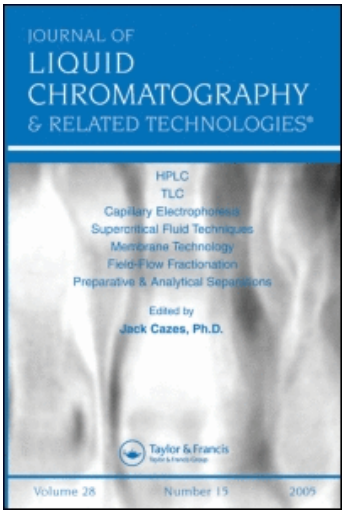

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ON THE IMPORTANCE OF TOPOLOGICAL INDICES IN RESEARCH OF *α*- AND *γ*-TERPINENE AS WELL AS *α*- AND *β*-PINENE SEPARATED BY TLC

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ABSTRACT

α- and γ-terpinene, as well as α- and β-pinene were separated on silica gel and on silica gel impregnated with various percentages of silver nitrate. It was stated that argentation thin-layer chromatography is an efficient technique for separation of isomeric α- and γ-terpinene as well as α- and β-pinene. The optimal conditions of separation of these compounds were determined. The electrotopological states of carbon atoms forming double bonds explain the separation of the terpenes. Qualitative relationships between physical and chromatographic parameters and topological indices, based on adjacency matrix and distance matrix, were formulated.

Key Words: TLC; Topological indices; Terpinene; Pinene

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INTRODUCTION

The monoterpenes are liquid or solid compounds with a strong smell. They are volatile in water vapour. These compounds are in gradients of essential oils distilled from plants. They are soluble in organic solvents and fats, but they are practically insoluble in water. α- and γ-terpinene, as well as α- and β-pinene, are monoterpenes with molecular formula $C_{10}H_{16}$. α- and γ-terpinene are monocyclic terpenes. They occur (in particular α-terpinene) in numerous essential oils. α- and β-pinene are hydrocarbons from a group of bicyclic terpenes with a strong turpentine smell. α-pinene is widespread and occurs in hundreds of plants as a component of essential oils. It is the main component of turpentine (Terebinthina) from wood of pine Pinus sylvestris (Pinaceae). α-pinene is an important parent substance for the synthesis of camphor, borneol, and a series of other compounds. β-pinene accompanies α-pinene. β-pinene is at present particularly plentiful in french turpentine.

α- and γ-terpinene have two double bonds, while α- and β-pinene have only one double bond. Hence, they can easily attach to halogens, giving crystalline compounds with characteristic melting points.

The presence of α- and β-pinene was stated in essential oils from: Achillea millefolium,[1] fruits of the West African peppertree Xylopia aethiopica,[2] roots, stems, leaves, and flowers of Echinacea angustifolia, Echinacea pallida, and Echinacea purpurea,[3] grapefruit,[4] needles and twigs of balkan pine (Pinus peuce grisebach) grown in Northern Greece,[5] lemon,[6] and loblolly pine (Pinus taeda).[7] α- and γ-terpinene are present, among others, in Artemisia annua L.,[8] in tea tree oil,[9] and essential oil obtained from Senecio graveolens.[10] The physical characteristics of α- and γ-terpinene, and α- and β-pinene are presented in Table 1.

For isolation of individual monoterpenes, fractional distillation is often applied. For identification of their presence, gas chromatography is used. It enables the separation and quantitative determination of monoterpene components. However, for the purpose of only qualitative determination of the

Table 1. General Physical Data of Terpenes Investigated

Terpene	Molar Mass [g/mol]	Boiling Point bp. [°C]	Flash Point Fp. [°C]	Density d [g/cm^3]	Refractive Index n_D^{20}
γ-Terpinene	136.24	182	51	0.849	1.4740
α-Terpinene	136.24	173–175	46	0.837	1.4780
α-Pinene	136.24	155–156	32	0.858	1.4650
β-Pinene	136.24	164–165	36	0.872	1.4780

composition of essential oils, thin-layer chromatography can be an alternative method.[11–20]

Thin-layer chromatography is a relatively cheap technique enabling the analysis of several samples on one chromatoplate. However, in each chromatographic method there are particular problems when the separated compounds are isomers.

The aim of this work was to establish the conditions for optimal separation by TLC of the isomeric α- and γ-terpinene, as well as α- and β-pinene, and using the topological indices chosen, as well as electrotopological states, for the evaluation of separation of monoterpenes investigated.

