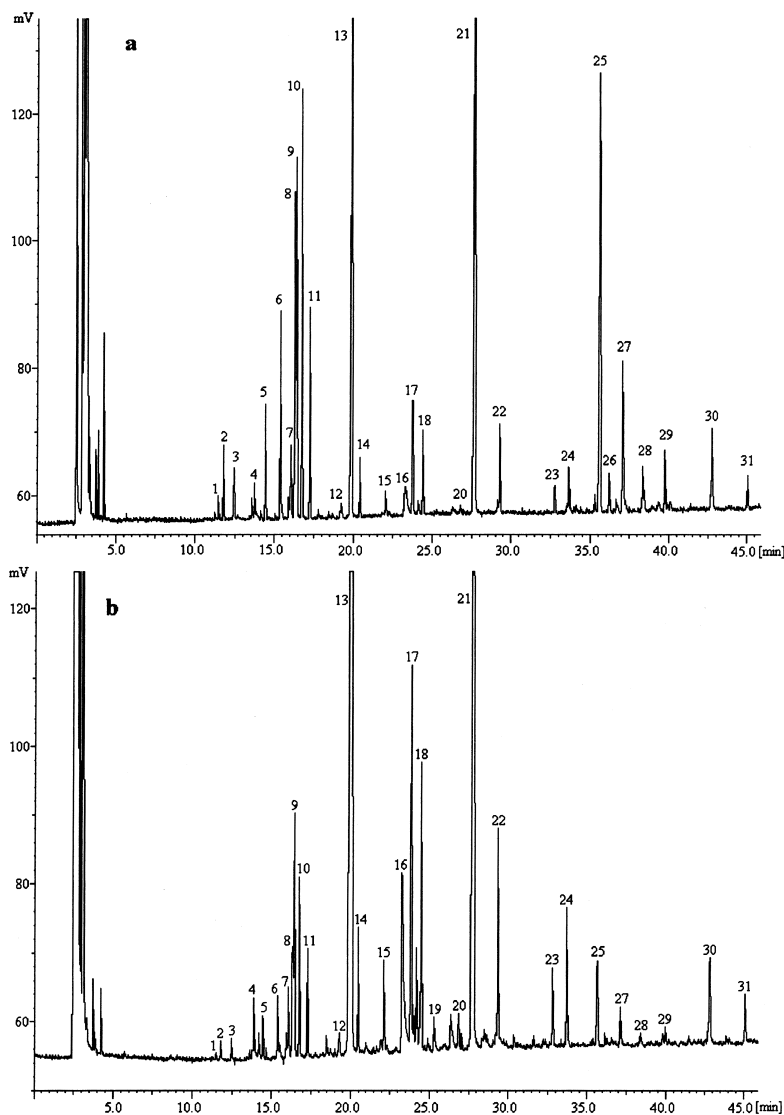


Fig. 1. Partition of the lavender essential oil components between hexane (a) and acetonitrile (b) phase. Identified components: 1 = tricyclene, 2 =  $\alpha$ -pinene, 3 = camphene, 4 =  $\beta$ -pinene, 5 = myrcene, 6 =  $\alpha$ -terpinene, 7 = 1,8-cineol, 8 = limonene, 9 =  $\beta$ -phellandrene, 10 =  $\beta$ -(Z)-ocimene, 11 =  $\beta$ -(E)-ocimene, 12 = fenchone, 13 = linalool, 14 = camphor, 15 = borneol, 16 = isopinocampheol(?), 17 = 4-terpineol, 18 =  $\alpha$ -terpineol, 19 = nerol, 20 = geraniol, 21 = linalool acetate, 22 = sabinyl acetate, 23 = neryl acetate, 24 = geranyl acetate, 25 =  $\beta$ -caryophyllene, 26 =  $\beta$ -(E)-farnesene, 27 =  $\gamma$ -bisabolene(?), 28 = vetivenene(?), 29 = cadinane-1,4-diene, 30 = longiborneol (juniperol), 31 = unknown sesquiterpenoid.

