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Gas chromatographic determination of vapour pressures of pheromone-like acetates

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ABSTRACT

The vapour pressures of nineteen *Z* and *E* monounsaturated C_{10}–C_{16} even-carbon acetates were determined using a method based on gas chromatographic (GC) retention data. Experimental measurements were carried out at six temperatures in the range 90–140°C on a 2-m HP-1 capillary column by utilizing n-C_{18} and n-C_{20} hydrocarbons as vapour pressure reference compounds. Corrections for the systematic errors were made by relating the experimentally determined vapour pressures P_{GC} to the literature values P_L through a linear regression relationship. Over a narrow temperature range of 25–45°C, the GC-measured vapour pressures were found to satisfy the Clausius–Clapeyron equation. Also, for structurally similar subseries of acetates, *e.g.*, for $\omega - 3$ or $\omega - 5$ unsaturated derivatives, the vapour pressures were shown to have a simple dependence on the number of carbon atoms per molecule. The vapour pressures at 25°C ranged from 2.633 Pa for (*Z*)-5-decenyl acetate to 0.005 Pa for (*E*)-13-hexadecenyl acetate.

INTRODUCTION

In recent years, research on the sex pheromones of moths and butterflies has opened up new possibilities for developing ecologically safe strategies for insect pest control as alternatives to the use of conventional insecticides [1]. Most of these pheromones are volatile, multi-component mixtures of unsaturated even-carbon (C_{10}–C_{18}) acetates or alcohols with one or two double bonds at various positions in the molecule in either the *Z* or *E* geometric configuration, and a precise ratio of the components is required for the full insect response [2]. In order to mimic a pheromone-releasing insect in practical applications, it became necessary to develop controlled-release systems for use in monitoring, mass trapping and aerial dissemination control programmes. The successful applications of synthetic pheromone blends however, require volatility considerations to be put on a quantitative basis. In this context, a knowledge of evaporative characteristics of the individual blend components is of great importance.

Among the physico-chemical properties that determine the transport and fate of chemicals in the environment, vapour pressure is one of the most important. Clearly, a compound's vapour pressure will affect its partitioning between the vapour and liquid (particulate-bond) phases and, in turn, its effectivity. For many organic chemicals of environmental relevance, including pheromones, low pressures cause difficulties [3] in direct measurements by conventional Knudsen effusion [4] and gas saturation [5,6] methods. As a consequence, the literature interlaboratory data often disagree by factors of 2–3 or more. Gas chromatography (GC) is an alternative method for measuring vapour pressures [7,8], offering advantages in terms of speed, solute sample size, purity and stability requirements.

The original idea of relating GC retention times to solute vapour pressure [9] has been improved by introducing a latent heat ratio term for unknown

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and reference compounds [10] and subsequently applied to estimate the vapour pressures of many polychlorinated biphenyls and dioxins [11,12], herbicide esters [10] and organophosphorus pesticides [8]. In addition, two different GC approaches have been used [13–15] to treat the retention time (or volume) – vapour pressure relationships for pheromone-like compounds. One [13] uses the substance under study directly as the liquid stationary phase in packed glass chromatographic columns, whereas the other [14,15] makes use of a cholesteryl *p*-chlorocinnamate-coated capillary column, suggesting that on liquid crystal phases the elution order expressed as equivalent chain length (*ECL*) is determined by the length-to-breath ratio of the compounds. Disregarding the fact that, for restricted sets of compounds, both these approaches have produced good vapour pressure estimates, there are two problems connected with them. The first approach is very time consuming as it requires a separate column for each substance, and the efficient use of liquid crystal columns is limited to a narrow temperature range of *ca.* ± 10°C about the mesophase transition temperature.

The purpose of this work was to examine if the rapid and simple GC method reported previously [7,10,16] to be useful for environmentally hazardous chemicals would provide an alternative to more sophisticated methods for determining vapour pressures of pheromone-like acetates with the same degree of accuracy.

