

Vaporization Enthalpies and Vapor Pressures of the Major Components of Opopanax Oil, α -Santalene, cis α Bisabolene, cis α -Bergamotene,

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Vaporization Enthalpies and Vapor Pressures of the Major Components of Opopanax Oil,
 α -Santalene, *cis* α Bisabolene, *cis* α -Bergamotene,

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Abstract: The vapor pressures and vaporization enthalpies of the major components of opopanax oil, a medicinal that has been in use since biblical times, are evaluated by correlation gas chromatography. Two sets of hydrocarbon standards are used, n-alkanes and a mixture of cyclic and polycyclic hydrocarbons. Two of the oil's sesquiterpene components, evaluated in a previous study, were used both as standards and also as targets. Their use as targets was in an effort to confirm both their identity in the oil and the reproducibility of their properties. All correlations produce reproducible vaporization enthalpies and vapor pressures at ambient temperatures. At elevated temperatures, the use of the two different sets of standards resulted in some divergence in vapor pressure. Experiments are described aimed at attenuating this divergence. The results are compared to existing data.

Keywords: Correlation gas chromatography; gas chromatography; vaporization enthalpy; vapor pressure; sesquiterpenes; opopanax oil

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Introduction

Opopanax essential oil, also known as Sweet Myrrh is steam distilled from the resin of trees of the same genus as Myrrh and their odors both share some similarities. Opopanax has been used for the treatment of wounds as an antiseptic since biblical times. Other properties of the opopanax essential oil includes use as an expectorant and as an antispasmodic. Much of its use is in the practice of traditional medicine [1]. An additional use of opopanax essential oil has been as a fixative in the perfume industry [2]. The chemical composition of the essential oil varies, depending on the species. The genus comprises of more than 200 species, all native to Africa, Arabia, Madagascar and India [1]. The volatile oils in the two species used in this study, *commiphora guidotti*, and *commiphora glabrescenes*, are rich in five sesquiterpenes, α -santalene, *cis* α -bisabolene, *cis* α -bergamotene, α *trans*-bergamotene, and β -bisabolene [3,4]. The structures of all the sesquiterpenes and cyclic standards involved in this study are provided in Figure 1.

α -Santalene (**1**), 1, 7-dimethyl-7-(4-methylpent-3-enyl)tricyclo[2.2.1.0^{2,6}]heptane, is the most abundant sesquiterpene present in opopanax oil. It is found in allspice and used as a flavoring ingredient [5]. It is an important intermediate in the synthesis of (*Z*)-(+)- α -santalol, a major constituent responsible for the sweet-woody and balsamic aroma of sandalwood oil used in perfumes [6]. The recent availability of santalenes from biomass sugars has triggered additional interest in them, since they exhibit a greater energy density when compared to JP-5 and F76 fuels. As a renewable energy source, this has been suggested as a means of reducing the carbon footprint produced by the military [7].

Another component in opopanax oil is *cis* α -bergamotene, (1*R*, 5*R*)-2,6-dimethyl-6-(4-methylpent-3-en-1-yl)-bicyclo[3.1.1]hept-2-ene (**3**), a substance found in a variety of plants, including carrot oil, bergamot and lime [8]. *cis* α -Bisabolene, (*Z*)- 2-methyl-6-(4-methyl-3-cyclohexen-1-yl)- 2,5-heptadiene (**4**), another major component, is also found in trace amounts in a variety of plant oils, including carrot seed oil and citrus lemon peel oil from Italy. It is present in bay laurel and in rosemary plants [8]. Another major compound found in the two varieties of opopanax oil examined is *cis* α -bisabolene (**5**), the immediate precursor of *trans/cis*-(*Z*)- α -bisabolene epoxide, the sex pheromone of the Southern green stink bug, *Nezara viridula* [9]. *trans* α -Bergamotene and *cis* α -bisabolene are two other sesquiterpenes found in opopanax oil; the properties of these two compounds have been described and studied, recently [10, 11].

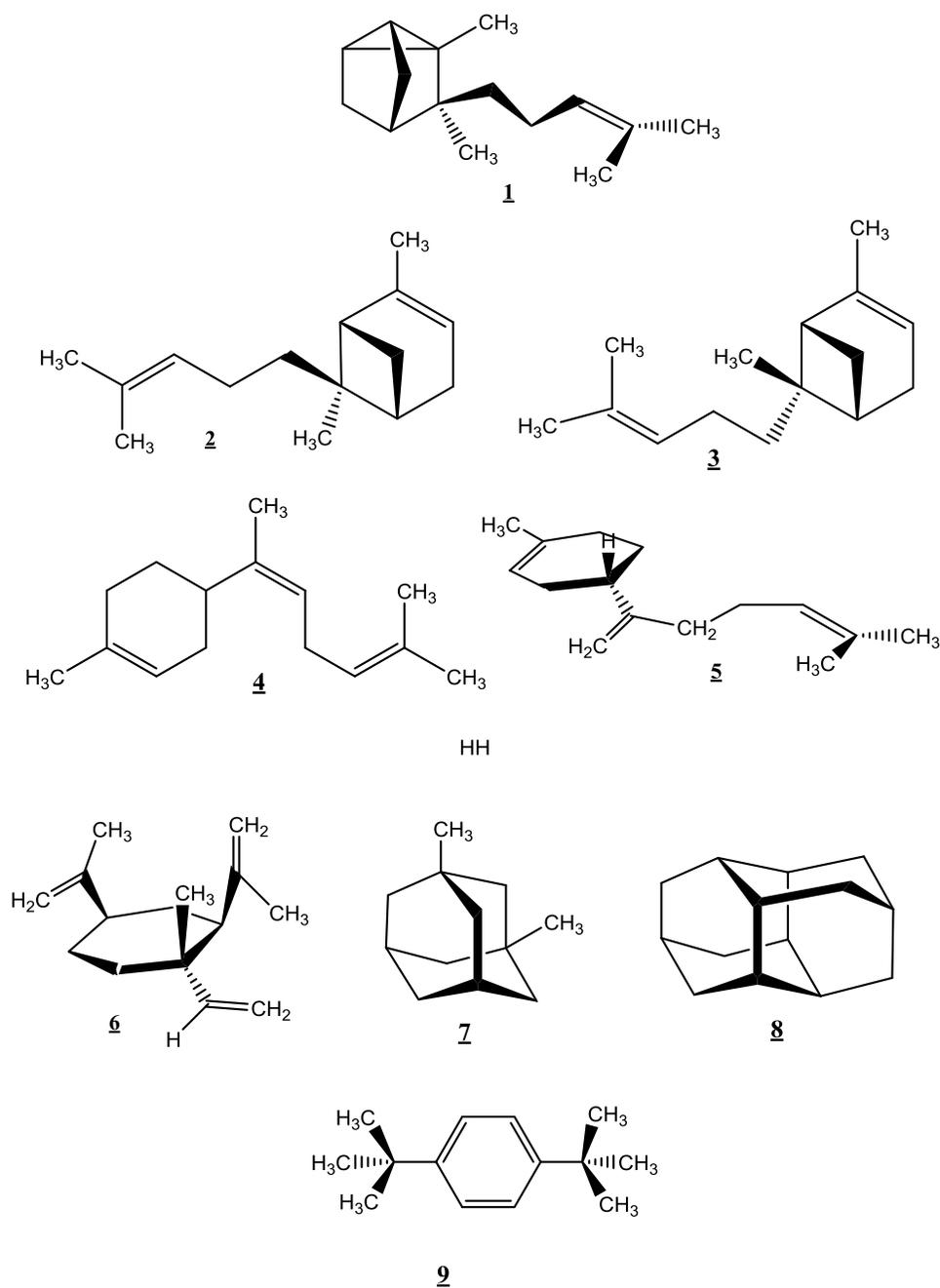


Figure 1. Structure of the targets and cyclic standards discussed in this article. From left to right: α -santalene (**1**), *trans* α -bergamotene (**2**), *cis* α -bergamotene (**3**), *cis* α -bisabolene (**4**), β -bisabolene (**5**). Standards: β -elemene (**6**), 1,3-dimethyladamantane (**7**), diamantane (**8**), 1,4-di-*t*-butylbenzene (**9**). Structures of the *n*-alkanes used as standards are not shown.

This study reports the vaporization enthalpies and vapor pressures of the sesquiterpenes reported above. The properties of the two sesquiterpenes reported previously and also present in

opopanax oil, *trans* α -bergamotene (**2**), and β -bisabolene (**5**), were also included in correlations as both targets and as internal standards [10, 11]. The main purpose for their inclusion as targets was as means of confirming their identity in the opopanax oil and for evaluating the reproducibility of previous work. Two sets of standards were used, a series of compounds that included in addition to the two mentioned above, 1,3-dimethyladamantane, 1,4-di-*t*-butylbenzene, β -elemene and diamantane and the following series of n-alkanes: n-C₁₃ to n-C₁₆. The former of these two sets of compounds are described in this article as oligocyclic compounds. *trans* α -Bergamotene (**2**), and β -bisabolene (**5**) are generally referenced separately, referred to as the sesquiterpenes. The vapor pressures of both of these sesquiterpenes were evaluated previously using similar oligocyclic standards. Their vapor pressures were also included in experiments with n-alkanes to determine the degree to which their vapor pressures correlated with those of the n-alkanes. This effort was directed toward identifying a protocol that could possibly attenuate some of the curvature observed with n-alkane standards in plots of $\ln(p/p^0)$ versus K/T and is discussed below.

