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# Gas chromatographic determination of vapour pressures of pheromone-like compounds

## III. Aldehydes<sup>☆</sup>

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### Abstract

Equilibrium vapour pressures of six saturated and seventy-four mono-unsaturated C<sub>10</sub>–C<sub>16</sub> even-carbon aldehydes were determined using a method based on gas chromatographic (GC) retention data. GC measurements were carried out on a 3-m HP-1 capillary column at five to seven temperatures in the range of 35–140°C by utilising saturated *n*-C<sub>12</sub>, *n*-C<sub>13</sub>, *n*-C<sub>17</sub> and *n*-C<sub>18</sub> hydrocarbons as vapour pressure reference standards. A close correlation, viz.  $\ln P [\text{Pa}] = 14.008 - 1.105n_c$  ( $r = 0.9996$ ) has been found between the vapour pressures  $P$  and the number of carbon atoms ( $n_c$ ), indicating a vapour pressure decrease by a factor of 3.02 for each CH<sub>2</sub> group added in the alkanal chain. For structurally similar subseries of alkenals ( $\omega$ -3,  $\omega$ -5 and  $\omega$ -7 unsaturation), the vapour pressures were also shown to have a simple dependence on  $n_c$ . Within each alkenal subseries, isomers having *Z*-configuration had mostly greater vapour pressures than their *E*-counterparts.

**Keywords:** Vapour pressure; Aldehydes; Pheromones

### 1. Introduction

The great majority of lepidopteran sex pheromones consists of even-carbon (C<sub>10</sub> to C<sub>18</sub>) straight-chain mono-unsaturated acetates, alcohols or aldehydes, the functional group always

being found on a terminal carbon atom [1,2]. It is now well-established [3] that these pheromones are generally multicomponent mixtures and, in most cases, a precise blend of two or more components is required for full insect response. For any adequate practical use of synthetic pheromone mixtures in pest control, one needs to be able to predict component ratios in the vapour considering the different volatilities of the compounds. Essential to this prediction is the quantitation of the emission and longevity

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<sup>†</sup> Dedicated to Professor Hans-Dieter Scharf on the occasion of his 65 birthday. For part II, see Ref. [14].

characteristics of the individual blend components [4].

Among the properties required to predict or understand a compound's distribution between condensed and gas phases, vapour pressure is one of the most important [5]. Since the direct measurement of vapour pressures for highly boiling compounds becomes difficult in the low pressure region (say  $P < 1$  kPa), alternative gas chromatographic (GC) methods have been developed to obtain this physico-chemical property. These methods are generally based on the use of non-polar stationary phases and isothermal conditions such that a compound's retention time is related directly to its vapour pressure. The fundamental expressions for most of these determinations (Eqs. 1 and 2) have been formulated by Hamilton [6]:

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

$$\ln P_T = \frac{\Delta H_T}{\Delta H_R} \ln P_R + C \quad (2)$$

where  $T$  refers to the compound under investigation and  $R$  to the reference compound,  $t'$ ,  $P$  and  $\Delta H$  are the GC (adjusted) retention time, vapour pressure and heat of vaporisation, respectively, and  $C$  is a constant.

Hence, plotting the measured relative retention times against known vapour pressures  $P_R$  at different temperatures yields  $\Delta H_T/\Delta H_R$  and  $C$  and, via Eq. 2, also  $P_T$  at any temperature if  $P_R$  at that temperature is known. A great deal of work has been done using this technique, especially by Bidleman and co-workers [7–9], Seiber and co-workers [10] and Hawker [11,12]. Recently, using this method, we have obtained the vapour pressures of some pheromone-like acetates [13] and alcohols [14].

In the work reported here, we utilise this approach to determine vapour pressures of pheromone-like aldehydes having 10, 12, 14 and 16 carbon atoms in the chain. This series of 80 congeners contains both alkanals and alkenals with varying positions and geometric configuration of double bonds. The work represents part of a broadly based program the aim of which is

to form a reliable vapour pressure database of pheromone-like compounds.

## 2. Experimental

### 2.1. Chromatography

The retention times of aldehyde samples were determined using a Hewlett-Packard HP 5890 gas chromatograph equipped with a flame ionisation detector (FID), split injection port and an HP 5895A ChemStation. A Hewlett-Packard fused-silica capillary column (HP-1, film thickness 0.52  $\mu\text{m}$ ) of length 3 m and I.D. 0.31 mm was used in the split mode with the split ratio set at 50:1. The gas chromatograph was operated isothermally with a hydrogen flow-rate of 5 ml/min at 5 or 10°C intervals in the range of 35–140°C as specified. *n*-Dodecane, *n*-tridecane, *n*-heptadecane and *n*-octadecane were used as reference standards. Adjusted retention times were calculated by subtracting the retention time of methane from the retention time of the analyte. All retention times of aldehydes used for vapour pressure determinations were the means of at least three separate runs (relative standard deviation 0.03%).

