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Gas chromatographic determination of vapour pressures of pheromone-like compounds II. [☆] Alcohols

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Abstract

The vapour pressures of 98 (*Z*)- and (*E*)-monounsaturated C₁₀-C₁₈ alcohols were determined using a method based on gas chromatographic retention data. This method, by utilizing a non-polar HP-1 capillary column, five experimental temperatures, four reference compounds (C₁₁, C₁₂, C₁₄ and C₁₆ alkanols) whose polarities approximated that of the test compounds and melting point corrections for compounds that are solids at ambient temperature, provided vapour pressures that agreed reasonably well with the available literature values. For alkenols belonging to structurally similar subseries, e.g., for ω -3, ω -5 and ω -7 unsaturated derivatives, the vapour pressures may be represented over a range of pressure by simple equations in which the number of carbon atoms is a parameter.

1. Introduction

The saturation properties of pure liquids play a major role in both the understanding of fluid phase behaviour and the design and operation of a multitude of industrial processes [1,2]. Such properties are essential not only when used directly in calculations, but also when

used as input to variety of models and applications.

At present, there is an increasing need for vapour pressures of high-molecular-mass organic compounds at ambient temperatures [3,4]. One of the most important reasons for this is the increased public sensitivity to the effect of chemicals on health and the environment generally. As the vapour pressure of an organic chemical exerts a large influence on its dispersal in the environment, a knowledge of the vapour pressures should allow one not only to model the fate of organic pollutants [5,6] but

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[☆] For Part I, see Ref. [20].

also to optimize the use of ecologically friendly behaviour-modifying chemicals [7]. An impetus for developing more effective design for practical applications of these compounds is the continuing value of pheromones for monitoring insect flight activity and the recent commercial success in controlling several pests by permeating the air with their sex pheromones [7]. Both the release rates and, in the case of blends, the release ratios of pheromone components from dispensers are governed, for the most part, by the vapour pressures of the compounds. It appears that environmental concerns are weighing against the use of traditional pesticides and expectations are [8] that pheromones will capture about 15–40% of the insecticide market within 10 years. Thus, an understanding of the pheromone evaporative process can aid in the optimization of selectivity conditions and the minimization of the loss of the biological activity of synthetic pheromone blends.

The vapour pressures of compounds of low volatility are commonly determined by either gas saturation [9,10] or effusion [11] methods. Gas chromatography (GC) is an alternative method for measuring vapour pressures [12,13], offering advantages in terms of speed, solute sample size, purity and stability requirements. It is based on the use of a non-polar stationary phase and isothermal conditions such that a compound's GC retention time is related directly to its vapour pressure. The GC method has been used to study polychlorinated biphenyls and dioxins [14,15], herbicide esters [12], organophosphorus pesticides [16], tetraorganostannanes [17], linear alkylbenzenes [18] and fatty acid methyl esters [19]. Using this approach, we have obtained [20] some vapour pressure data on pheromone-like acetates.

In this paper we show that the GC method yields equally good results in determining equilibrium vapour pressures of more polar compounds, viz. monounsaturated (C_{10} – C_{18}) pheromone-like alcohols. The extensive set of 98 compounds studied also allowed the influence of subtle structural differences in chain length and the positions of double bonds on vapour pressures to be revealed.

2. Experimental

2.1. Chromatography

Samples were analysed on a Hewlett-Packard HP 5890 chromatograph equipped with a $3\text{ m} \times 0.31\text{ mm}$ I.D. fused-silica capillary column (cross-linked 5% methylsilicone, HP-1, film thickness $0.52\ \mu\text{m}$) with split injection and a flame ionization detector. The length of the column employed (3 m) is a compromise between the need for acceptable resolution when working with mixtures and the need to avoid prohibitively long retention times, particularly at lower temperatures. The chromatograph was operated isothermally with a hydrogen flow-rate of 5 ml/min at 10°C intervals in the range 50 – 160°C as specified. C_{11} , C_{12} , C_{14} and C_{16} alkanols were used as reference standards. Retention times were determined on a Hewlett-Packard HP 5895A ChemStation. Adjusted retention times were calculated by subtracting the retention time of methane from the retention time of the chemical. As recommended [13], long retention times of compounds producing unsymmetrical peaks at low temperatures were not taken at the peak maximum, but were estimated at the centre of gravity of the peak. The reproducibility of retention time measurements expressed as the relative standard deviation of at least three measurements for each compound was 0.03%.

2.2. Chemicals

The alcohols were either obtained from the Research Institute for Plant Protection (IPO-DLO) (Wageningen, Netherlands) and used as received or synthesized in our laboratory. In the latter instance, the purity of the chemicals was at least 97% as determined by capillary GC. Condensed nomenclature for alcohols is used: the letters after the colon indicate the functional type (OH = alcohol), the number between the dash and colon indicate the number of carbon atoms in the chain and the letters and numbers before the dash indicate the configuration and

position of the double bonds, e.g., Z3-10:OH is (Z)-3-decenol.

