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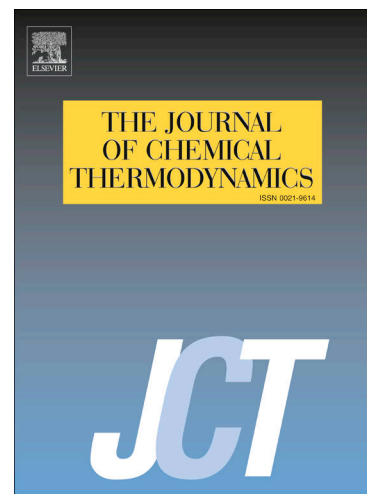
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Heat Capacity of Some Terpenes in the Temperature Range between (293.15 and 353.15) K and at 85.1 kPa

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Abstract

The heat capacity of several terpenes ((-)-carveol, (1R)-(-)-nopyl acetate, γ -terpinene, carvacrol, 3 carene, (1R)-(-)-myrtenol, (S)-(-)-perillyl alcohol, α -pinene oxide and (+)-limonene oxide) were estimated at Medellín (Colombia) atmospheric pressure and in the temperature range from 293.15 K to 353.15 K with a heating rate of 0.5 K/min. All measurements were performed by means of a Setaram E/ μ DSC 7 Evo-1A microcalorimeter. Heat capacities dependence with temperature were fitted to a third order polynomial equation. Furthermore, heat capacities were estimated using group contribution with Dvorkin et al model, the Dadgostar–Shaw universal correlation and a modified correlation of Dadgostar-Shaw and compared with experimental data. The reliability of the results was evaluated using water as a known substance; the experimental uncertainty measured using naphthalene was lower than 1.5%.

Keyword: Micro DSC; heat capacity; terpenes; temperature effect.

1. Introduction

The knowledge of the thermodynamic properties is of great importance to obtain information that is needed for example in the design of equipment. One of these properties is the heat capacity at constant pressure, C_p , that can be obtained using differential scanning

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calorimetry (DSC). Differential scanning microcalorimetry, μ DSC, has been used in food, chemical and pharmaceutical industries because it is not a destructive technique and this instrument offers very high sensitivity and require not much quantity of sample [1]. Terpenes and terpenoids have applications in medicine, perfumery, cosmetics, fragrance and food industry [2]; for example nopyl acetate is used in perfumery [3], carveol in cosmetics or medical uses [4], γ -terpinene have also pharmaceutical and therapeutical uses [5], and carvacrol is employed as an antioxidant [6].

Heat capacity of some terpenes, that are the main components of essential oils, has been reported by other authors; the study of heat capacity of the α -pinene+ β -pinene mixture at atmospheric pressure and temperatures between 313 and 418 K was obtained by DSC [7]. The evaluation of the isobaric heat capacity in the range between 326.15 and 348.15 K of menthol and α -terpineol enantiomers has also been obtained [8]. It was reported values of heat capacities of limonene, turpentine, α -pinene and β -pinene using DSC (313 to 403 K) [9]. In other research, it was reported isobaric heat capacity (290-343 K) for limonene, terpinolene, (1R)-(-)-myrtenal, and α -terpinyl acetate [10]. Other studies that are reported on terpenes include the estimation of the liquid heat capacity of *p*-cymene [11], α -terpineol [12]; in the study of the chemical composition and thermal and thermodynamic properties of the essential oil *Coriandrum sativum* [13] it was reported heat capacities of β -linalool, camphor, nerol, γ -terpinene (gas phase), limonene, camphene, *p*-cymene, geranyl acetate and α -pinene at standard conditions. It was reported a decreased of excess molar heat capacities with increased of temperature for the excess isobaric molar heat capacity for (R)-(+)- α -pinene + (S)-(-)- α -pinene at several temperatures and as function of composition [14]. Vapor pressure plots for clove oil and eucalyptus oil were constructed using DSC [15].

Additionally, since the heat capacity of some compounds could be not reported in the literature, correlations or models that are based on substance properties or group contribution techniques are used to estimate unknown heat capacities or compare their reliability with already reported information. These models depend on the system to be studied, for organic liquids for example, there are some reported models in the literature [16]–[19].

In the present work, the heat capacity of several terpenes (carveol, nopyl acetate, γ -terpinene, carvacrol, 3 carene, (1R)-(-)-myrtenol, perillyl alcohol, α -pinene oxide and

limonene oxide), Figure 1, in liquid phase at 85.1 kPa using a Setaram μ sc μ DSC 7 microcalorimeter at different temperatures (293.15 to 353.15 K) is reported. The experimental results were adjusted to theoretical models that are used for estimating the heat capacity of terpenes, using contribution of groups, or fitting the models.

