Investigation of the thermodynamic and thermal properties of clary sage (*Salvia sclarea* L.) essential oil and its main components

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Abstract: The some physochemical and chemical properties of the clary sage (*Salvia sclarea* L.) essential oil were determined. The main constituents in the clary sage essential oil (above 2%) were: linalyl acetate (34.62%), β-linalool (17.67%), α-muurolene (8.27%), β-caryophyllene (5.60%), α-ylangene (5.18%), α-terpineol (4.84%), n-docosane (3.00%), and neryl acetate (2.34%).The thermodynamic and thermal properties of essential oil and its main components were investigated.

1 Introduction

Clary sage essential oil is obtained by steam distillation of flowering tops and foliage of cultivated *Salvia sclarea* L. (Lamiaceae). The main compounds in the oil were linalyl acetate (56-78%) and linalool (6.5-24%) [1-8]. In the plant were identified polyphenolic compounds, sesqui- and diterpenes [9-12].

The thermal properties of borage (*Borago officinalis* L.) seeds were determined at temperatures ranging from 6 to 20°C and moisture contents from 1.2 to 30.3% [13].

Some authors were reported of viscosities and densities, at T = 298.15 K of the phases formed after diterpenation of bergamot, lemon and mint essential oils, by (liquid + liquid) extraction [14].

In the literature do not found data for determination of thermodynamic parameters of clary sage essential oil as well as its main components which is also the aim of the present study.

2 Material and methods

2.1 Materials. Clary sage oil was provided by Kateco Ltd, Bulgaria. The oil was kept in the refrigerator at 4 °C before analysis.

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2.1.1 Determination of refractive index. The refractive index (n_D^{20}) was determined according to ISO 280:1998 [15].

2.1.2 Determination of relative density. The refractive density (d_{20}^{20}) was determined according to ISO 279:1998 [16].

2.1.3 Infrared spectroscopy of clary sage oil. The infrared spectrum was recorded using a Nicolet iS 50 Thermo Scientific FT-IR spectrometer in the frequency region of 4000–400 cm^{-1}, with the samples embedded in KBr matrixes.

2.1.4 Chemical composition of the essential oil. GC analysis was performed using gas chromatograph Agilent 7890A [17]

2.1.5 Thermodynamic and thermal properties of the essential oil and its main compounds. Specific heat capacity is obtained by eq. (1) [18]:

$$C_p = \left(\frac{\mathrm{dH}}{\mathrm{dT}}\right)_P \tag{1}$$

where: C_p - specific heat capacity, $J.mol^{-1}K^{-1}$; H - enthalpy, $J.mol^{-1}$; T - temperature, ° K. Dependence between specific heat capacity, thermal conductivity and coefficient of thermal conductivity were determined according to [13, 18] by eq. (2).

$$a = \frac{\lambda}{\rho C_p} \tag{2}$$

where: a - coefficient of thermal conductivity, $m^2.s^{-1}$; λ - thermal conductivity, $W.m^{-1}K^{-1}$; C_p - specific heat capacity, $J.mol^{-1}K^{-1}$; ρ -density, $kg.m^{-3}$.

2.1.6 Statistical analysis. The experimental data were obtained after three replicates. The results are presented as a mean value of the individual measurements with the corresponding standard deviation (SD).

3 Results and Discussions

The clary sage essential oil presented light yellow with a specific odor and had followed properties: density 0.8623 ± 0.0 and a refractive index (n_D^{20}) 1.4635 ± 0.0. The obtained values didn`t exhibited differences with similar data from literature [1, 2].

The IR spectrum of clary sage essential oil is presented in Table 1. The analysis of FT-IR of studied oil represents mainly strong vibrations of the components in this oil. Intense line at 3423 cm^{-1} appears stronger connected with conformation in the β-linalool molecule. In this case the mixture OH-groups lose steric factor.

Another connection with the spectrum of pure β-linalool is the band at 2973 cm^{-1} and associated with CH_2-asymmetric vibrations. The probable cause of this behavior can be explained with antagonism with different bands from different components in the investigated oil. The other components does not show strong absorption bands because the limitations of FT-IR method which detects chemical compounds with concentration above 5%.