EXPERIMENTAL

Chromatography and chemicals

Samples were analysed on a Hewlett-Packard HP 5880 chromatograph equipped with a flame ionization detector and a 2-m fused-silica capillary column (cross-linked 5% methylsilicone, HP-1, film thickness 0.52 μm) with splitless injection. Chromatography was carried out isothermally at 10°C intervals from 90° to 140°C with a hydrogen flow-rate of 10 ml/min. n-C_{18} and n-C_{20} hydrocarbons were used as reference standards. Retention times were determined using an HP 3396A integrator. As recommended [7], long retention times of compounds producing asymmetric peaks at low temperatures were not taken at the peak maximum, but were calculated at the mid-point between the beginning and the end of the peak.

The acetates were either obtained from Sigma (St. Louis, MO, USA) and used as received or were synthesized in our laboratory. In the latter instance the purity of the compounds was at least 97% as determined by capillary GC. In the abbreviated nomenclature used for the acetates, the letters after the colon indicate the functional type (Ac = acetate); the number between the dash and colon indicates 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.

Data treatment

The equations for calculating vapour pressures from GC retention data were derived by Hamilton [10]. Briefly, pressures of the substances at the same temperature are related through

$$\ln P_t = H_t/H_r \ln P_r + c \qquad (1)$$

where the subscripts t and r refer to the test and reference compounds, respectively, and H is the latent heat of vaporization. These vapour pressures are also related to their retention times (t):

$$\ln P_t = \ln P_r - \ln (t_t/t_r) \qquad (2)$$

Combining eqns. 1 and 2 and rearranging yields

$$\ln (t_t/t_r) = (1 - H_t/H_r) \ln P_r - c \qquad (3)$$

Therefore, a plot of $\ln (t_t/t_r)$ *versus* $\ln P_r$ would have a slope $1 - H_t/H_r$ and an intercept c. Eqn. 1 can then be used to determine the vapour pressure of a test compound at any temperature given the vapour pressure of the reference compound at that temperature.

RESULTS AND DISCUSSION

Table I gives the GC retention time data measured isothermally at six temperatures. Before using these data in the vapour pressure calculations, it seemed useful to analyse them with respect to the molecular structure of the analytes. As the Kováts system of retention indices is known to permit correlations of this type, the measured retention times in Table I were first converted into retention indices I defined by the equation

$$I = 100N + 100n\,[(\log t_a - \log t_N)/(\log t_{N+n} - \log t_N)]$$

TABLE I

GC RETENTION TIMES (min) OF THE PHEROMONE-LIKE ACETATES

Compound	90°C	100°C	110°C	120°C	130°C	140°C
10:Ac	1.074	0.688	0.423	0.285	0.188	0.128
12:Ac	4.023	2.341	1.338	0.822	0.509	0.568
14:Ac	14.496	7.554	4.391	2.555	1.506	0.913
*Z*5–10:Ac	0.986	0.604	0.395	0.266	0.175	0.121
*E*5–10:Ac	0.916	0.582	0.365	0.237	0.161	0.108
*Z*7–12:Ac	3.522	2.108	1.194	0.744	0.465	0.298
*E*7–12:Ac	3.526	2.055	1.178	0.728	0.454	0.284
*Z*9–12:Ac	3.845	2.228	1.272	0.791	0.484	0.307
*E*9–12:Ac	3.826	2.235	1.261	0.782	0.478	0.303
*Z*9–14:Ac	13.186	6.771	4.091	2.471	1.514	0.951
*E*9–14:Ac	13.051	7.045	4.049	2.463	1.484	0.922
*Z*11–14:Ac	13.032	6.784	4.215	2.423	1.433	0.881
*E*11–14:Ac	13.724	6.975	4.195	2.422	1.441	0.886
*Z*9–16:Ac	44.199	22.145	11.127	6.233	3.395	1.961
*E*9–16:Ac	45.026	22.638	11.505	6.291	3.458	1.955
*Z*11–16:Ac	46.495	23.522	11.706	6.423	3.567	1.997
*E*11–16:Ac	49.529	24.865	12.193	6.689	3.622	2.047
*Z*13–16:Ac	52.051	26.513	12.935	7.066	3.839	2.156
*E*13–16:Ac	52.639	26.435	12.922	7.087	3.821	2.156
n-$C_{18}H_{38}$	15.521	8.395	4.441	2.571	1.483	0.884
n-$C_{20}H_{42}$	58.501	26.909	14.277	7.424	3.994	2.223

where t_A, t_N and t_{N+n} are the adjusted retentions of the analyte and of n-alkanes possessing N and $N + n$ carbon atoms, respectively.