Table 1

Partition coefficient ( $K_p$ ) of some components of essential oils

| Compound                                       | $I_{cal}$ | $I_{lit}$ [9] | $K_p \pm \sigma$ | $n$ | Essential oil <sup>a</sup> |
|--|-----------|---------------|------------------|-----|----------------------------|
| <b>(I) Monoterpene hydrocarbons</b>            |           |               |                  |     |                            |
| (1) Cyclofenchene                              | 896       | —             | 8.87             | 2   | 1                          |
| (2) Tricyclene                                 | 920±1     | 926           | 7.99±0.10        | 3   | 1, 3, 5–9                  |
| (3) $\alpha$ -Pinen                            | 933±2     | 939           | 7.02±0.20        | 10  | 1–10                       |
| (4) Camphene                                   | 946±2     | 953           | 6.16±0.36        | 10  | 1–5, 7, 9                  |
| (5) Sabinene                                   | 971±3     | 976           | 6.50             | 3   | 1, 4, 5, 7, 8              |
| (6) $\beta$ -Pinen                             | 974±3     | 980           | 7.14±0.25        | 9   | 1–5, 7–9                   |
| (7) Myrcene                                    | 989±1     | 991           | 3.30±0.20        | 9   | 1–5, 7–9                   |
| (8) 3-Carene                                   | 1010±1    | 1011          | 6.70±0.43        | 8   | 1–4                        |
| (9) $\alpha$ -Terpinene                        | 1016±1    | 1018          | 4.31±0.28        | 3   | 1–6                        |
| (10) Limonene                                  | 1028±2    | 1031          | 4.76±0.45        | 7   | 1–9                        |
| (11) $\beta$ -Phellandrene                     | 1031      | 1031          | 4.90             | 2   | 1, 2                       |
| (12) $\beta$ -(Z)-Ocimene                      | 1037±2    | 1040          | 2.99±0.19        | 3   | 1, 2, 9                    |
| (13) $\beta$ -(Z)-Ocimene                      | 1046±2    | 1050          | 3.03±0.07        | 3   | 1, 2, 9                    |
| (14) $\gamma$ -Terpinene                       | 1057±2    | 1062          | 4.69±0.28        | 5   | 1–9                        |
| (15) Terpinolene                               | 1088±1    | 1089          | 4.78±0.15        | 7   | 1–4, 6–8                   |
| <b>(II) Monoterpene alcohols</b>               |           |               |                  |     |                            |
| (1) Linalool                                   | 1100±1    | 1089          | 0.35±0.07        | 6   | 7–11                       |
| (2) Fenchol, exo                               | 1115      | 1117          | 0.32             | 2   | 4, 5                       |
| (3) Isopulegol <sup>b</sup>                    | 1150      | 1156          | 0.25             | 1   | 5                          |
| (4) Isoborneol                                 | 1156±1    | 1156          | 0.36±0.02        | 3   | 1, 2, 5                    |
| (5) Borneol                                    | 1166±1    | 1165          | 0.37±0.02        | 6   | 1–3, 5, 9, 11              |
| (6) Pinocampheol, iso <sup>b</sup>             | 1178      | 1178          | 0.50             | 2   | 5, 9                       |
| (7) $\alpha$ -Terpineol                        | 1189±1    | 1189          | 0.36±0.06        | 8   | 1–5, 9, 11                 |
| (8) Nerol                                      | 1227      | 1228          | 0.30             | 2   | 6, 9                       |
