

# Predictive strategies for determining retention indices of some allylic alcohols and their esters by gas chromatography

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## Abstract

Improved structure retention index relationships were used to predict retention index values for some allylic alcohols and unsaturated esters on polar and non-polar stationary phases. Using this method, we were also able to establish group retention factors, for these systems. In these computations, it was found that our predicted retention index values had percentage differences to within  $\pm 3.00\%$  of the observed retention index in more than 95% of the experiments performed. This reconfirmed the applicability of the retention index increment methodology. The importance of  $n-\pi$  orbital overlap of lone pairs of electrons and C=C bonds in these molecules was also shown to be a crucial factor in establishing the strength of intra- and intermolecular interactions between solute and stationary phases.

**Keywords:** Structure–retention relationships; Retention indices; Group retention factors; Allylic alcohols

## 1. Introduction

Over the past two decades, extensive study of structure retention index relationships (SRIR) has led to the development of sophisticated computerized methods, which relate molecular structure to gas chromatographic retention phenomena [1–10]. These approaches have provided insight into both the intra- and intermolecular interactions that affect and influence solute–stationary phase absorption processes.

In a study of cyclohexane and cyclohexene ring systems, Buchman et al. [11] reported that by looking at the effect of a particular substituent on a homologous series of a few reference compounds, retention index increments ( $\delta I$ ) due to that substituent could be established on both polar and non-

polar columns. In other words, if  $I_{\text{subst}}$  is the retention index of a compound bearing a substituent and  $I_o$  is the retention index of that compound without the substituent, then

$$\delta I = I_{\text{subst}} - I_o \quad (1)$$

Following on this work, Peng et al. [12–15], outlined a method for the prediction of retention indices using three parameters: (i) the total number of carbon atoms ( $N$ ) or the total number of carbon atoms and carbon atom equivalents ( $Z$ ) in the molecule, (ii) the retention index increment and (iii) the group retention factor (GRF) for substituents and functional groups. From this information, the retention index ( $I_{\text{cp}}$ ) could be predicted by using the following expression:

$$I_{\text{cp}} = 100Z + \sum m_i - \sum n_i \quad (2)$$

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where 100Z represents the retention index contribution from the atoms in the molecule,  $m_i$  and  $n_i$  represent the GRFs of the  $i$ th functional group or substituent [11–13] and are given by

$$m, n = \delta I - 100Z \quad (3)$$

We needed to investigate some volatile terpenes using the SRIR system presented by Peng et al. [12,13]. They proposed that the allylic alcohol moiety should be considered as a combination of groups – the 1° alcohol and the non-terminal C=C bond. The GRF of the allylic alcohol would therefore be a composite of the GRFs of both of these groups. The possibility of intramolecular interaction between the two functionalities [16], however, suggested that better approximations could be obtained if such systems were treated as one group. We explored this and now report our findings.

We also investigated the effect of changing the hydroxyl group of linalool and geraniol to the esters – methanoate through to pentanoate. In their work to determine GRFs for esters, Peng et al. [12] stated that the retention of esters on the polar column could be predicted using the column difference ( $\Delta I$ ) between polar and non-polar columns. This value is added to the base value as follows:

$$I_{cp} = 100Z + \sum m_i - \sum n_i + \Delta I \quad (4)$$

We felt that an examination of the GC retention characteristics of the linalyl and geranyl esters would possibly lead us to a better understanding of the retention mechanisms involved for these systems and thus add to the literature on unsaturated esters [17,18].

## 2. Experimental

Standards and reference chemicals were obtained from Aldrich, BDH and Sigma and were used without further purification. *n*-Butyl esters of linalool and geraniol were prepared by the method of Brewster and Ciotti [19].

GC experiments were performed on a Varian 3700 gas chromatograph equipped with a flame ionization detector. High purity N<sub>2</sub> was used as the carrier gas, at a flow-rate of 1.0 ml/min through the column and

