

CHROM. 21 303

## DISPERSION AND SELECTIVITY INDICES IN GAS CHROMATOGRAPHY

### PART II<sup>a</sup>. STUDIES OF HOMOLOGOUS CARBONYL AND CARBOXYL COMPOUNDS

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#### SUMMARY

The division of the retention indices of simple carbonyl-containing compounds into components indicative of apolar and polar interactions is reported. About 200 compounds in 40 homologous series were studied, including simple esters with branching and unsaturation in both the alkyl or alcohol and acyl chains, simple and difunctional ketones and simple and branched-chain pyruvate esters. The effects of the various structural parameters are compared with those observed in earlier studies which considered the relationship between retention behaviour and structural parameters.

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#### INTRODUCTION

An extension of the retention index scheme has recently been reported<sup>1</sup> in which the retention index of a solute was divided to show the contributions of apolar forces and polar interactions moderated by steric effects. The apolar forces, described as dispersion indices ( $I_M$ ), are assumed to be related to the molecular weight of the solute and the polar interactions, described as selectivity indices ( $I^*$ ), are influenced by structure and the stationary phase used. The relationship is

$$I = I_M + I^* \quad (1)$$

where  $I_M$  is defined as the retention index of a hypothetical *n*-alkane having the same molecular weight as the solute and determined by eqn. 2 and  $I^*$  is determined by subtraction.

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<sup>a</sup> For Part I, see ref. 1.

$$I_M = \frac{MW - 2.016}{0.14026} \quad (2)$$

It has been shown generally that solutes possessing polar functional groups tend towards positive  $I^*$  values whereas solutes with screened electrons yield negative  $I^*$  values. The selectivity parameter has also been shown to be influenced by structural considerations and the effects were examined using a wide range of carbonyl compounds in which the functional groups are of varying but modest polar character using stationary phases that are generally regarded as being of low polarity and to possess donor and acceptor characteristics.

## EXPERIMENTAL

The retention indices were determined isothermally at 150°C using 12 ft.  $\times$  1/4 in. O.D. aluminium columns packed with 10% stationary phase on 62-72-mesh acid-washed, silanized Celatom as reported previously<sup>2-5</sup>.

## RESULTS AND DISCUSSION

Dispersion and selectivity indices for the various homologous compounds considered are shown in Table I. It is apparent that the values of  $I^*$  for the *n*-alkyl alkanoates with a constituent carboxyl group of modest polarity decrease both as the

TABLE I  
DISPERSION ( $I_M$ ) AND SELECTIVITY ( $I^*$ ) INDICES FOR CARBONYL AND CARBOXYL COMPOUNDS AT 150°C ON SE-30, OV-25 AND SILAR 5CP

Series	Compound	$I_M$	$I^*$		
			SE-30	OV-25	SILAR 5CP
Formates	<i>n</i> -C <sub>1</sub>	413.8	-27.8	157.2	348.2
	<i>n</i> -C <sub>2</sub>	513.8	-18.8	141.2	346.2
	<i>n</i> -C <sub>3</sub>	613.8	-11.8	142.2	341.2
	<i>n</i> -C <sub>4</sub>	713.8	-6.8	138.2	345.2
	<i>n</i> -C <sub>5</sub>	813.8	-3.8	138.2	342.2
	<i>n</i> -C <sub>6</sub>	913.8	-6.8	133.2	340.2
	Isopropyl	613.8	-61.8	72.2	255.2
	Isobutyl	713.8	-43.8	89.2	301.2
	Isopentyl	813.8	-36.8	101.2	299.2
Acetates	<i>n</i> -C <sub>1</sub>	513.8	-4.8	179.2	336.2
	<i>n</i> -C <sub>2</sub>	613.8	-21.8	146.2	309.2
	<i>n</i> -C <sub>3</sub>	713.8	-18.8	139.2	299.2
	<i>n</i> -C <sub>4</sub>	813.8	-19.8	135.2	302.2
	<i>n</i> -C <sub>5</sub>	913.8	-22.8	130.2	298.2
	<i>n</i> -C <sub>6</sub>	1013.8	-25.8	119.2	389.2
	Isopropyl	713.8	-70.8	68.2	200.2
	Isobutyl	813.8	-63.8	84.2	249.2
	Isopentyl	913.8	-54.8	87.2	258.2