| <b>(III) Monoterpene aldehydes and ketones</b> |           |               |                  |     |                            |
| (1) Fenchone                                   | 1087      | 1087          | 0.59             | 2   | 5, 9, 11                   |
| (2) Thujone, <i>trans</i> <sup>b</sup>         | 1116      | 1114          | 0.60             | 2   | 4, 5                       |
| (3) Camphor                                    | 1143±1    | 1143          | 0.46±0.01        | 4   | 2, 3, 5, 9                 |
| (4) 3-Pinanone                                 | 1176±2    | 1173          | 0.58±0.05        | 8   | 1, 3                       |
| (5) Neral ( $\beta$ -citral)                   | 1241±1    | 1240          | 0.38±0.02        | 3   | 11                         |
| (6) Geranial ( $\alpha$ -citral)               | 1271±1    | 1270          | 0.40±0.03        | 3   | 10, 11                     |
| <b>(IV) Monoterpene acetates</b>               |           |               |                  |     |                            |
| (1) Linalool                                   | 1256±3    | 1257          | 0.83±0.06        | 4   | 7–10                       |
| (2) Chrysanthenyl, <i>cis</i> <sup>b</sup>     | 1261      | 1262          | 1.40             | 1   | 5                          |
| (3) Bornyl                                     | 1288±2    | 1285          | 1.26±0.05        | 10  | 1–5                        |
| (4) Sabiny, <i>trans</i>                       | 1292±1    | 1291          | 1.21±0.08        | 4   | 4, 5, 9                    |
| (5) Verbenyl, <i>trans</i> <sup>b</sup>        | 1294      | 1292          | 0.98             | 1   | 5                          |
| (6) $\alpha$ -Terpenyl                         | 1350±1    | 1350          | 1.18±0.05        | 5   | 1–4                        |
| (7) Neryl                                      | 1364±1    | 1365          | 1.40±0.03        | 3   | 7–9, 11                    |
| (8) Geranyl                                    | 1384±1    | 1383          | 1.42±0.02        | 3   | 7–11                       |
| <b>(V) Sesquiterpenes</b>                      |           |               |                  |     |                            |
| (1) Thujopsene                                 | 1428±3    | 1429          | 6.40             | 2   | 4, 5,                      |
| (2) $\beta$ -Caryophyllene                     | 1427±4    | 1418          | 9.04±0.04        | 5   | 1, 2, 4, 9, 10             |
| (3) $\alpha$ -Humulene                         | 1451±2    | 1454          | 8.79±0.15        | 5   | 1, 2                       |
| (4) $\beta$ -(E)-Farnesene                     | 1482±3    | 1477          | 7.97±0.23        | 3   | 4, 9, 11                   |
| (5) $\gamma$ -Muuroleone                       | 1489±5    | 1480          | 12.08±0.10       | 6   | 1, 3, 4, 10                |
| (6) D-Germacrene                               | 1489±5    | 1480          | 7.11±0.13        | 3   | 10                         |
| (7) $\gamma$ -Cadinene                         | 1510±1    | 1513          | 6.02±0.09        | 5   | 1, 2, 10                   |
| (8) $\gamma$ -Bisabolene <sup>b</sup>          | 1517±1    | 1517          | 9.64±0.61        | 4   | 1, 3, 4, 9                 |
| (9) Vetivenene <sup>b</sup>                    | 1527±2    | 1526          | 10.44±1.03       | 3   | 4, 9                       |
| (10) Cadina-1,4-diene                          | 1528±2    | 1532          | 10.99±2.00       | 6   | 1–4, 9                     |

