

## GAS CHROMATOGRAPHIC BEHAVIOR OF THE DIAGNOSTIC COMPONENTS OF SOME ESSENTIAL OILS

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The natural essential oils are highly complex matrices. Their isolated constituents are extensively utilized for their flavor fragrance, anti-microbial, pharmacological, and medicinal properties.

According to the bibliography, gas chromatography (GC) or gas chromatography-mass spectrometry (GC-MS) is the most common method for the qualitative and quantitative analysis of the volatile organic compounds in different essential oils from various parts of the world, e.g., [1–7].

Our literature survey revealed that comparatively minimal study of the chromatographic behavior of essential oils components has been published [8, 9]. Jalavi-Heravi et al. [8] investigated the retention behavior of 53 noncyclic and monocyclic terpenes on the polar stationary phase Carbowax 20M. A detailed discussion of the retention behavior of six pine terpenes on six different liquid phases with a wide range of polarity was reported by Diaz et al. [9].

Thus, on the basis of the literature survey and taking into account that most of the essential oils are primarily composed of terpenes and their oxygenated derivatives, we decided to study the GC behavior of the diagnostic components of some Bulgarian essential oils: linalool and linalyl acetate (lavender),  $\alpha$ -pinene and sabinene (juniper), thymol and carvacrol (thyme), limonene and citral (lemon), borneol and 1,8-cineole (rosemary), menthol (spearmint), and germacrone (geranium).

This paper is limited to the determination of the retention indices of some monoterpenes, terpenoids, and nonterpenoid compounds on three liquid phases of increasing polarity and different molecular compact packing in order to interpret their chromatographic behavior. The stationary phases were selected to include different functional groups and potential interactions.

The gas chromatographic analyses were carried out on a Perkin-Elmer Model Sigma 2000 gas chromatograph (Norwalk, CT, USA), equipped with a flame-ionization detector and the Chromatographics 2 Data System. The chromatograph was fitted with Permaphase DMS, Permaphase CPMS-1701, and Carbowax 20M fused-silica capillary columns.

For the investigated compounds more than five injections were made at two temperatures, and the mean retention times were used for further calculations. The gas holdup time was determined according to the method of Peterson and Hirsch [10]. Retention indices were calculated from the adjusted retention times according to the generally known expression used today [11]. Homologous series of  $n$  C<sub>7–n</sub> C<sub>20</sub> alkanes were used.

Table 1 lists the retention indices of the compounds studied on the three capillary columns (McReynolds polarity: DMS = 229; CPMS-1701 = 789; Carbowax-20M = 2262), measured at two temperatures. The table also gives the retention index increments (dI/dT) per 10°C.

On the nonpolar DMS column, the elution of the monoterpene hydrocarbons follows the order of their boiling points. The monocyclic monoterpene (limonene) is more strongly retained than the bicyclic terpenes ( $\alpha$ -pinene and sabinene). This may be attributed to the effect of the isopropyl group on the double bonded ring, so the latter is more polarized. It is observed that the bicyclic monoterpene sabinene, having a double bond outside the ring, shows a higher retention than the bicyclic monoterpene  $\alpha$ -pinene. These facts are in good agreement with those of other authors [9, 12].

Among terpenoids, the elution of the acyclic ones (citral, linalool, and linalyl acetate) follows the order of their molecular weight. The monocyclic terpenoid menthol is more strongly retained than the bicyclic 1,8-cineole and borneol, and the elution follows the order of their boiling point.

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TABLE 1. Retention Indices of the Compounds Studied on DMS, CPMS-1701, and Carbowax 20M Columns at Two Temperatures, and the Corresponding Temperature Increments

Compound	I <sub>DMS</sub> 160°C	I <sub>DMS</sub> 170°C	dI/10°C*	I <sub>CPMS</sub> 160°C	I <sub>CPMS</sub> 170°C	dI/10°C*	I <sub>C-20M</sub> 140°C	I <sub>C-20M</sub> 150°C	dI/10°C**
$\alpha$ -Pinene	963.3	965.6	2.3	1102.8	1108.8	6.0	1300.1	1305.7	5.6
Sabinene	989.6	992.0	2.4	1298.8	1305.3	6.5	1629.4	1634.8	5.4
Citral	1007.7	1010.9	3.2	1374.0	1378.8	4.8	1685.7	1692.4	6.7
Limonene	1045.5	1048.5	3.0	1412.0	1417.8	5.8	1766.7	1773.0	6.3
1,8-Cineole	1051.8	1056.0	4.2	1115.4	1122.8	7.4	1257.1	1267.0	9.9
Linalool	1093.3	1095.0	1.7	1202.1	1204.2	2.1	1552.0	1559.0	7.0
Carvacrol	1097.8	1100.8	3.0	1303.4	1207.9	4.5	1550.7	1556.4	5.7
Borneol	1160.9	1164.5	3.6	1314.4	1322.1	7.7	1573.2	1579.0	5.8
Linalyl acetate	1244.1	1246.2	2.1	1337.5	1339.3	2.2	1629.4	1634.8	5.1
Thymol	1273.8	1276.9	3.1	1329.7	1334.6	4.9	1720.7	1725.7	5.0
Menthol	1286.2	1290.0	3.8	1419.1	14.26.2	7.1	1863.8	1868.7	4.9
Germacrone	1460.2	1466.4	6.2	1576.8	1586.0	9.2	1982.0	1994.1	12.1

\*Calculated as  $I^{170^\circ\text{C}} - I^{160^\circ\text{C}}$ ; \*\*calculated as  $I^{150^\circ\text{C}} - I^{140^\circ\text{C}}$ .

The compounds selected are more strongly retained on the moderately polar phase CPMS, and the elution order is not the same as on the nonpolar DMS. Similarly, to the DMS column, the retention index of limonene (monocyclic monoterpene) is greater than those of  $\alpha$ -pinene and sabinene (bicyclic monoterpenes). There is an increase in the retention of limonene and sabinene (their retention is slightly less than that of menthol and borneol). However, the contributions due to the shape and the size of these molecules, the presence of cyanopropyl and phenyl functional groups, and the nonlinear chain in the molecule of the stationary phase (noncompact packing) may be the most significant. The elution of the acyclic terpenoids (linalool, linalyl acetate, and citral), 1,8-cineole and borneol (bicyclic terpenoids), and menthol (monocyclic terpenoid) follows the order of their boiling point.

On the polar Carbowax 20 M column the order in which the compounds appear is greatly influenced by their structure, the presence of strong electron-acceptor functional groups, the high amount of electron-donor methoxy groups, and the molecular compact packing of the stationary phase. The elution order of the compounds studied on the polar and moderately polar columns was with one exception the same: 1,8-cineole was eluted from Carbowax 20 M before  $\alpha$ -pinene, but it is not the same as on the nonpolar DMS column (except for menthol and germacrone). Thus, the solute-solvent interaction depends on the solvent properties and structure. The retention of 1,8-cineole may be due to the slightly polar ether bond of this compound and the compact packing of Carbowax 20 M molecule, which decreases this retention.

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