2.3. Data treatment

The method has been discussed in detail by Bidleman [13] and Hinckley et al. [21] and will therefore be only briefly reviewed here. At a constant temperature, the vapour pressures of a test and of a reference compound (subscripts T and R, respectively) are related by the ratio of their latent heats of vaporization:

$$\ln P_T = \frac{\Delta H_T}{\Delta H_R} \cdot \ln P_R + C \quad (1)$$

where ΔH is the latent heat of vaporization and C is a constant. A similar equation has been developed for the GC (adjusted) retention times t' :

$$\ln \left(\frac{t'_T}{t'_R} \right) = \left(1 - \frac{\Delta H_T}{\Delta H_R} \right) \ln P_R - C \quad (2)$$

Hence, a plot of $\ln(t'_T/t'_R)$ versus $\ln P_R$ should have a slope $1 - \Delta H_T/\Delta H_R$ and an intercept $-C$. Eq. 1 can then be used to determine the vapour pressure of the test compound at any temperature if the vapour pressure of the reference compound at that temperature is known.

Since the GC method gives the subcooled liquid vapour pressure (defined as the liquid vapour pressure extrapolated below the melting point) [22], it was necessary to convert the literature-based solid vapour pressures (P_S) into subcooled liquid vapour pressures (P_L) by using the equation developed by Mackay et al. [23]:

$$\ln \left(\frac{P_S}{P_L} \right) = -\frac{\Delta S_F}{R} \left(\frac{T_M}{T} - 1 \right) \quad (3)$$

where T_M and T are the absolute melting and ambient temperatures, respectively, R is the gas constant and ΔS_F is the entropy of fusion. The usually employed "average" value of $\Delta S_F = 56.5$ J/K·mol (or the corresponding value $\Delta S_F/R = 6.79$) seems to be too low for alcohols, however. Based on the value of enthalpy of fusion (ΔH_F) published [24] for 1-hexadecanol (34.286 kJ/mol), ΔS_F for this compound amounts 106.34

J/K·mol and, as a consequence, $\Delta S_F/R = 12.789$. Hence this constant was used to convert literature P_S values of 1-hexadecanol and 1-pentadecanol into P_L .

2.4. Statistical analysis

The data were subjected to statistical analyses utilizing the Statgraphics Plus 7.0 software package (Manugistic, Rockville, MD, USA).

3. Results and discussion

The accuracy of the GC method as represented by Eqs. 1 and 2 depends to a large extent on two factors: (i) the accuracy of the P_R values and (ii) the similarity of infinity dilution activity coefficients γ in the stationary phase between the test and reference compounds to which Eq. 2 is applied. Strictly, an additional term, $-\ln(\gamma_T/\gamma_R)$, should appear (see discussion in Ref. [21]) on the right-hand side of this equation and only when $\gamma_T \sim \gamma_R$ (or at least $\gamma_T/\gamma_R \sim \text{constant}$) can the use of Eq. 1 lead to reasonable results. As values of γ on a squalane liquid phase have been found [25] to range from 0.48 to 0.73 for hydrocarbons and from 17 to 34 for alcohols, the frequently employed reference hydrocarbons seemed to be disqualified for our purposes. Therefore, we chose to use *n*-alkanols (i.e., compounds of the same chemical class as the test compounds) as the reference standards. When literature vapour pressure values were being selected for the reference *n*-alkanols, some judgment was necessary. We favoured recent static measurements [26] that have been especially focused on the low vapour pressure field. The literature values of the four reference compounds given in Table 1 in the form of the Antoine equation are thus from a single report. In most instances vapour pressures were calculated from the Antoine constants by interpolation. In those instances where some extrapolation was necessary (14:OH, 15:OH and 16:OH), the temperature range of extrapolation was usually less than 40 K.

As the choice of the P_R is critical for the

Table 1
Vapour pressures (P_R) of the reference n -alkanols

Alkanol	Constants of the Antoine equation ^a			P_R (25°C) (Pa)
	A	B	C	
11:OH	7.094	2105.005	176.145	0.4255
12:OH	6.860	2011.634	162.769	0.1402
14:OH	6.916	2217.995	165.381	0.01844
16:OH	5.964	1781.618	120.726	0.00207 ^b

^a Ref. [26]; $\log P$ (kPa) = $A - B/(t + C)$.