2. Experimental

2.1 Compounds: Identity and purity controls

The origin of the standards and their mass fractions are reported in Table 1. The first portion of the table describes the properties of the standards available in relatively pure form. *trans* α -Bergamotene was the major component in bergamotene oil studied previously; its mass fraction in the oil was 0.56 [10]. Its retention time was used to confirm the identity of same in the opopanax oil; similarly for β -bisabolene. The composition of the major components in the two opopanax oils follow. The major components in the two different species were each identified by their composition as reported by their suppliers [3, 4], and by their retention index. A comparison of the compositions of the two opopanax oils by gas chromatography to those reported by the suppliers is provided in the last column of Table 1. Retention index results used to confirm their identity are provided in Table S5 (Supporting information). Two different opopanax oils were examined since they differed regarding the presence of β -bisabolene as reported by their suppliers. The presence of β -bisabolene in both opopanax oils was identified and confirmed by co-injection with a sample from a different supplier [11]; *trans*-bergamotene was identified

similarly. Gas chromatograms of the two opopanax oils used in this study are provided as Figures S1 and S2

Table 1

Origin and composition of the standards and targets

	CAS No.	Supplier	Mass Fraction ^a
Methylene chloride	75-09-2	Fisher Chemical	0.995
n-Tridecane	629-50-5	Sigma Aldrich	0.99
n-n-Tetradecane	629-59-4	Sigma Aldrich	0.99
n-Pentadecane	629-62-9	Sigma Aldrich	0.98+
n-Hexadecane	544-76-3	Sigma Aldrich	0.99+
1,3-Dimethyladamantane	702-79-4	Sigma Aldrich	0.99+
1,4-Di-t-butylbenzene	1012-72-2	Sigma Aldrich	0.98
Diamantane	2292-79-7	TCI	0.98
(-)- β -Elemene (6)	515-13-9	Essential Oil University	0.94
(-)- β -Bisabolene (5)	495-61-4	Essential Oil University	0.91
Bergamotene oil		Aramacs ^c	Found ^d
<i>α trans</i> -Bergamotene	13474-59-4		0.56
Opopanax oil (<i>Commiphora guidotti</i>)		Pompeii Organics ³	(Supplier/Found) ^d
<i>cis α</i> -Bergamotene (3)	18252-46-5		0.008/0.029
<i>α</i> -Santalene (1)	512-61-8		0.198/0.201
<i>α trans</i> -Bergamotene (2)	13474-59-4		0.053/0.064
<i>cis α</i> -Bisabolene (4)	29837-07-8		0.163/0.159
<i>β</i> -Bisabolene (5)	495-61-4		NR ^e /0.030
Opopanax-Wild (<i>Commiphora glabrescenes</i>)		Eden Botanicals ⁴	(Supplier/Found)
<i>cis α</i> -Bergamotene (3)	18252-46-5		0.045/0.033
<i>α</i> -Santalene (1)	512-61-8		0.278/0.223
<i>α trans</i> -Bergamotene (2)	13474-59-4		0.091/0.075
<i>cis α</i> -Bisabolene (4)	29837-07-8		0.231/0.224
<i>β</i> -Bisabolene (5)	495-61-4		0.032/0.040

^a Mass fractions reported by the suppliers unless noted otherwise;

^b Source: www.essentialoil.university/terpenes; accessed: [11/20/2019].

^c Source: B-94/8 Joshi colony I. P. Extn, Patpar Ganj Delhi 110,092 India; identified by GCMS and the NIST/EPA/NIH MS library [10].

^d Mass fractions by gas chromatography; the value(s) directly below refer to the composition in the mixture, not the purity.

^e Not reported.

(Supplementary Information (SI)). As mentioned above, once α *trans*-bergamotene and β -bisabolene were identified in the two oils, the two present naturally in the oil were used to confirm that their properties reproduced previous work [10, 11] and to evaluate the effects of combining their vapor pressures with those of the n-alkanes generated from the simultaneous use of a mixture of both. The stereochemistry at the chiral carbon of β -bisabolene in opopanax oil in Figure 1 is not shown. We were not locate any literature information as to whether it has been assigned in opopanax oil; we presume the structure represents a single enantiomer.

2.2 Methods

The gas chromatographic experiments were conducted isothermally on an HP 5980 gas chromatograph using a 15 m SPB-5 capillary column with He as the carrier gas at a split ratio of approximately 80/1 and a head pressure of approximately 150 kPa. Duplicate experiments were performed under similar conditions of pressure and temperature. All retention times, and correlations pertaining to vaporization enthalpies both with and without the use of α *trans*-bergamotene and β -bisabolene as standards and details regarding their associated uncertainties are provided in the SI in Tables S1A-S4A, S1B-S4B, and S1C-S4C respectively.

2.3. Vaporization enthalpy

A basic premise in correlation gas chromatography is that the amount of time a substance spends on the column, its residence time, t_r , is related inversely to the substance's vapor pressure off the column. Residence time is evaluated by subtracting the retention time of a non-retained reference included in the chromatography from the retention time of each analyte. In these experiments, the non-retained reference, methylene chloride, was also the solvent. A plot of $\ln(t_o/t_r)$ versus K/T over a 30 K temperature range at approximately 5 K intervals was linear and the product of the absolute value of the slope of the line and the gas constant, $R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, provided the enthalpy of transfer of the analyte from the stationary phase of the column to the gas phase, $\Delta_{trn}^g H_m(T_m)$; t_o refers to the reference time, 60 s. Thermodynamically, this enthalpy should be equal to the sum of two terms, the vaporization enthalpy and an enthalpy of interaction of the analyte with the column, Eq. 1 [12].

$$\Delta_{trn}^g H_m(T_m) = \Delta_l^g H_m(T_m) + \Delta H_{intr}(T_m) \quad (1)$$

Additionally, we have observed that if $\Delta_l^g H_m(T_m)$ of a series of substances, functionally related to the target(s) with known $\Delta_l^g H_m(298.15 \text{ K})$ values are correlated against their values of $\Delta_{trn}^g H_m(T_m)$, a linear relationship ensues. The equation of this linear relationship and values of $\Delta_{trn}^g H_m(T_m)$ of the targets provides their vaporization enthalpy.

2.4. Vapor pressure

The same premise regarding the relationship between $1/t_r$ and the vapor pressure of an analyte off the column suggests that $1/t_r$ may also be related to p , the vapor pressure of the pure analyte, provided the standards and targets share a similar compositional and structural relationship. Indeed, a linear relationship has been observed between $\ln(p/p^\circ)$ and $\ln(t_\circ/t_r)$, where p° and t_\circ are a reference pressure and reference residence time. The linear relationship observed at $T = 298.15 \text{ K}$ has often been found to extend over a broad range of temperatures. In this work p° refers to 101325 Pa. The retention times in the Supporting Information are reported as t/t_\circ where $t_\circ = 60 \text{ s}$. Vapor pressures evaluated in this work as a function of temperature are reported either directly from the correlation at each temperature or are evaluated from fits of the correlated data to a second order polynomial, Eq. (2).

$$\ln(p/p^\circ) = A_s + B_s(K/T) + C_s(K/T)^2 \quad (2)$$

2.5 Uncertainties

All uncertainties reported in this work refer to one standard deviation unless expressed otherwise [13]. Both linear and non-linear least squares were performed using Excel and Sigma Plot 14. All regression coefficients exceeded $r^2 > 0.99$. Uncertainties evaluated from logarithmic terms are reported as an average. Evaluation of uncertainties in boiling temperature at $p^\circ = 101325 \text{ Pa}$ is described below. Uncertainties evaluated from correlations, generally reflect how well the property of the standards correlate. Actual uncertainties in the target(s) may exceed the value(s) tabulated.

2.6 Estimations of vaporization enthalpy

A simple but usually reliable method of estimating vaporization enthalpies is provided by Eq. (3) [14]. Results are generally within 5%. For hydrocarbons, the equation is depended on two variables, the total number of carbon atoms, n_C and the number of quaternary sp^3 hybridized carbon atoms, n_Q .

$$\Delta_l^g H_m(298.15 K)/\text{kJ mol}^{-1} = 4.69(n_C - n_Q) + 1.3n_Q + 3.0 \quad (3)$$

2.7 Vaporization enthalpies and vapor pressures of the standards

The vaporization enthalpies and vapor pressure parameters of the standards used in this work are summarized in Table 2. Vaporization enthalpies of the n-alkanes and vapor pressures as a function of temperature used in this study are taken from the critically evaluated values reported by Ruzicka and Majer [15]. The vapor pressures reported by these workers are in the form of the Cox equation, Eq (4). Constants for this equation are also included in Table 2 next to their corresponding vaporization enthalpies. The vaporization enthalpies for \square -elemene, diamantane, *trans* α -bergamotene and β -bisabolene are from previous work from this laboratory [11, 16]. The three sesquiterpenes were evaluated using oligocyclic compounds. Vapor pressures for both are reported in the form of Eq. (2) also found next to their vaporization enthalpy. Finally, vaporization enthalpies and vapor pressure constants for 1,3-dimethyladamantane and 1,4-di-*t*-butylbenzene are from the work of Steele et al [17] and Chirico and Steel [18], respectively. Their properties are included at the bottom of the table. The vapor pressure constants for these two compounds are reported in the form of the Wagner equation and are located below their vaporization enthalpies. Unlike Eqs. (2) and (4) which are referenced to $p^0 = 101,325$ Pa, the constants for the Wagner equation, Eq. (5), are referenced to the critical pressure, p_c . Before use, it was necessary to convert $\ln(p/p_c)$ to $\ln(p/p^0)$.