The correlations between the retention indices corresponding to 110°C, I^{110}, and the number of the carbon atoms N in the acetate chain were established by means of the equation $I = a + bN$ and are shown in Figs. 1 and 2. For n-alkenyl compounds, the position of the double bond relative to the non-polar end of the molecule will affect the GC retention times. Thus, considering the different structural features of the $\omega - 3$ (9–12:Ac, 11–14:Ac and 13–16:Ac) and $\omega - 5$ (5–10:Ac, 7–12:Ac, 9–14:Ac and 11–16:Ac) unsaturated acetates, both subseries were treated separately. The linear dependence of the retention indices of a homologous series with normal alkyl chain on carbon number N represents a common trend among the GC data. Therefore, also given in Figs. 1 and 2 are similar dependences of 3- and 5-alkenes based on literature data [17,18]. The retention indices of Kuningas *et al.* [18] were

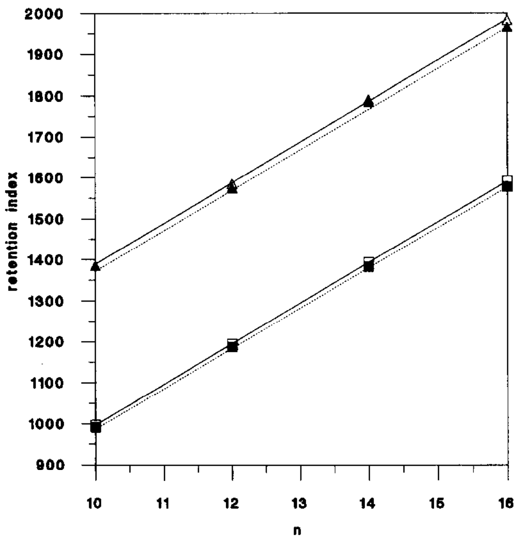

Fig. 1. Retention indices (I^{110}) for (*Z*)-alkenyl acetates and (*Z*)-alkenes plotted against the respective carbon number. △ = $\omega - 3$-Acetates; ▲ = $\omega - 5$-acetates; □ = $\omega - 3$-alkenes; ■ = $\omega - 5$-alkenes.

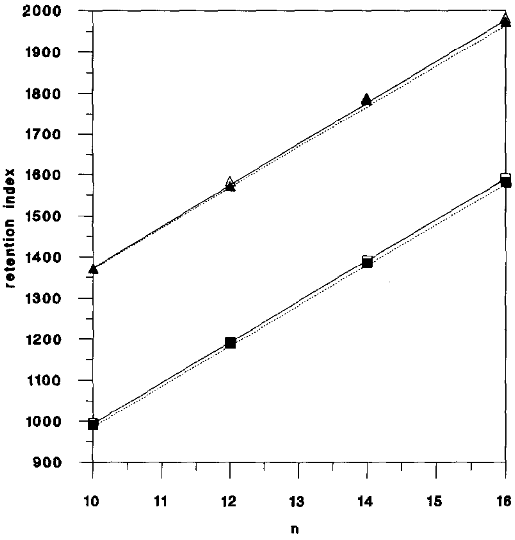

Fig. 2. Retention indices (I^{110}) for (*E*)-alkenyl acetates and (*E*)-alkenes plotted against the respective carbon number. Symbols as in Fig. 1.

TABLE II

COEFFICIENTS OF THE EQUATION $I = a + bN$

In all instances $r^2 = 0.999$ or better.

Compound	Configuration	*a*	*b*
ω−5-Acetates	*Z*	409.23	97.61
	E	366.23	100.71
5-Alkenes	*Z*	15.39	97.66
	E	5.88	98.54
ω−3-Acetates	*Z*	396.38	99.31
	E	390.95	99.64
3-Alkenes	*Z*	4.69	99.21
	E	0.96	99.36

used for this purpose, as both the stationary phase (OV-101) and temperature (110°C) that they used are comparable to our experimental conditions.