EXPERIMENTAL

Thin-Layer Chromatography

20×20 cm glass plates precoated with 0.25 mm layers of silica gel (#5715, E. Merck) were impregnated with an aqueous solution of silver nitrate (0%, 5%, 10%, 15%, 20%, or 25%). Solutions of the investigated terpenes (Sigma-Aldrich, USA) were spotted on a chromatographic plate in quantities of 10 μg of each terpene in 2 μL of ethanol. Benzene was used as a mobile phase. The development distance was 14 cm. The terpene isomers were detected by UV illumination at 254 nm. The R_F values obtained were counted over again on R_M values according to the formula:

$$R_M = \log\left(\frac{1}{R_F} - 1\right) \tag{1}$$

Calculation of the Topological Indices and Electrotopological States

The topological indices based on connectivity: Randic ($^0\chi$, $^1\chi$, $^2\chi$),[21–25] Gutman (M),[23] on distance matrix: Wiener (W),[23,26] Balaban (I_B),[27] and Pyka (A, ^0B, ^1B, ^2B, ^2B_q, C, D, χ_{012})[28,29] indices were calculated for the terpenes. The S_i index was also calculated.[30] The Wiener, Balaban, Pyka, and S_i indices were calculated by building the distance matrix and determining its elements by means of values given by Barysz et al.[30] The electrotopological states (E) of each atom in a molecule of the terpines investigated were calculated.[31,32]

The elements necessary for calculating topological indices and electrotopological states are presented in Table 2.

The methods of calculation of the topological indices and electrotopological states were presented in numerous review works.[23,31–35]

Table 2. The Elements Needed for Calculating Topological Indices and Intrinsic State Values

Atom	Delta Values δ (23)	Atom	Diagonal Elements d_{ii} (30)	Type of Bond	Off-Diagonal Elements d_{ij} (30)	Skeletal Hydride Group	Intrinsic State Values I (31,32)
$-CH_3$	1	C	0	C–C	1.000	$-CH_3$	2.00
$=CH_2$	2			C=C	0.500	$-CH_2-$	1.50
$\equiv CH$	3					$=CH_2$	3.00
$=C=$	4					$=CH-$	2.00
						$>CH-$	1.33
						$>C=$	1.67
						$>C<$	1.25

RESULTS AND DISCUSSION

The separation of the isomeric organic compounds is an important analytical and physicochemical task. A great many papers are concerned with the separation of the organic isomers by TLC, HPLC, and GC techniques. Chromatographic techniques allow the establishment of certain rules concerning the separation sequences of the investigated isomers. There were chromatographed isomeric α- and γ-terpinene, as well as α- and β-pinene by means of the TLC technique on silica gel and silica gel with various percentages of impregnation with silver nitrate. The results of these analyses are presented in the form of R_F and R_M values in Table 3, and in Figure 1, where the plot of the R_M values versus impregnation percentage of $AgNO_3$ on silica gel is shown for the investigated compounds.

From these figures it was found, that on non-impregnated silica gel (0% of impregnation) the isomeric terpinene and pinene, were not separated easily. The best separations of α- and γ-terpinene were obtained on silica gel with impregnation of 5%, 10%, and 25%. The good separations of α- and β-pinene were obtained on silica gel with all the impregnation percentage with silver nitrate. The best α- and β-pinene separation was obtained by 25% impregnation. The confirmation of this fact is separation factors ($\alpha_{1,2}$ and $\alpha_{3,4}$), separation parameters ($\mathbf{R}^{\alpha}_{F(1,2)}$ and $\mathbf{R}^{\alpha}_{F(3,4)}$) counted, and the differences between R_F values of spots of isomers on the chromatogram (ΔR_F).

One of the current tendencies in chemical investigations is the prediction of physical, physicochemical, and biological properties of molecules from their structural parameters. The fundamental finding of these investigations is the fact that the structure of a molecule determines its properties.[31,38–40] Only quantum mechanics completely describes the structure of a molecule, characterizing its geometrical and electron structure. The topological indices, which descend from a graph theory, are the simplest means of the structural description of a molecule. The topological indices encode the structural information of a molecule. The topological index characterizes a molecule by a simple number.[39,40] In this connection, the selected topological indices and electrotopological states of each atom in a molecule graph were used to show the dependence among the numerical values of the topological indices and electrotopological states, and the chromatographic separation of the investigated terpenes. The numerical values of topological indices based on adjacency matrix and distance matrix are presented in Table 4.