Cox Eq.:

$$\ln(p/p^0) = [1 - T_o/T] \exp[A_{co} + A_{c1}(T/K) + A_{c2}(T/K)^2]; p^0 = 101,325 \text{ Pa} \quad (4)$$

Wagner Eq.:

$$\ln(p/p_c) = (1/T_r)(A_w(1 - T_r) + B_w(1 - T_r)^{1.5} + C_w(1 - T_r)^{2.5} + D_w(1 - T_r)^5); \quad (5)$$

$$\text{where } T_r = T/T_c$$

Table 2

Vaporization enthalpies and vapor pressure constants of the Cox equation, Eq. (4), and the Wagner equation of the compounds used as standards; $p^{\circ} = 101325 \text{ Pa}$

n-Alkanes [15]	$\Delta_l^g H_m(298.15 \text{ K})/$	Parameters of the Cox equation (Eq. 4)			
	$\text{kJ}\cdot\text{mol}^{-1 \text{ a}}$	T_0/K	A_{co}	$-A_{\text{c1}}$	A_{c2}
n-Tridecane	66.68±0.67	508.602	3.10403	0.002071819	1.611600□10 ⁻⁶
n-Tetradecane	71.73□0.72	526.691	3.13624	0.002063853	1.541507□10 ⁻⁶
Pentadecane	76.77±0.76	543.797	3.16774	0.002062348	1.487263□10 ⁻⁶
Hexadecane	81.35□0.81	559.978	3.18271	0.002002545	1.384476□10 ⁻⁶

Compounds	$\Delta_l^g H_m(298.15 \text{ K})/$	Parameters of Equation (2); $p^{\circ} = 101325 \text{ Pa}$		
	$\text{kJ}\cdot\text{mol}^{-1 \text{ b}}$	A_s	$-B_s$	$-C_s$
□-Elemene [11]	66.8□3.0	11.512±0.007	5221.9±4.9	391829±882
Diamantane [16]	65.0±4.4	11.243±0.267	5682.1±214	286764±41846
<i>trans</i> α -bergamotene [10]	69.5±2.0	12.025±0.004	5545.1±2.9	385490±521
β -Bisabolene [11]	73.9±3.0	12.488±0.025	5863.9±19	415352±33404

Vaporization Enthalpy and Parameters of the Wagner Equation		
Compound	1,3-Dimethyladamantane [17]	1,4-Di-t-butylbenzene [18]
$\Delta_l^g H_m(298 \text{ K})/ \text{kJ}\cdot\text{mol}^{-1}$	49.37±0.33 ^c	62.98±0.14 ^c
A_w	-8.1734	-9.2795
B_w	3.28872	3.87697
C_w	-3.4732	-5.5302
D_w	-2.486	-3.3734
T_c/K	708	708
p_c/kPa	3000	2300

^aUncertainties represent probable error.

^bUncertainties for □-elemene, diamantane, α *trans*-bergamotene, and β –Bisabolene represent one standard deviation.

^c Estimated combined expanded uncertainty (confidence level: 0.95).

3. Results

3.1 Vaporization Enthalpies

Enthalpies of transfer, $\Delta_{trn}^g H_m(T_m)$, were evaluated from plots of $\ln(t_o/t_r)$ versus K/T as described above. Vaporization enthalpies of the standards were then correlated against their enthalpies of transfer. Tables 3A and 3C summarize the results of one of two duplicate runs using both *trans* α -bergamotene (**2**) and β -bisabolene (**5**) as standards. In Table 3A, the correlation involved the use of structurally similar standards; standards in Table 3C include use of the n-alkanes. In Tables 3B and 3D, the two sesquiterpenes are used as targets. The correlation coefficients of Eqs. (6) through (9) describe the quality of the correlations. Results from these correlations and their duplicates along with the uncertainties associated with the slopes and intercepts of all runs are reported in the Supporting Information. Table 4 summarizes the vaporization enthalpies of all four runs using *trans* α -bergamotene and β -bisabolene both as standards and targets; results are also compared to estimated or literature values and are discussed below.

Table 3

Oligocyclic standards: correlation of $\Delta_l^g H_m(298.15\text{ K})$ of the standards with their $\Delta_{trn}^g H_m(402\text{ K})$ values ^a

A. (2) and (5) as standards (Run S1B)	-slope/K	intercept	$\Delta H_{trn}(402\text{ K})$ kJ·mol ⁻¹	$\Delta_l^g H_m(298.15\text{ K})/ \text{kJ}\cdot\text{mol}^{-1}$	
				Lit.	Calc
1,3-Dimethyladamantane	4,542.5	10.83	37.76±0.27	49.37±0.33 ^b	49.4±0.9
1,4-Di- <i>t</i> -butylbenzene	5,636.3	12.65	46.86±0.21	62.98±0.14 ^b	63.0±1.0
(-) β -Elemene (6)	5,918.8	12.85	49.21±0.20	66.8±3.0	66.5±1.0
<i>cis</i> α -Bergamotene (3)	6,061.4	13.09	51.15±0.18		68.3±1.1
α -Santalene (1)	6,007.4	12.93	48.32±0.11		67.6±1.1
<i>trans</i> α -Bergamotene (2)	6,152.3	13.21	39.2±0.18	69.5±2.0	69.4±1.1
Diamantane	5,811.8	11.98	49.94±0.14	65.0±4.4	65.2±1.0
<i>cis</i> α -Bisabolene (4)	6,572.2	13.92	54.64±0.17		74.6±1.1
β -Bisabolene (5)	6,524.7	13.76	54.24±0.45	73.9±3.0	74.0±1.1

$$\Delta_l^g H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.495 \pm 0.015)\Delta_{trn}^g H_m(402\text{ K}) - (7.07 \pm 0.73); r^2 = 0.9996 \quad (6)$$

B. (2) and (5) as targets (Run S1C)					
1,3-Dimethyladamantane	4,542.5	10.83	37.76±0.27	49.37±0.33 ^b	49.3±1.5
1,4-Di-t-butylbenzene	5,636.3	12.65	46.86±0.21	62.98±0.14 ^b	63.0±1.7
(-)- β -Elemene (6)	5,918.8	12.85	49.21±0.20	66.8±3.0	66.6±1.7
<i>cis</i> α -Bergamotene (3)	6,061.4	13.09	51.15±0.18		68.3±1.7
α -Santalene (1)	6,007.4	12.93	48.32±0.11		67.7±1.7
α <i>trans</i> -Bergamotene (2)	6,152.3	13.21	39.2±0.18		69.5±1.8
Diamantane	5,811.8	11.98	49.94±0.14	65.0±4.4	65.2±1.7
<i>cis</i> α Bisabolene (4)	6,572.2	13.92	54.64±0.17		74.7±1.8
β -Bisabolene (5)	6,524.7	13.76	54.24±0.45		74.1±1.8

$$\Delta_l^g H_m(298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.505 \pm 0.026)\Delta_{trn}^g H_m(402 \text{ K}) - (7.48 \pm 1.17); \quad r^2 = 0.9994$$

C. (2) and (5) as standards (Run S3B)	-slope/K	intercept	$\Delta H_{trn}(402 \text{ K})$ kJ·mol ⁻¹	$\Delta_l^g H_m(298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	
				Lit.	Calc
n-Tridecane	5,877.5	13.351	48.86	66.68±0.67 ^c	66.6±2.7
n-Tetradecane	6,320.5	13.904	52.55	71.73±0.72 ^c	71.6±2.8
<i>cis</i> α -Bergamotene (3)	6,050.1	13.11	50.30		68.6±2.8
α -Santalene (1)	6,026.1	13.022	50.10		68.3±2.8
α <i>trans</i> -Bergamotene (2)	6,176.9	13.321	51.35	69.5±2.0	70.0±2.8
n-Pentadecane	6,766.6	14.469	56.25	76.77±0.77 ^c	76.5±2.9
<i>cis</i> α Bisabolene (4)	6,510.3	13.811	54.12		73.7±2.9
β -Bisabolene (5)	6,505.4	13.767	54.08	73.9±3.0	73.6±2.9
n-Hexadecane	7,220.2	15.057	60.03	81.35±0.81 ^c	81.6±3.0

$$\Delta_l^g H_m(298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.34 \pm 0.04)\Delta_{trn}^g H_m(407 \text{ K}) - (1.26 \pm 2.0); \quad r^2 = 0.9969 \quad (8)$$

D. (2) and (5) as targets (Run S3C)					
n-Tridecane	5,877.5	13.351	48.86	66.68±0.67 ^c	66.8±2.0
n-Tetradecane	6,320.5	13.904	52.55	71.73±0.72 ^c	71.7±2.0
<i>cis</i> α -Bergamotene (3)	6,050.1	13.110	50.30		68.7±2.0
α -Santalene (1)	6,026.1	13.022	50.10		68.4±2.0
α <i>trans</i> -Bergamotene (2)	6,176.9	13.321	51.35		70.1±2.0
n-Pentadecane	6,766.6	14.469	56.25	76.77±0.77 ^c	76.5±2.1
<i>cis</i> α Bisabolene (4)	6,510.3	13.811	54.12		73.7±2.0
β -Bisabolene (5)	6,505.4	13.767	54.08		73.7±2.0
n-Hexadecane	7,220.2	15.057	60.03	81.35±0.81 ^c	81.5±2.2

$$\Delta_l^g H_m(298 \text{ K})/\text{kJ}\cdot\text{mol}^{-1} = (1.318 \pm 0.027)\Delta_{trn}^g H_m(407 \text{ K}) - (2.38 \pm 1.45); \quad r^2 = 0.9992 \quad (9)$$

^a All Uncertainties represent one standard deviation unless noted otherwise.