TABLE I (continued)

Series	Compound	$I_M$	$I^*$		
			SE-30	OV-25	SILAR 5CP
Propionates	<i>n</i> -C <sub>1</sub>	613.8	3.2	161.2	333.2
	<i>n</i> -C <sub>2</sub>	713.8	-21.8	131.2	284.2
	<i>n</i> -C <sub>3</sub>	813.8	-24.8	120.2	284.2
	<i>n</i> -C <sub>4</sub>	913.8	-27.8	118.2	281.2
	<i>n</i> -C <sub>5</sub>	1013.8	-33.8	111.2	275.2
	<i>n</i> -C <sub>6</sub>	1113.8	-39.8	101.2	274.2
	Isopropyl	813.8	-80.8	57.2	187.2
	Isobutyl	913.8	-65.8	71.2	227.2
	Isopentyl	1013.8	-65.8	72.2	229.2
Butanoates	<i>n</i> -C <sub>1</sub>	713.8	-11.8	154.2	318.2
	<i>n</i> -C <sub>2</sub>	813.8	-35.8	117.2	271.2
	<i>n</i> -C <sub>3</sub>	913.8	-38.8	108.2	265.2
	<i>n</i> -C <sub>4</sub>	1013.8	-44.8	100.2	258.2
	<i>n</i> -C <sub>5</sub>	1113.8	-51.8	97.2	248.2
	<i>n</i> -C <sub>6</sub>	1213.8	-57.8	78.2	237.2
	Isopropyl	913.8	-93.8	41.2	177.2
	Isobutyl	1013.8	-80.8	51.2	203.2
	Isopentyl	1113.8	-74.8	49.2	202.2
Pentanoates	<i>n</i> -C <sub>1</sub>	813.8	-6.8	147.2	317.2
	<i>n</i> -C <sub>2</sub>	913.8	-37.8	100.2	265.2
	<i>n</i> -C <sub>3</sub>	1013.8	-42.8	97.2	207.2
	<i>n</i> -C <sub>4</sub>	1113.8	-50.8	91.2	242.2
	<i>n</i> -C <sub>5</sub>	1213.8	-58.8	91.2	200.2
	<i>n</i> -C <sub>6</sub>	1313.8	-66.8	68.2	225.2
	Isopropyl	1013.8	-98.8	32.2	166.2
	Isobutyl	1113.8	-85.8	42.2	193.2
	Isopentyl	1213.8	-81.8	39.2	191.2
Hexanoates	<i>n</i> -C <sub>1</sub>	913.8	-11.8	142.2	311.2
	<i>n</i> -C <sub>2</sub>	1013.8	-37.8	104.2	261.2
	<i>n</i> -C <sub>3</sub>	1113.8	-49.8	93.2	249.2
	<i>n</i> -C <sub>4</sub>	1213.8	-57.8	81.2	200.2
	<i>n</i> -C <sub>5</sub>	1313.8	-67.8	70.2	225.2
	<i>n</i> -C <sub>6</sub>	1413.8	-76.8	56.2	212.2
	Isopropyl	1113.8	-95.8	17.2	161.2
	Isobutyl	1213.8	-94.8	32.2	183.2
	Isopentyl	1313.8	-101.8	28.2	180.2
Isobutanoates	<i>n</i> -C <sub>1</sub>	713.8	-48.8	98.2	243.2
	<i>n</i> -C <sub>2</sub>	813.8	-81.8	61.2	202.2
	<i>n</i> -C <sub>3</sub>	913.8	-77.8	54.2	193.2
	<i>n</i> -C <sub>4</sub>	1013.8	-82.8	45.2	187.2
	<i>n</i> -C <sub>5</sub>	1113.8	-89.8	41.2	180.2
	<i>n</i> -C <sub>6</sub>	1213.8	-96.8	24.2	169.2
	<i>iso</i> -C <sub>3</sub>	913.8	-133.8	-25.8	200.2
	<i>iso</i> -C <sub>4</sub>	1013.8	-114.8	-6.8	135.2
	<i>iso</i> -C <sub>5</sub>	1113.8	-119.8	-5.8	135.2