subsequently increased to 30 ml/min through the detector. The flow-rates of O<sub>2</sub> and H<sub>2</sub> were set at 300 and 30 ml/min, respectively. Injector and detector temperatures were set at 250 and 270°C, respectively. Injections (1.0 μl) of the samples were made and peak data collected and analyzed on a Hewlett-Packard model 3350C electronic integrator. GC–MS experiments were performed on a Varian 3400 gas chromatograph with a Finnigan MAT Ion Trap 800 mass spectrometer. The capillary columns used in these experiments were a fused-silica SE-30 column (30 m × 0.25 mm × 0.25 μm film thickness) with the initial column temperature set at 40°C for 4.0 min and programmed to increase at a rate of 3.0°C/min to 250°C and held for 5.0 min and a Supelcowax 10 column (30 m × 0.32 mm × 0.25 μm film thickness), with the initial column temperature set at 40°C, without an initial hold time and programmed to increase to 190°C at a ramp rate of 3.0°C/min. Both capillary columns were obtained from Supelco. The injector temperature for GC–MS experiments was set at 250°C and the carrier gas flow-rate through the column was optimized to 1.0 ml/min with high purity helium. All experiments were performed in the splitless mode. The transfer line temperature from GC to the mass spectrometer was set at 260°C, for both columns. The ion trap detector (ITD) was operated at an electron energy of 70 eV, with the multiplier voltage optimized at between 1500 and 1850 V. Retention indices ( $I_{obs}$ ) were computed using the Van den Dool and Kratz equation [20] and predicted retention indices ( $I_p$ ) were obtained by the method of Peng et al. [12–15].

## 3. Results and discussion

The elution characteristics of an homologous series of allylic alcohols, from C<sub>4</sub>–C<sub>7</sub>, was examined on both polar and non-polar stationary phases. Plots of  $I_{obs}$  versus the number of carbon and oxygen atoms ( $Z$ ) as well as of carbon atoms ( $N$ ) gave the following regression equations, which are used to predict the retention indices ( $I_p$ ) of this series;

### 3.1. Supelcowax 10 (polar) column

$$I_p = 98.90(\pm 1.51)Z + 731.30(\pm 8.43) \quad (5a)$$

$$I_p = 98.90(\pm 1.51)N + 830.20(\pm 6.99) \quad (5b)$$

$$(n = 4, R^2 = 0.9995, p = 2.32 \times 10^{-4})$$

### 3.2. SE-30 (non-polar) column

$$I_p = 107.50(\pm 1.47)Z + 102.00(\pm 8.23) \quad (6a)$$

$$I_p = 107.50(\pm 1.47)N + 209.50(\pm 6.80) \quad (6b)$$

$$(n = 4, R^2 = 0.9996, p = 2.00 \times 10^{-4})$$

where  $R^2$  = coefficient of determination,  $n$  = number of compounds examined,  $p$  = significance probability (significance of getting a greater  $F$ -statistic than that obtained if the hypothesis is true), and standard errors for regression coefficients and intercepts are given in parenthesis.

From these equations, it was noted that the intercepts (i.e. GRFs) for the allylic alcohol group were larger than the  $\text{GRF}_{\text{cp}}$  (that proposed by Peng's calculations) on the polar column and smaller than  $\text{GRF}_{\text{cp}}$  on the non-polar column (Table 1). It is possible that the retention of this system is being influenced by: (i) inductive effects resulting in increased electron density on the oxygen atom of the hydroxyl group, (ii) intramolecular cyclization between  $\text{C}=\text{C}$  bond and the hydroxyl oxygen atom, i.e.,  $n-\pi$  orbital overlap and (iii) the relative polarities of the stationary phases [16,21]. The polyethylene glycol (PEG) chain of the polar column can

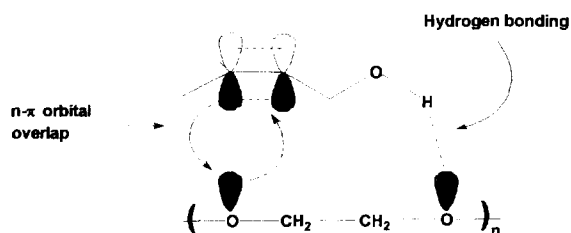


Fig. 1. Intermolecular interactions between allylic alcohol and a polyethylene glycol (polar) stationary phase.

accommodate increased intermolecular interactions through hydrogen bonding and  $n-\pi$  orbital overlap with the allylic alcohol. These interactions would be facilitated by a linear conformation of the alcohol along the backbone of the stationary phase, resulting in increased retention of the system relative to an isolated  $1^\circ$  alcohol and  $\text{C}=\text{C}$  bond (Fig. 1).

For the non-polar column, approach of the allylic alcohol to the polydimethyl siloxane stationary phase interface, in a linear conformation, should be slightly hindered by the presence of the two methyl groups on the silicon atoms. In such a case, intramolecular cyclization between the lone pair of electrons on the hydroxyl oxygen and the  $\text{C}=\text{C}$  bond would be enhanced, resulting in decreased intermolecular interaction with the stationary phase (Fig. 2) and, thus, a lowering of the GRF relative to Peng's proposed values. The data are summarized in Table 2 Table 3.