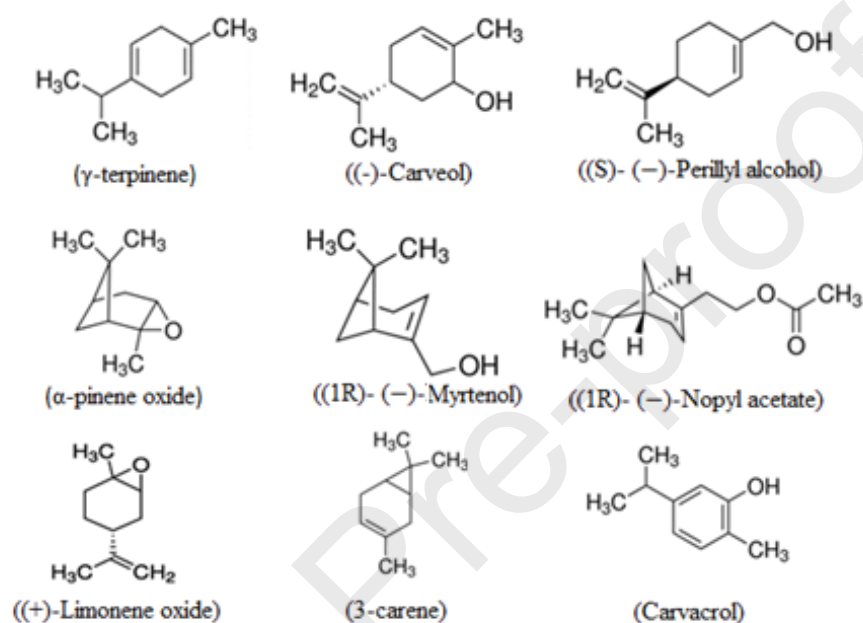


Figure 1. Structural formula of analyzed terpenes

2. Experimental

2.1. Material and methods

Chemicals used for this study were taken from original manufacturer's packaging (**Table 1**); all the chemicals were liquids, except naphthalene that was solid.

Table 1 Source and purity of used chemicals ^a

Name	CAS	Batch number	Optical rotation ^b	Mole fraction	Source
				purity ^c	
3-Carene	13466-78-9	MKBV3310V	13.4° (C = Neat); enantiomeric excess of (+)-3- carene 78.8% ^d	0.961	Sigma- Aldrich
Carvacrol	499-75-2	SHBL1384	-	0.994	Sigma- Aldrich
(-)-Carveol, mixture of <i>cis</i> and <i>trans</i> isomers	99-48-9	MKCL8608	-107.8° (C = 1%, CHCl ₃); enantiomeric excess of (-)- carveol 96.25% ^d .	0.975	Sigma- Aldrich
(+)-Limonene oxide, mixture of <i>cis</i> and <i>trans</i>	203719-54-4	13421AJV	+68.5° (C = Neat); enantiomeric excess 98.8%	0.983	Sigma- Aldrich
(1R)-(-)-Myrtenol	19894-97-4	STBG1227V	-49.3° (C = Neat)	0.978	Sigma- Aldrich
(1R)-(-)-Nopyl acetate	35836-72-7	20922CUV	-31.7° (C = Neat)	0.985	Sigma- Aldrich
(S)-(-)-Perillyl alcohol	18457-55-1	MKAA4409V	-88.1° (C = 1% in methanol)	0.965	Sigma- Aldrich
α-Pinene oxide	1686-14-2	MKCK8699	-337° (C = 0.1% in CHCl ₃); enantiomeric excess of (-)-α-	0.965	Sigma- Aldrich

			pinene oxide		
			61.3% ^e		
γ -Terpinene	99-85-4	STBH9503	-	0.988	Sigma-Aldrich

^a Also distilled water (conductivity = 5 $\mu\text{S cm}^{-1}$) and standard naphthalene 0.9997 mol (LGC corporation, reference S60/58180, batch number LC20569-72) were used.

^b Information provided by the supplier available in the certificate of analysis, that are presented in the supporting information.

^c Provided by the supplier

^d Calculated with the optical rotation of the used compound and the optical rotation of the pure compound.

^e Optical rotation obtained with Digital Polarimeter P-2000 WI – JASCO equipment and enantiomeric excess calculated with the optical rotation of the used compound and the optical rotation of the pure compound.

2.2. Measurement of heat capacity

Heat capacities were measured using a Setaram E/ μ DSC 7 Evo-1A microcalorimeter, with two standard cells of 1 cm^3 placed in parallel, one cell contained the sample and the other was the reference cell that was empty; during measurements continuous nitrogen flow at 0.8 bar was used. A blank was obtained using the two cells empty, a heating rate of 0.5 K min^{-1} was used with a scanning constant heat followed by an isothermal delay of 1800 s, the background noise provided by the supplier was less than 0.3 μW . The amount of sample was 100 $\text{mg} \pm 0.1 \text{ mg}$ that was weighted in a Sartorius BP2105 balance. The μ DSC was calibrated following reported procedure [20] measuring the enthalpy of fusion and melting temperature of pure naphthalene (99.97% mol), **Table S1 in supplementary information** shows the values obtained in the equipment and reported values. To guarantee repeatability and reproducibility of the data, experimental tests were carried out to obtain calibration constants and temperature correction; the accuracy of heat capacity was measured using water (conductivity = 5 $\mu\text{S cm}^{-1}$) as a reference (data deviation less than 0.5% at room temperature respect to the literature value [21]); the results are shown in **Table S2 in supplementary information**. The estimated uncertainty [22], [23] was 0.1 K for temperature and less to 1.5% for heat capacity with a confidence level of 95% using a k factor of 2. To guarantee the

reliability of the results, the experiments were carried out in triplicate. The heat capacity was determined using the software Calisto Processing; with the data obtained, a mathematical adjustment was proposed to find an equation that represents the heat capacity as a function of temperature.

2.3 Modeling of the theoretical values of the heat capacity

Predictive correlations for isobaric liquid specific heat capacity of liquids to absolute temperature and elemental composition were used. The data were compared with the values predicted using the Dadgostar-Shaw universal correlation, equation (2); a modified Dadgostar-Shaw universal correlation, equation (3) [24]; and a contribution group model, equation (4) [25].