^b Estimated combined expanded uncertainty (confidence level: 0.95) [17, 18].

^c Uncertainty represents probable error [15].

Table 4

A summary of the vaporization enthalpies of runs 1-4 in $\text{kJ}\cdot\text{mol}^{-1}$ using *trans* α -bergamotene (**2**) and β - bisabolene (**5**) as both standards and as targets; comparisons to estimated or literature values ^a

$\Delta_l^g H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	Oligocyclic Compounds		n-Alkanes		Average	Est ^b
	Run 1B	Run 2B	Run 3B	Run 4B		
2 and 5 as standards						
α -Santalene (1)	67.6±1.1	67.2±1.9	68.3±2.8	68.5±1.6	67.9±1.9	66.6±3.3
<i>cis</i> α -Bergamotene (3)	68.3±1.0	68.1±2.0	68.6±2.8	68.6±1.6	68.4±1.9	70.0±3.5
<i>cis</i> α -Bisabolene (4)	74.6±1.1	74.6±1.1	73.7±2.9	74.0±1.7	74.2±1.7	73.4±3.7
$\Delta_l^g H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1}$	Oligocyclic Compounds		n-Alkanes		Average	Est/Lit ^b
2 and 5 as targets	Run 1C	Run 2C	Run 3C	Run 4C		
α -Santalene (1)	67.7±1.7	67.4±1.3	68.4±2.0	68.4±1.4	68.0±1.6	66.6±3.3
<i>trans</i> α -Bergamotene (2)	69.5±1.8	69.4±1.4	70.1±2.0	69.3±1.4	69.6±1.7	69.5±2.0 ^c
<i>cis</i> α -Bergamotene (3)	68.3±1.7	68.2±1.4	68.7±2.0	68.5±1.4	68.4±1.6	70.0±3.5
<i>cis</i> α -Bisabolene (4)	74.7±1.8	74.9±1.4	73.7±2.0	73.9±1.5	74.3±1.7	73.4±3.7
β -Bisabolene (5)	74.1±1.8	74.1±1.4	73.7±2.0	73.6±1.5	73.9±1.7	73.9±3.0 ^d

^a All uncertainties represent one standard deviation.

^b Estimate unless noted otherwise.

^c Experimental, ref. [10].

^d Experimental, ref. [11].

3.2 Vapor Pressures: oligocyclic standards

Vapor pressures of the targets were evaluated from plots of $\ln(p/p^0)$ versus $\ln(t_0/t_r)$ of the standards. Duplicate runs of each set of correlations were obtained under similar conditions of temperature and head pressure. Values of t_0/t_r evaluated from the slopes and intercepts of runs (1 and 2 at each similar temperature evaluated were averaged; similarly for runs 3 and 4. *trans* α -Bergamotene (**2**) and β - bisabolene (**5**) were treated both as standards and as targets in separate

sets of correlations. All correlations using the group of oligocyclic standards with or without the two sesquiterpenes as standards were conducted at $T = (298.15, 310)$ and at 10 K intervals up to 450 K, Table 5, A and B. Equations. (6) and (7) summarize the quality of the results at $T = 298.15$ K. Correlation coefficients (r^2) for both set of correlations varied from a minimum of 0.9928 at 450 K to a maximum of 0.9998.

Table 5

Correlation of $\ln(p/p^0)$ versus $\ln(t_0/t_a)_{\text{avg}}$ at $T = 298.15$ K of all the major sesquiterpenes of opananax oil for combined runs 1 and 2 using oligocyclic compounds with and without the use *trans* α -bergamotene (**2**) and β -bisabolene (**5**) as standards; $p^0 = 101325$ Pa

A. 2 and 5 as standards	$\ln(t_0/t_r)$	$\ln(p/p^0)$	$\ln(p/p^0)_{\text{calc}}$	$p_{\text{calc}}/\text{Pa}$	p_{lit}/Pa
1,3-Dimethyladamantane	-4.468	-6.894	-6.920±0.139	100±14	100 [17]
1,4-Di-t-butylbenzene	-6.314	-9.448	-9.392±0.159	8.4±1.3	8.0 [18]
\square -Elemene	-7.056	-10.410	-10.386±0.168	3.1±0.5	3.1±1.0 [11]
<i>cis</i> α -Bergamotene	-7.283		-10.689±0.170	2.3±0.4	NA ^a
α -Santalene	-7.261		-10.660±0.170	2.4±0.4	5.3 [8] ^b , 10.2 [19] ^c
<i>trans</i> α -Bergamotene (2)	-7.466	-10.910	-10.935±0.173	1.8±0.3	1.9±0.7 [10], 2.8 [8] ^b
Diamantane	-7.567	-11.041	-11.070±0.174	1.6±0.3	1.6±0.55 [16]
<i>cis</i> α -Bisabolene (5)	-8.179		-10.869±0.182	0.69±0.13	1.1 [8] ^b
\square -Bisabolene	-8.166	-11.852	-11.873±0.182	0.71±0.13	0.72±0.0.2 [11]
$\ln(p/p^0) = (1.340 \pm 0.0173) \cdot \ln(t_0/t_r) - (0.937 \pm 0.115)$				$r^2 = 0.9995$	(10)
B. 2 and 5 as targets					
1,3-Dimethyladamantane	-4.468	-6.894	-6.917±0.165	100±17	100 [17]
1,4-Di-t-butylbenzene	-6.314	-9.448	-9.398±0.190	8.4±1.6	8.0 [18]
\square -Elemene	-7.056	-10.410	-10.396±0.201	3.1±0.6	3.1±1.0 [11]
<i>cis</i> α -Bergamotene	-7.283		-10.700±0.205	2.3±0.5	NA ^a
α -Santalene	-7.261		-10.671±0.205	2.4±0.5	5.3 [8] ^b , 10.2 [19] ^c
<i>trans</i> α -Bergamotene (2)	-7.466		-10.947±0.208	1.8±0.4	1.9±0.7 [10], 2.8 [8] ^b
Diamantane	-7.567	-11.041	-11.082±0.209	1.6±0.3	1.6±0.55 [16]
<i>cis</i> α -Bisabolene (5)	-8.179		-11.906±0.219	0.68±0.15	1.1 [8] ^b

\square -Bisabolene	-8.166	-11.888±0.219	0.70±0.15	0.72±0.2 [11]
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$$\ln(p/p^{\circ}) = (1.344 \pm 0.021) \cdot \ln(t_0/t_r) - (0.911 \pm 0.136) \quad r^2 = 0.9995 \quad (11)$$

^a Not available.

^b Estimate.

^c Estimate, sub-cooled liquid.

3.2 Vapor Pressures: *n*-alkane standards

Table 6 summarizes the results at $T = 298.15$ K of plots of $\ln(p/p^{\circ})$ versus $\ln(t_0/t_r)$ using *n*-alkanes as standards that included both *trans* α -bergamotene (**2**) and *cis* α -bisabolene (**5**) as standards (Table 6A) and as targets (Table 6B). The vapor pressures used in correlations that included both of these sesquiterpenes as standards were those previously evaluated for the two sesquiterpenes using a series of oligocyclic compounds. Correlations were conducted at temperatures from $T = (298.15, 310)$ and at 10 K intervals up to 410 K. Correlation coefficients (r^2) varied from 0.999 at $T = 298.15$ to 0.9931 at $T = 410$ K. Above 410 K, correlation coefficients rapidly dropped below $r^2 = 0.99$. As a result, these correlations were terminated at $T = 410$ K. Correlations using *n*-alkanes that included (**2**) and (**5**) as targets were extended to 450 K without any significant changes in the correlation coefficients; all r^2 values exceeded 0.999. Eqs. 8 and 9 in Table 6 describe the quality of the results at $T = 298.15$ K. Both sets of vapor pressures evaluated were fit independently to Eq. (2). Constants for Eq. (2) generated using *n*-alkanes and the two sesquiterpenes as targets and as standards are reported in Table 7C and 7D, respectively. A summary and comparison of all vapor pressure at $T = 298.15$ K and boiling temperatures evaluated at $p^{\circ} = 101325$ Pa using both sets of standards are provided in Table 8; results are discussed below.