Three other allylic alcohols – geraniol, nerol and linalool – were subsequently examined. For the  $E/Z$ -isomers, geraniol and nerol,  $I_p$  values were computed using the GRFs for the allylic alcohol moiety. The

Table 1

Group retention factors for  $1^\circ$  alcohol, non-terminal  $\text{C}=\text{C}$  bond and an experimentally determined allylic alcohol group on polar and non-polar columns

Group	Polar $\text{GRF}_{\text{cp}}$	Column $^a\text{GRF}_p$	Non-polar $\text{GRF}_{\text{cp}}$	Column $^a\text{GRF}_p$
$1^\circ$ Alcohol	+647	+731.30	+156	+102.00
NT $\text{C}=\text{C}$	+60	–	+27	–
Total	+707	+731.30	+183	+102.00

NT = non-terminal carbon–carbon double bond;  $\text{GRF}_{\text{cp}}$  = group retention factor using Peng's calculations.

$^a\text{GRF}_p$  = group retention factors from linear regression equations (see text).

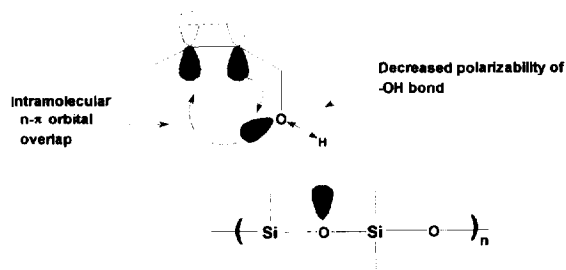


Fig. 2. Intramolecular interactions within allylic alcohol on a polydimethylsiloxane (non-polar) stationary phase.

Table 2

Comparison of % differences between  $I_{cp}$  and  $I_p$  for allylic alcohols, linalyl and geranyl esters on the polar column GRF ( $m_i$  and  $n_i$ ) for (1) primary alcohol = +647 I.U., (2) non-terminal C=C bond = +60 I.U., (3) terminal C=C bond = +40 I.U. and (4) tertiary carbon atom = -75 I.U.

Compound	$I_{obs}$ [19]	% Diff <sub>cp</sub>	% Diff <sub>p</sub>
<i>Allylic alcohols</i>			
2-Propen-1-ol	1125	+3.38	+0.36
2-Buten-1-ol	1227	+1.63	+0.57
2-Penten-1-ol	1328	+1.58	+0.75
2-Hexen-1-ol	1421	+0.99	+0.28
<i>Linalyl ester series</i>			
Methanoate	1579	-8.04	+7.41
Ethanoate	1551	-11.86	+1.16
Propanoate	1586	-12.93	+3.34
Butyrate	1663	-12.33	-0.84
Pentanoate	1765	-12.75	+0.91
<i>Geranyl ester series</i>			
Methanoate	1697	-9.31	+0.41
Ethanoate	1752	-8.68	-0.28
Propanoate	1816	-9.86	-0.38
Butyrate	1889	-10.27	0.00
Pentanoate	1960	-9.59	+0.25

$$\%Diff_{cp} = (I_{obs} - I_{cp}) \times 100 / (I_{obs})$$

$$\%Diff_p = (I_{obs} - I_p) \times 100 / (I_{obs})$$

$I_{cp}$  determined as stated by Peng et al. [13].

$I_p$  determined from Eqs. (5a), (9a), (10a) for allylic alcohols, linalyl and geranyl esters, respectively.

differences in  $I_{obs}$  for nerol and geraniol on the polar and non-polar columns were -20 and -13 I.U., respectively. These latter values represented the corrections due to "isomeric effects" and were included in our computations of  $I_p$  [12,13], resulting in significant improvements in  $I_p$  over  $I_{cp}$  for nerol and geraniol, particularly on the non-polar column (Table 4 Table 5). In the case of linalool,  $\pi$ - $\pi$  orbital overlap between the terminal and non-terminal C=C bonds would effectively reduce electron density around the terminal C=C bond and hence decrease the possibility of n- $\pi$  orbital overlap, thus, the GRF for allylic alcohols was not used.

In the second study, the effect of unsaturation in the alcohol moiety of methanoate through pentanoate esters of linalool and geraniol were investigated. Retention of both groups of esters was found to be governed by Eqs. (7a)-(10b) on the respective stationary phases.

Table 3

Comparison of % differences  $I_{cp}$  and  $I_p$  for allylic alcohols, linalyl and geranyl esters on the non-polar column GRF ( $m_i$  and  $n_i$ ) for (1) primary alcohol = +156 I.U., (2) non-terminal C=C bond = +27 I.U., (3) terminal C=C bond = -10 I.U. and (4) tertiary carbon atom = +15 I.U.