- Dadgostar-Shaw universal correlation

$$C_{p,l} = 24.5 (a_{1,1}\alpha + a_{1,2}\alpha^2) + (a_{2,1}\alpha + a_{2,2}\alpha^2)T + (a_{3,1}\alpha + a_{3,2}\alpha^2)T^2 \quad (2)$$

- Modified Dadgostar-Shaw universal correlation

$$C_{p,l} = 24.5 (a_{1,1}\alpha + a_{1,2}\alpha^2) + (a_{2,1}\alpha + a_{2,2}\alpha^2)T + (a_{3,1}\alpha + a_{3,2}\alpha^2)T^2 + b_1 \frac{R}{M} \left[\frac{1}{(T_r)^{b_2}} - 1 \right] \quad (3)$$

Where $C_{p,l}$ is in $\text{J K}^{-1} \text{g}^{-1}$, T is the temperature in K; the variable α is defined as the number of atoms in a molecule divided by its molecular mass and it has units of mol g^{-1} . The values of the coefficient of equation (2) and equation (3) are listed in **Table 2**. The modified equation takes account the differences between isomers, in this case R is in $\text{J K}^{-1} \text{mol}^{-1}$, M is the molecular weight in g mol^{-1} and T_r is the reduced temperature, calculated with critical temperature obtained with Aspen Plus software,

Table 3.

Table 2. Values of the coefficients for equation (2) and equation (3) ^a

Coefficient	Value
a _{1,1}	-0.3416
a _{1,2}	2.2671
a _{2,1}	0.1064
a _{2,2}	-0.3874
a _{3,1}	-9.8231E-05
a _{3,2}	4.182E-04
b ₁	1.6704
b ₂	0.5509

^a Reference [24]**Table 3.** Critical temperature of the compounds

	Critical temperature /K ^a	Molar mass / g mol ⁻¹ ^b	α value ^c / mol g ⁻¹
3-Carene	654.83	136.22	0.191
Carvacrol	764.5	150.20	0.166
(-)-Carveol, mixture of <i>cis</i> and <i>trans</i> isomers	731.65	152.22	0.177
(+)-Limonene oxide, mixture of <i>cis</i> and <i>trans</i>	678.77	152.22	0.177
(1R)-(-)-Myrtenol	734.16	152.22	0.177
(1R)-(-)-Nopyl acetate	698	208.28	0.168
(S)-(-)-Perillyl alcohol	736.52	152.22	0.177
α -Pinene oxide	676.49	152.22	0.177
γ -Terpinene	661	136.22	0.191

^a Estimate with UNIFAC contribution group model using Aspen Plus software^b Reference [26]^c $\alpha = \frac{N}{M}$; M = Molecular mass; N = number of atoms in a molecule

- Contribution group model

The heat capacity calculated by group contribution consists of breaking down the molecule into smaller functional groups (-CH₃, -CH₂OH, ...), equation (4) [25].

$$C_{p,m} = \sum n_i \left(A_i + B_i \left(\frac{T}{100} \right) + C_i \left(\frac{T}{100} \right)^2 + D_i \left(\frac{T}{100} \right)^3 \right) \quad (4)$$

$C_{p,m}$ in cal K⁻¹ mol⁻¹, parameters A, B, C, D for each functional group i , T is temperature (K), n is the number of times that the functional group is in the molecule.

3. Results and discussion

3.1. Determination of heat capacity

The isobaric heat capacity values experimentally obtained for all the compounds as a function of temperature are presented in **Table 4**, and fitted to a cubic polynomial function, equation (5), although many experimental points are obtained, in the table values are reported every 5 K.

$$C_{p,m} = A + BT + CT^2 + DT^3 \quad (5)$$

where T is in Kelvin and $C_{p,m}$ in J·mol⁻¹·K⁻¹. The parameters A, B, C and D for each compound are listed in **Table 5**. A good adjustment of the data with the polynomial regression was found, a low standard error and a determination coefficient close to unity were obtained.

Table 4 Isobaric heat capacity of liquid terpenes, C_p , and terpenoids as a function of temperature and at pressure ($P = 85.1$ kPa)^a

$C_p / \text{J mol}^{-1} \text{K}^{-1}$									
T / K	α -Pinene oxide	Carvacrol	(-)-Carveol, mixture of cis and trans isomers	(+)-Limonene oxide, mixture of cis and trans	(1R)-(-)-Myrtenol	(1R)-(-)-Nopyl acetate	(S)-(-)-Perillyl alcohol	3-Carene	γ -Terpinene
298.15	274.03	331.37	341.10	288.83	321.91	368.84	329.82	264.18	259.80
303.15	281.51	333.53	351.29	293.09	330.29	374.71	337.54	268.93	262.92
308.15	288.89	337.57	360.39	299.10	338.94	380.41	346.02	272.75	265.49
313.15	295.72	339.28	369.32	304.65	346.40	384.14	354.34	276.21	268.07
318.15	303.32	340.61	378.27	309.37	354.36	389.55	361.81	276.95	270.10
323.15	309.60	342.91	385.72	314.60	361.07	394.55	369.83	278.28	271.23
328.15	316.01	345.08	393.70	319.78	367.91	399.01	376.69	276.99	270.74
333.15	322.67	347.18	401.35	324.45	374.98	403.33	382.06	279.26	270.35
338.15	326.89	349.07	406.95	329.48	381.31	408.34	387.12	280.95	NA
343.15	329.14	351.19	410.84	333.37	385.10	412.30	390.63	280.21	NA
348.15	329.88	355.27	414.49	337.77	390.14	416.23	392.21	278.22	NA
353.15	330.98	357.61	414.65	338.96	392.66	416.83	392.31	277.42	NA

NA: not available.