The linearity of the plots provides evidence for the incremental nature of the sorbate–sorbent interaction energy irrespective of the homologous series considered. Inspection of the least-squares regres-

TABLE III

PARAMETERS OF EQN. 3 AND VAPOUR PRESSURES (25°C) OF THE PHEROMONE-LIKE ACETATES

Compound[a]	H_t/H_r	*c*	*P*(Pa)				Error[e] (%)
			Eqn. 1	Eqn. 4	Exp.[c]	Exp.[d]	
10:Ac	0.7821	3.1977	1.392	2.179	2.262	2.181	−1.9
12:Ac	0.8996	1.5954	0.1827	0.279	–	0.276	1.1
14:Ac[b]	0.8575	1.5142	0.0298	0.0201	–	0.0349	−14.6
*Z*5–10:Ac	0.7685	3.3373	1.678	2.633	2.659	–	1
*E*5–10:Ac	0.7846	3.354	1.609	2.523	2.524	–	0
*Z*7–12:Ac	0.8854	1.7581	0.235	0.359	0.319	0.337	9.5
*E*7–12:Ac	0.8958	1.7363	0.212	0.324	–	–	–
*Z*9–12:Ac	0.8995	1.6427	0.191	0.292	–	–	–
*E*9–12:Ac	0.9035	1.6342	0.1862	0.284	–	–	–
*Z*9–14:Ac[b]	0.8147	1.6744	0.0309	0.0461	0.0495	–	7
*E*9–14:Ac[b]	0.8261	1.6486	0.0279	0.0416	–	–	–
*Z*11–14:Ac[b]	0.8364	1.6367	0.0259	0.0386	–	–	–
*E*11–14:Ac[b]	0.8489	1.5524	0.0228	0.0339	–	–	–
*Z*9–16:Ac	1.0723	−1.2107	0.0058	0.0085	–	–	–
*E*9–16:Ac	1.0781	−1.2511	0.0055	0.008	–	–	–
*Z*11–16:Ac	1.0812	−1.2909	0.0052	0.0076	–	0.0065	16.9
*E*11–16:Ac	1.0944	−1.2864	0.0045	0.0066	–	–	–
*Z*13–16:Ac	1.0947	−1.4442	0.0042	0.0061	–	–	–
*E*13–16:Ac	1.0992	−1.4623	0.0041	0.005	–	–	–

[a] Standard: *n*-octadecane.

[b] Standard: *n*-eicosane.

[c] Ref. 13.

[d] Refs. 14 and 15.

[e] Error = $100(p_{GC}-p_{exp})/p_{exp}$.

sion coefficients of the equation $I = a + bN$ (Table II) further reveals that (i) the values of the coefficient b vary only slightly (by *ca.* ±1.5%) around a mean value of 99.03 i.u., demonstrating an approximate constancy of the methylene group contribution to the sorbate–stationary phase interaction energy within all subseries of compounds compared; slightly higher slopes, however, are invariably found for the E isomers; (ii) specific interactions between the sorbent and terminal functional groups, in addition to double bonds, are reflected almost exclusively in the intercept a; and (iii) reasonable statistics of the I *vs.* N linear dependences ($r > 0.999$ in all instances) permit the I values of non-available acetates to be predicted with good accuracy by prudent extrapolation.

As the method used for vapour pressure determination is a comparative one, vapour pressures being calculated from that of a standard compound, it became important to assess the values given in the literature. The vapour pressures of *n*-octadecane over the temperature range 40–130°C have been shown [7,19] to fit the equation $\ln P\,(\text{Torr}) = A + B/T$ with $A = 25.548$ and $B = -10\,165$. On the other hand, the Antoine equation, $\log P\,(\text{Torr}) = A + B\,/\,(t + C)$, with $A = 7.99897$, $B = -2607.622$ and $C = 177.32$, has been proposed [20] for the vapour pressure–temperature (80–170°C) dependence of *n*-eicosane. Similar parameters have also been found by other workers [21]. Therefore, the above-mentioned constants A, B and C were used to calculate the vapour pressures of the reference standards in this work. Accordingly, the vapour pressure values for *n*-octadecane and *n*-eicosane extrapolated to 25°C are 0.02546 and 0.00172 Pa, respectively.