3.3 Boiling temperature at $p^{\circ} = 101,325$ Pa

Boiling temperatures (T_B) were evaluated by extrapolating Eq. 2 until $\ln(p/p^{\circ}) = 0$. Uncertainties in boiling temperature (p_u) were evaluated by combining the vapor pressures with their uncertainties evaluated at each temperature, fitting the results to Eq. 2 for each substance and solving for the new temperature where $\ln((p+p_u)/p^{\circ}) = 0$. The uncertainties stated in the last

column of Table 7 are reported as the difference in the two boiling temperatures evaluated. These uncertainties reflect the quality of the correlation; uncertainties in T_B may be larger.

Table 6

Correlation of $\ln(p/p^0)$ versus $\ln(t_0/t_a)_{\text{avg}}$ at $T = 298.15$ K of all the major sesquiterpenes of opopanax oil for combined runs 3 and 4 using n-alkanes with and without the use *trans* α -bergamotene (**2**) and β -bisabolene (**5**) as standards; $p^0 = 101325$ Pa

A. 2 and 5 as standards	$\ln(t_0/t_r)$	$\ln(p/p^0)$	$\ln(p/p^0)_{\text{calc}}$	$p_{\text{calc}}/\text{Pa}$	p_{lit}/Pa
n-Tridecane	-6.371	-9.789	-9.771±0.218	5.8±1.2	5.7 [15]
n-Tetradecane	-7.304	-10.936	-10.907±0.231	1.9±0.4	1.8 [15]
<i>cis</i> α -Bergamotene	-7.179		-10.754±0.229	2.2±0.5	NA ^a
α -Santalene	-7.199		-10.780±0.239	2.1±0.5	5.3 [8] ^b , 10.2 [19] ^c
<i>trans</i> α -Bergamotene (2)	-7.373	-10.910	-10.991±0.232	1.7±0.4	1.9±0.7 [10], 2.8 [8] ^b
n-Pentadecane	-8.25	-12.078	-12.059±0.245	0.59±0.15	0.58 [15]
<i>cis</i> α -Bisabolene (5)	-8.049		-11.814±0.242	0.75±0.18	1.1 [8] ^b
β -Bisabolene	-8.062	-11.85	-11.830±0.242	0.74±0.14	0.72±0.2 [11]
n-Hexadecane	-9.177	-13.181	-13.188±0.260	0.19±0.05	0.19 [15]
$\ln(p/p^0) = (1.218 \pm 0.169) \cdot \ln(t_0/t_r) - (2.012 \pm 0.169)$				$r^2 = 0.9987$	(8)
B. 2 and 5 as targets					
n-Tridecane	-6.371	-9.789	-9.798±0.063	5.6±0.4	5.7 [15]
n-Tetradecane	-7.304	-10.936	-10.926±0.066	1.8±0.12	1.8 [15]
<i>cis</i> α -Bergamotene	-7.179		-10.774±0.066	2.1±0.14	NA ^a
α -Santalene	-7.199		-10.799±0.066	2.1±0.14	5.3 [8] ^b , 10.2 [19] ^c
<i>trans</i> α -Bergamotene (2)	-7.373		-11.009±0.067	1.7±0.11	1.9±0.7 [10], 2.8 [8] ^b
n-Pentadecane	-8.25	-12.078	-12.069±0.070	0.58±0.04	0.58 [15]
<i>cis</i> α -Bisabolene	-8.049		-11.826±0.070	0.74±0.05	1.1 [8] ^b
β -Bisabolene (5)	-8.062		-11.842±0.070	0.73±0.05	0.72±0.2 [11]
n-Hexadecane	-9.177	-13.181	-13.190±0.075	0.19±0.14	0.19 [15]
$\ln(p/p^0) = (1.209 \pm 0.006) \cdot \ln(t_0/t_r) - (2.096 \pm 0.049)$				$r^2 = 0.9995$	(9)

^b Estimate.

^c Estimate, sub-cooled liquid.

Table 7

Constants of Eq. (2) evaluated for the targets from runs 1-4; $p^0 = 101325$ Pa; vapor pressures evaluated from $T = (298.15 \text{ to } 450)$ K unless stated otherwise; nBT : normal boiling temperature at $p^0 = 101325$ Pa, uncertainties: 1 standard deviation

A. Oligocyclic compounds: Constants using <i>trans</i> α -bergamotene and β -bisabolene as standards				
	A_s	- B_s	- C_s	$[(nBT_{\text{calc}}/nBT_{\text{lit}})/K]^a$
<i>cis</i> α -Bergamotene	11.777 \pm 0.01	5,369.1 \pm 7.5	396,361 \pm 1355	(520.5 \pm 3.3)/(532.7 \pm 7) [21] ^b
α -Santalene	11.568 \pm 0.006	5,310.7 \pm 4.3	392,560 \pm 777	(523.8 \pm 3.4)/521.2 [8], 525.7 [20]
<i>trans</i> α -Bergamotene	11.992 \pm 0.007	5,526.1 \pm 5.1	390,467 \pm 918	(523.0 \pm 3.4)/((533 \pm 7)[21] ^b , 533.2) [8]
<i>cis</i> α Bisabolene	13.110 \pm 0.004	6,197.8 \pm 3.1	374,450 \pm 552	(526.9 \pm 3.9)/(550 \pm 25)[21] ^b , 549.2 [8]
β -Bisabolene	12.927 \pm 0.005	6,150.9 \pm 3.3	370,621 \pm 589	(529.9 \pm 4.2)/548.2 [8]
B. Oligocyclic compounds: Constants using <i>trans</i> α -bergamotene and β -bisabolene as targets				
<i>cis</i> α -Bergamotene	11.770 \pm 0.01	5,364.5 \pm 9.2	398,174 \pm 1,664	(520.7 \pm 0.8)/(532.7 \pm 7) [21] ^b
α -Santalene	11.561 \pm 0.008	5,306.2 \pm 6.0	394,314 \pm 1,087	(524 \pm 5)/521.2 [8], 525.7 [20]
<i>trans</i> α -Bergamotene	11.986 \pm 0.009	5,521.6 \pm 6.9	392,366 \pm 1,244	(523.2 \pm 4.9)/(533 \pm 7) [21] ^b , 533.2 [8]
<i>cis</i> α Bisabolene	13.105 \pm 0.006	6,193.5 \pm 4.3	376,757 \pm 770	(527.1 \pm 5.6)/(550 \pm 25) ^b , 549.2 [8]
β -Bisabolene	12.922 \pm 0.004	6,146.7 \pm 2.5	372,878 \pm 458	(530.1 \pm 5.9)/548.2 [8]
C. Alkanes: Constants using <i>trans</i> α -bergamotene and β -bisabolene as targets;				
<i>cis</i> α -Bergamotene	8.182 \pm 0.086	2,941.2 \pm 63	808,911 \pm 11,364	(541.9 \pm 0.8)/(532.7 \pm 7)[21] ^b
α -Santalene	8.070 \pm 0.090	2,903.7 \pm 65	812,324 \pm 11,757	(544.6 \pm 0.8)/521.2 [8], 525.7 [20]
<i>trans</i> α -Bergamotene	8.265 \pm 0.88	2,998.0 \pm 64	820,318 \pm 11,576	(544.8 \pm 0.7)/(533 \pm 7) [21] ^b , 533.2 [8]
<i>cis</i> α Bisabolene	8.707 \pm 0.090	3,249.5 \pm 66	857,131 \pm 11,844	(551.6 \pm 0.8)/(550 \pm 25)[21] ^b , 549.2 [8]
<i>B</i> -Bisabolene	8.580 \pm 0.093	3,204.2 \pm 68	860,847 \pm 12,250	(554.4 \pm 0.9)/(548.2) [8]
D. Alkanes: Constants using <i>trans</i> α -bergamotene and β -bisabolene as standards: $410 \geq T/K > 298.15$				
<i>cis</i> α -Bergamotene	9.659 \pm 0.066	3,949.0 \pm 46	637,450 \pm 7,970	(532.7 \pm 11.7)/(532.7 \pm 7)[19] ^b
α -Santalene	9.571 \pm 0.066	3,949.0 \pm 46	638,048 \pm 7,967	(535.0 \pm 12.2)/521.2 [8], 525.7 [20]
<i>trans</i> α -Bergamotene	9.782 \pm 0.062	4,032.1 \pm 43	644,646 \pm 7,452	(535.3 \pm 12)/(533 \pm 7)[21] ^b , 533.2 [8]
<i>cis</i> α Bisabolene	10.336 \pm 0.046	4,358 \pm 32	669,901 \pm 5,601	(541.3 \pm 13.2)/(550 \pm 25)[21] ^b , 549.2 [8]
<i>B</i> -Bisabolene	10.233 \pm 0.047	4,329.0 \pm 32	670,803 \pm 5,623	(543.6 \pm 13.6)/(548.2) [8]

^a Uncertainties in calculated boiling temperatures are a reflection of the quality of the correlations; uncertainties can be larger.

^b Estimate.