(Continued on p. 220)

TABLE I (continued)

Series	Compound	$I_M$	$I^*$		
			SE-30	OV-25	SILAR 5CP
Isopentanoates	<i>n</i> -C <sub>1</sub>	813.8	-50.8	88.2	249.2
	<i>n</i> -C <sub>2</sub>	913.8	-74.8	53.2	200.2
	<i>n</i> -C <sub>3</sub>	1013.8	-84.8	45.2	192.2
	<i>n</i> -C <sub>4</sub>	1113.8	-92.8	35.2	182.2
	<i>n</i> -C <sub>5</sub>	1213.8	-101.8	24.2	176.2
	<i>n</i> -C <sub>6</sub>	1313.8	-109.8	22.2	160.2
	<i>iso</i> -C <sub>3</sub>	1013.8	-139.8	-24.8	113.2
	<i>iso</i> -C <sub>4</sub>	1113.8	-128.8	-17.8	132.2
<i>iso</i> -C <sub>5</sub>	1213.8	-132.8	-18.8	129.2	
Isohexanoates	<i>n</i> -C <sub>1</sub>	913.8	-38.8	105.2	263.2
	<i>n</i> -C <sub>2</sub>	1013.8	-70.8	64.2	205.2
	<i>n</i> -C <sub>3</sub>	1113.8	-78.8	51.2	199.2
	<i>n</i> -C <sub>4</sub>	1213.8	-90.8	38.2	188.2
	<i>n</i> -C <sub>5</sub>	1313.8	-98.8	26.2	176.2
	<i>n</i> -C <sub>6</sub>	1413.8	-107.8	13.2	160.2
	<i>iso</i> -C <sub>3</sub>	1113.8	-134.8	-18.8	115.2
	<i>iso</i> -C <sub>4</sub>	1213.8	-124.8	-11.8	126.2
<i>iso</i> -C <sub>5</sub>	1313.8	-132.8	-15.8	128.2	
2-Methylpentanoates	<i>n</i> -C <sub>1</sub>	913.8	-60.8	75.2	217.2
	<i>n</i> -C <sub>2</sub>	1013.8	-96.8	39.2	159.2
	<i>n</i> -C <sub>3</sub>	1113.8	-104.8	22.2	152.2
	<i>n</i> -C <sub>4</sub>	1213.8	-116.8	9.2	138.2
	<i>n</i> -C <sub>5</sub>	1313.8	-126.8	-3.8	126.2
	<i>n</i> -C <sub>6</sub>	1413.8	-136.8	-15.8	113.2
	<i>iso</i> -C <sub>3</sub>	1113.8	-161.8	-53.8	62.2
	<i>iso</i> -C <sub>4</sub>	1213.8	-149.8	-34.8	88.2
<i>iso</i> -C <sub>5</sub>	1313.8	-159.8	-64.8	80.2	
2-Ethylbutanoates	<i>n</i> -C <sub>1</sub>	913.8	-68.8	65.2	202.2
	<i>n</i> -C <sub>2</sub>	1013.8	-99.8	23.2	157.2
	<i>n</i> -C <sub>3</sub>	1113.8	-111.8	16.2	146.2
	<i>n</i> -C <sub>4</sub>	1213.8	-120.8	3.2	129.2
	<i>n</i> -C <sub>5</sub>	1313.8	-130.8	-10.8	120.2
	<i>n</i> -C <sub>6</sub>	1413.8	-140.8	-20.8	106.2
	<i>iso</i> -C <sub>3</sub>	1113.8	-159.8	-56.8	-39.8
	<i>iso</i> -C <sub>4</sub>	1213.8	-153.8	-46.8	-19.8
<i>iso</i> -C <sub>5</sub>	1313.8	-164.8	-50.8	-26.8	
Pivalates	<i>n</i> -C <sub>1</sub>	713.5	-107.8	-30.8	137.2
	<i>n</i> -C <sub>2</sub>	813.5	-142.8	-71.8	86.2
	<i>n</i> -C <sub>3</sub>	913.5	-143.8	-74.8	83.2
	<i>n</i> -C <sub>4</sub>	1013.5	-148.8	-82.8	87.2
	<i>n</i> -C <sub>5</sub>	1113.5	-152.8	-89.8	80.2
	<i>n</i> -C <sub>6</sub>	1213.5	-	-	77.2
	<i>iso</i> -C <sub>3</sub>	913.5	-206.8	-150.8	-19.7
	<i>iso</i> -C <sub>4</sub>	1013.5	-177.8	-120.8	28.2
<i>iso</i> -C <sub>5</sub>	1113.5	-183.8	-126.8	34.2	