GC-determined vapour pressures P_{GC} of all nineteen acetates at 25°C were calculated from relative retention times (Table I) by using eqns. 1 and 3. The results are given in Table III. It should be noted that the difficulties in separating the C_{18} hydrocarbon and C_{14} acetates resulted in a substantial scatter of the points of the $\ln t_{rel.}$ *vs.* P_r plot. Therefore, *n*-eicosane was used as reference compound for all C_{14} acetates.

To test the validity of this approach, it was useful to compare the P_{GC} values from Table III (eqn. 1) with the limited amount of vapour pressure data on unsaturated acetates (P_L) that have been published previously [13–15]. When literature values were selected for this comparison, some judgement was necessary, as different reports for a single compound sometimes agreed very well but in other cases poorly. Of the three data sources [13,14,22] dealing with vapour pressures of acetates in Table III, we favoured the more recent results. The older data [22], based on a gas saturation approach, had been already questioned [13,23], and were not considered further. The literature P_L values in Fig. 3 and Table III are therefore those based on refs. 13, 14 and 15. They correspond to two different experimental techniques, (i) the GC method [13] which uses the substance under study as the stationary phase, if necessary these data being extrapolated 5°C below the temperature range at which they were measured, and (ii) the GC method [14,15] which uses a liquid crystal stationary phase (as the vapour pressures obtained by the latter method were measured at 30°C they were recalculated to 25°C by making use of the Clausius–Clapeyron equation and the corresponding heats of vaporization given in ref. 23). The results of comparison of our P_{GC} data with those taken from the literature (P_L) are depicted in Fig. 3. As can be seen, the regression line obtained parallels the $y = x$ line. The equation of the regression line by a linear least-squares fit is

$$\ln P_L\,(\text{Pa}) = 1.0126 \ln P_{GC} + 0.444 \qquad (4)$$
$$(n = 8,\ r = 0.9991,\ \text{S.E.} = 0.094)$$

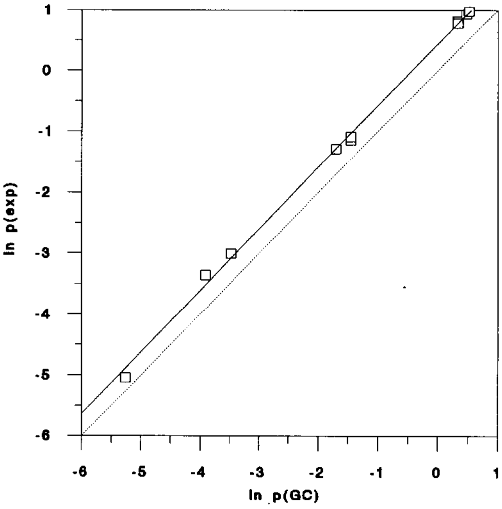

Fig. 3. Logarithmic plot of literature vapour pressures P_L *versus* P_{GC} data from the present work. The regression line (solid) and the $y = x$ line (dashed) are shown.

Although both data sets for 10:Ac, 12:Ac, 14:Ac, *E*5–10:Ac, *Z*5–10:Ac, *Z*7–12:Ac, *Z*9–14:Ac and *Z*11–16:Ac are well correlated on the HP-1 column, the P_{GC} underestimated P_L by a factor of about 1.6. Two reasons have been identified [16] that might cause this inequality. One could occur if the difference in activity coefficients γ among the test and reference compounds were related to compound volatility, while the other could be due differences in γ which were not correlated with volatility. As no significant scatter of points about the regression line in Fig. 3 was observed, the deviations in the present instance are probably attributable to a systematic error connected with the GC column. This systematic error can be eliminated and the accuracy improved by using Fig. 3 as a calibration plot to correlate P_{GC} with P_L. Hence, the final vapour pressures P_L of test compounds (Table III, eqn. 4) were obtained from measured P_{GC} data by correcting them according to eqn. 4. It is shown that this correction provides vapour pressures within a factor of about 1.17 of average literature values, thus achieving better precision of vapour pressure determinations than reported interlaboratory results. The mean relative error for the testing set of eight acetates was found to be less than ± 7%.