### 2.2. Chemicals

The saturated aldehydes up to  $C_{12}$  were acquired from Aldrich (97–99% pure by weight). The other alkanals as well as the alkenals are not commercially available as pure compounds. Thus, structurally relevant alcohols provided by the Research Institute for Plant Protection (IPO–DLO) Wageningen (Netherlands) were oxidised in situ to corresponding aldehydes using an excess of pyridinium chlorochromate (PCC). In a typical experiment, the alcohol (2  $\mu\text{mol}$ ) and PCC (2.4  $\mu\text{mol}$ ) were stirred in dichloromethane for 2 h at R.T. A small amount of activated carbon (Darco, Aldrich) was then added and the reaction mixture was filtered over a short-path column of neutral aluminium oxide (10% water) and washed with ether. The solvent was removed by blowing an argon stream on the surface of the

solution and the remaining aldehyde was diluted with hexane. With exception of two (*Z*)-allylic alcohols, i.e. of (*Z*)-2-dodecenol and (*Z*)-2-tetradecenol, where the oxidation procedure afforded a 3:1 mixture of corresponding (*Z*)- and (*E*)-enals with the *Z*-isomer eluting first, the purity of all other chemicals was at least 97%, as determined by capillary GC. Condensed nomenclature for aldehydes is used: the letters after the colon indicate the functional type (Al = aldehyde), 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, e.g. Z5-12:Al is (*Z*)-5-dodecenal.

### 2.3. Statistical analysis

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

## 3. Results and discussion

One of the basic requirements for a useful application of Eqs. 1 and 2 is the selection of appropriate reference compounds. In addition to having data on vapour pressure variation with temperature, it is desirable [12,14] that the reference compound be similar to the compounds of interest or at least to have small retention volume differences. Unfortunately, an extensive literature search of vapour pressures on *n*-aldehydes ( $C_{10}$  to  $C_{18}$ ) over the temperature range of interest for this study (25–140°C) showed that the experimental values are too fragmentary and too inaccurate to provide the basis for reliable computations. Undoubtedly, the scarcity of experimental data on the physical properties of pure aldehydes derives from the considerable difficulties associated with working with aldehydes in the laboratory, resulting from their instability due to oxidation and polymerisation. Since aldehydes may be ranked among the only slightly polar compounds, however, we chose to use several *n*-alkanes as reference standards. Of

the numerous vapour pressure–temperature relationships available for *n*-alkanes (e.g. [15–18]), the most recent results [18], based on a simultaneous treatment of vapour pressures and thermal data, were favoured. The data in this critical compilation are mutually consistent over the  $C_5$ – $C_{20}$  alkane homologous series, thus forming probably the best database of vapour pressures presently available, especially in the low vapour pressure region. For *n*-dodecane, *n*-tridecane, *n*-heptadecane and *n*-octadecane, which were selected as reference standards in this work, the data were found to fit the Cox equation  $\ln(P/P_0)$  [kPa] =  $(1 - T_0/T) \exp(A_0 + A_1T + A_2T^2)$  with parameters as follows: *n*-dodecane,  $A_0 = 3.05854$ ,  $A_1 = -2.018454 \cdot 10^{-3}$ ,  $A_2 = 1.606849 \cdot 10^{-6}$  and  $T_0 = 489.438$  K; *n*-tridecane,  $A_0 = 3.10403$ ,  $A_1 = -2.071819 \cdot 10^{-3}$ ,  $A_2 = 1.611600 \cdot 10^{-6}$  and  $T_0 = 508.602$  K; *n*-heptadecane,  $A_0 = 3.21826$ ,  $A_1 = -2.036553 \cdot 10^{-3}$ ,  $A_2 = 1.383899 \cdot 10^{-6}$  and  $T_0 = 575.375$  K; *n*-octadecane,  $A_0 = 3.24741$ ,  $A_1 = -2.048039 \cdot 10^{-3}$ ,  $A_2 = 1.362445 \cdot 10^{-6}$  and  $T_0 = 590.023$  K; for all compounds  $P_0 = 101.325$  kPa. These parameters were used to interpolate vapour pressure values at the temperatures selected to develop the *P*–*T* relationships (35–140°C). Accordingly, the vapour pressures for *n*-dodecane, *n*-tridecane, *n*-heptadecane and *n*-octadecane at 25°C are 18.02, 5.682, 0.06148 and 0.02007 Pa, respectively.