^b Vapour pressure is for the subcooled liquid; it was calculated from the original solid vapour pressure ($5.4726 \cdot 10^{-4}$ Pa) using Eq. 3 and m.p. 56°C.

accuracy of vapour pressures determined by the comparative GC method, the literature P_R data were checked for internal consistency. Examination of the logarithm of vapour pressure (corrected for melting point) as a function of the number of carbon atoms in alkanol series (Fig. 1) confirms that an excellent linear correlation, $\ln P = (-1.0675 \pm 0.0058)n_C + (10.8973 \pm 0.0734)$ ($n = 7$, S.E. = 0.0374, $r^2 = 0.9999$), does exist.

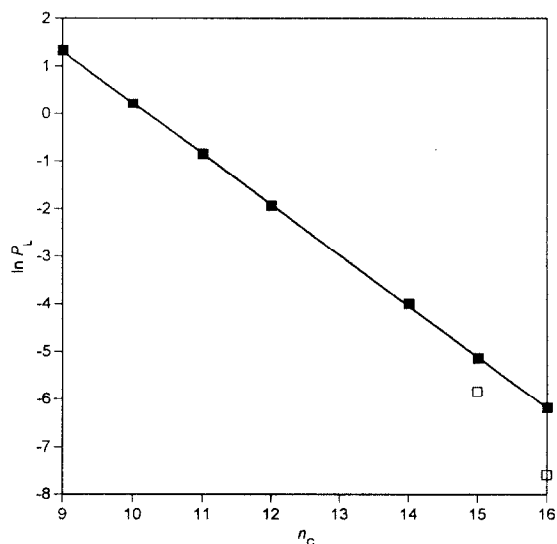


Fig. 1. Liquid vapour pressures (Pa) (25°C) of alkanols [25] as a function of the number of carbon atoms. □ = Original (solid) vapour pressures of 15:OH and 16:OH.

Table 2
Adjusted GC retention times (min) of the n -alkanols

Alkanol	80°C	90°C	100°C	110°C	120°C
9:OH	0.773	0.482	0.332	0.237	0.172
10:OH	1.553	0.926	0.605	0.409	0.283
11:OH	3.162	1.800	1.123	0.724	0.481
12:OH	6.557	3.541	2.122	1.313	0.837
14:OH	26.696	13.305	7.385	4.242	2.256
15:OH	53.448	25.600	13.698	7.600	4.379
16:OH	110.337	50.162	25.846	13.914	7.757

3.1. Validation of the method

Six n -alkanols with known P_L [26] were chromatographed along with the 14:OH reference, and P_{GC} values at 25°C were calculated from the relative retention data (Table 2) using Eqs. 1 and 2. In Fig. 2, these P_{GC} values are compared with P_L . As can be seen, the regression line obtained closely parallels the $y = x$ line. The equation of the regression line by a linear least-squares fit is

$$\ln [P_L \text{ (Pa)}] = (1.02536 \pm 0.0049) \ln P_{GC} \quad (4)$$

($n = 6$, S.E. = 0.0402, $r^2 = 0.9999$)

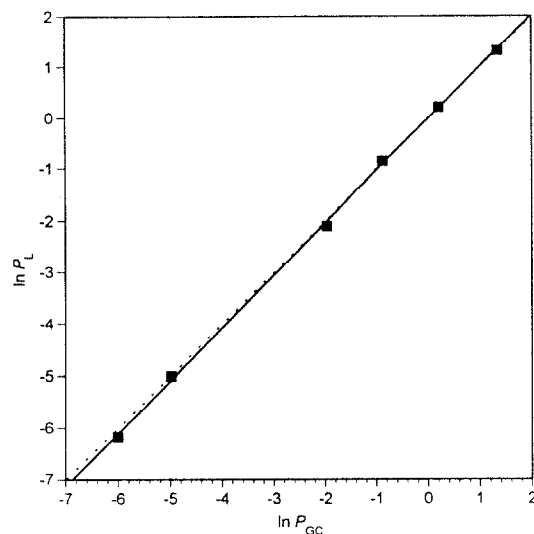


Fig. 2. Logarithmic plot of the literature vapour pressures P_L of alkanols (25°C) vs. the corresponding P_{GC} data (Eq. 1) from the present work. The regression line (solid) and $y = x$ line (dashed) are shown.

with a slope nearly equal to 1. Note that in Eq. 4 the intercept has not been included at the 0.05% probability level. The quality of fit produced by the proposed vapour pressure correlation is excellent, thus demonstrating the validity of the GC method even for polar compounds.