^a Standard uncertainty is $u(T) = \pm 0.1$ K; $u(P) = \pm 2.0$ kPa [27], uncertainty of values is less than 1.5% (0.95 level of confidence, coverage factor $k=2$).

Table 5 Parameters of polynomial heat capacities dependence of temperature ^a

Compounds	A (J·K ⁻¹ ·mol ⁻¹)	B (J·K ⁻² ·mol ⁻¹)	C x 10³ (J·K ⁻³ ·mol ⁻¹)	D x 10⁶ (J·K ⁻⁴ ·mol ⁻¹)	SE^b	R^{2 c}
3-Carene	-3813.16	33.92	-93.10	84.49	0.904	0.964
Carvacrol	-2846.97	28.65	-86.89	89.09	0.418	0.998
(-)-Carveol, mixture of <i>cis</i> and <i>trans</i> isomers	8811.13	-85.73	283.53	-306.07	0.470	0.999
(+)-Limonene oxide, mixture of <i>cis</i> and <i>trans</i>	7071.94	-65.85	210.10	-219.83	0.906	0.997
(1R)-(-)-Myrtenol	6163.95	-59.61	197.66	-212.81	0.549	0.999
(1R)-(-)-Nopyl acetate	5735.46	-52.57	168.87	-177.39	0.856	0.996
(S)-(-)-Perillyl alcohol	7972.92	-77.95	259.63	-282.24	0.387	0.999
α-Pinene oxide	10294.53	-99.14	322.56	-344.71	0.479	0.999
γ-Terpinene	-4773.90	43.36	-123.91	117.76	0.728	0.975

^a Temperature range (293.15 to 353.15 K) except γ-terpinene (293.15 to 333.15 K), polynomial adjust given by: $C_p [J \cdot mol^{-1} \cdot K^{-1}] = A + B \cdot T + C \cdot T^2 + D \cdot T^3$

^b SE is the standard error = $\sqrt{\frac{\sum_i (C_{p_i} - \hat{C}_{p_i})^2}{n-2}}$; n is the total number of measurements, \hat{C}_{p_i} is the value predicted with the model and C_{p_i} is the experimental value

R^2 is the coefficient of determination = $\frac{\sum_i(\hat{c}_{p_i} - \bar{c}_p)^2}{\sum_i(c_{p_i} - \bar{c}_p)^2}$; \bar{c}_p is the mean value of heat capacity for the entire temperature range for each substance

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Figure 2 to **Figure 10** show the experimental values for molar heat capacity as function of temperature of α -pinene oxide, 3-carene, carvacrol, carveol, γ -terpinene, limonene oxide, (1R)-(-)-myrtenol, nopyl acetate, and perillyl alcohol. Figures also include a comparison between experimental data and values obtained by the predictive correlations of the Dadgostar-Shaw universal correlation, equation (2), and the Dadgostar-Shaw universal correlation, equation (3), and a group contribution method, equation (4). The percentage deviation between the heat capacity estimated with the models ($C_{p,m}^{mod}$) and the values experimentally obtained ($C_{p,m}^{exp}$) are also presented in the figures. The data are available in **Table S3** to **Table S5** in Supplementary Information.

The two epoxides (**Figure 2** and **Figure 7**) have similar heat capacities, and they are lower than for the other isomers (**Figure 4**, **Figure 8**, **Figure 10**), which values decrease in the following order: carveol > perillyl alcohol > (1R)-(-)-myrtenol. For nopyl acetate (**Figure 9**), carvacrol (**Figure 4**), and the two isomers γ -terpinene (**Figure 6**) and 3-carene (**Figure 3**) the temperature effect on heat capacity is lower and, in some cases, (γ -terpinene and 3-carene) heat capacity tends to be constant at higher temperatures. Additional experiments varying the load of the (1R)-(-)-nopyl acetate was carried out, for confirming the large temperature dependence of its heat capacity. Data in **Table S6** in Supporting Information show that the values obtained did not vary regardless of the mass used, which shows the large dependence on temperature for the heat capacity of (1R)-(-)-nopyl acetate.

The heat capacity of carvacrol at some temperatures studied is reported in the literature [28], as evidenced in **Table 6**, it can be seen that the differences obtained between the authors and the values reported in this work are less than 2.5%. Experimentally, the equipment used is different as well as the heating rate (0.1 K min^{-1}) used by the author.

Table 6. Experimental and literature heat capacity for carvacrol at different temperatures.

<i>T</i> / K	$C_p / \text{J mol}^{-1} \text{K}^{-1}$		
	Experimental ^a $C_{p,m}^{l,exp}$	Literature ^b $C_{p,m}^{l,lit}$	Difference (%) ^c
298.15	331.4	325.1	-1.9
308.15	337.6	329.7	-2.3
318.15	340.6	335.0	-1.6
328.15	345.1	339.3	-1.7

^a Data taken from **Table 4**

^b Reference [28]

^c Difference: $100 (C_{p,m}^{l,lit} - C_{p,m}^{l,exp}) / C_{p,m}^{l,exp}$ of experimental liquid heat capacity of carvacrol from this work $C_{p,m}^{l,exp}$ and reported by Martínez-López et al. $C_{p,m}^{l,lit}$ [28]

The heat capacity of 3-carene at several temperatures was compared with reported values for (+)-3-carene [28]; **Table 7** shows that there are some differences between those data. Those differences could be attributed to the purities of the reagents, the working pressures, some variations in the heating rate, or differences in the equipment used.