### 3.1. Vapour pressures of alkanals—testing of the method

Table 1 lists the GC retention time data of five alkanals measured isothermally at five or seven temperatures. Using these data and the general framework given by Eqs. 1 and 2, the calculated  $P_{GC}$  values are presented in Table 2 along with the scarce experimental literature data available [19–21]. Also included is a comparison of the present work with the estimates resulting from two correlative approaches. The first of them uses a linear correlation found experimentally [19] between the logarithm of *P* at 25°C and the number of carbon atoms  $n_C \in <5, 10>$ , viz.  $\ln P = 14.025 - 1.112n_C$  ( $n = 6$ ,  $r = 0.9999$ , S.E. =

Table 1  
GC retention times (min) of *n*-alkanals and alkane standards

Compound	Adjusted retention time (min) at													
	35°C	40°C	45°C	50°C	55°C	60°C	65°C	70°C	75°C	80°C	85°C	90°C	100°C	110°C
9:Ald	-	-	-	1.715	1.326	1.035	0.825	0.652	-	-	-	-	-	-
10:Ald	8.711	6.202	4.589	3.421	-	1.918	-	1.117	-	0.708	-	-	-	-
11:Ald	-	-	-	9.657	6.911	5.127	3.509	2.558	-	-	-	-	-	-
12:Ald	67.068	45.492	31.697	22.339	-	11.372	-	6.018	-	3.459	-	-	-	-
14:Ald	-	-	-	-	-	-	-	22.179	16.211	11.747	8.578	6.392	3.651	2.151
16:Ald	-	-	-	-	-	-	-	101.639	69.579	48.582	34.059	24.313	12.909	7.092
<i>n</i> -C <sub>12</sub> H <sub>26</sub>	-	-	-	4.636	3.464	2.621	1.978	1.544	-	-	-	-	-	-
<i>n</i> -C <sub>13</sub> H <sub>28</sub>	26.301	18.187	12.908	9.312	-	4.918	-	2.712	-	1.588	-	-	-	-
<i>n</i> -C <sub>17</sub> H <sub>36</sub>	-	-	-	-	-	-	-	52.941	37.408	26.388	18.819	13.647	7.422	4.169

Table 2  
Regression parameters of Eq. 2 and comparison of vapour pressures (25°C) of *n*-alkanals with literature data

Alkanal	$\Delta H_T/\Delta H_R$	C	P (Pa)				
			Eq. 2	Eq. 3	Exp.	Ref. [19]	Ref. [22]
8:Ald	–	–	–	175.4	169 <sup>d</sup>	169.4*	191.7
9:Ald <sup>a</sup>	0.8975	–1.4843	59.12	58.10	57.00 <sup>d</sup>	55.70*	60.04
10:Ald <sup>b</sup>	0.9072	–1.3509	18.67	19.24	18.00 <sup>d</sup>	18.33*	18.72
11:Ald <sup>a</sup>	1.1268	1.3439	6.78	6.37	8.22 <sup>c</sup>	6.03*	5.88
12:Ald <sup>b</sup>	1.0531	1.0756	2.125	2.110	–	1.984*	1.883
13:Ald	–	–	–	0.699	–	0.653*	0.622
14:Ald <sup>c</sup>	0.9279	–0.9858	0.201	0.231	0.167 <sup>f</sup>	0.215*	0.215
15:Ald	–	–	–	0.0766	–	0.0707*	0.0785
16:Ald <sup>c</sup>	1.0374	0.6976	0.0276	0.0254	0.0212 <sup>f</sup>	0.0233*	0.0307
17:Ald	–	–	–	0.00840	–	0.00765*	0.0130
18:Ald	–	–	–	0.00278	–	0.00252*	0.00612

<sup>a</sup> Standard *n*-dodecane.

<sup>b</sup> Standard *n*-tridecane.

<sup>c</sup> Standard *n*-heptadecane.

<sup>d</sup> Ref. [19], the values marked with an asterisk were determined from the regression equation given in the text.

<sup>e</sup> Ref. [20].

<sup>f</sup> Ref. [21].

0.0159) to obtain extrapolated vapour pressures for aldehydes up to C<sub>16</sub>, while the other is based on a newly reported [22] group contribution method.

The literature vapour-pressure data are based on three different experimental techniques, (i) the dynamic (ebulliometric) method [19], (ii) the static method [20] and (iii) the GC method [21], which uses a liquid crystal stationary phase. Regarding the accuracy of the literature data one should consider the following: The only precise values in the literature with which a comparison can be made are those of Djakova et al. [19] on 9:Al and 10:Al. For these compounds, their data yield 57.00 ± 1.0 and 18.00 ± 1.00 Pa at 25°C, which values are to be compared with the values 59.12 and 18.67 Pa, respectively, from the present investigation. The vapour pressures for 14:Al and 16:Al obtained by the GC method [21] were measured at “room” temperature which probably corresponded to ca. 30°C and they had to be recalculated to 25°C by making use of the Clausius–Clapeyron equation and the corresponding heats of vaporisation given in Ref. [23]. Considering the lack of precise temperature

information, our data for 14:Al (0.201 Pa) and 16:Al (0.0276 Pa) are in satisfactory and perhaps somewhat fortuitous agreement (within 20.3 and 30.2%, respectively) with those of Heath et al. [21].