Another noteworthy feature of this correlation is that it appears to be applicable over a range of pressures that covers three orders of magnitude. Table 3 presents a comparison between the GC-based and literature vapour pressure data. Our corrected (Eq. 4) vapour pressures differ from those given by N'Guimbi et al. [26] by values ranging from 0.6% (for 10:OH) to 5.3% (for 12:OH). In addition to the original database [26] employed in deriving Eq. 4, Table 3 also includes a complete data set [3] obtained from the Chebyshev-type polynomial in x of degree 3 by extrapolation. This polynomial has been proposed to allow extrapolation for about 150 K with fair confidence. The slightly lower (about 10%) but consistently similar vapour pressure values following from the use of this equation might be regarded as a notable agreement between the two literature data sets. It is noticeable that vapour pressures of 10:OH (1.233 Pa) and 12:OH (0.1328 Pa) following from the use of Eq. 4 compare favourably with the values 1.190 and 0.1397 Pa obtained [27] for these compounds from a simultaneous correlation of vapour pres-

sure and thermal data. Hence it appears that the GC method is capable of yielding vapour pressures of saturated alcohols with an error below 10%.

This conclusion finds further support in the estimated heats of vaporization. In deriving vapour pressures from GC retention time data, $\Delta H_T/\Delta H_R$, the ratio of the enthalpies of vaporization of a test to that of the reference compound is obtained. Hence, by utilizing the literature [28] experimental ΔH_R value for our reference standard, 14:OH (102.2 ± 2.4 kJ mol⁻¹), the remaining enthalpies of vaporization of alkanols may be calculated from the $\Delta H_T/\Delta H_R$ ratios given in Table 3. The results calculated by this approach are 72.17 kJ mol⁻¹ for 9:OH, 79.27 kJ mol⁻¹ for 10:OH and 91.69 kJ mol⁻¹ for 12:OH. These values compare well with the corresponding calorimetric data, viz. 76.86 ± 0.75 , 81.50 ± 0.75 and 91.96 ± 0.59 kJ mol⁻¹, respectively, yielding a maximum error of 6.1%.

3.2. Vapour pressures of alkenols

Vapour pressures of all measured alkenols were determined by the same approach as described above for saturated compounds. Taking advantage of the internal consistency of the vapour pressure data for saturated derivatives demonstrated above, the test compounds were

Table 3
Parameters of Eq. 2 and vapour pressures (25°C) of the *n*-alkanols

Alkanol ^a	$\Delta H_T/\Delta H_R$	C	P · 1000 (Pa)				Error ^e (%)
			Eq. 1	Eq. 4	Exp. ^b	Exp. ^d	
9:OH	0.7062	4.1446	3760	3888	3738	3334	4.0
10:OH	0.7756	3.3008	1226	1233	1241	1087	-0.6
11:OH	0.8379	2.4614	412.9	403.7	425.0	378.1	-5.0
12:OH	0.8972	1.6137	139.6	132.8	140.2	136.1	-5.3
15:OH	1.0493	-0.7941	6.846	6.033	5.894 ^c	5.335	2.4
16:OH	1.1007	-1.6180	2.446	2.100	2.069 ^c	1.842	1.5

^a Standard 14:OH.

^b Ref. [25].

^c Corrected by using Eq. 3.

^d Ref. [3].

^e Error = $100(P_{GC} - P_{EXP})/P_{EXP}$; P_{EXP} taken from Ref. [25].

Table 4
GC data and vapour pressures (25°C) of decenols

Alcohol	Relative retention time ^a					P (Pa)	
	50°C	60°C	70°C	80°C	90°C	Eq. 1	Eq. 4
Z3-10:OH	0.128	0.146	0.168	0.189	0.210	1.669	1.691
E3-10:OH	0.125	0.142	0.163	0.183	0.204	1.704	1.727
Z4-10:OH	0.135	0.153	0.174	0.193	0.214	1.536	1.553
E4-10:OH	0.141	0.160	0.179	0.198	0.218	1.432	1.445
Z5-10:OH	0.144	0.162	0.183	0.202	0.223	1.406	1.418
E5-10:OH	0.147	0.165	0.185	0.205	0.225	1.367	1.378
Z6-10:OH	0.147	0.166	0.186	0.206	0.227	1.380	1.391
E6-10:OH	0.147	0.165	0.185	0.205	0.225	1.365	1.376
Z7-10:OH	0.153	0.171	0.192	0.212	0.232	1.311	1.320
E7-10:OH	0.153	0.171	0.191	0.210	0.229	1.294	1.303
Z8-10:OH	0.175	0.195	0.217	0.237	0.258	1.109	1.112
E8-10:OH	0.165	0.183	0.204	0.224	0.244	1.187	1.192

^a Standard 12:OH.

chromatographed using four reference standards: 11:OH (for C₁₂ alkenols), 12:OH (for C₁₀, C₁₃ and C₁₄ alkenols), 14:OH (for C₁₅ and C₁₆ alkenols) and 16:OH (for C₁₈ alkenols).