Table 7. Experimental and literature heat capacity for 3-carene at different temperatures.

T / K	$C_p / \text{J mol}^{-1} \text{K}^{-1}$		
	Experimental ^a $C_{p,m}^{l,exp}$	Literature ^b $C_{p,m}^{l,lit}$	Difference (%) ^c
300.15	266.5	254.8	4.4
305.15	270.4	257.2	4.9
310.15	273.7	259.6	5.2

^a Data are taken from **Table 4**

^b Reference [28]

^c Difference: $100 (C_{p,m}^{l,lit} - C_{p,m}^{l,exp}) / C_{p,m}^{l,exp}$ of experimental liquid heat capacity of 3-carene from this work $C_{p,m}^{l,exp}$ and Štejfa et al $C_{p,m}^{l,lit}$ [28]

In general, the correlations [24] allow to obtain a good approximation to the heat capacity of the different substances except for those that contain alcohols. the modified equation also has the advantage that it allows to differentiate between the heat capacity of the substances that have isomers. On the other hand, the model chosen by group contribution for organic liquids [25] generally predicts with good accuracy the experimental data obtained for the different substances taking into account that the error is not usually greater than 5% in most of the cases, which is a good approximation for this type of measurements, as they are complex substances, containing cyclic structures and different functional groups.

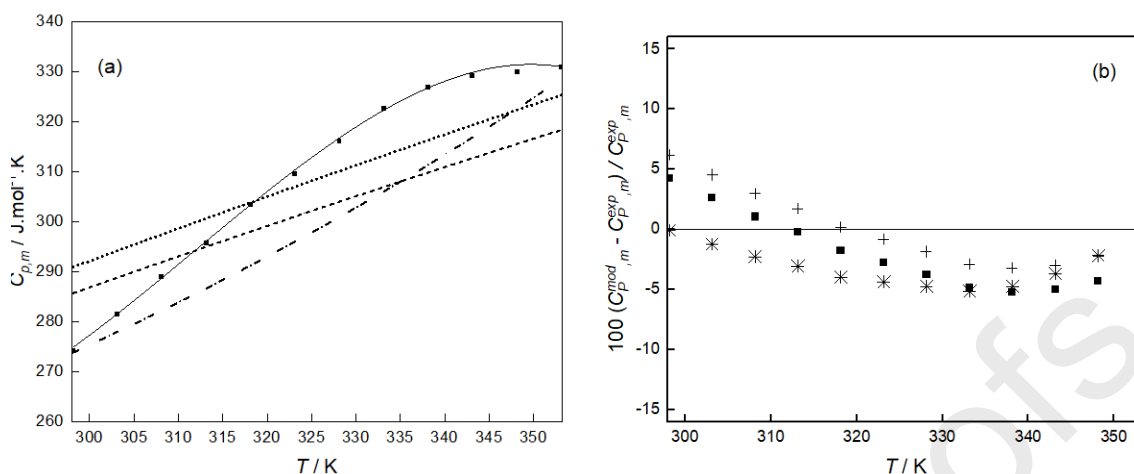


Figure 2. (a) Molar heat capacity $C_{p,m}$ for α -pinene oxide: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (· ·) modified Dadgostar–Shaw universal correlation; (- · -) group-contribution method. (b) Relative deviations $100 (C_{p,m}^{\text{mod}} - C_{p,m}^{\text{exp}})/C_{p,m}^{\text{exp}}$; with $C_{p,m}^{\text{mod}}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

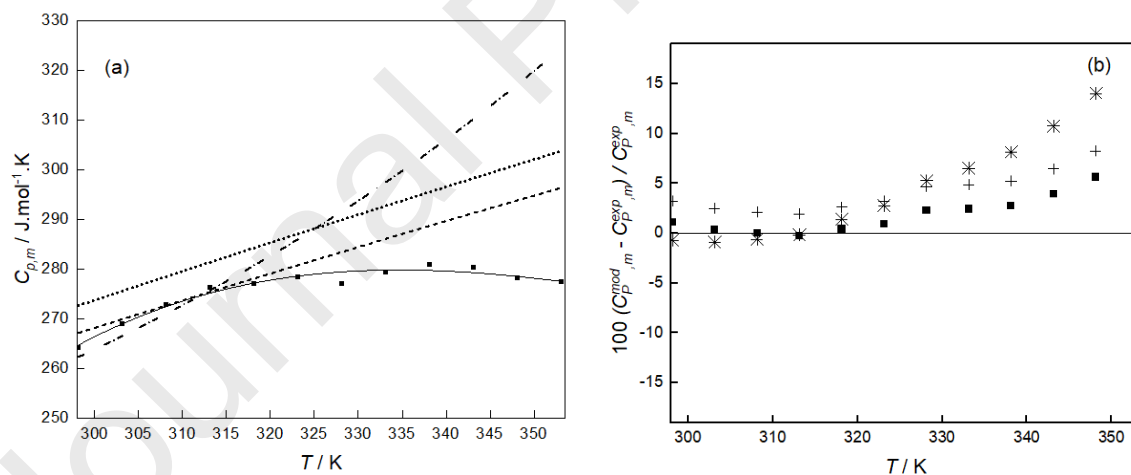


Figure 3. (a) Molar heat capacity $C_{p,m}$ for 3-carene: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (· ·) modified Dadgostar–Shaw universal correlation; (- · -) group-contribution method. (b) Relative deviations $100 (C_{p,m}^{\text{mod}} - C_{p,m}^{\text{exp}})/C_{p,m}^{\text{exp}}$; with $C_{p,m}^{\text{mod}}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