Hence, our vapour pressures,  $P_{GC}$ , differ from those determined experimentally by other methods by values ranging from 3.7% (for 9:Al and 10:Al) to 30.2% (for 16:Al). On the other hand, an agreement of our results with those based on the correlative approaches is substantially better, with mean average deviations under 9 and 8%, respectively.

Owing to the fact that only a limited amount of literature experimental data ( $P_L$ ) of uncertain accuracy was available, we did not attempt to calibrate our  $P_{GC}$  values for possible systematic errors by relating  $P_{GC}$  to  $P_L$  through a regression equation. Instead, we decided to correlate and smooth the vapour pressures of *n*-alkanals on the assumption that for the members of the series the values should fall on smooth curves or lines when plotted against  $n_C$ . Smoothing of the data by a linear least-squares routine allowed detection of possible errors in the experimental  $P_{GC}$

data set. The equation of the regression line by a linear least-squares fit is

$$\ln P_{GC}[\text{Pa}] = (14.0085 \pm 0.1877) - (1.1051 \pm 0.0153)n_C \quad (3)$$

( $n = 5$ ,  $r = -0.9996$ , S.E. = 0.0894).

The smoothed values that slightly differ from those observed are also included in Table 2. This procedure served also to generate the vapour pressure data for those aldehydes where no experimental information was available. Fig. 1 illustrates the overall comparison showing the linear regression line (Eq. 3) with experimental data from other sources, as well as predicted (both interpolated and extrapolated) values. While our smoothed values compare very well with those reported by Djakova et al. [19] and even the extrapolated data agree within a 95% confidence limit, the data based on the group contribution method [22] appear to be overestimated for  $n_C \geq 16$ . Note, however, that experimental vapour pressures of lower aldehydes ( $n_C < 16$ ) had to be probably used as data base in

deriving the appropriate group contribution equations. Thus, strictly speaking, the validity of this group contribution approach might be restricted to the lower carbon span region. The slope of the regression line is  $-1.1051$ , which indicates that the vapour pressure decreases by a factor of 3.02 for each  $\text{CH}_2$  group added to the chain. This value compares quite well with the previously estimated [19] value (3.04). It is worth mentioning that the extrapolated vapour pressure of 5:Al (4831 Pa) following from the use of Eq. 3 still compares favourably (within 1.9%) with the values 4750 and 4579 Pa obtained experimentally [19,23] by two independent methods. Additional support for the reliability of Eqs. 1 and 2 comes from a comparison between estimated and experimental vaporisation enthalpies  $\Delta H_V$ . By utilising the in the literature [18] recommended values at 298.15 K for our reference standards ( $n$ -dodecane: 61.52 kJ/mol,  $n$ -tridecane: 66.68 kJ/mol and  $n$ -heptadecane: 86.47 kJ/mol), the enthalpies of vaporisation of alkanals may be calculated from the  $\Delta H_T/\Delta H_R$  ratios given in Table 2. The  $\Delta H_V$  values (in kJ/mol) are in reasonable agreement with those reported by Djakova et al. [19] and by McDonough [24] for 9:Al, 10:Al, 14:Al and 16:Al from their calorimetric and half-lives measurements (56.31, 60.39, 78.12 and 87.36, respectively, versus our values of 55.21, 60.49, 80.23 and 89.70). Our values agree within 1.9% with those of Djakova [19] and are by about 2.7% lower than those of McDonough [23]. Hence, the assessment of the overall value of the present results, based on the comparison, and the potential for simple extrapolation, shows it to be highly viable and perhaps superior to others evaluated. It may be interesting to note at this point that the use of several  $n$ -alkane reference standards as applied in this work corresponds with a recently developed [25] model relating the Kováts indices and the McReynolds numbers to the isothermal pure liquid vapour pressures.

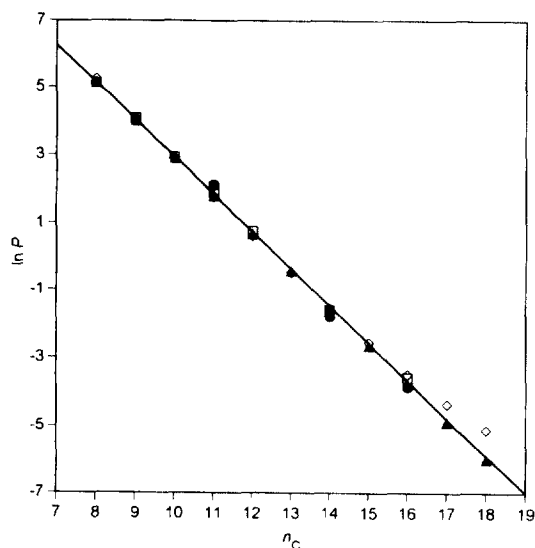


Fig. 1. Scatter plot of the observed ( $\square$  = Eq. 2) and literature ( $\bullet$  = experimental, Refs. [19–21];  $\blacktriangle$  = correlated data from Ref. [19];  $\diamond$  = group contribution method, Ref. [22]) data of vapour pressures for  $n$ -alkanals versus number of carbon atoms  $n_C$ . The line corresponds to Eq. 3.