Compound	$I_{obs}$ [19]	%Diff <sub>cp</sub>	%Diff <sub>p</sub>
<i>Allylic alcohols</i>			
2-Propen-1-ol	530	-3.02	-0.38
2-Buten-1-ol	641	-6.55	+0.23
2-Penten-1-ol	750	-4.40	+0.40
2-Hexen-1-ol	852	-3.64	-0.29
<i>Linalyl ester series</i>			
Methanoate	1198	-11.18	+1.59
Ethanoate	1241	-15.39	-1.37
Propanoate	1320	-16.06	-1.21
Butyrate	1420	-14.93	+0.42
Pentanoate	1500	-15.47	+0.53
<i>Geranyl ester series</i>			
Methanoate	1262	-7.29	-0.32
Ethanoate	1368	-6.87	+0.88
Propanoate	1441	-7.84	-0.35
Butyrate	1526	-14.93	-0.65
Pentanoate	1632	-7.47	+0.43

$$\%Diff_{cp} = (I_{obs} - I_{cp}) \times 100 / (I_{obs})$$

$$\%Diff_p = (I_{obs} - I_p) \times 100 / (I_{obs})$$

$I_{cp}$  determined as stated by Peng et al. [12].

$I_p$  determined from Eqs. (6a), (7a), (8a) for allylic alcohols, linalyl and geranyl esters, respectively.

Table 4

Comparison of  $I_{obs}$ ,  $I_{cp}$  and  $I_p$  for the allylic alcohols on the polar column GRF ( $m_i$  and  $n_i$ ) for (1) primary alcohol = +647 I.U., (2) non-terminal (NT) carbon-carbon double bond = +60 I.U., (3) terminal carbon-carbon double bond = +40 I.U., (4) chain branching/iso-carbon = -50 I.U., (5) <sup>a</sup>hyperconjugation = -8 I.U., (6) allylic alcohol = +731 I.U., (7) <sup>b</sup>trans-cis isomers = -20 I.U. and (8) tertiary alcohol = +410 I.U.

Compound	I/I.U.	%Diff.
Linalool ( $I_{obs} = 1545$ )		
$1100 + 40 + 60 + 410 - 75 = I_{cp}$	1535	+0.65
$1100 + 40 + 60 + 410 - 75 - (8 \times 2) = I_p$	1519	+1.68
Nerol ( $I_{obs} = 1824$ )		
$1100 + 647 + (60 \times 2) = I_{cp}$	1867	-2.36
$1100 + 731 + 60 - (8 \times 3) - 20 = I_p$	1847	-1.26
Geraniol ( $I_{obs} = 1844$ )		
$1100 + 647 + (60 \times 2) = I_{cp}$	1867	-1.25
$1100 + 731 + 60 - (8 \times 3) = I_p$	1867	-1.25

<sup>a</sup> Increment for hyperconjugation estimated from Soják et al. [22].

<sup>b</sup> Increment for trans-cis isomerism calculated as described by Peng et al. [12,13].

Table 5

Comparison of  $I_{\text{obs}}$ ,  $I_{\text{cp}}$  and  $I_{\text{p}}$  for the allylic alcohols on the non-polar column GRF ( $m_i$  and  $n_i$ ) for (1) primary alcohol = +156 I.U., (2) non-terminal (NT) carbon-carbon double bond = +27 I.U., (3) terminal carbon-carbon double bond = -10 I.U., (4) chain branching/iso-carbon = -40 I.U., (5) <sup>a</sup>hyperconjugation = +10 I.U., (6) allylic alcohol = +102 I.U., (7) <sup>b</sup>*trans-cis* isomers = -13 I.U. and (8) tertiary alcohol = +15 I.U.

Compound	I/I.U.	%Diff.
Linalool ( $I_{\text{obs}} = 1081$ )		
$1100 + 27 + 15 - 40 - 10 = I_{\text{cp}}$	1092	-1.02
$1100 + 27 + 15 - 40 - 10 + (10 \times 2) = I_{\text{p}}$	1112	-2.87
Nerol ( $I_{\text{obs}} = 1218$ )		
$1100 + 156 + (27 \times 2) = I_{\text{cp}}$	1310	-7.55
$1100 + 102 + 27 + (10 \times 3) - 13 = I_{\text{p}}$	1246	-2.30
Geraniol ( $I_{\text{obs}} = 1231$ )		
$1100 + 156 + (27 \times 2) = I_{\text{cp}}$	1310	-6.42
$1100 + 102 + 27 + (10 \times 3) = I_{\text{p}}$	1259	-2.27

<sup>a</sup> Increment for hyperconjugation estimated from Soják et al. [22].