The relative retention times and calculated

vapour pressures for C₁₀, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆ and C₁₈ alkenols are listed in Tables 4–10. Inspection of these tables reveals that the vapour pressures of all alkenols are similar to those of the corresponding alkanols. In spite of this, two

Table 5
GC data and vapour pressures (25°C) of dodecenols

Alcohol	Relative retention time ^a					P (Pa)	
	60°C	70°C	80°C	90°C	100°C	Eq. 1	Eq. 4
Z2-12:OH	2.034	1.961	1.894	1.827	1.780	0.167	0.160
Z2-12:OH	2.083	2.002	1.933	1.854	1.806	0.162	0.155
Z3-12:OH	1.768	1.726	1.691	1.649	1.624	0.204	1.196
E3-12:OH	1.719	1.682	1.646	1.606	1.591	0.212	0.204
Z4-12:OH	1.793	1.743	1.701	1.652	1.612	0.196	0.188
E4-12:OH	1.896	1.832	1.775	1.715	1.665	0.181	0.173
Z5-12:OH	1.864	1.803	1.753	1.698	1.662	1.187	0.179
E5-12:OH	1.944	1.870	1.811	1.745	1.701	0.175	0.167
Z6-12:OH	1.867	1.800	1.753	1.697	1.664	0.187	0.179
E6-12:OH	1.913	1.839	1.787	1.726	1.673	0.178	0.170
Z7-12:OH	1.901	1.829	1.780	1.720	1.672	0.181	0.173
E7-12:OH	1.951	1.871	1.813	1.748	1.700	0.174	0.166
Z8-12:OH	2.002	1.922	1.855	1.789	1.738	1.169	0.162
E8-12:OH	2.002	1.914	1.855	1.784	1.732	0.169	0.162
Z9-12:OH	2.078	1.986	1.920	1.840	1.789	0.161	0.154
E9-12:OH	2.096	1.998	1.924	1.837	1.775	0.156	0.149
Z10-12:OH	2.402	2.273	2.171	2.065	1.979	0.132	0.125
E10-12:OH	2.246	2.128	2.041	1.946	1.886	1.145	0.138

^a Standard 11:OH.

Table 6
GC data and vapour pressures (25°C) of tridecenols

Alcohol	Relative retention time ^a					P (Pa)	
	70°C	80°C	90°C	100°C	110°C	Eq. 1	Eq. 4
Z7-13:OH	1.762	1.721	1.675	1.633	1.590	0.0673	0.0628
E7-13:OH	1.817	1.769	1.713	1.666	1.619	0.0639	0.0596
Z9-13:OH	1.890	1.839	1.776	1.719	1.674	0.0607	0.0565
E9-13:OH	1.939	1.856	1.790	1.728	1.678	0.0575	0.0534
Z11-13:OH	2.266	2.177	2.077	1.999	1.920	0.0472	0.0436
E11-13:OH	2.167	2.077	1.982	1.900	1.833	0.0491	0.0455

^a Standard 12:OH.

subtle trends are apparent in all series considering the influence of double bond position: (i) the vapour pressures of series members with a double bond located near the centre of the carbon chain are generally higher than those of the corresponding saturated compounds and (ii) the

vapour pressures of isomers with a double bond positioned on the second carbon atom of the chain (irrespective of the end of the molecule from which the numbering starts) are either close to or lower than those of the saturated compounds. It appears that the double bond position

Table 7
GC data and vapour pressures (25°C) of tetradecenols

Alcohol	Relative retention time ^a					P (Pa)	
	80°C	90°C	100°C	110°C	120°C	Eq. 1	Eq. 4
Z2-14:OH	3.820	3.538	3.299	3.113	2.911	0.0211	0.0191
E2-14:OH	3.883	3.586	3.345	3.140	2.925	0.0203	0.0184
Z3-14:OH	3.389	3.186	3.013	2.847	2.685	0.0256	0.0234
E3-14:OH	3.286	3.083	2.912	2.767	2.609	0.0267	0.0243
Z4-14:OH	3.358	3.157	2.966	2.811	2.650	0.0256	0.0233
E4-14:OH	3.526	3.289	3.079	2.902	2.723	0.0234	0.0213
Z5-14:OH	3.408	3.217	3.017	2.843	2.663	0.0246	0.0224
E5-14:OH	3.551	3.308	3.096	2.917	2.729	0.0230	0.0209
Z6-14:OH	3.343	3.138	2.954	2.798	2.634	0.0257	0.0234
E6-14:OH	3.462	3.243	3.050	2.865	2.686	0.0240	0.0218
Z7-14:OH	3.340	3.134	2.959	2.798	2.634	0.0258	0.0235
E7-14:OH	3.485	3.259	3.057	2.883	2.704	0.0239	0.0217
Z8-14:OH	3.412	3.209	3.004	2.840	2.665	0.0246	0.0224
E8-14:OH	3.616	3.301	3.087	2.922	2.719	0.0220	0.0200
Z9-14:OH	3.512	3.285	3.079	2.898	2.725	0.0236	0.0215
E9-14:OH	3.622	3.376	3.157	2.961	2.768	0.0222	0.0202
Z10-14:OH	3.682	3.473	3.223	3.016	2.819	0.0217	0.0196
E10-14:OH	3.731	3.464	3.221	3.025	2.815	0.0211	0.0191
Z11-14:OH	3.881	3.587	3.335	3.117	2.909	0.0200	0.0181
E11-14:OH	3.834	3.548	3.300	3.079	2.864	0.0201	0.0182
Z12-14:OH	4.346	4.024	3.714	3.447	3.185	0.0169	0.0153
E12-14:OH	4.102	3.774	3.495	3.250	3.004	0.0180	0.0163