### 3.2. Vapour pressures of alkenals

The relative retention times and calculated vapour pressures for  $C_{10}$ ,  $C_{12}$ ,  $C_{14}$  and  $C_{16}$

Table 3  
GC data and vapour pressures (25°C) of decenals

Aldehyde	Relative retention time <sup>a</sup>					Eq. 1		P (Pa)
	50°C	55°C	60°C	65°C	70°C	Intercept	Slope	
Z3-10:Ald	0.752	0.761	0.770	0.778	0.789	-0.4640	0.03734	25.73
E3-10:Ald	0.788	0.795	0.804	0.808	0.817	-0.3691	0.02751	24.08
Z4-10:Ald	0.755	0.764	0.773	0.781	0.790	-0.4513	0.03557	25.54
E4-10:Ald	0.781	0.786	0.794	0.799	0.807	-0.3689	0.02538	24.22
Z5-10:Ald	0.725	0.735	0.746	0.756	0.772	-0.5566	0.04876	27.31
E5-10:Ald	0.764	0.772	0.778	0.789	0.802	-0.4512	0.03766	25.38
Z6-10:Ald	0.778	0.786	0.794	0.804	0.813	-0.4248	0.03602	24.83
E6-10:Ald	0.782	0.789	0.805	0.804	0.815	-0.4003	0.03250	24.48
Z7-10:Ald	0.814	0.817	0.822	0.832	0.841	-0.3329	0.02594	23.33
E7-10:Ald	0.804	0.809	0.823	0.828	0.831	-0.3524	0.02819	23.63
Z8-10:Ald	0.925	0.930	0.934	0.940	0.946	-0.1606	0.01722	20.13
E8-10:Ald	0.870	0.873	0.881	0.886	0.894	-0.2478	0.02231	21.65

<sup>a</sup> Standard *n*-dodecane.

alkenals are listed in Tables 3–6. Inspection of these tables reveals that, in comparison to alkanals, most of the alkenals have greater vapour pressures. Additionally, three trends may be generally observed: First, the position of the

double bond affects the vapour pressures of aldehydes in a similar manner as found in alcohols [14]. Its position to both the polar ( $\Delta$ -unsaturation) and non-polar ( $\omega$ -unsaturation) end of the molecule is significant. However, how

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

Aldehyde	Relative retention time <sup>a</sup>					Eq. 1		P (Pa)
	50°C	60°C	70°C	80°C	90°C	Intercept	Slope	
Z2-12:Ald	7.088	6.283	5.693	5.146	4.639	2.809	-0.1781	1.81
E2-12:Ald	7.150	6.260	5.725	5.085	4.669	2.825	-0.1805	1.80
Z3-12:Ald	4.107	3.748	3.481	3.233	3.005	2.039	-0.1315	3.43
E3-12:Ald	4.308	3.896	3.604	3.339	3.082	2.128	-0.1403	3.22
Z4-12:Ald	4.008	3.649	3.409	3.183	2.943	1.999	-0.1284	3.54
E4-12:Ald	4.202	3.801	3.539	3.286	3.028	2.083	-0.1363	3.32
Z5-12:Ald	3.810	3.491	3.249	3.052	2.842	1.921	-0.1227	3.76
E5-12:Ald	4.065	3.686	3.432	3.204	2.971	2.022	-0.1307	3.48
Z6-12:Ald	3.966	3.610	3.376	3.156	2.941	1.968	-0.1246	3.61
E6-12:Ald	4.122	3.720	3.470	3.232	2.990	2.047	-0.1332	3.42
Z7-12:Ald	4.022	3.708	3.422	3.201	2.977	2.001	-0.1274	3.52
E7-12:Ald	4.119	3.751	3.486	3.248	3.010	2.040	-0.1313	3.42
Z8-12:Ald	4.272	3.846	3.563	3.295	3.088	2.099	-0.1370	3.28
E8-12:Ald	4.226	3.839	3.557	3.305	3.060	2.085	-0.1353	3.31
Z9-12:Ald	4.468	4.039	3.729	3.469	3.204	2.157	-0.1391	3.11
E9-12:Ald	4.491	4.030	3.722	3.434	3.184	2.186	-0.1443	3.07
Z10-12:Ald	5.180	4.623	4.262	3.905	3.577	2.380	-0.1547	2.61
E10-12:Ald	4.848	4.333	3.983	3.673	3.365	2.302	-0.1524	2.80

<sup>a</sup> Standard *n*-dodecane.