The experimental FT-IR spectrum of clary sage essential oil is the presented in Fig. 1.

Table 1. IR spectrum of clary sage essential oil

Characteristic bands (cm^{-1})		Group type
Experimental data	Reference data	
3423	3550 – 3400 3590 – 3420	γOH intramolecular H – bond
2973	2970 – 2950	linear γ_{as} CH_3
2928	2940 – 2915	γ_{as} $-CH_2-$
1735	1740 – 1720	R – CHO $\gamma_{C=O}$; characteristic band of carbonyl group
1640	1648 – 1640	non-conjugated C=C, low intensity. HRC=CH_2 end vinyl
1450	1465 – 1440	aromatic ring
1412	1435 – 1405	- CH_2–CO–; vibrations of ketones, δ CH_2
1375	1385 – 1370	a structural fragment of the type $C(CH_3)_2$
1250	1260 – 1240	a characteristic band for ether bond, of the type γ^{as} C–O–C
1172	1175 – 1165	a characteristic band for ether bond, of the type CH_3–CH–CH_3
1088	1150 – 1050	γ^{as} C–O–C, ether bond
1047	1070 – 1020	=C–O–C, γ^{s} C–O–C, aromatic and vinyl
921	925 – 9 05	C–H bond of the type HRC=CH_2
879	900 – 865	trisubstituted aromatic ring γ Ar – H in positions 1,2,4

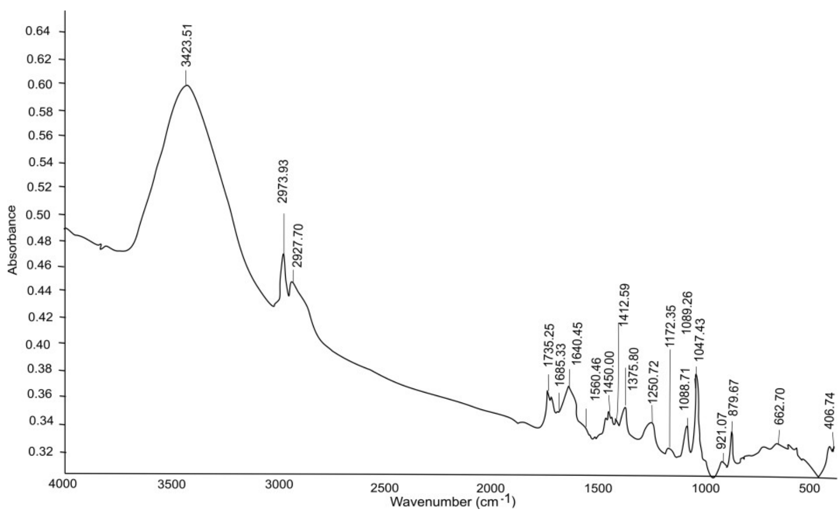

Fig. 1. IR spectrum of clary sage essential oil

Chemical composition of the clary sage essential oil is listed in Table 2.

From Table 2 as can see the oil contained 33 components representing 98.39% of the total content were identified. Fourteen of them were in concentrations over 1% and the rest 19 constituents were in concentrations under 1%. The main components in the essential oil (above 2%) from fruits were: linalyl acetate (34.62%), β-linalool (17.67%), α-muurolene (8.27%), β-caryophyllene (5.60%), α-ylangene (5.18%), α-terpineol (4.84%), n-docosane (3.00%), and neryl acetate (2.34%).