These indices can be useful for estimation of relative changes of physical quantities and retention parameters (R_F and R_M) of investigated terpenes presented in Table 1. These relationships were worked out for couples: α- and γ-terpinene, as well as α- and β-pinene. Observed qualitative relationships between

Table 3. R_F, ΔR_F, and R_M Values, Separation Factors (α), and Separation Parameter ($\mathbf{R}_F^{\alpha}$) of the Terpene Isomers Investigated

		% of Silver Nitrate											
		0%		5%		10%		15%		20%		25%	
Code	Terpene	R_F^a	R_M^a	R_F^a	R_M^a	R_F^a	R_M^a	R_F^a	R_M^a	R_F^a	R_M^a	R_F^a	R_M^a
1	γ-Terpinene	0.721	−0.412	0.726	−0.423	0.678	−0.323	0.621	−0.214	0.566	−0.115	0.528	−0.049
2	α-Terpinene	0.713	−0.395	0.615	−0.203	0.586	−0.151	0.552	−0.091	0.508	−0.014	0.446	0.094
	$\boldsymbol{\alpha_{1,2}(36)}$[b]	1.040		**1.660**		**1.486**		1.327		1.262		**1.390**	
	$\mathbf{R^{\alpha}_{F(1,2)}(37)}$[c]	1.011		**1.180**		**1.157**		1.125		1.114		**1.184**	
	$\mathbf{\Delta R^{\alpha}_{F(1,2)}}$[d]	0.008		**0.145**		**0.092**		0.069		0.058		**0.082**	
3	α-Pinene	0.722	−0.414	0.726	−0.423	0.715	−0.399	0.685	−0.337	0.652	−0.273	0.614	−0.202
4	β-Pinene	0.709	−0.387	0.623	−0.218	0.575	−0.131	0.532	−0.056	0.481	0.033	0.432	0.119
	$\boldsymbol{\alpha_{3,4}(36)}$[b]	1.064		**1.603**		**1.854**		**1.910**		**2.023**		**2.094**	
	$\mathbf{R^{\alpha}_{F(3,4)}(37)}$[c]	1.018		**1.165**		**1.243**		**1.288**		**1.355**		**1.421**	
	$\mathbf{\Delta R_{F(3,4)}}$[d]	0.013		**0.103**		**0.140**		**0.153**		**0.171**		**0.182**	

[a]Average from 10 measurements.
[b]$\alpha_{1,2} = (1/R_{F1} - 1)/(1/R_{F2} - 1)$ or $\log \alpha_{1,2} = R_{M2} - R_{M1}$; $\alpha_{3,4} = (1/R_{F3} - 1)/(1/R_{F4} - 1)$ or $\log \alpha_{3,4} = R_{M4} - R_{M3}$.
[c]$R^{\alpha}_{F(1,2)} = R_{F1}/R_{F2}$; $R^{\alpha}_{F(3,4)} = R_{F3}/R_{F4}$.
[d]$\Delta R_{F(1,2)} = R_{F1} - R_{F2}$; $\Delta R_{F(3,4)} = R_{F3} - R_{F4}$.

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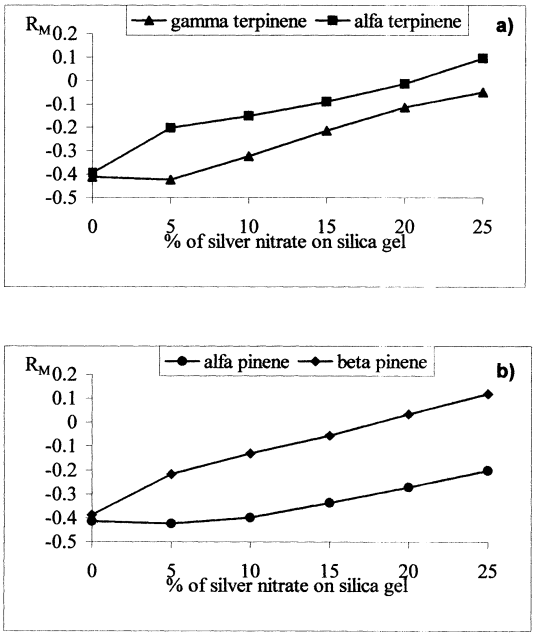