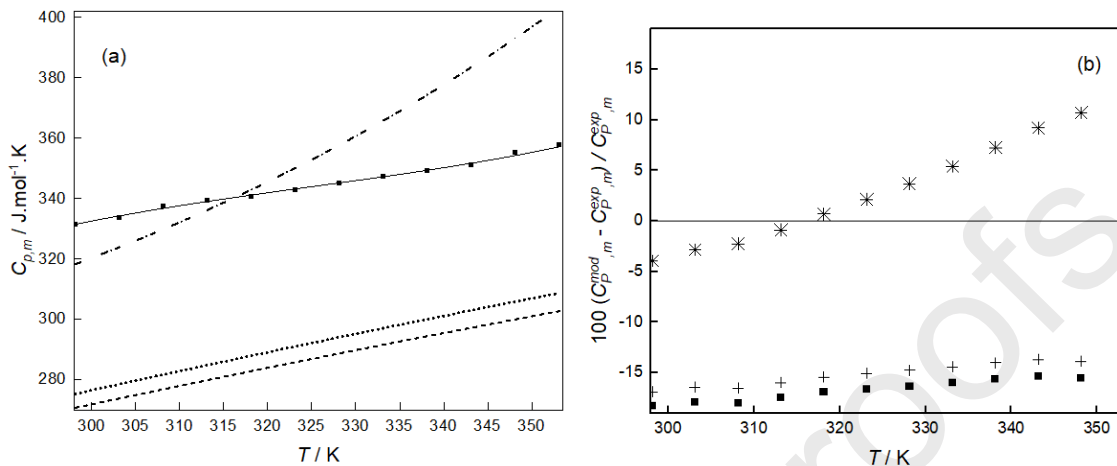


Figure 4. (a) Molar heat capacity $C_{p,m}$ for carvacrol: (■) experimental data; (—) polynomial regression; (---) Dadgostar–Shaw universal correlation; (··) modified Dadgostar–Shaw universal correlation; (-·-) group-contribution method. (b) Relative deviations $100(C_{p,m}^{\text{mod}} - C_{p,m}^{\text{exp}}) / C_{p,m}^{\text{exp}}$; with $C_{p,m}^{\text{mod}}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

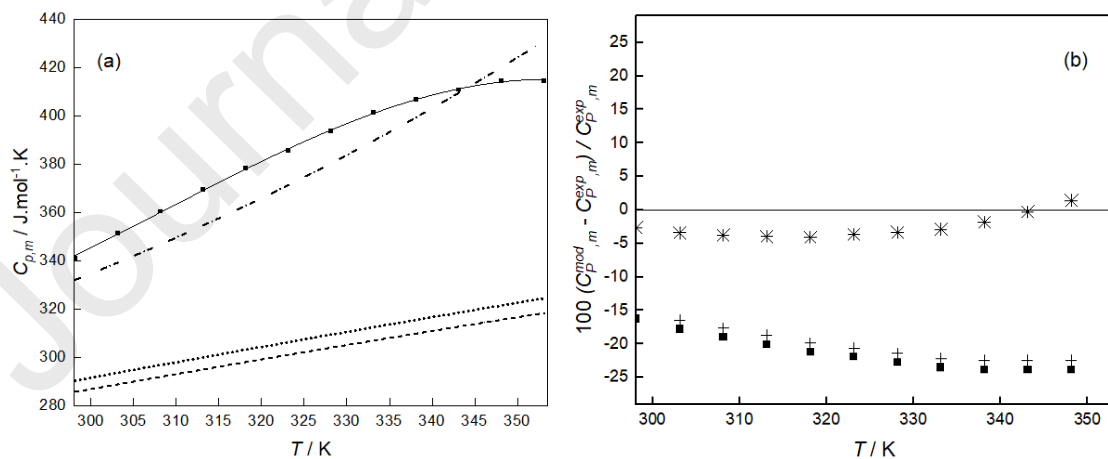


Figure 5. (a) Molar heat capacity $C_{p,m}$ for (-)-carveol: (■) experimental data; (—) polynomial regression; (---) Dadgostar–Shaw universal correlation; (··) modified Dadgostar–Shaw universal correlation; (-·-) group-contribution method. (b) Relative deviations $100(C_{p,m}^{\text{mod}} - C_{p,m}^{\text{exp}}) / C_{p,m}^{\text{exp}}$ —

$C_{p,m}^{exp}/C_{p,m}^{exp}$); with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