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

Aldehyde	Relative retention time <sup>a</sup>					Eq. 1		P (Pa)
	80°C	90°C	100°C	110°C	120°C	Intercept	Slope	
Z2-14:Ald	0.317	0.344	0.369	0.394	0.419	-1.303	0.09829	0.108
E2-14:Ald	0.320	0.349	0.372	0.396	0.421	-1.289	0.09637	0.106
Z3-14:Ald	0.200	0.223	0.244	0.267	0.291	-1.817	0.1318	0.207
E3-14:Ald	0.207	0.229	0.250	0.272	0.295	-1.772	0.1244	0.192
Z4-14:Ald	0.195	0.218	0.239	0.262	0.286	-1.846	0.1342	0.214
E4-14:Ald	0.203	0.225	0.247	0.268	0.291	-1.795	0.1267	0.198
Z5-14:Ald	0.184	0.207	0.229	0.252	0.275	-1.919	0.1427	0.239
E5-14:Ald	0.196	0.218	0.240	0.263	0.286	-1.845	0.1346	0.215
Z6-14:Ald	0.187	0.210	0.232	0.256	0.279	-1.899	0.1411	0.233
E6-14:Ald	0.197	0.219	0.242	0.263	0.286	-1.836	0.1326	0.211
Z7-14:Ald	0.187	0.209	0.230	0.254	0.277	-1.902	0.1398	0.232
E7-14:Ald	0.194	0.216	0.238	0.261	0.283	-1.853	0.1342	0.216
Z8-14:Ald	0.190	0.213	0.234	0.258	0.281	-1.879	0.1379	0.225
E8-14:Ald	0.198	0.219	0.241	0.264	0.287	-1.834	0.1327	0.211
Z9-14:Ald	0.197	0.220	0.241	0.266	0.289	-1.839	0.1353	0.214
E9-14:Ald	0.201	0.224	0.246	0.268	0.290	-1.812	0.1307	0.205
Z10-14:Ald	0.207	0.230	0.253	0.275	0.298	-1.781	0.1294	0.197
E10-14:Ald	0.207	0.229	0.251	0.274	0.296	-1.776	0.1268	0.194
Z11-14:Ald	0.217	0.241	0.263	0.284	0.306	-1.719	0.1218	0.180
E11-14:Ald	0.217	0.241	0.260	0.283	0.306	-1.715	0.1198	0.178
Z12-14:Ald	0.243	0.267	0.290	0.313	0.337	-1.600	0.1162	0.156
E12-14:Ald	0.229	0.253	0.272	0.296	0.319	-1.658	0.1162	0.166

<sup>a</sup> Standard *n*-octadecane.

close the double bond can be to the polar and non-polar end without mutual interaction occurring, is uncertain. Thus, considering the different structural features of the  $\omega$ -3 (7-10:Al, 9-12:Al, 11-14:Al and 13-16:Al),  $\omega$ -5 (5-10:Al, 7-12:Al, 9-14:Al and 11-16:Al) and  $\omega$ -7 (3-10:Al, 5-12:Al, 7-14:Al and 9-16:Al) alkenals, these subseries were treated separately. Despite the rather good linear correlation of the type  $\ln P [\text{Pa}] = a - bn_C$  achieved for all the  $\omega$ -subseries investigated ( $r^2 \geq 0.994$ ), inspection of the least-squares regression coefficients  $a$  and  $b$  reveals that the changes in the parameters are small and nearly always within the range of the 95% confidence limits. Both the intercepts  $a$  and slopes  $b$  vary only slightly (by ca.  $\pm 1\%$ ) around mean values of 14.835 and 1.1547, respectively. Note that the value of the slope  $b$  is similar to the slope of Eq. 3 ( $1.1051 \pm 0.0153$ ), indicating an approximate constancy of the  $\text{CH}_2$  contribution irrespective of

the homologous subseries considered. Second, (*Z/E*)-2-alkenals behave exceptionally, probably because of the presence of the conjugated enal system. Thus, the vapour pressures of (*Z/E*)-2-12:Al and (*Z/E*)-2-14:Al are markedly lower than the vapour pressures of corresponding saturated compounds. Third, in an approximate ( $\Delta$ -5,  $\omega$ -6) interval, the vapour pressures of alkenals, while higher than those of their saturated equivalents, change only insignificantly regardless of the double-bond position in the chain. The same effect as illustrated in Fig. 2 for the *Z*-homologous series may be observed for *E*-isomers with all curves closely resembling those shown in Fig. 2. Within each alkenal subseries, *Z*-isomers have mostly greater vapour pressures than their *E*-counterparts. However, a reverse behaviour may be invariably observed for  $\omega$ -2 alkenals (8-10:Al, 10-12:Al and 12-14:Al).