Table 8

(A) Comparison of vapor pressures evaluated at $T = 298.15$ K using oligocyclic compounds and n-alkanes; (B) normal boiling temperatures (nBT) at $p^0 = 101325$ Pa ^a

A. Vapor pressures	Oligocyclic Compounds		n-Alkanes		p/Pa
	Runs 1 & 2 ^b	Runs 1 & 2 ^c	Runs 3 & 4 ^b	Runs 3 & 4 ^c	Average
<i>cis</i> α -Bergamotene	2.3±0.5	2.3±0.4	2.1±0.1	2.2±0.2	2.2±0.3
α -Santalene	2.4±0.5	2.4±0.4	2.1±0.1	2.1±0.5	2.3±0.4
<i>trans</i> α -Bergamotene	1.8±0.4	1.8±0.3	1.7±0.1	1.7±0.4	1.8±0.3
<i>cis</i> α -Bisabolene	0.68±0.2	0.69±0.1	0.74±0.05	0.75±0.2	0.72±0.14
β -Bisabolene	0.70±0.2	0.71±0.1	0.73±0.05	0.74±0.1	0.72±0.12
B. Boiling Temp/K	Oligocyclic compounds		n-Alkanes		nBT/K
	Runs 1 & 2 ^b	Runs 1 & 2 ^c	Runs 3 & 4 ^b	Runs 3 & 4 ^c	Lit.
<i>cis</i> α -Bergamotene	520.7±0.8	520.5±3.3	541.9±0.8	532.7±11.7	532.7±7 [21] ^d
α -Santalene	524±5	523.8±3.4	544.6±0.8	535.0±12.2	521.2 [8], 525.7[20]
<i>trans</i> α -Bergamotene	523.2±4.9	523.2±4.9	544.8±0.7	535.3±12.2	533.2 [8], 533±7 [21] ^d
<i>cis</i> α -Bisabolene	527.1±5.6	526.9±3.9	551.6±0.8	541.3±13.2	549.2 [8]
β -Bisabolene	530.1±5.9	529.9±4.2	554.4±0.9	543.6±13.6	548.2 [8]

^a Uncertainties represent one standard deviation; uncertainties only reflect the quality of the correlation and may be larger; vapor pressures and uncertainties evaluated by correlation.

^b Using *trans* α -bergamotene and β -bisabolene as targets.

^c Using *trans* α -bergamotene and β -bisabolene as standards.

^d Estimate.

4. Discussion

As noted in the introduction, two of the components in opopanax oil, *trans* α -bergamotene and β -bisabolene, were studied previously. *trans* α -Bergamotene was studied in a complex mixture; the mass fraction of β -bisabolene was 0.91. An objective of this work was to determine the

reproducibility of the various physical properties evaluated for these two components identified in opananax oil and also present in a complex mixture.

4.1 Vaporization enthalpies

As indicated in Table 4, the vaporization enthalpies at $T = 298.15$ K evaluated in all correlations using *trans* α -bergamotene and β -bisabolene either as targets or standards at $T = 298.15$ K result in values for all that are reproducible and reside within their experimental uncertainties. Treated as targets, both *trans* α -bergamotene and β -bisabolene reproduce their literature values and provide additional confirmation of their identity in the opananax oil. Consistent with previous results on other similar sesquiterpenes [11], α -santalene, a tricyclic sesquiterpene with two quaternary centers, has the smallest vaporization enthalpy followed by the two bicyclic α -bergamotenes with one quaternary center and then the two bisabolenes. Estimated values using Eq. (3) also reproduce the vaporization enthalpy values within the uncertainties cited for all compounds studied.

4.2 Vapor pressures

As has been observed previously, the use of either n-alkanes or oligocyclic hydrocarbons as standards in correlations of $\ln(p/p^0)$ versus $\ln(t_o/t_r)$ produce similar vapor pressures for the targets at and near room temperature. All vapor pressures in Table 8 evaluated at $T = 298.15$ K, with and without the use of *trans* α -bergamotene and β -bisabolene as standards, agree within their stated uncertainties. For the mixture containing n-alkanes and both sesquiterpenes, as the temperature is raised, the vapor pressures evaluated for the two sesquiterpenes (derived from oligocyclic compound) begin to diverge from those of the n-alkane standards, resulting in a rapid decrease in the correlation coefficient. For this specific mixture of n-alkanes and sesquiterpenes, the decrease occurs above $T = 410$ K. This divergence results from the slightly greater curvature exhibited by the n-alkanes in plots of $\ln(p/p^0)$ versus K/T . Consequently, somewhat larger boiling temperatures are predicted at $p^0 = 101325$ Pa when using n-alkanes as compared to using only oligocyclic compounds as standards. As indicated in the last column of Table 7 (B and C), roughly a 20 K difference is observed in boiling temperatures evaluated at $p^0 = 101,325$ Pa when vapor pressures are extrapolated over a temperature range of about 100 K using these two different sets of standards.

The n-alkanes and oligocyclic compounds are each representative of a class of compounds that appear at opposite ends of the spectrum with regards to intramolecular flexibility. The n-alkanes have structures with the potential for great internal flexibility while the oligocyclic compounds are substances that are relatively rigid in comparison. The bergamotenes and bisabolenes are likely examples of substances with some intermediate degree of flexibility. As mentioned above, in an effort to better model somewhat more flexible sesquiterpene systems, vapor pressures derived from the set of constants of Eq. (2) for α *trans*-bergamotene and β -bisabolene evaluated previously using oligocyclic standards, were combined together with vapor pressures for the n-alkanes in correlations of $\ln(p/p^\circ)$ versus $\ln(t_o/t_r)$ as a function of temperature. The experiments were designed to evaluate whether at the lower temperatures, where both sets of vapor pressures correlate reasonably well, inclusion of the two sesquiterpenes would result in a new set of hybrid constants for both that would cause some attenuation of the curvature observed with the n-alkanes and simultaneously perhaps, somewhat enhance the curvature observed for the two sesquiterpenes. The last column of Table 7 lists the predicted boiling temperatures of each compound according to the standards used. A comparison of Table 7C, which only used n-alkanes as standards, to 7D, which used a combination of standards, resulted in a decrease of roughly 10 K in the predicted boiling temperatures of the targets. This is about half the difference observed previously (Table 7B and 7C). A comparison of the boiling temperatures reported in Table 7A and Table 7D, show roughly a similar increase in boiling temperature evaluated for the targets. Changes reported in Table 7D come at the expense of limiting the temperature range of the correlations, in this case from $T = (298,15- 410)$ K, and in an increase in the uncertainty associated in boiling temperature predictions at $p^\circ = 101,325$ Pa. Nevertheless, the use of such mixtures or the hybrid constants of Eq. (2) derived from them, may prove useful in evaluating similar properties of other cyclic hydrocarbons that would be expected to exhibit some intermediate degree of curvature as a function of temperature relative to the two sets of standards currently employed.

Tables (S6) and (S7) (Supporting Information) compare the vapor pressures evaluated in this work by correlation for the two bisabolenes and the two bergamotenes, respectively, using three different sets of standards, oligocyclics combined with the two sesquiterpenes, n-alkanes including the two sesquiterpenes and just n-alkanes. A fourth comparison, using only oligocyclic compounds resulted in virtually identical results to those including the two sesquiterpenes and

are not tabulated. Vapor pressures rounded to two significant figures reported from $T = 298.15$ K to either $T = (410 \text{ or } 450)$ K were evaluated by correlation and those at higher temperatures are extrapolations of Eq. 2 evaluated by fitting each set of data evaluated from $T = (298.15 \text{ to either } (410 \text{ or } 450))$ K as described above. The vapor pressures of *trans* α -bergamotene and β -bisabolene were both not used in correlations involving their own evaluation with either set of standards. A gradual decrease in the evaluated vapor pressures is generally observed in going from oligocyclic compounds (with or without the two sesquiterpenes) to a combination of n-alkanes and the two sesquiterpenes to the sole use of n-alkanes as standards. In the case of the bisabolenes (Table S6), the absolute average deviation between vapor pressures calculated using only oligocyclic standards (OC) and the mix of n-alkanes and the two sesquiterpenes as standards (A & αB) was approximately 13 %. This decreased to approximately 11% for the bergamotenes (Table S7), primarily due to their lower boiling temperature. The major differences in vapor pressure between the use of the different sets of constants of Eq. (2) occurred at elevated temperatures. Availability of some reliable experimental vapor pressures evaluated at elevated temperatures would be extremely useful in future studies for fine tuning the fits. Unfortunately, very little experimental data, some of questionable reliability, are available for many of the materials in this study.

The vapor pressures of the n-alkanes evaluated in these correlations were also affected by inclusion of the vapor pressures of the two sesquiterpenes as standards, but only minimally. Fitting the calculated vapor pressures of the n-alkanes that resulted from inclusion of the two sesquiterpenes as standards to Eq. 2 and extrapolating the resulting equations from $T = 420$ K to temperatures where $\ln(p/p^\circ) = 0$, resulted in temperature decreases of $\Delta T = (5.8, 3.0, 4.5 \text{ and } 6.4)$ K for n-tridecane to n-hexadecane, respectively (all normal boiling temperatures > 500 K). The vaporization enthalpies at $T = 298.15$ K calculated using these hybrid alkane constants and the predicted boiling temperatures at $p^\circ = 101,325$ Pa are provided in Table S8. As indicated in the table, the vaporization enthalpies calculated at $T = 298.15$ K using Eq. (2) and the hybrid constants still remain within their original uncertainties. The vaporization enthalpies of two smaller n-alkanes decreased in value while the two larger n-alkanes increased slightly.

