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CHEMICAL COMPOSITION OF VOATILE OIL FROM STACHYS SPECTABILIS USING CARBON NANOTUBE PROFILE

M.H.MESHKATALSADAT[a*], SABAH SALHVARZI [b], R. AMINIRADPOUR[a]
[a]*Department of basic engineering, Qom University of technology Qom, Iran*
[b]*Departement of Chemistry, Azad University of khoramabad, khoramabad.Iran*

Multi-wall carbon nanotubes (MWCNTs) were used for he first time to extract the volatile oil of the *Stachys spectabilis* stem bark through non-covalent interactions between the surface of MWCNTs and oil segments. Analyzing the absorbed volatile oil using GC and GC-MS showed that it is containing twenty-nine different compounds major compound such as Benzaldehyde (30.69%), Caryophyllene oxide(10.53%), Trans-Caryophyllene (9.8%) and Chrysanthenyl acetate (6.22%) total compound identified is 97.17%. A comparison of the chemical composition of the oil was made with that of others methods on earial parts of *Stachys spectabilis* using nano tube and hydrodistillaion methods. MWCNTs were washed by water and organic solvents and they were used repeatedly. Results showed no sign of the decreasing the extraction capacity of MWCNTs after multiple cycles.

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1. Introduction

Carbon nanotubes (CNTs) have attracted much attention because of their unique atomic structure, high surface area-to-volume ratio and excellent electronic, mechanical and thermal properties [1]. They have a wide range of potential applications including nanoelectronic, sensors, fillers in composites materials and others [2-4]

Due to the high surface area-to-volume ratio, high hydrophobicity and electronic structure of CNTs, they can be used to absorbed and delivery variety of molecules and macromolecules through “noncovalent“ interactions. This approach is based on poor vander Waals or π-π interactions between CNTs and guest molecules such as polymers and small organic molecules and without disrupting the primary structure, thus maintaining electronic and mechanical properties of nanotubes [7]. insome causes the modification of surface of CNTs is essential for improving their interactions with polymers and the interfacial adhesion to the matrix and finally a good dispersion in the polymer matrix. To have a good interaction with the surface of a CNT, an essential structural factor in a polymer is the presence of hydrophobic segments or π-bonds which can interact with the hydrophobic surface and π-bonds of CNTs. An advantage of this procedure is the use of macromolecules containing two or more types of functional groups in which one type interacts with sidewall of CNT and others can be used to react with other molecules [8] With increasing production and application of carbon nanotubes (CNTs), it becomes necessary to understand the interaction between CNTs and aromatic compounds, an important group of organic contaminants and structural components of large organic molecules in biological systems. However, so far few experimental studies have been conducted to systematically investigate the sorption mechanism of polar aromatics to CNTs. Therefore, cyclohexanol, phenol, catechol, pyrogallol, 2-phenylphenol, 1-naphthol, and naphthalene were selected to investigate the role of aromatic structure and -OH substitution in the polar aromatics-CNTs system. Sorption affinity of these compounds by CNTs increased with increasing number of aromatic rings, with an order of

[*]Corresponding author: mhmeshkatalsadat@yahoo.com, meshkatalsadat.m@qut.ac.i

cyclohexanol < phenol <2-phenylphenol <1-naphthol, and was greatly enhanced by -OH substitution, with an order of phenol (1 -OH) < catechol (2 -OH) < pyrogallol (3-OH). Four possible solute-sorbent interactions, i.e., hydrophobic effect, electrostatic interaction, hydrogen bonding, and π-π bonds, were discussed to address the underlying mechanism of the enhanced sorption affinity by -OH substitution. It was evident that electron-donating substitution on the aromatic rings strengthened the π-π interaction between the aromatics and CNTs and thus the adsorption affinity. These results will advance the understanding of the sorption behavior of CNTs in the environmental systems adsorption of Phenolic compounds by Carbon Nanotubes .

CNTs have been used to study the surface–protein and protein–protein binding which may lead to develop the highly specific electronic bimolecular detectors [10].

Initiators containing aromatic segments have been supported by CNTs. The resulting CNT/initiator hybrid has been used for the polymerization of monomers leading to a nanocomposite containing a CNT core and polymeric shell [11].

Based on above explanations it can be understand that CNTs are able to form complexes with hydrophobic molecules or those containing conjugated π-bonds through non-covalent interactions, hence the volatile oil of many plants which are containing molecules and macromolecules with these characteristics can be extracted using CNTs as supporter probably.