To extend further the scope of the method, the effect of temperature on vapour pressures was also investigated. The Clausius–Clapeyron equation

$$\ln P = -H_v/RT + C \qquad (5)$$

where H_v is the enthalpy of vaporization and R and C are the gas (8.3144 J $\text{mol}^{-1}\text{K}^{-1}$) and integration constants, respectively, was found to be adequate for describing the vapour pressure–temperature dependence over the range 25–45°C.

The method of least squares was used to fit eqn. 5 to the data using H_v and C as parameters. The resulting parameter estimates were further found to depend systematically on the carbon number N within the saturated and the monoenic ω-3 and ω-5 acetate subseries. As a consequence, an empirical relationship given by the equation

$$\ln P\,(\text{Pa}) = -(AN + B)/T + (CN + D) \qquad (6)$$

resulted, where the constants *A*–*D* varied depending on the subseries type. The numerical values of the constants are summarized in Table IV. Tests of this empirical equation are provided by comparison of both the vapour pressures at 25°C and heats of vaporization as they are predicted by this equation with original P_{GC} data based on eqn. 1 and vaporization enthalpies obtained previously [23] from independent measurements. The agreement found between P_{GC} (eqn. 1) and P (eqn. 6) values with a relative error not exceeding 2% demonstrates the predicative validity of eqn. 6. Additional support for its reliability comes from a comparison between estimated and experimental H_v data. For compounds in common with ours, the H_v values (kJ mol^{-1}) found by McDonough *et al.* [23] and ourselves are, respectively: 10:Ac, 67.78 and 66.1; 12:Ac, 77.58 and 77.4; 14:Ac, 87.37 and 88.7; *Z*7–12:Ac, 75.91 and 74.91 and 74.9; *Z*9–14:Ac, 85.7 and 83.8; Z11–16:Ac, 95.46 and 92.7. Hence the experimental enthalpies are reproduced to within about ± 3%.

TABLE IV

PARAMETERS OF EQN. 6

Acetate subseries	*A*	*B*	*C*	*D*
Saturated	679.7	1154.3	1.218	14.853
ω−3-(*Z*)	499.4	3297.2	0.725	20.768
ω−3-(*E*)	500.7	3360.5	0.726	20.966
ω−5-(*Z*)	536.3	2572.4	0.833	18.759
ω−5-(*E*)	533.8	2742.9	0.822	19.299

At a constant temperature of 25°C, eqn. 6 with parameters from Table IV can be substituted into the correction eqn. 4, yielding corrected vapour pressure relationships as shown in Table V. These equations enable vapour pressures at 25°C to be

TABLE V

PROPOSED RELATIONSHIPS FOR PREDICTING VAPOUR PRESSURES AT 25°C

Acetate subseries	$\ln P_L = a + bN^a$	
	a	*b*
Saturated	11.563	−1.075
ω−3-(*Z*)	10.275	−0.962
ω−3-(*E*)	10.261	−0.965
ω−5-(*Z*)	10.702	−0.978
ω−5-(*E*)	10.67	−0.981

[a] Vapour pressure in Pa.

predicted for selected homologous subseries of acetates from the carbon numbers *N*. Based on a restricted set of available experimental data, it is believed that these equations should predict vapour pressures with an average error of less than 10%.

A specific comment is needed regarding the intercepts and slopes in Table V. Whereas significant differences in these parameters are observed among the saturated, ω-3 and ω-5 monoenic subseries, the same differences in parameters between *Z* and *E* isomeric subseries (although they might be real) are all within the 95% confidence interval limits.

The conclusion reached from the results is that the present GC method can provide vapour pressures of pheromone-like acetates with average deviations of less than ± 10% of the literature values, well within the interlaboratory precision of other techniques. Taking into account its other advantages, *e.g.*, simplicity, speed, sample size and purity requirements, the approach presented here can be considered as a viable means for calculating vapour pressures of a large variety of compounds. In this respect, we believe the present results for acetates to be prototypical for a number of related systems. We are currently examining the potential of this method for determining vaporization properties of other classes of pheromone components, such as alcohols and dienes.

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