^a Standard 12:OH.

Table 8
GC data and vapour pressures (25°C) of pentadecenols

Alcohol	Relative retention time ^a					P (Pa)	
	90°C	100°C	110°C	120°C	130°C	Eq. 1	Eq. 4
Z9-15:OH	1.633	1.598	1.564	1.533	1.505	0.00917	0.00814
E9-15:OH	1.692	1.649	1.605	1.568	1.536	0.00851	0.00754
Z10-15:OH	1.696	1.651	1.608	1.574	1.541	0.00845	0.00749
E10-15:OH	1.729	1.681	1.638	1.593	1.557	0.00815	0.00721
Z11-15:OH	1.768	1.721	1.676	1.629	1.590	0.00794	0.00702
E11-15:OH	1.769	1.721	1.673	1.623	1.581	0.00781	0.00691
Z12-15:OH	1.841	1.790	1.735	1.677	1.639	0.00739	0.00652
E12-15:OH	1.830	1.771	1.714	1.660	1.614	0.00730	0.00644
Z13-15:OH	2.071	1.988	1.915	1.849	1.792	0.00617	0.00542
E13-15:OH	1.955	1.880	1.811	1.744	1.695	0.00654	0.00576

^a Standard 14:OH.

Table 9
GC data and vapour pressures (25°C) of hexadecenols

Alcohol	Relative retention time ^a					P (Pa)	
	100°C	110°C	120°C	130°C	140°C	Eq. 1	Eq. 4
Z3-16:OH	2.973	2.801	2.673	2.524	2.401	0.00329	0.00285
E3-16:OH	2.900	2.741	2.605	2.465	2.343	0.00336	0.00291
Z4-16:OH	2.919	2.758	2.629	2.486	2.364	0.00337	0.00292
E4-16:OH	3.054	2.872	2.719	2.559	2.422	0.00302	0.00261
Z5-16:OH	2.944	2.779	2.639	2.494	2.369	0.00327	0.00283
E5-16:OH	3.033	2.851	2.703	2.546	2.412	0.00307	0.00265
Z6-16:OH	2.854	2.704	2.575	2.440	2.320	0.00348	0.00301
E6-16:OH	2.962	2.794	2.657	2.506	2.378	0.00323	0.00279
Z7-16:OH	2.809	2.664	2.545	2.414	2.299	0.00362	0.00314
E7-16:OH	2.993	2.798	2.659	2.507	2.377	0.00312	0.00270
Z8-16:OH	2.849	2.702	2.576	2.433	2.323	0.00350	0.00303
E8-16:OH	2.967	2.799	2.656	2.510	2.377	0.00321	0.00278
Z9-16:OH	2.880	2.711	2.586	2.447	2.335	0.00344	0.00298
E9-16:OH	3.001	2.825	2.679	2.521	2.393	0.00312	0.00270
Z10-16:OH	2.962	2.795	2.658	2.506	2.377	0.00323	0.00279
E10-16:OH	3.058	2.873	2.719	2.563	2.426	0.00302	0.00261
Z11-16:OH	3.050	2.870	2.719	2.572	2.430	0.00308	0.00266
E11-16:OH	3.125	2.930	2.757	2.604	2.457	0.00288	0.00248
Z12-16:OH	3.191	2.997	2.822	2.665	2.510	0.00282	0.00243
E12-16:OH	3.198	2.996	2.810	2.651	2.499	0.00276	0.00238
Z13-16:OH	3.330	3.110	2.922	2.746	2.588	0.00261	0.00224
E13-16:OH	3.294	3.066	2.884	2.705	2.544	0.00260	0.00224

^a Standard 14:OH.