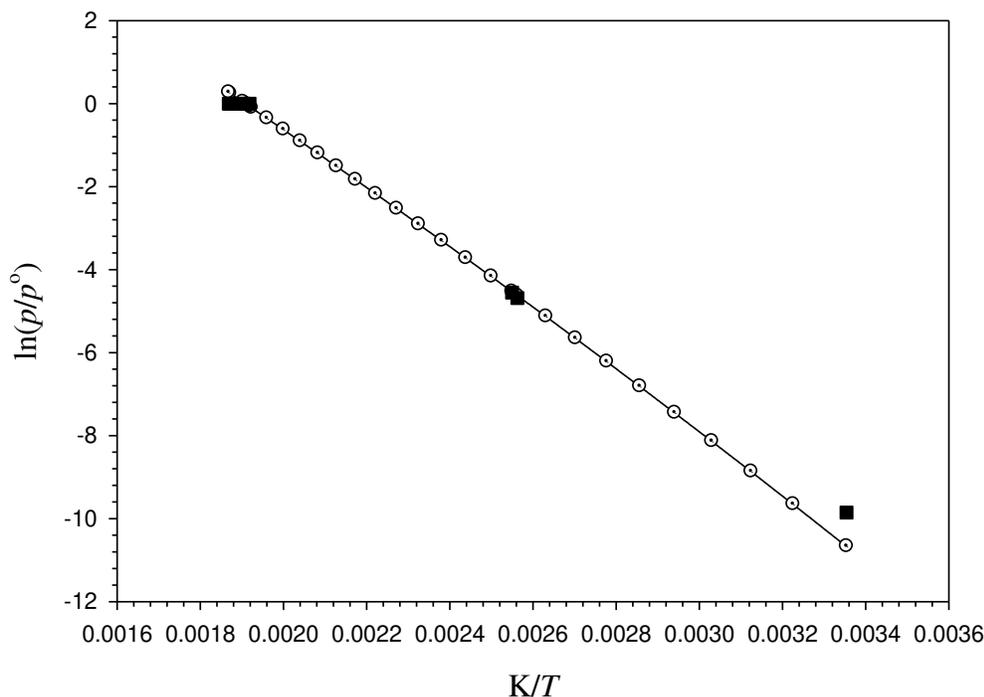
As noted in the introduction, a goal of this work was to confirm reproducibility of properties evaluated previously. The vaporization enthalpies of *trans* α -bergamotene and to a lesser extent β -bisabolene, were both evaluated from complex mixtures; similarly in this study. While

vaporization enthalpies are reproduced, it seem prudent to also examine the reproducibility of the vapor pressures evaluated. Table S9 compares the vapor pressures evaluated for β -bisabolene and *trans* α -bergamotene evaluated previously to results from this work using a similar set of oligocyclic compounds. For β -bisabolene, and *trans* α -bergamotene average absolute fractional deviations of 0.026 and 0.024 were obtained prior to rounding the results to two significant figures, confirming that results obtained from complex mixtures, provided the compounds are properly identified and reasonably separated from other components, are reproducible.

Despite the availability of some experimental vapor pressure data for the compounds investigated, most data are in the region where vapor pressure differences between the predictions by the different standards studied are small and the scatter in the experimental data is sufficient to make unequivocal decisions difficult. Recommendations are based mainly on reproduction of the experimental boiling temperatures at various pressures; structure was also an important consideration, particularly with geometric isomers.

A limited amount of vapor pressure data from the literature was located for α -santalene. Results from this work and the data we have been successful in locating are summarized in Figure 2. The line in Figure 2 represents $\ln(p/p^\circ)$ data evaluated using oligocyclic standards when both *trans* α -bergamotene and β -bisabolene are included as standards and the circles are results when the two sesquiterpenes were evaluated as targets. The solid squares represent literature values. The square at $T = 298.15$ K represents an estimated value (lower right). More quantitative comparisons are provided in Table S10. This table compares vapor pressures evaluated using as standards, n-alkanes, n-alkanes with both sesquiterpenes, and oligocyclic compounds without and with both sesquiterpenes; literature values are listed in the final column. As indicated in Table S10, vapor pressures evaluated by boiling temperatures at reduced pressures are generally fit by all sets of standards. The selection of the preferred standards for α -santalene is based on two criteria, a single vapor pressure, the experimental boiling temperature of 521.2 K at $p^\circ = 101325$ Pa (the other is an estimate), and the structural similarities of α -santalene to the oligocyclic standards. The following progression in estimated boiling temperatures is generally observed: n-alkanes > n-alkanes with both sesquiterpenes > oligocyclic compounds \square oligocyclic compounds with both sesquiterpenes. The constants of Eq. (2) generated using oligocyclic

standards that include both sesquiterpenes have been selected as providing best vapor pressure model. The properties recommended for α -santalene are summarized in Table 9.



on an estimated T_B and the structural relationship to its *trans* isomer. Properties selected for both bergamotenes are also summarized in Table 9.

For β -bisabolene (**5**) and similarly for *cis* α -bisabolene (**4**), assignment of which constants to recommend is more problematic. Previously, the constants derived using oligocyclic standards were selected for (**5**) based on an overall fit to literature data. In the present work, the combination of the n-alkanes with the two sesquiterpenes reproduce boiling temperatures at reduced pressures nearly as well as the oligocyclic compounds and do slightly better at predicting the boiling temperature at $p^\circ = 101325$ Pa of β -bisabolene as indicated in Table S12. While there may be an inclination to recommend the same mixture of n-alkanes and sesquiterpenes for *cis* α -bisabolene (**4**) based on functional group similarities, in this case, the n-alkanes may provide slightly better overall predictions, admittedly, on the basis of very limited data (Table S12).

Table 9

A summary of the recommended vaporization enthalpies (kJ mol^{-1}), vapor pressures at $T = 298.15$ K from this study and suggested constants of Eq (2) ^a

	$\Delta_l^g H_m(298\text{ K})$	A_s	$-B_s$	$-C_s$	$p/\text{Pa}(298\text{ K})$ ^b
α -Santalene	67.9±1.7	11.568±0.006	5,310.7±4.3	392,560±777	2.3±0.4
<i>cis</i> α -Bergamotene	68.4±1.7	9.659±0.066	3,949.0±46	637,450±7970	2.2±0.3
<i>trans</i> α -Bergamotene	69.5±1.7 ^c	9.782±0.062	4,032.1±43	644,646±7452	1.8±0.3 ^d
β -Bisabolene	73.9±2.2	10.233±0.047	4,329.0±32	670,803±5,623	0.71±0.14 ^d
<i>cis</i> α -Bisabolene	74.3±2.2 ^d	8.707±0.090	3,249.5±66	857,131±11844	0.72±0.2

^a Uncertainties represent one standard deviation; vapor pressures and vaporization enthalpies are an average of the eight entries from Table 4 unless noted otherwise.

^b Uncertainties in vapor pressure are an measure of the overall quality of the correlations; actual uncertainties may be larger.

^c An average of eight runs, four from this work, plus, four from reference [10].

^d An average of six runs, four from this work, plus, two from reference [11].

5. Summary

The vapor pressures and vaporization enthalpies of three of the major sesquiterpenes present in opopanax oil were evaluated by correlation gas chromatography using several different sets of standards. Both vaporization enthalpy and vapor pressures results at $T = 298.15$ K obtained for *trans* α -bergamotene and β -bisabolene are consistent with their assignment in opopanax oil and with previous work [10, 11]. Vaporization enthalpies at $T = 298.15$ K evaluated for the target substances using the different sets of standards are all well within their stated uncertainties. Values from from this and previous studies are provided in Table 9. The vaporization enthalpies for *cis* α -bergamotene, β -santalene and *cis* α -bisabolene are an average of all eight entries from Table 4. The vaporization enthalpies reported for both *trans* α -bergamotene and β -bisabolene are an average of the four entries from this work where they were used as targets and the four entries reported in references [10] and [11], respectively.

The oligocyclic standards appear to provide the best agreement with available literature vapor pressures for α -santalene. Comparisons are provided in Table S10 and summarized in Table 9. For the two bergamotene isomers, the combination of n-alkanes and the two sesquiterpenes as standards seem to provide the best fit as summarized in Table S11, albeit on very limited data. As noted above, assignment of which constants to recommend for β -bisabolene (**5**) and *cis* α -bisabolene (**4**) is more problematic. Constants generated using n-alkanes are recommended for *cis* α -bisabolene and the the n-alkanes combined with the two sesquiterpenes are recommended for β -bisabolene.