Table 1. Continued

| Compound                                       | $I_{\text{cal}}$ | $I_{\text{lit}}$ [9] | $K_p \pm \sigma$ | $n$ | Essential oil <sup>a</sup> |
|--|------------------|----------------------|------------------|-----|----------------------------|
| <b>(VI) Sesquiterpenoids</b>                   |                  |                      |                  |     |                            |
| (1) ( <i>Z</i> )-Nerolidol                     | 1537±1           | 1534                 | 0.70±0.02        | 3   | 11                         |
| (2) ( <i>E</i> )-Nerolidol                     | 1569±1           | 1564                 | 0.79±0.02        | 3   | 11                         |
| (3) Juniperol                                  | 1592±2           | 1592                 | 0.94±0.03        | 3   | 4, 5, 9                    |
| (4) Caryophyllene alcohol                      | 1570±3           | 1568                 | 1.10±0.06        | 3   | 1, 11                      |
| (5) Piconia (isolongi-folanone)                | 1620             | 1618                 | 1.31             | 1   | 11                         |
| (6) $\gamma$ -Eudesmol <sup>b</sup>            | 1632             | 1630                 | 0.96             | 1   | 5                          |
| (7) $\alpha$ -Muurolol                         | 1649±2           | 1645                 | 1.09±0.07        | 6   | 1–4, 10                    |
| (8) $\beta$ -Eudesmol<br>( $\beta$ -Selinanol) | 1651             | 1649                 | 0.89             | 2   | 3, 4                       |
| (9) $\alpha$ -Cadinol                          | 1654±2           | 1653                 | 0.52±0.06        | 5   | 1–4, 10                    |
| (10) Coniferyl alcohol                         | 1663             | 1664                 | 1.02             | 2   | 1–4                        |
| (11) $\alpha$ -Santanol                        | 1683             | 1678                 | 0.88             | 1   | 11                         |
| (12) $\beta$ -Bisabolol                        | 1685             | 1683                 | 0.88             | 2   | 10, 11                     |
| (13) ( <i>Z,E</i> )-Farnesol                   | 1700±1           | 1697                 | 0.78±0.02        | 3   | 11                         |
| (14) Nerolidol acetate                         | 1715             | 1714                 | 2.76             | 1   | 11                         |
| (15) $\beta$ -( <i>Z</i> )-Santalol            | 1720             | 1720                 | 0.96             | 1   | 11                         |
| (16) ( <i>E,E</i> )-Farnesol                   | 1722±1           | 1722                 | 0.79±0.02        | 4   | 10, 11                     |
| (17) (6 <i>R</i> ,7 <i>R</i> )-Bisabolene      | 1735             | 1733                 | 0.79             | 1   | 11                         |
| (18) $\beta$ -( <i>E</i> )-Santalol            | 1741             | 1741                 | 1.05             | 1   | 11                         |
| (19) (6 <i>S</i> ,7 <i>R</i> )-Bisabolone      | 1742             | 1744                 | 0.65             | 1   | 11                         |
| (20) $\beta$ -Bisabolen-12-ol                  | 1759             | 1760                 | 0.94             | 1   | 11                         |
| <b>(VII) Sesquiterpene epoxide</b>             |                  |                      |                  |     |                            |
| (1) Cedranoxoyde                               | 1544             | 1540                 | 3.23             | 1   | 11                         |
| (2) Caryophyllene oxide                        | 1584±3           | 1581                 | 4.30±0.45        | 3   | 1, 11                      |
| (3) Andrane ( $\alpha$ -cedrene epoxide)       | 1585             | –                    | 2.72             | 1   | 11                         |
| <b>(VIII) Nonterpene components</b>            |                  |                      |                  |     |                            |
| (1) Anisole, <i>p</i> -methyl                  | 1018             | 1019                 | 0.49             | 2   | 10                         |
| (2) <i>p</i> -Cymene                           | 1026±1           | 1026                 | 2.29±0.30        | 3   | 3, 8, 9                    |
| (3) Methyl benzoate                            | 1092             | 1091                 | 0.23             | 2   | 10                         |
| (4) Benzyl acetate                             | 1161             | 1163                 | 0.14             | 1   | 10                         |
| (5) Eugenol                                    | 1356             | 1356                 | 0.68             | 2   | 10                         |
| (6) Hexenyl benzoate <sup>b</sup>              | 1587             | 1583                 | 2.77             | 2   | 10                         |
| (7) 3-Hexenylphenyl acetate <sup>b</sup>       | 1626             | 1631                 | 2.33             | 1   | 10                         |

<sup>a</sup> Essential oils: *Pinus sylvestris* (1); *Picea abies* (2); *Larix europaeae* (3); *Juniperus communis* (4); *Thuja occidentalis* (5); lemon (6); tangerine (7); bergamot (8); lavender (9); ylang-ylang (10); authentic preparations (11).

<sup>b</sup> Identified tentatively.

though  $I$  values can differ by 10–20 index units (in the case of DB-1 and Carbowax 20M this difference is on the average about 150 units for hydrocarbons and attains 400–500 units for alcohols).

These differences in the values of partition coefficients for different classes of compounds provide the possibility of carrying out group identification of components of complex mixtures, which is particularly important in performing ‘prospective’ analyses. The advantage of this approach as compared to traditional analysis on columns with different polarities is the absence of the problem of mutual

assignment of peaks of the same compounds on different chromatograms. It is also important that in this method complex preliminary sample preparation including precise control of concentrations, solvent volumes, and temperature is not required.