Figure 1. Relationships between the experimental R_M values and the impregnation percentages of silver nitrate on silica gel for γ- and α-terpinene (a), and α- and β-pinene (b).

bp, Fp, d values for α-terpinene, α-pinene	<	**bp, Fp, d** values for γ-terpinene, β-pinene
W, and A values for α-terpinene, α-pinene	<	**W, and A** values for γ-terpinene, β-pinene
I_B, ^oB, ^1B, ^2B, ^2B_q, and C values for α-terpinene, α-pinene	>	**I_B, ^oB, ^1B, ^2B, ^2B_q, and C** values γ-terpinene, β-pinene

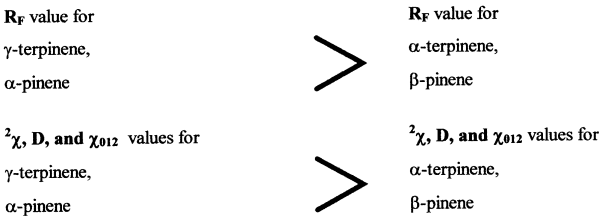
Scheme 1. The qualitative relationships between boiling point (bp), flash point (Fp), density (d), and topological indices for the terpenes investigated.

Table 4. Topological Indices for Terpenes Investigated

	Topological Indices														
	Gutman	Randić			Wiener	Balaban	Pyka								
Terpene	M	$^0\chi$	$^1\chi$	$^2\chi$	W	I_B	A	^0B	^1B	^2B	^2B_q	C	D	χ_{012}
γ-Terpinene	70	7.1463	4.6217	4.6643	108.0	1.8513	69.86	2.1867	0.6171	0.2240	0.3869	10.199	22.444	5.3607
α-Terpinene	70	7.1463	4.6386	4.6065	104.0	1.9416	67.20	2.2278	0.6472	0.2401	0.4147	10.262	21.888	5.3450
α-Pinene	70	7.1463	4.5763	5.1500	96.0	2.0508	61.61	2.3070	0.6836	0.2851	0.4605	11.881	22.235	5.5225
β-Pinene	68	6.9831	4.6515	4.9576	97.5	1.9800	62.31	2.2830	0.6600	0.2601	0.4335	11.318	21.986	5.4405

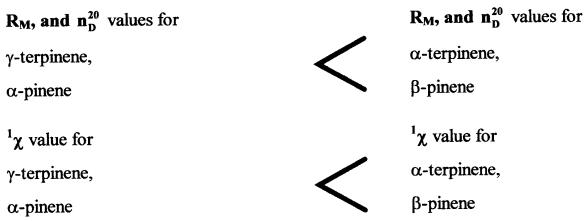
boiling point (bp), flash point (Fp), density (d), and topological indices are presented on Scheme 1

The γ-terpinene has higher R_F values from α-terpinene in all chromatographic separations obtained. Likewise, α-pinene has higher R_F values from β-pinene. The qualitative correlations between R_F values and topological index values of investigated terpenes are listed in Scheme 2.



Scheme 2. The qualitative correlations between R_F values and topological indices values of the terpenes investigated.

The observed qualitative relationships between R_M values, refractive index ($\mathbf{n_D^{20}}$) and topological indices are shown in Scheme 3.



Scheme 3. The observed qualitative relationships between R_M values, refractive index ($\mathbf{n_D^{20}}$), and topological indices for the terpenes investigated.

Impregnation with silver nitrate is especially important in this investigation. The Ag^+ ions are able to form complexes with π systems. In this way, selectivity is achieved with respect to the number, position, and geometry of double bonds.[41] In our earlier work, we showed that the S_i index well describes the separation of selected quinones, which were investigated by means of adsorption thin-layer chromatography on non-impregnated silica gel.[42] The values of the S_i index for individual atoms of molecular graphs for investigated terpenes are presented in Figure 2.