Table 2. Chemical composition of clary sage essential oil

№	Compounds	RI	Content, %
1.	(2E,4E)-Hexadienol	912	0.15 ± 0.0
2.	*β*-Myrcene	988	1.82 ± 0.01
3.	Limonene	1025	1.05 ± 0.01
4.	(Z)-*β*-Ocimene	1039	0.22 ± 0.0
5.	(E)-*β*-Ocimene	1049	1.59 ± 0.01
6.	*α*-Terpinolene	1084	0.56 ± 0.0
7.	*β*-Linalool	1090	17.67 ± 0.17
8.	*α*-Terpineol	1188	4.84 ± 0.04
9.	Linalyl formate	1215	0.18 ± 0.0
10.	Nerol	1230	0.15 ± 0.0
11.	Geraniol	1249	0.83 ± 0.0
12.	Linalyl acetate	1254	34.62 ± 0.33
13.	Geranyl formate	1297	0.10 ± 0.0
14.	Citronellyl acetate	1350	0.15 ± 0.0
15.	Neryl acetate	1361	2.34 ± 0.02
16.	*β*-Ylangene	1373	5.18 ± 0.05
17.	*β*-Cubebene	1386	0.33 ± 0.0
18.	*β*-Bourbonene	1389	0.38 ± 0.0
19.	*β*-Caryophyllene	1420	5.60 ± 0.05
20.	Aromadendrene	1439	0.27 ± 0.0
21.	*α*-Caryophyllene	1455	0.30 ± 0.0
22.	*γ*-Muurolene	1478	0.60 ± 0.0
23.	*α*-Muurolene	1496	8.27 ± 0.08
24.	Viridiflorene	1499	0.74 ± 0.0
25.	*γ*-Cadinene	1513	1.61 ± 0.01
26.	*δ*-Cadinene	1522	0.97 ± 0.0
27.	*β*-Cadinene	1537	1.56 ± 0.01
28.	Spathulenol	1577	0.72 ± 0.0
29.	(2-Z,6-E)-Farnesyl acetate	1821	1.12 ± 0.01
30.	*n*-Nonadecane	1900	0.53 ± 0.0
31.	*n*-Eicosane	2000	0.37 ± 0.0
32.	*n*-Heneicosane	2100	0.57± 0.0
33.	*n*-Docosane	2200	3.00 ± 0.03

The difference in the quantities of chemical composition of our essential oil and the reported data [1-8] may be due to environmental conditions under which the plant has grown as well as the variation in conditions of analysis.

Distribution of major groups of aroma substances in the essential oil is shown in Figure 2. The dominant groups in the oil were oxygenated monoterpenes (61.88%); then followed by sesquiterpene hydrocarbons (26.23%), monoterpene hydrocarbons (5.33%), and hydrocarbons (4.54%), oxygenated sesquiterpenes (1.87%), and oxygenated hydrocarbons (0.15%).

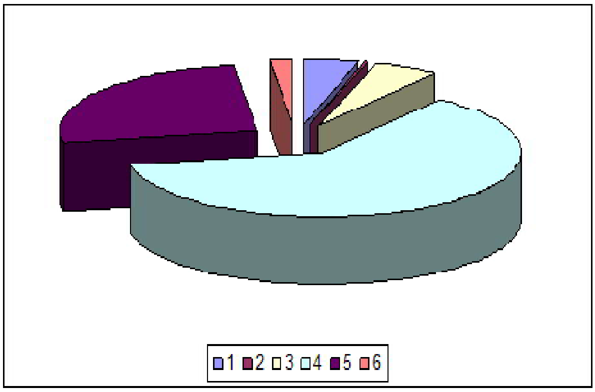

Fig.2. Group of components in clary sage essential oils, %.

1 - hydrocarbons; 2 - oxygenated hydrocarbons; 3 - monoterpene hydrocarbons; 4 - oxygen monoterpenes; 5 - sesquiterpene hydrocarbons; 6 - oxygenated sesquiterpenes.

In Table 3 are presented some chemical properties of the main nine aromatic substances, which formed 82.85% from total composition. It was determined scent and properties of the essential oil, too. The investigated substances were β-linalool, α-terpineol, linalyl acetate, and neryl acetate which are the main components from oxygen monoterpenes group, α-muurolene, β-caryophyllene, and β-ylangene – from sesquiterpene hydrocarbons group and n-docosane from hydrocarbons group. There distribution by functional groups and structure is: hydrocarbons (α-muurolene, β-caryophyllene, β-ylangene, and n-docosane), two alcohols (linalool and α-terpineol), and two esters (linalyl acetate and neryl acetate).

The calculations of thermo physical characteristics of the clary sage essential oil as well as thermal conductivity, specific heat capacity and coefficient of thermal conductivity are presented in Table 4. The values are obtained according to the chemical composition presented in Table 2.