Table 10
GC data and vapour pressures (25°C) of octadecenols

Alcohol	Relative retention time ^a					P (Pa)	
	120°C	130°C	140°C	150°C	160°C	Eq. 1	Eq. 4
Z3-18:OH	2.676	2.500	2.400	2.288	2.200	0.000377	0.000309
E3-18:OH	2.583	2.448	2.346	2.244	2.149	0.000406	0.000333
Z9-18:OH	2.465	2.339	2.254	2.160	2.083	0.000453	0.000373
E9-18:OH	2.596	2.455	2.366	2.247	2.157	0.000402	0.000330
Z11-18:OH	2.534	2.405	2.311	2.216	2.130	0.000431	0.000354
E11-18:OH	2.637	2.497	2.391	2.275	2.181	0.000386	0.000316
Z13-18:OH	2.712	2.555	2.439	2.326	2.221	0.000363	0.000296
E13-18:OH	2.753	2.585	2.463	2.342	2.234	0.000345	0.000282

^a Standard 16:OH.

relative to both the polar and non-polar ends of the molecule is significant. As illustrated in Figs. 3 and 4, these trends may be observed both for the *Z*- and *E*-isomers in all the series investigated.

For homologous subseries such as *Z*- or *E*-isomers of 7-10:OH, 9-12:OH, 11-14:OH and 13-16:OH (ω -3 unsaturation), 5-10:OH, 7-12:OH, 9-14:OH and 11-16:OH (ω -5 unsatura-

tion) and 3-10:OH, 5-12:OH, 9-14:OH and 11-16:OH (ω -7 unsaturation), the double bond is at a constant position with respect to the non-polar end of the molecule. Analysis of the double bond effect in these subseries reveals that the vapour pressures of alkenols having different positions of unsaturation decrease in the order ω -7 > ω -5 > ω -3 > saturated. The empirical relationships given by the $\ln P$ vs. n_C expression

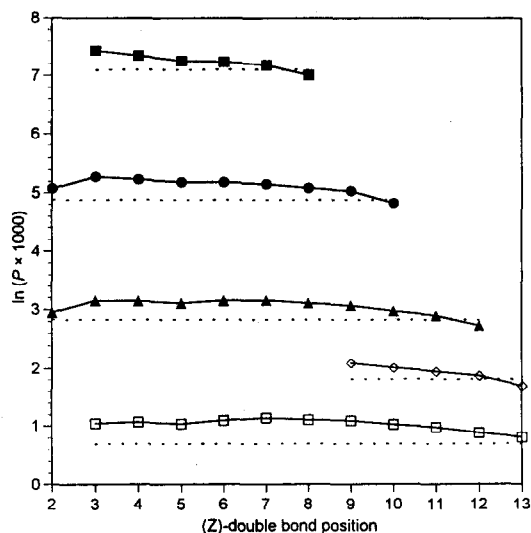


Fig. 3. Vapour pressures (Eq. 4) for (*Z*)-alkenols plotted against the respective double bond position. ■ = Decenols; ● = dodecenols; ▲ = tetradecenols; ◇ = pentadecenols; □ = hexadecenols. Dashed lines show the vapour pressures of the corresponding saturated compounds.

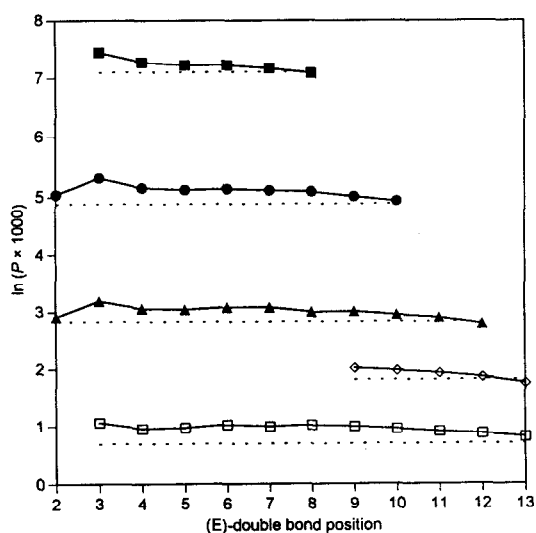


Fig. 4. Vapour pressures (Eq. 4) for (*E*)-alkenols plotted against the respective double bond position. ■ = Decenols; ● = dodecenols; ▲ = tetradecenols; ◇ = pentadecenols; □ = hexadecenols. Dashed lines show the vapour pressures of the corresponding saturated compounds.