The only data on vapour pressures of enals



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

Aldehyde	Relative retention time <sup>a</sup>					Eq. 1		P (Pa)
	100°C	110°C	120°C	130°C	140°C	Intercept	Slope	
Z3-16:Ald	0.838	0.853	0.868	0.882	0.896	-0.2627	0.02750	0.0291
E3-16:Ald	0.863	0.874	0.886	0.896	0.908	-0.2113	0.02046	0.0269
Z4-16:Ald	0.825	0.832	0.849	0.866	0.885	-0.2905	0.02954	0.0301
E4-16:Ald	0.837	0.853	0.866	0.878	0.898	-0.2642	0.02750	0.0291
Z5-16:Ald	0.773	0.796	0.815	0.833	0.854	-0.3797	0.03965	0.0343
E5-16:Ald	0.819	0.831	0.849	0.865	0.883	-0.2981	0.03074	0.0305
Z6-16:Ald	0.775	0.796	0.818	0.838	0.852	-0.3751	0.03906	0.0340
E6-16:Ald	0.809	0.824	0.843	0.860	0.874	-0.3136	0.03227	0.0311
Z7-16:Ald	0.764	0.785	0.806	0.824	0.842	-0.3931	0.03992	0.0348
E7-16:Ald	0.800	0.815	0.834	0.850	0.862	-0.3217	0.03140	0.0313
Z8-16:Ald	0.768	0.786	0.809	0.828	0.849	-0.3930	0.04091	0.0349
E8-16:Ald	0.800	0.814	0.836	0.851	0.867	-0.3301	0.03371	0.0318
Z9-16:Ald	0.783	0.795	0.820	0.836	0.856	-0.3653	0.03743	0.0335
E9-16:Ald	0.819	0.825	0.848	0.865	0.881	-0.3036	0.03148	0.0307
Z10-16:Ald	0.800	0.813	0.835	0.852	0.871	-0.3365	0.03536	0.0323
E10-16:Ald	0.830	0.837	0.857	0.872	0.886	-0.2788	0.02817	0.0296
Z11-16:Ald	0.823	0.838	0.857	0.874	0.891	-0.2977	0.03259	0.0307
E11-16:Ald	0.846	0.854	0.870	0.885	0.898	-0.2483	0.02502	0.0284
Z12-16:Ald	0.869	0.890	0.895	0.910	0.922	-0.2094	0.02292	0.0271
E12-16:Ald	0.857	0.875	0.885	0.898	0.910	-0.2264	0.02376	0.0276
Z13-16:Ald	0.900	0.922	0.923	0.935	0.948	-0.1614	0.01917	0.0254
E13-16:Ald	0.895	0.905	0.911	0.920	0.932	-0.1609	0.01585	0.0251

<sup>a</sup> Standard *n*-octadecane.

were provided by Heath et al. [21]. The aldehydes studied and the vapour pressures in Pa reported were: Z9-14:Al, 0.4062 and Z11-16:Al, 0.0549. Using the same procedure as described for 14:Al and 16:Al, with the  $\Delta H$  values ( $\text{kJ mol}^{-1}$ ) found by McDonough [24] for 14:Al (78.12) and 16:Al (87.36) to recalculate their "room" temperature values to 25°C we obtain 0.241 and 0.031 Pa, respectively. If this is done, then the results of the present study (0.262 and 0.039 Pa) agree with those reported in [21] within 25%, with the literature values being consistently lower. It is to be noted, however, that the vapour pressure data on aldehydes reported in Ref. [21] seem to be slightly underestimated (see also Table 2). A similar conclusion has been drawn from a comparative study of evaporative half-lives of the aldehydes from rubber septa [24].

In summary, the equilibrium vapour pressures of aldehydes ranging in length from C<sub>9</sub> to C<sub>16</sub>

may be satisfactorily determined by the capillary GC method, provided that four alkanes, each covering a part of the total vapour pressure range ( $2 \cdot 10^1$ – $2 \cdot 10^{-2}$  Pa at 25°C) are used as vapour pressure reference standards. The vapour pressures show relations to the chain length and are affected to varying degrees by the presence of a double bond in the chain. For example, the vapour pressures always increased as the position of double bond became more internal on the alkyl chain. Some irregular trends were also observed. Due to the paucity of appropriate experimental data, especially on the low-volatility end of the scale, it is difficult to draw any definite conclusion on the accuracy of the method in determining the vapour pressures of aldehydes. However, based on the agreement of our  $P_{GC}$  values with some ebulliometric data, as well as on very good extrapolation ability of our model to the high-volatility region (up to C<sub>5</sub>