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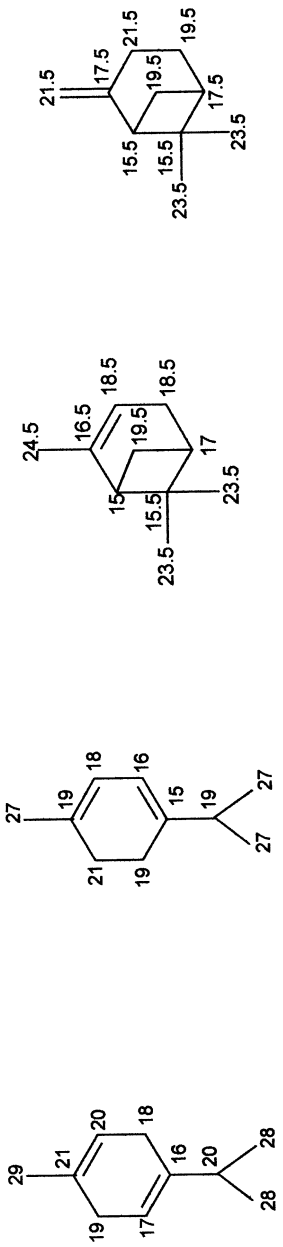

Figure 2. The S_i index values calculated of atoms for terpenes investigated.

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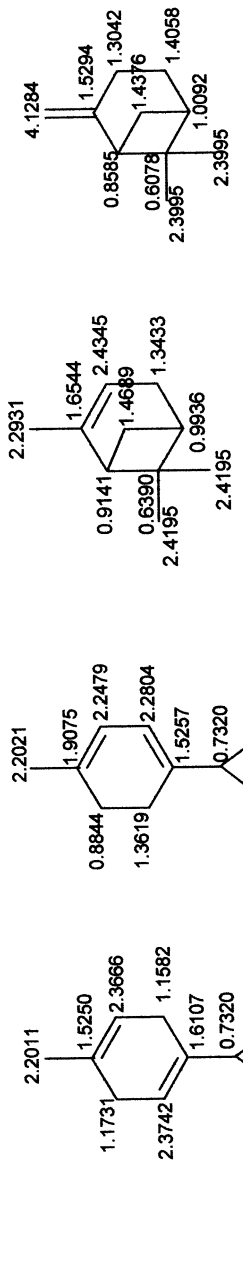

Figure 3. The E-state values calculated of atoms for terpenes investigated, and sum of electrotopological states ($\sum E_{C=C}$) of all carbon atoms forming double bonds.

The S_i index is equal to the sum of elements in the ith row in the distance matrix. This index measures the connection of atom *i* to the rest of the molecule. Low values of the S_i index indicate strongly connected positions, whereas high values of S_i are characteristic of weakly connected positions. The usefulness of this index is that it indicates the effect of the substituents on the physical, chemical, and biological properties of the molecule.[42] The values of S_i indices for individual vertexes were analysed, particularly taking into consideration graph vertexes forming double bonds. It was stated that with the aid of the S_i index it can't explain the separation terpenes investigated in argentation thin-layer chromatography. As we applied argentation thin-layer chromatography for separation of α- and γ-terpinene, as well as α- and β-pinene for that reason, it seemed necessary to count the electrotopological states of individual vertexes in graphs. The electrotopological states of individual graph vertexes counted of the terpenes investigated, are presented on Figure 3. The E-state index is a structural descriptor for an atom within a covalently bonding molecule. The index is formulated to encode information about the electronegativity, pi and lone-pair electron content, topological status, and the environment of an atom within a molecule. In argentation TLC, the interactions between Ag^+ ions and double bonds of substances separated, decide the separation. For that the reason, the electrotopological states of carbon atoms forming double bonds were analysed. It was stated that the sum of electrotopological states of all carbon atoms forming double bonds is lower for γ-terpinene than for α-terpinene (Figure 3).

This sum is also lower for α-pinene than for β-pinene (Figure 3). For that reason, γ-terpinene should form weaker complexes with Ag^+ ions (higher R_F values) in relation to α-terpinene (lower R_F values). The α-pinene also should form weaker complexes with Ag^+ ions (higher R_F values) in relation to β-pinene (lower R_F values).

CONCLUSION

It was shown that argentation thin-layer chromatography is an efficient technique for separation of isomeric α- and γ-terpinene, as well as α- and β-pinene. Optimal conditions for their separation were determined. The electrotopological states of carbon atoms forming double bonds explain the separation of terpenes mentioned above.

The above observations allow us to formulate definite rules concerning relationships between chromatographic separation sequence and topological indices of the investigated terpenes. These rules can be applied with qualitative importance, for an estimation sequence during isomer preparative separation, which can be the subject of further physical, chemical, physicochemical, and pharmaceutical investigations.

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