The hexane–acetonitrile heterogenous system is not the only system suitable for determining  $K_p$  for analytical purposes. Similar results can be obtained by using the hexane–nitromethane system [10,11].

One of the factors preventing wide practical application of the above parameters is the absence of sufficiently detailed databases. This problem can be

Table 2  
Average  $K_p \pm \sigma$  values for the principal groups of terpene compounds

| Group  | <i>n</i> | $K_p \pm \sigma$ |
|--|----------|------------------|
| (I) Monoterpene hydrocarbons including         | 12       | 5.27 ± 1.81      |
| acyclic  | 3        | 3.10 ± 0.17      |
| monocyclic                                     | 4        | 4.61 ± 0.27      |
| bicyclic                                       | 4        | 6.76 ± 0.44      |
| tricyclene                                     | 1        | 7.99             |
| (II) Monoterpene alcohols                      | 7        | 0.35 ± 0.06      |
| (III) Monoterpene aldehyde and ketone          | 6        | 0.50 ± 0.10      |
| (IV) Acetate of monoterpene alcohols including | 8        | 1.08 ± 0.26      |
| acyclic  | 3        | 0.78 ± 0.09      |
| cyclic   | 5        | 1.21 ± 0.15      |
| (V) Sesquiterpenes                             | 10       | 8.89 ± 1.91      |
| (VI) Sesquiterpene alcohols                    | 14       | 0.84 ± 0.15      |
| (VII) Sesquiterpene epoxide                    | 4        | 3.77 ± 0.16      |

solved by the calculation of the  $K_p$  values on the bases of the ‘partitioning–structure’ relationships similar to the ‘retention–structure’ relationships used for calculating *I* [12–17]. An example of these correlation equations can be given by the three-parameter equation

$$\log K_p = a \log X + bY + c \quad (4)$$

Various physicochemical constants can be used as *X* and *Y* descriptors. They must be characterised by a monotonic change in the homological groups considered. Such constants as molar refraction, molar volume, dissolution heat, etc. may be applied. Table 3 lists the results of calculating the  $K_p$  of monoterpene hydrocarbons from Eq. (4) by using the ring numbers in the molecule as the descriptor *Y* and an empirical parameter  $\delta_i$  proposed in [16] as the descriptor *X*. It is calculated according to Eq. (5):

$$\delta_{t_i}^2 = -0.02085 \cdot \frac{T_i^2}{V_i} + 58.93 \cdot \frac{T_i}{V_i} - 6892.14 \cdot \frac{1}{V_i} - 26.76 \quad (5)$$

where *T* is the boiling temperature (K) at the atmospheric pressure and *V* is the molar volume.

The first part of Table 3 contains the initial data for calculating of the coefficients *a*, *b*, and *c* from Eq. (4). The second part (control set) includes

terpenes that have not been used in calculating the coefficients in Eq. (4). The average value of relative error is 3.5%, whereas the maximum value does not exceed 10%. However, the use of Eq. (4) is hindered by the fact that for many compounds boiling tem-

Table 3  
Calculation of  $K_p$  for monoterpene hydrocarbons according to Eq. (4) (variable parameters *X* and *Y* are the total solubility  $\delta_i$  and the number of rings *n* in the molecule, respectively)