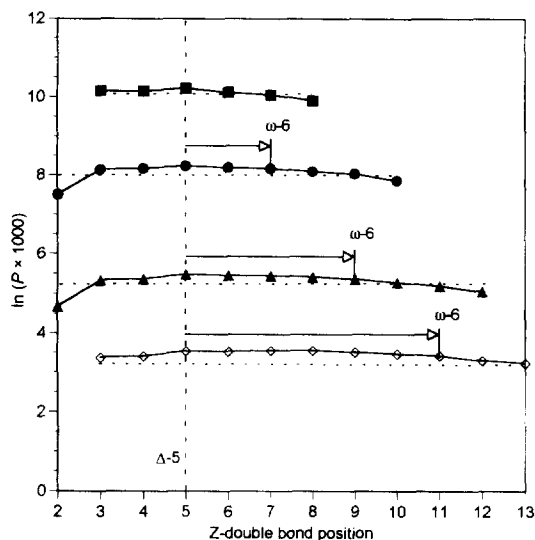


Fig. 2. Vapour pressures for Z-alkenals plotted against the respective double-bond position. (■) decenals; (●) dodecenals; (▲) tetradecenals; (◇) hexadecenals. Dashed lines show the vapour pressures of the corresponding saturated compounds.

aldehyde), we tentatively assume that the relative error should be under  $\pm 15\%$ .

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### References

- [1] J.C. Baker, *Experientia*, 45 (1989) 248.
- [2] D. Schneider, *Naturwissenschaften*, 79 (1992) 241.
- [3] M.S. Mayer and J.R. McLaughlin (Editors), *CRC Handbook of Insect Pheromones and Sex Attractants*, CRC Press, Boca Raton, FL, 1991.
- [4] J.H. Tumlinson, in R.L. Ridgway, R.M. Silverstein and M.N. Inscoe (Editors), *Behaviour-Modifying Chemicals for Insect Management—Applications of Pheromones and Other Attractants*, Marcel Dekker, New York, 1990, Ch. 5.
- [5] D. Mackay and S. Paterson, *Environ. Sci. Technol.*, 25 (1991) 427.
- [6] D.J. Hamilton, *J. Chromatogr.*, 195 (1980) 75.
- [7] J.W. Westcott and T.F. Bidleman, *J. Chromatogr.*, 210 (1981) 331.
- [8] T.F. Bidleman, *Anal. Chem.*, 56 (1984) 2490.
- [9] D.A. Hinckley, T.F. Bidleman, W.T. Foreman and J.R. Tushall, *J. Chem. Eng. Data*, 35 (1990) 232.
- [10] Y.-Kim, J.E. Woodrow and J.N. Seiber, *J. Chromatogr.*, 314 (1984) 37.
- [11] D.W. Hawker, *Environ. Sci. Technol.*, 23 (1989) 1250.
- [12] D.W. Hawker, *Chemosphere*, 25 (1992) 427.
- [13] B. Koutek, M. Hoskovec, K. Konečný and J. Vrkoč, *J. Chromatogr.*, 626 (1992) 215.
- [14] B. Koutek, M. Hoskovec, P. Vrkočová, K. Konečný and L. Felzl, *J. Chromatogr. A*, 679 (1994) 307.
- [15] S.E. Stein, *J. Chem. Soc. Faraday Trans. 1*, 77 (1981) 1457.
- [16] S. Salerno, M. Cascella, D. May, P. Watson and D. Tassios, *Fluid Phase Equilibria*, 27 (1986) 15.
- [17] N. Allemand, J. Jose and J.C. Merlin, *Thermochim. Acta*, 105 (1986) 79.
- [18] K. Růžička and V. Majer, *J. Phys. Chem. Ref. Data*, 23 (1994) 1.
- [19] G.N. Djakova, G.L. Korichev, A.D. Korkhov, T.F. Vasiljeva and I.A. Vasiljev, *Zh. Prikl. Khim.*, 54 (1981) 1644.
- [20] J. Dykyj, M. Repáš and J. Svoboda, *Tlak Nasýtenej Pary Organických Zlúčenin*, Vydavateľstvo Slovenskej Akadémie Vied, Bratislava, Czechoslovakia, Vol. I, 1979; Vol. II, 1984.
- [21] R.R. Heath, P.E.A. Teal, J.H. Tumlinson and L.J. Mengelkoch, *J. Chem. Ecol.*, 12 (1986) 2133.
- [22] Chei-Hsiun Tu, *Fluid Phase Equilibria*, 99 (1994) 105.
- [23] R.C. Reid, J.M. Prausnitz and B.E. Poling, *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York, 1987.
- [24] L.M. McDonough, in P.A. Hedin (Editor), *Naturally Occurring Pest Bioregulators*, ACS Symp. Ser. Vol. 449, American Chemical Society, Washington, DC, 1991, Ch.8.
- [25] W. Spieksma, R. Luijk and H.A.J. Govers, *J. Chromatogr. A*, 672 (1994) 141.