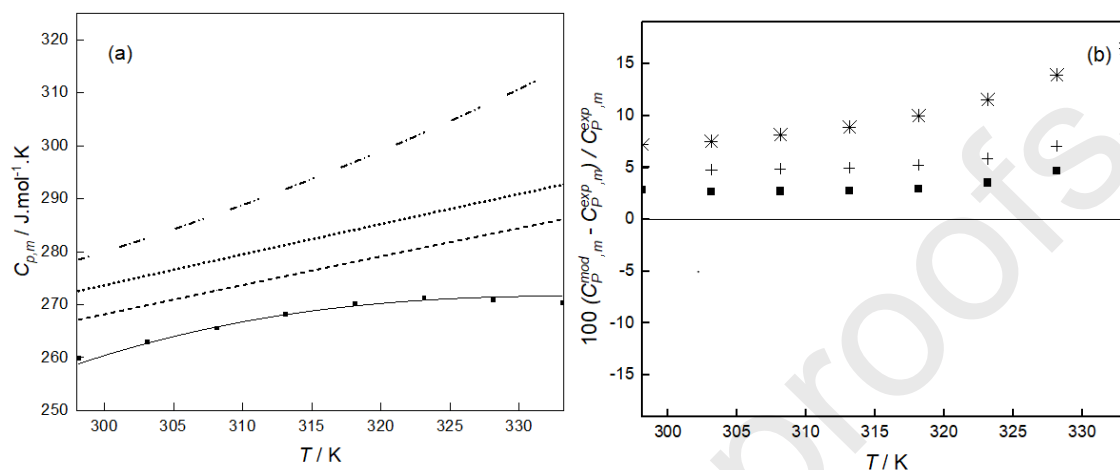


Figure 6. (a) Molar heat capacity $C_{p,m}$ for γ -terpinene: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (· ·) modified Dadgostar–Shaw universal correlation; (- · -) group-contribution method. (b) Relative deviations $100(C_{p,m}^{mod} - C_{p,m}^{exp})/C_{p,m}^{exp}$; with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

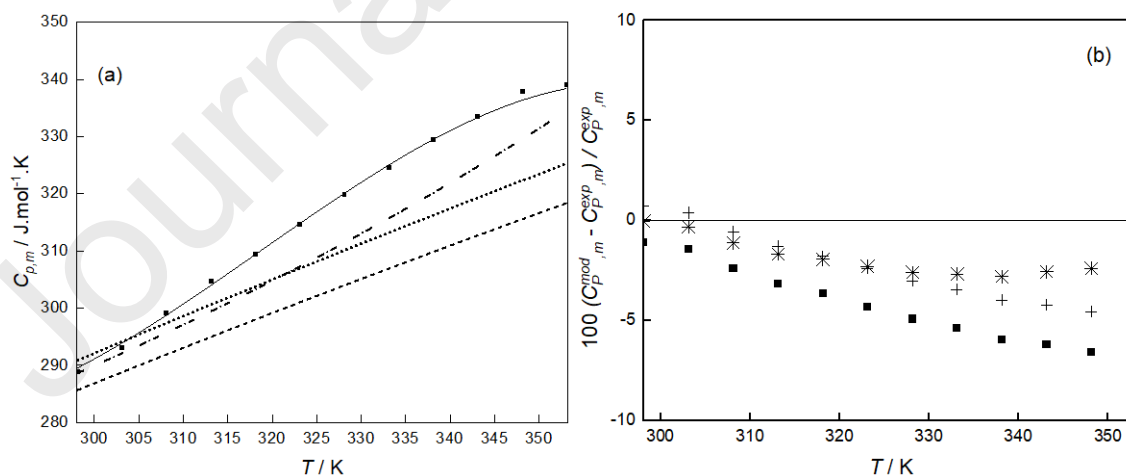


Figure 7. (a) Molar heat capacity $C_{p,m}$ for (+)-limonene oxide: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (· ·) modified Dadgostar–Shaw universal correlation; (- · -) group-contribution method. (b) Relative deviations $100(C_{p,m}^{mod} - C_{p,m}^{exp})/C_{p,m}^{exp}$; with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

$C_{p,m}^{mod} - C_{p,m}^{exp} / C_{p,m}^{exp}$; with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

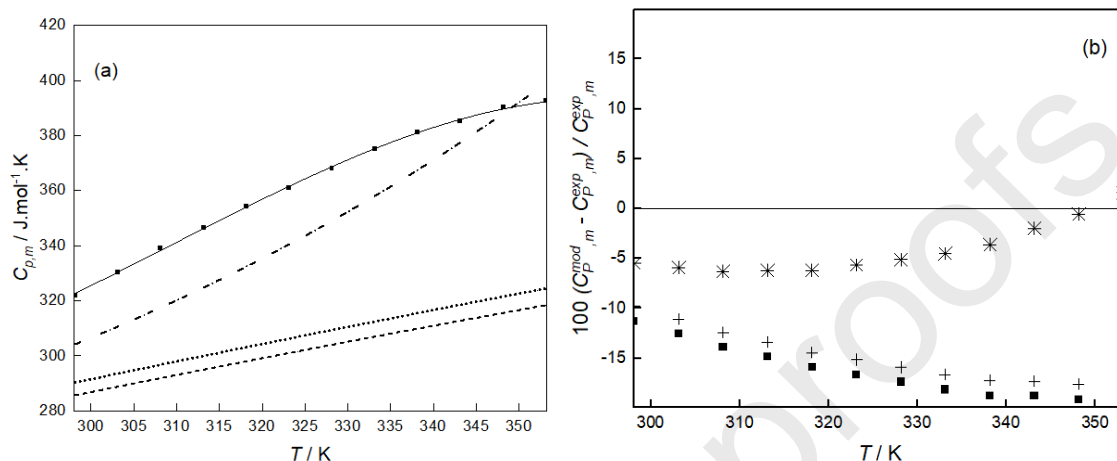


Figure 8. (a) Molar heat capacity $C_{p,m}$ for (1R)-(-)-myrtenol: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (· ·) modified Dadgostar–Shaw universal correlation; (-·-) group-contribution method. (b) Relative deviations $100 (C_{p,m}^{mod} - C_{p,m}^{exp}) / C_{p,m}^{exp}$; with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