<sup>b</sup> Increment for *trans-cis* isomerism calculated as described by Peng et al. [12,13].

## 4. Non-polar column

### 4.1. Linalyl ester series

$$I_{\text{p}} = 78.30(\pm 5.68)Z + 161.30(\pm 85.58) \quad (7a)$$

$$I_{\text{p}} = 78.30(\pm 5.68)N + 317.90(\pm 74.28) \quad (7b)$$

$$(n = 5, R^2 = 0.9845, p = 8.00 \times 10^{-4})$$

### 4.2. Geranyl ester series

$$I_{\text{p}} = 89.80(\pm 3.27)Z + 98.80(\pm 9.24) \quad (8a)$$

$$I_{\text{p}} = 89.80(\pm 3.27)N + 278.40(\pm 42.74) \quad (8b)$$

$$(n = 5, R^2 = 0.996, p = 1.00 \times 10^{-4})$$

## 5. Polar column

### 5.1. Linalyl ester series

$$I_{\text{p}} = 71.90(\pm 10.66)Z + 526.80(\pm 165.68) \quad (9a)$$

$$I_{\text{p}} = 71.90(\pm 10.66)N + 670.60(\pm 144.42) \quad (9b)$$

$$(n = 5, R^2 = 0.9579, p = 0.021)$$

### 5.2. Geranyl ester series

$$I_{\text{p}} = 66.30(\pm 2.11)Z + 828.30(\pm 31.83) \quad (10a)$$

$$I_{\text{p}} = 66.30(\pm 2.11)N + 960.90(\pm 27.63) \quad (10b)$$

$$(n = 5, R^2 = 0.9969, p = 7.11 \times 10^{-5})$$

Significant improvements in  $I_{\text{p}}$  over  $I_{\text{cp}}$  calculations were observed on non-polar and polar columns for both ester series. Our study showed that unsaturation in the alcohol portion of the molecule does affect ester retention. The effect is seen as a reduction in the atom increment or regression coefficient [15], from 100 to between 89.90 and 66.00 I.U. for both ester series (Eqs. (7a)–(10b)). Percentage differences between  $I_{\text{obs}}$  and  $I_{\text{cp}}$  or  $I_{\text{p}}$  highlighted the importance of establishing GRFs for each class of compounds. Improvements of better than 7.0% were observed for  $I_{\text{p}}$  over  $I_{\text{cp}}$  on either stationary phase, and ranged between  $\pm 3.40\%$  of  $I_{\text{obs}}$  for all but linalyl methanoate on the polar column (Tables 2 and 3).

For linalyl esters on the polar column, the methanoate and ethanoate showed a reversal in the expected order of elution. This was highlighted by the large standard error of  $\pm 10.66$  for the gradient relative to that observed in Eqs. (9a), (9b). We attributed this anomaly in elution to stronger intramolecular cyclization between the lone pair of electrons on the oxygen atom of the ethanoate carbonyl and the  $\pi$ -orbital of the terminal C=C bond, leading to the formation of a pseudo-six-membered ring system (Fig. 3). It is likely that electron density around the carbonyl oxygen in linalyl ethanoate is higher than in methanoate, due to the inductive effect of the methyl group of the ester moiety in the former, versus the -H atom in the latter. As the ester series progresses, steric effects begin to predominate and the elution pattern becomes more ordered.

On the non-polar column, such cyclic structures, from the methanoate to pentanoate esters of linalool, would render the esters increasingly non-polar and, hence, increase intermolecular interactions as the

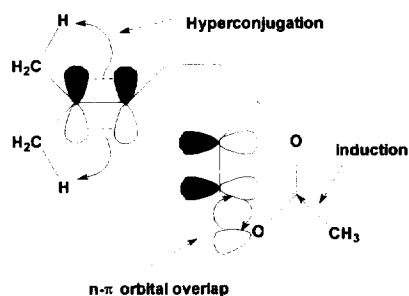


Fig. 3. Intramolecular orbital overlap occurring in linalyl ethanoate on the polar column.

series progresses. Pseudo cyclic structures would be unlikely in the geranyl esters since the allylic system is locked in the *cis*-geometry.

## 6. Conclusions

For simple allylic alcohols, GRFs may be better treated as a composite of both the primary hydroxyl and the non-terminal C=C bond. One explanation for this may be the possibility of intramolecular interactions within the system. For the unsaturated esters, the difference in elution order of methanoate and ethanoate esters of linalool on the polar column may be explained in terms of the likelihood of these compounds assuming cyclic conformations. Taking these factors into consideration resulted in significant improvements of  $I_p$  over  $I_{cp}$  for the compounds studied.

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