Table 11
Proposed relationships for predicting vapour pressures at 25°C

Alcohol subseries ^a	Ln[P (Pa)] = $a - bn_c$		S.E. ^b	r^2
	a	b		
Saturated	10.772 ± 0.135	1.058 ± 0.010	0.0458	0.9998
ω -3-(Z)	10.904 ± 0.065	1.064 ± 0.005	0.0220	1.0000
ω -3-(E)	10.844 ± 0.081	1.060 ± 0.006	0.0276	0.9999
ω -5-(Z)	10.805 ± 0.018	1.046 ± 0.001	0.0061	1.0000
ω -5-(E)	10.849 ± 0.020	1.053 ± 0.002	0.0067	1.0000
ω -7-(Z)	10.995 ± 0.222	1.053 ± 0.017	0.0751	0.9995
ω -7-(E)	11.178 ± 0.307	1.071 ± 0.023	0.1040	0.9991

^a Number of data points, $n = 6$.

^b S.E. = standard error of estimate.

were obtained from analyses of the calculated (Tables 4–10) $\ln P$ data. The relevant equations, listed in Table 11, may be used to estimate vapour pressures for any set of ω -3, ω -5 and ω -7 alkenols. The quality of the fit obtained with MAD (mean average deviation) 2.3% (ω -3), 1.9% (ω -5) and 4.8% (ω -7) combined with the convenience of only one substance-specific input variable makes this an attractive approach in predicting vapour pressures of some other structurally similar derivatives.

At this point some comment should be made regarding literature vapour pressure values of unsaturated alcohols. To our knowledge, only four of the alkenols investigated in this work had literature data available for comparison. Heath and Tumlinson [29] determined the vapour pressures of Z7-12:OH, Z9-14:OH, Z11-14:OH and Z11-16:OH as 1.25, 0.177, 0.160 and 0.039 Pa, respectively. They carried out these determinations on capillary liquid crystal GC columns at “room temperature”, which probably corresponded to 30°C. At that temperature our GC method yields vapour pressures of 0.344, 0.044, 0.037 and 0.0057 Pa, respectively, for the same compounds. Hence our values are significantly (3.6–6.8 times) lower than those in Ref. [29]. Note, however, that a high degree of correlation exists between both data sets. The linear fit

may be expressed as $\ln P = (1.1716 \pm 0.0666) \ln P_{\text{Heath}} - (1.231 \pm 0.137)$ ($n = 4$, S.E. = 0.164, $r^2 = 0.9936$).

By utilizing the reliable literature [26] values at 30°C (see Table 1) for 12:OH (0.266 Pa) and 14:OH (0.0366 Pa), the ratio $P_{\text{alkenol}}/P_{\text{alkanol}}$ for compounds with the same number of carbon atoms may be adopted as an approximate measure of the “effect of non-terminal monounsaturations”. This vapour pressure ratio following from our data is about 1.2–1.3, which seems to be a reasonable value considering its similarity to the corresponding values common for non-terminal alkene [1] and unsaturated acetate series [20]. On the other hand, the ratio of 4.7–4.8 which follows from the use of the data from Ref. [29] appears to be unrealistically high. The reasons for this discrepancy are not clear. However, besides the imprecisely defined temperature they used, another factor might be important, viz. the use of cholesteryl *p*-chlorocinnamate as a stationary phase. It may be that the polar alcohols interact in a specific manner with this phase and then this factor would account for the differences in the two studies.

As the errors in the reported vapour pressures depend both on experimental uncertainties and on the accuracy of the literature vapour pressure data adopted for the reference standards, it is difficult to determine any inherent error in the present method for alcohols. Some discussion is possible, however: as to the latter error factor, recent inter-laboratory data [25,27] for 10:OH and 12:OH agree to within $\pm 5\%$, which may be regarded as a very good agreement. Hence the differences between our data and those taken from the literature for alkanols are generally not greater than the experimental errors (see Table 3). On the other hand, when admitting a propagation of errors, the uncertainty might reach about 10%. Moreover, the vapour pressures for 15:OH and 16:OH were obtained by (prudent) extrapolation and additionally corrected for melting points. It is unlikely that they are in serious error (see the internal homogeneity of the alkanol data illustrated in Fig. 1), but we have to accept their lower accuracy. Taken

together, we assume that, at worst, the errors may combine to give an overall uncertainty in vapour pressures of about 15%.

4. Conclusions

This study has demonstrated the successful application of the capillary GC method to the determination of the vapour pressures of unsaturated alcohols whose generally low thermal stability causes difficulties in direct measurements by conventional physico-chemical methods. The method yields reasonable vapour pressure values for both the alkanols and alkenols at 25°C provided that a compound of similar structure and polarity is used as the reference standard. It is hoped that these new values may considerably extend the database for the vapour pressures of alcohols, and enable entomologically oriented chemists to study and model the physical behaviour of pheromone-like compounds in the environment more accurately.

The method is currently being used to determine vapour pressures of unsaturated aldehydes and will be the subject of a separate report.

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