| Monoterpene   | $\delta_i$ | <i>n</i> | $K_p^{\text{exp}}$ | $K_p^{\text{calc}}$ | $ \Delta K_p $ |
|---|------------|----------|--------------------|---------------------|----------------|
| (1) Myrcene   | 7.86       | 0        | 3.30               | 3.27                | 0.07           |
| (2) $\beta$ -( <i>Z</i> )-Ocimene   | 8.29       | 0        | 2.99               | 3.12                | 0.13           |
| (3) Limonene  | 8.28       | 1        | 4.76               | 4.60                | 0.16           |
| (4) $\gamma$ -Terpinene   | 8.43       | 1        | 4.69               | 4.53                | 0.16           |
| (5) $\alpha$ -Pinene  | 8.06       | 2        | 7.02               | 6.93                | 0.09           |
| (6) Camphene  | 8.25       | 2        | 6.16               | 6.79                | 0.63           |
| (7) $\beta$ -Pinene   | 8.27       | 2        | 7.14               | 6.78                | 0.36           |
| Average   |            |          |                    |                     | 0.23           |
| Parameters of Eq. (5): <i>a</i> = -0.84825, <i>b</i> = 0.16790, <i>c</i> = 1.2738; <i>R</i> = 0.988 |            |          |                    |                     |                |
| Control set <sup>a</sup>  |            |          |                    |                     |                |
| (1) $\beta$ -( <i>E</i> )-Ocimene   | 7.89       | 0        | 3.03               | 3.26                | 0.23           |
| (2) $\alpha$ -Terpinene   | 8.21       | 1        | 4.21               | 4.63                | 0.42           |
| (3) Terpinolene   | 8.56       | 1        | 4.69               | 4.75                | 0.06           |
| (4) 3-Carene  | 8.36       | 2        | 6.72               | 6.70                | 0.02           |
| Average   |            |          |                    |                     | 0.18           |

<sup>a</sup>  $K_p^{\text{exp}}$  values were not used for calculation above coefficients.

peratures at atmospheric pressure or density required for calculating  $\delta_{t_1}$  are not known. In these cases  $I$  values can be used as the descriptor  $X$ . The average relative error for the same 12 monoterpenes is 6%, and the maximum error does not exceed 15% ( $R = 0.978$ ). Table 4 gives the results of these calculations

performed by using  $I$ . The second part of the table contains the calculated values of  $K_p$  for a series of monoterpenes that are not often encountered in the composition of essential oils.

Consequently, the method of group identification considered here could be easily implemented in

Table 4

Calculation of  $K_p$  for monoterpene hydrocarbons according to Eq. (4) (variable parameters  $X$  and  $Y$  are the retention index and the number of rings in the molecule, respectively)

| Monoterpene              | $I$  | $n$ | $K_p^{\text{exp}}$ | $K_p^{\text{calc}}$ | $ \Delta K_p $ |
|--------------------------|------|-----|--------------------|---------------------|----------------|
| (1) Myrcene              | 991  | 0   | 3.30               | 3.12                | 0.18           |
| (2) $\beta$ -(Z)-Ocimene | 1040 | 0   | 2.99               | 3.19                | 0.20           |
| (3) $\beta$ -(E)-Ocimene | 1050 | 0   | 3.03               | 3.20                | 0.17           |
| (4) $\alpha$ -Terpinene  | 1016 | 1   | 4.21               | 4.55                | 0.34           |
| (5) Limonene             | 1058 | 1   | 4.76               | 4.57                | 0.19           |
| (6) $\gamma$ -Terpinene  | 1062 | 1   | 4.69               | 4.63                | 0.06           |
| (7) Terpinolene          | 1088 | 1   | 4.78               | 4.68                | 0.10           |
| (8) $\alpha$ -Pinene     | 939  | 2   | 7.02               | 6.34                | 0.68           |
| (9) Camphene             | 953  | 2   | 6.16               | 6.38                | 0.22           |
| (10) $\beta$ -Pinene     | 980  | 2   | 7.14               | 6.45                | 0.69           |
| (11) 3-Carene            | 1011 | 2   | 6.70               | 6.54                | 0.16           |
| (12) Tricyclene          | 926  | 3   | 7.99               | 9.08                | 1.09           |
|                          |      |     |                    | Average             | 0.34           |

Parameters of Eq. (5):  $a = 0.42952$ ,  $b = 0.15880$ ,  $c = -0.79261$ ;  $R = 0.978$