The results compared with literature data of the same parameters, which is obtained experimentally [13] where: λ = 0.11-0.28 $W.m^{-1}$ K^{-1}; Cp = 0.77–1.99 $кJ.mol^{-1}K^{-1}$; a = $2.32.10^{-7}$- $3.18.10^{-7}$ $m^2.s^{-1}$.

Table 3. Thermo physical parameters of the main compounds [19]

Compounds	Ylangene	β-Caryophyllene	α-Muurolene	n-Docosane	β-Linalool	α-Terpineol	Neryl acetate	Linalyl acetate
Empirical Formula	$C_{15}H_{24}$	$C_{15}H_{24}$	$C_{15}H_{24}$	$C_{22}H_{46}$	$C_{10}H_{18}O$	$C_{10}H_{18}O$	$C_{12}H_{20}O_2$	$C_{12}H_{20}O_2$
Molecular Weight	204.35	204.32	204.35	310.60	154.25	154.25	196.29	196.29
ΔfG°, kJ.mol^{-1}	242.55	196.63	179.03	134.36	58.85	-55.88	-40.42	-21.41
ΔfH°gas, kJ.mol^{-1}	-125.10	-112.68	-164.97	-497.41	-177.85	-310.08	-320.95	-311.70
ΔfusH°, kJ.mol^{-1}	20.07	14.82	21.69	52.74	15.94	11.00	27.41	19.82
ΔvapH°, kJ.mol^{-1}	47.69	65.50	50.71	[111.90; 115.60]	65.00	54.62	51.54	49.53
*log*Potc/wat	4.27	4.73	4.58	8.83	2.67	2.50	3.24	3.24
Pc, kPa	2001.91	2027.23	1921.98	10000.00	2581.96	2950.48	2047.46	2054.89
Tboil, K	561.69	576.30	576.33	641.80	[468.70; 471.80]	490.70	407.20	493.20
Tc, K	775.53	802.06	791.72	786.00	697.57	740.92	748.06	740.67
Tfus, K	322.81	323.71	287.93	[313.20; 318.30]	244.90	308.15	259.08	278.78
Vc, m^3.kg^{-1}mol^{-1}	0.71	0.72	0.72	1.27	0.57	0.52	0.69	0.68
Cp, gas, J.mol^{-1}K^{-1}	503.35	501.77	503.29	962.02	347.03	353.52	426.65	428.80
Cp, liquid, J.mol^{-1}K^{-1}	-*	-	-	739.00	372.40	-	-	-
Cp, solid, J.mol^{-1}K^{-1}	-	-	-	563.60	-	-	-	-

$\Delta_c H°_{liquid}$ - standard liquid enthalpy of combustion (kJ.mol^{-1}); $\Delta_f G°$ - standard Gibbs free energy of formation (kJ.mol^{-1}); $\Delta_f H°_{gas}$ - enthalpy of formation at standard conditions (kJ.mol^{-1}); $\Delta_{fus} H°$ - enthalpy of fusion at standard conditions (kJ.mol^{-1}); $\Delta_{vap} H°$ - enthalpy of vaporization at standard conditions (kJ.mol^{-1}); P_c - critical pressure (kPa); T_{boil} - normal boiling point Temperature (K); T_c - critical temperature (K); $C_{p,gas}$ - ideal gas heat capacity (J.mol^{-1}K^{-1}); $C_{p,liquid}$ - liquid phase heat capacity (J.mol^{-1}K^{-1}); * no data.

Table 4. Thermal parameters of the clary sage essential oil

Thermal parameters	R_{cm}, J.mol^{-1}K^{-1}	E_a, kJ.mol^{-1}	C_p, J.mol^{-1}K^{-1}	λ.10^3, W.m^{-1}K^{-1}	a.10^6, m^2.s^{-1}
Clary sage oil	43.58	-1796.75	6026.32	330.31	1.49
Thermal Parameters	$M_{cm,}$ kg.mol^{-1}	ΔH, kJ.mol^{-1}	ΔS, kJ.mol^{-1}K^{-1}	ΔG, kJ.mol^{-1}	
Clary sage oil	190.77	1796.75	-14.34	6072.31	

R_{cm} - universal gas constant, J.mol^{-1}K^{-1}; E_a - activation energy, kJ.mol^{-1}; C_p - specific heat capacity, J.mol^{-1}K^{-1}; λ - thermal conductivity, W.m^{-1}K^{-1}; a - coefficient of thermal conductivity, m^2.s^{-1}; $M_{cm,}$ - molar mass of the main components, kg.mol^{-1}; ΔH - enthalpy, kJ.mol^{-1}; ΔS - entropy, kJ.mol^{-1}K^{-1}; ΔG - energy of Gibb`s, kJ.mol^{-1}.