The subcosmopoltion genus *Stachys* L.comprises more than 270 species [12] and is justifiably considered as one of the largest genera of the Labiatae. In the old World area there are two main centers of diversity for the genus, as assessed by the number and distribution of the species. One is confined to South and East Anatolia, Caucasian, North West Iran and North Iraq, the other to the Balkan Peninsula [13]. In Iran, 34 species of the this genus are present, among which, 13 are endemic [14]. The plant is known as Chaye-kuhi in Iran and is antiveplant, which has been used as an antixiolytic and sedative in Iranian folk medicine [15]. At present, it is unknown in which way the composition of volatile oils truly reflects taxonomic relationships in *Stachys*, since many of its members remain to be investigated. However, the chemistry of volatile compounds has been proven particularly helpful in assessing taxonomic relationships of several genera in Labiatae [16]. Major compounds present such as Benzaldehyde (30.69%), Caryophyllene oxide(10.53%), Trans-Caryophyllene (9.8%) and Chrysanthenyl acetate (6.22%) and total compound identified is 97.17%. Based on above idea, ability of CNTs for extracting the volatile oil of plants, and significance of the oil of *S. spectabilis* mentioned above, in this work different chemical compounds of the volatile oil of the stem bark of *S. spectabilis* were extracted using MWCNTs. The yields of extractions were calculated using usual mass spectroscopy methods and they were compared with those from other reported methods. Numbers of the cycles which CNTs were recyclable to use in extractions were also investigated.

2. Materials and methods

2.1 Plant material

About1 kg of fresh aerial part of *Stachys spectabilis* at maturity were collected from agriculture college garden of the university. The dried aerial parts were stored in a dark place at 4°C.

2.2 Isolation of volatile components

Fresh powdered (10 g) of plant were subjected to nanotube (NWNTs 20-40 nm length 5-15 micro meter S.S.area 40-300 m^2/g) in a Petri dish-type apparatus heated for 4 h. at 40 C then washed by n-hexane. The yield (v/w) of volatile oil was 0.2%. The volatile oil was dried over anhydrous sodium sulfate and stored at 4 C for analysis.

2.3 GC-MS analysis

GC/MS analysis of the oil was carried out on an Agilent HP-6890 gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with an Agilent HP-5973 mass selective detector in the electron impact mode (ionization energy: 70eV), operating under the same conditions as described above, using a HP-5MS 5% phenylmethylsiloxane capillary column (30 m × 0.25 mm, 0.25 μm film thickness; Restek, Bellafonte, PA). Retention indices were calculated for all components using a homologous series of n-alkanes injected in conditions equal to the sample one. Identification of components of essential oil was based on retention indices (RI) relative to n-alkanes and computer matching with the Wiley7n.L libraries, as well as comparisons of the fragmentation pattern of the mass spectra with data published in the literature [17]. Some commercially available components of the essential oil were also co-injected for further confirmation of their identification.

3. Results and discussion

For the first time, the volatile oil of barks of *S. spectabilis* was extracted by nanotube and was analyzed by GC and GC-MS. Retention indices for all compounds were determined according to the Kovats method using n-alkanes as standards[17]. Wherever possible, by co injection with an authentic sample and by matching their fragmentation patterns in mass spectra with those stored in NIST library and published mass spectra [17] and Wiley7n.L libraries of GC/MS. The chemical composition of the *S. spectabilis* is presented in Table I. A total of twenty-four compounds were identified, which constitute 98% of the volatile oil. The volatile oil of buds of *S. spectabilis* contains Benzaldehyde (30.69%), Caryophyllene oxide(10.53%), Trans-Caryophyllene (9.8%) and Chrysanthenyl acetate (6.22%) total compound identified is 97.17%. More over some similarities as it contains many other compounds that are present in two methods extract oils as well.

Table I. composition of essential oil S. spectabilis by nano tube

row	Compound	KI	RI	Percentage
1	Methyl Benzene	0790	9.97	4.41
2	Alpha-Pinene	0939	9.56	1.69
3	Benzaldehyde	0960	26.49	30.69
4	Beta-Myrcene	0991	12.55	1.90
5	Decane	1000	14.24	0.77
6	Para-Cymene	1025	22.75	1.70
7	Cis-Ocimene	1037	14.74	0.42
8	Gamma-Terpinene	1061	15.58	0.91
9	Alpha-Terpinolene	1089	16.94	0.76
10	Naphthalene,decahydro	1100	45.35	1.17
11	Dodecane	1200	13.18	1.02
12	Cuminaldehyde	1242	36.22	3.25
13	Chrysanthenyl acetate	1265	27.79	6.22
14	Cinnamaldehyde	1270	45.11	2.90
15	Tridecane	1300	16.43	0.73
16	Z-Citral	1318	46.74	0.93
17	Tetradecane	1400	20.08	1.61
18	Trans-Caryophyllene	1419	29.35	9.80
19	Alpha-Humulene	1455	32.12	1.35
20	Trans-Beta-Farnesene	1457	30.84	0.95
21	Gamma-Gurjunene	1477	46.31	0.86
22	Pentadecane	1500	14.08	4.82
23	Caryophyllene oxide	1583	43.13	10.53
24	Hexadecane	1600	20.97	2.14
25	Cis 3-Hexenyl Phenyl Acetate	1634	50.58	1.06
26	Heptadecane	1700	21.60	1.44
27	Heptadecane	1700	28.30	1.47
28	Octadecane	1800	35.22	0.48
29	Heneicosane	2100	18.36	1.19
	Total			97.17

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