Results of calculation

|                                       |      |   |   |      |  |
|---------------------------------------|------|---|---|------|--|
| (1) Achillene                         | 894  | 0 | — | 2.99 |  |
| (2) <i>allo</i> -Ocimene              | 1124 | 0 | — | 3.29 |  |
| (3) <i>allo</i> -Ocimene, neo-        | 1139 | 0 | — | 3.31 |  |
| (4) $\alpha$ -Pyronene                | 944  | 1 | — | 4.40 |  |
| (5) $\beta$ -Pyronene                 | 999  | 1 | — | 4.51 |  |
| (6) $\alpha$ -Phellandrene            | 1011 | 1 | — | 4.54 |  |
| (7) $\beta$ -Terpinene                | 1020 | 1 | — | 4.59 |  |
| (8) $\beta$ -Phellandrene             | 1030 | 1 | — | 4.57 |  |
| (9) Sylvestrene                       | 1032 | 1 | — | 4.58 |  |
| (10) 1-Methyl-3-iso-propylcyclohexane | 1037 | 1 | — | 4.59 |  |
| (11) Isoterpinolene                   | 1085 | 1 | — | 4.86 |  |
| (12) Sylvoterpinolene                 | 1146 | 1 | — | 4.79 |  |
| (13) $\delta$ -Fenchene               | 864  | 2 | — | 6.11 |  |
| (14) $\xi$ -Fenchene                  | 899  | 2 | — | 6.22 |  |
| (15) $\beta$ -Thujene                 | 899  | 2 | — | 6.22 |  |
| (16) $\gamma$ -Fenchene               | 903  | 2 | — | 6.23 |  |
| (17) Bornylene                        | 908  | 2 | — | 6.24 |  |
| (18) $\epsilon$ -Fenchene             | 912  | 2 | — | 6.26 |  |
| (19) $\beta$ -Fenchene                | 921  | 2 | — | 6.28 |  |
| (20) $\alpha$ -Thujene                | 929  | 2 | — | 6.30 |  |
| (21) $\alpha$ -Fenchene               | 951  | 2 | — | 6.37 |  |
| (22) 4-Carene                         | 960  | 2 | — | 6.40 |  |
| (23) Sabinene                         | 976  | 2 | — | 6.44 |  |
| (24) 2-Carene                         | 994  | 2 | — | 6.52 |  |
| (25) Cyclofenchene                    | 890  | 3 | — | 8.92 |  |

practice, and databases for partitioning coefficients can be supplemented by using calculation methods.

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### References

- [1] I.G. Zenkevich, J. Ecol. Chem. 4 (1993) 257.
- [2] G. Guiochon, C.L. Guillemin, Quantitative Gas Chromatography for Laboratory Analyses and On-line Process Control. Elsevier, Amsterdam, Oxford, 1988.
- [3] V.G. Berezkin, V.D. Loshilova, A.G. Pankov, V.D. Yagodovskii, Khromato-Raspredelitelnyi Metod. Nauka, Moscow, 1976, (in Russian).
- [4] M. Beroza, M.C. Bowman, Anal. Chem. 37 (1965) 291.
- [5] M.C. Bowman, M. Beroza, Anal. Chem. 38 (1966) 1427.
- [6] M.C. Bowman, M. Beroza, Anal. Chem. 37 (1965) 291.
- [7] M.C. Bowman, M. Beroza, Anal. Chem. 38 (1966) 1427.
- [8] I.G. Zenkevich, A.V. Vasil'ev, Russ. J. Anal. Chem. (in Russian) 48 (1993) 473.
- [9] R.P. Adams, Identification of Essential Oil Components by GC–MS, Allurd, Carol Stram, IL, 1995.
- [10] I.G. Zenkevich, I.A. Tzibulskaya, Russ. J. Phys. Chem. 71 (1997) 341.
- [11] I.G. Zenkevich, Russ. J. Org. Chem. 32 (1996) 1460.
- [12] I.G. Zenkevich, L.M. Kuznezova, Collect. Czech. Chem. Commun. 56 (1991) 2042.
- [13] R. Kaliszan, Quantitative Structure–Chromatographic Retention Relationships, Wiley, New York, 1987.
- [14] K. Heberger, Chromatographia 29 (1990) 375.
- [15] M.A. Diez, M.D. Guillen, C.G. Blanco, J. Bernejo, J. Chromatogr. 508 (1990) 363.
- [16] Z. Hu, H. Zhang, J. Chromatogr. A 653 (1993) 275.
- [17] V. Isidorov, I. Zenkevich, T. Sacharewicz, Chem. Anal. (Warsaw) 42 (1997) 627.