The activation energy was calculated about -1796.75 kJ.mol^{-1}. The negative value specified that processes were non-spontaneous occurring as a result of heat and light. The molar mass of clary sage oil was determined experimentally using GC/MS analysis (190.77 kg.mol^{-1}). The thermodynamic parameters of Gibbs energy, enthalpy and entropy of the main components of sage essential oil were calculated. The thermodynamic parameters for salvia oil-ethanol-water solution were found in the literature [20], as the values obtained for the Gibbs energy are from -8968.87 to -10037.77 kJ.mol^{-1}, for the enthalpy (ΔH) -2490.24 kJ.mol^{-1} and for entropy (ΔS) from 21.71 to 24.83 kJ.mol^{-1}K^{-1}. The differences in the values obtained are probably due to the different composition of the studied essential oils. In pure oils the values of the thermodynamic parameters depend mainly on the chemical composition of the obtained essential oil, and when used in solution the values are also influenced by the solvents. Gibbs energy represents a thermodynamic potential and shows the possibility of the process. The positive values of Gibbs energy mean that the process that takes place in the main components of the essential oil is spontaneous and irreversible. Entropy as a thermodynamic parameter gives a connection about the mechanism of the reaction and the activation complexes. In this case the entropy values are negative, which means that the process is irreversible. The enthalpy values are positive too, which also means that the process is irreversible. In this case the enthalpy of the process is equal to the activating energy with the opposite sign. This means that the process will proceed with the adding of energy.

Table 5 presented values of heat capacity and enthalpy of main components of clary sage oil. Composition of the all components are summarised to 100% needs for calculations of the molar heat capacity and enthalpy for each one of main components. Comparison between results given in Table 3 and Table 5 are done for n-docosane and *β*-linalool. Differences which appeared between literature data [14, 19] (Table 3) and experimental values from this work probably connected for different composition of components in the essential oil. It didn`t found data for molar enthalpy of clary sage essential oil at 25^{0}C in literature and for this reason no comparison was made of the results obtained in this work.

Table 5. Specific heat capacity and enthalpy of main components of clary sage essential oil

Compounds	Ylan gene	*β*-Caryo phyllene	*α*-Muuro lene	*n*-Doco sane	*β*-Linalool	*α*-Terpi-eol	Neryl acetate	Linalyl acetate
Content,%	5.18	5.60	8.27	3.00	17.67	4.84	2.34	34.62
C_p, J.mol^{-1}.K^{-1}	229.87	248.50	366.99	87.59	1038.79	284.54	108.10	1599.38
$h_{i,}$ kJ.mol^{-1}	68.54	74.09	109.42	26.11	309.71	84.83	32.23	476.86

C_p - specific heat capacity, J.mol^{-1}K^{-1}; h_i - enthalpy, kJ.mol^{-1}.

4 Conclusions

Some thermodynamic and thermo physical properties of the industrial clary sage essential oil and its major compounds were investigated. The chemical characteristic was done with two experimental methods FT-IR and GC/MS. The FT-IR analysis of studied oil represented mainly strong vibrations of major components in the studied oil.

1. Thermal conductivity λ and coefficient of thermal conductivity were calculated as $330.31.10^{-3}$ $W.m^{-1}K^{-1}$ and $1.49.10^{-6}$ $m^2.s^{-1}$ respectively.
2. The thermodynamic parameters of sage essential oil were calculated on the basis of its main components, too: Gibbs energy (ΔG) - 6072.31 $kJ.mol^{-1}$, enthalpy (ΔH) - 1796.75 $kJ.mol^{-1}$, and entropy (ΔS) -14.34 $kJ.mol^{-1}K^{-1}$.
3. The specific heat capacity of sage oil and its main components are calculated, as well as the molar enthalpy of the main components.

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