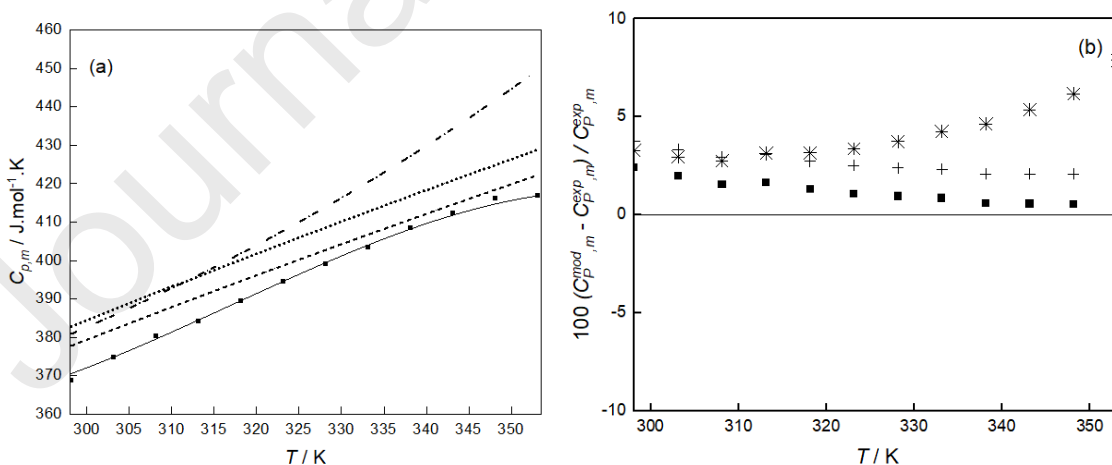


Figure 9. (a) Molar heat capacity $C_{p,m}$ for (1R)-(-)-nopyl acetate: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (· ·) modified Dadgostar–Shaw universal correlation; (-·-) group-contribution method. (b) Relative deviations $100 (C_{p,m}^{mod} - C_{p,m}^{exp}) / C_{p,m}^{exp}$

$C_{p,m}^{mod} - C_{p,m}^{exp} / C_{p,m}^{exp}$; with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

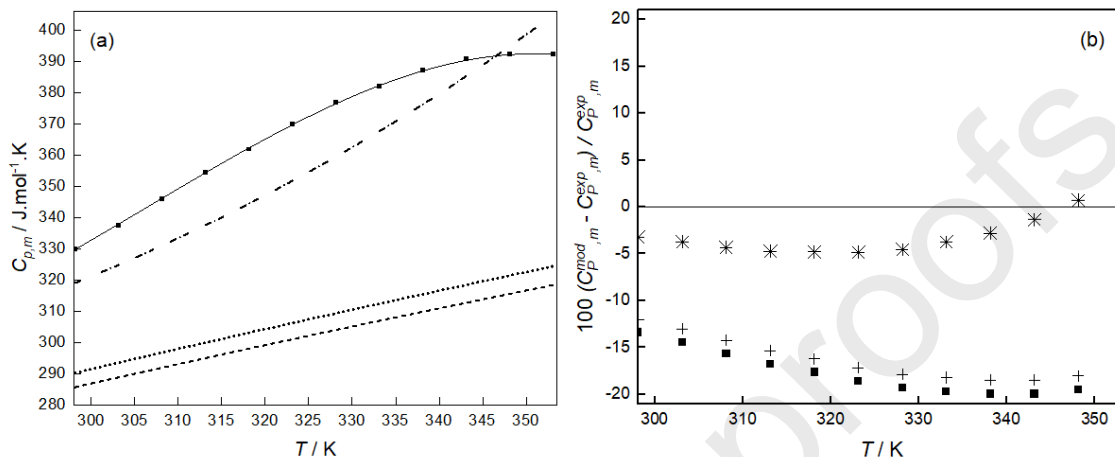


Figure 10. (a) Molar heat capacity $C_{P,m}$ for (S)-(-)-perillyl alcohol: (■) experimental data; (-) polynomial regression; (- -) Dadgostar–Shaw universal correlation; (- · -) modified Dadgostar–Shaw universal correlation; (- · -) group-contribution method. (b) Relative deviations $100 (C_{p,m}^{mod} - C_{p,m}^{exp}) / C_{p,m}^{exp}$; with $C_{p,m}^{mod}$ the heat capacity estimated with a model: (■) Dadgostar–Shaw universal correlation; (+) modified Dadgostar–Shaw universal correlation; (*) group-contribution method.

4. Conclusions

The heat capacities of nine terpenes and terpenoids were measured in liquid phase in the temperature range 293.15 and 353.15 K, obtaining a third-order polynomials equations for describing the heat capacity dependence with temperature. Several models were used for predicting heat capacities; it was found that the group contribution model satisfactorily predicts the experimental results except for γ -terpinene and nopyl acetate; the deviation with experimental data was lower than 5%, except for 3-carene and carvacrol at temperature higher than 330K. When the Dadgostar–Shaw universal correlation was modified, the deviation of predicted values respect to experimental data was lower than in the case of using the no modified equation and in some cases the predicted values were like the values obtained

with the group contribution model. The Dadgostar–Shaw universal correlation was the most adequate model to predict the behavior of 3-carene, γ -terpinene and nopyl acetate. In this contribution data for substances whose thermal properties have not been extensively studied were obtained, which is of special interest in the fine chemical industry.

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Highlights

- Heat capacity was measured as a function of temperature for several terpenes
- Experimental data were compared with some theoretical models
- The results were fitted to third order polynomials equation

Author statement

Nicolás Stiven Castellanos: Methodology, Data curation, Validation, Investigation, Writing- Original draft preparation

Aída Luz Villa: Conceptualization, Supervision, Resources, Writing- Reviewing and Editing, Funding acquisition.