The set of hybrid constants for the n-alkanes generated in this study may also prove useful for evaluating vapor pressures of other sesquiterpenes whose curvature in plots of $\ln(p/p^\circ)$ versus $\ln(t_0/t_r)$ at elevated temperatures is less than that of the n-alkanes, but more than the oligocyclic standards currently used. These hybrid constants are provided in the Supporting Information, Table S8. Finally, as noted previously, the availability of a reliable experimental vapor pressure at elevated temperatures would be extremely useful for fine tuning the results obtained by correlation at elevated temperatures when appropriate standards are not available.

7. Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org>

8. Declarations

Ethics approval: The ethical guidelines cited in the “Instructions for Authors” have been followed.

Consent to participate: The authors approve the version of the manuscript to be published.

Consent for publication: the authors consent.

Authors contributions: Dustin Barton: experimental; James Chickos: all else.

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Availability of data and material: Supporting Information on-line.

Code availability: Not applicable.

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Figures

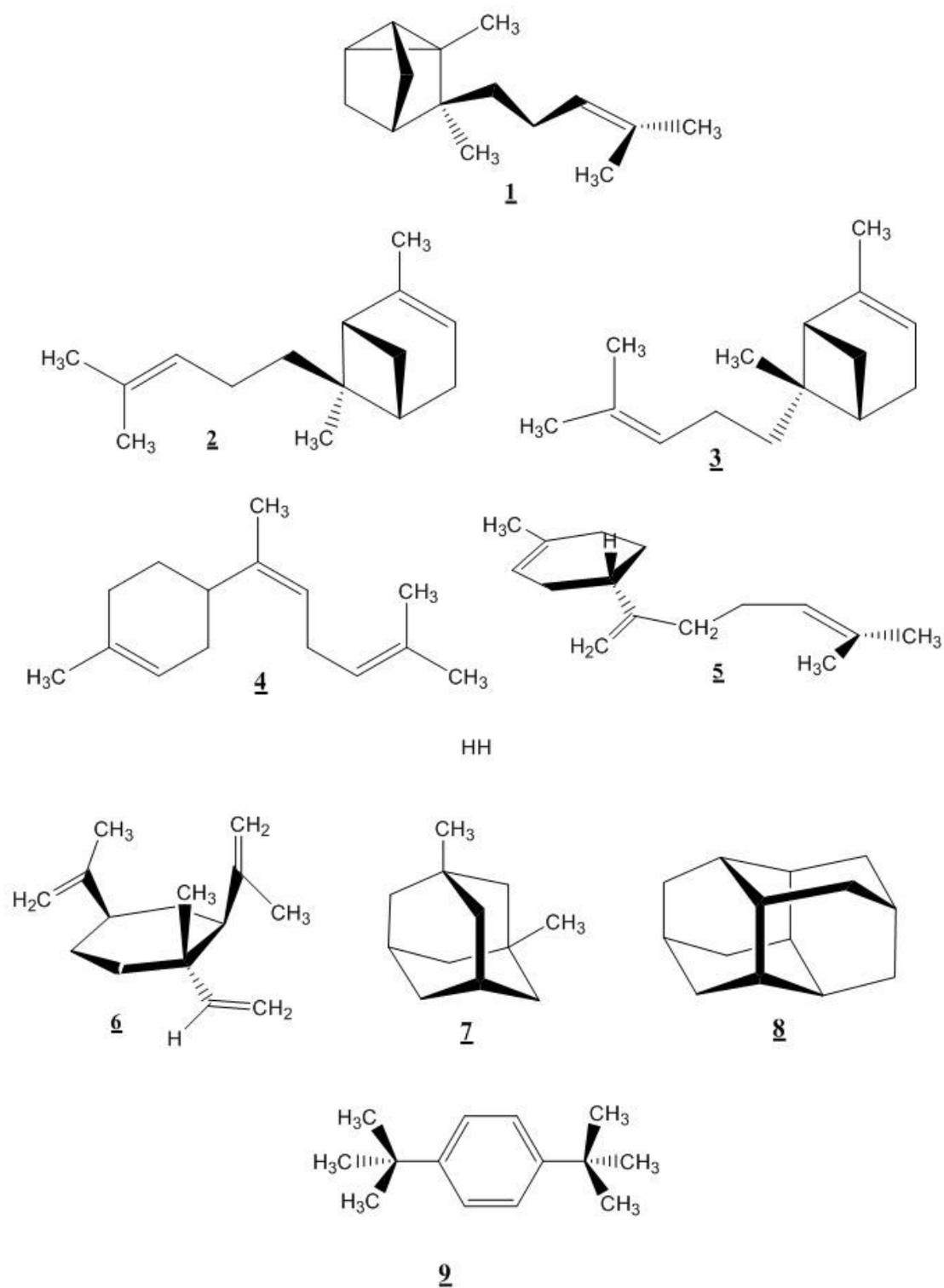


Figure 1

Structure of the targets and cyclic standards discussed in this article. From left to right: α -santalene (1), trans α -bergamotene (2), cis α -bergamotene (3), cis α -bisabolene (4), β -bisabolene (5). Standards: β -

elemene (6), 1,3-dimethyladamantane (7), diamantane (8), 1,4-di-t-butylbenzene (9). Structures of the n-alkanes used as standards are not shown.

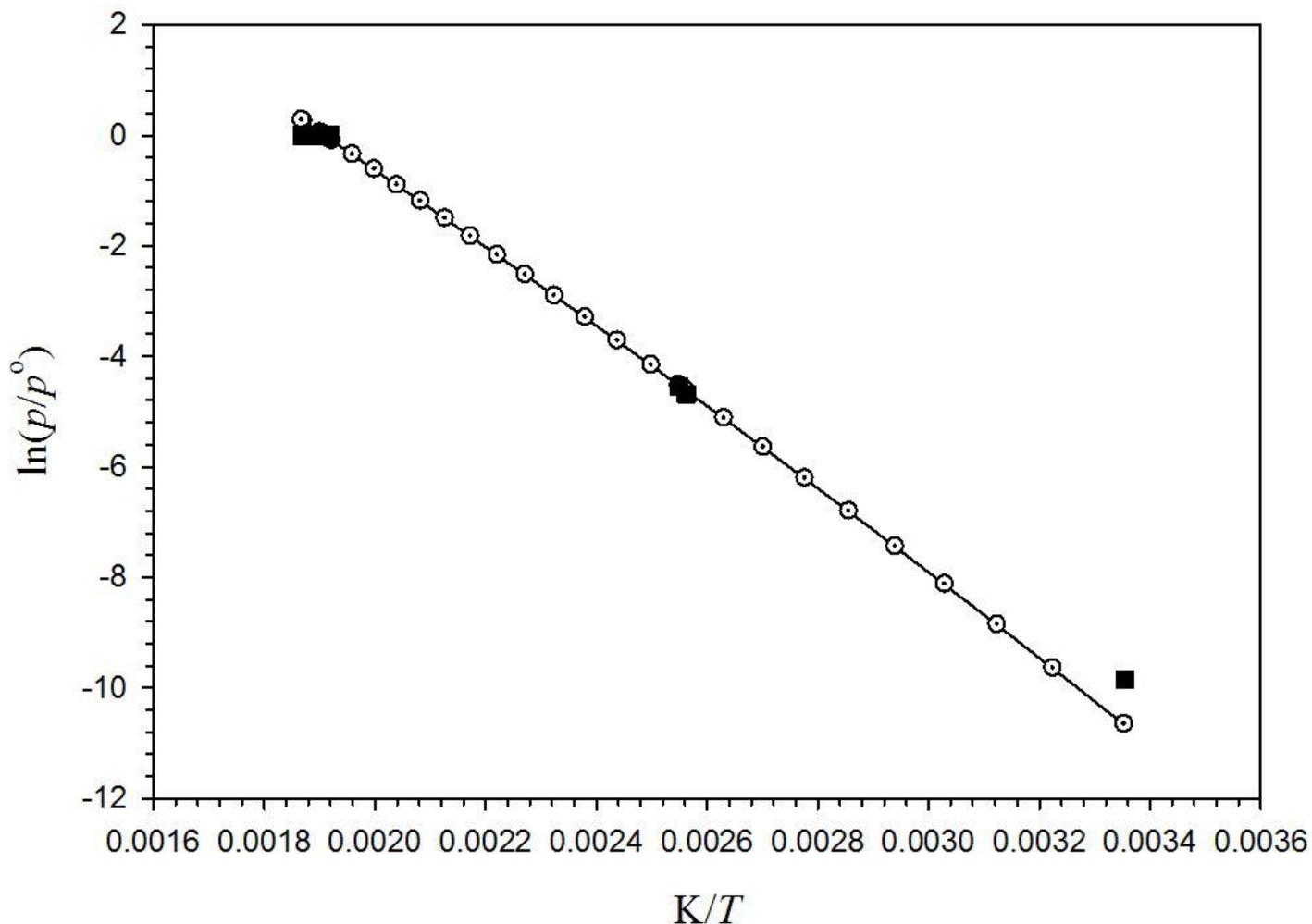


Figure 2

A plot of $\ln(p/p_0)$ versus K/T for α -santalene. The circles represent data using oligocyclic standards exclusive of $\text{trans } \alpha$ -bergamotene and β -bisabolene and the line represents results that included both as standards. The solid squares represent literature data. The value at $T = 298.15$ K (lower right) represents an estimated value.

Supplementary Files

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