TABLE I (continued)

Series	Compound	$I_M$	$I^*$		
			SE-30	OV-25	SILAR 5CP
2-Propenoates	<i>n</i> -C <sub>1</sub>	599.7	3.3	177.3	352.3
	<i>n</i> -C <sub>2</sub>	699.7	-13.7	136.3	314.3
	<i>n</i> -C <sub>3</sub>	799.7	-14.7	144.3	312.3
	<i>n</i> -C <sub>4</sub>	899.7	-19.7	137.3	309.3
	<i>n</i> -C <sub>5</sub>	999.7	-24.7	131.3	302.3
	<i>n</i> -C <sub>6</sub>	1099.7	-31.7	121.3	292.3
	<i>iso</i> -C <sub>3</sub>	799.7	-70.7	57.3	227.3
	<i>iso</i> -C <sub>4</sub>	899.7	-57.7	87.3	250.3
	<i>iso</i> -C <sub>5</sub>	999.7	-57.7	89.3	256.3
2-Methyl-2-propenoates	<i>n</i> -C <sub>1</sub>	699.7	-0.7	160.3	326.3
	<i>n</i> -C <sub>2</sub>	799.7	-27.7	121.3	272.3
	<i>n</i> -C <sub>3</sub>	899.7	-34.7	115.3	273.3
	<i>n</i> -C <sub>4</sub>	999.7	-37.7	108.3	264.3
	<i>n</i> -C <sub>5</sub>	1099.7	-45.7	99.3	256.3
	<i>n</i> -C <sub>6</sub>	1199.7	-53.7	88.3	245.3
	<i>iso</i> -C <sub>3</sub>	899.7	-90.7	32.3	182.3
	<i>iso</i> -C <sub>4</sub>	999.7	-74.7	56.3	110.3
	<i>iso</i> -C <sub>5</sub>	1099.7	-77.7	57.3	113.3
2-Butenoates	<i>n</i> -C <sub>1</sub>	699.7	53.3	240.3	443.3
	<i>n</i> -C <sub>2</sub>	799.7	26.3	209.3	399.3
	<i>n</i> -C <sub>3</sub>	899.7	22.3	205.3	392.3
	<i>n</i> -C <sub>4</sub>	999.7	17.3	198.3	386.3
	<i>n</i> -C <sub>5</sub>	1099.7	10.3	190.3	379.3
	<i>n</i> -C <sub>6</sub>	1199.7	2.3	180.3	367.3
	<i>iso</i> -C <sub>3</sub>	899.7	-35.6	211.3	304.3
	<i>iso</i> -C <sub>4</sub>	999.7	-24.6	248.3	337.3
	<i>iso</i> -C <sub>5</sub>	1099.7	-27.6	250.3	333.3
3-Butanoates	<i>n</i> -C <sub>1</sub>	699.7	-7.6	173.3	368.3
	<i>n</i> -C <sub>2</sub>	799.7	-29.6	137.3	323.3
	<i>n</i> -C <sub>3</sub>	899.7	-37.3	129.3	310.3
	<i>n</i> -C <sub>4</sub>	999.7	-42.3	120.3	302.3
	<i>n</i> -C <sub>5</sub>	1099.7	-51.3	111.3	295.3
	<i>n</i> -C <sub>6</sub>	1199.7	-58.3	100.3	282.3
	<i>iso</i> -C <sub>3</sub>	899.7	-93.8	56.3	226.3
	<i>iso</i> -C <sub>4</sub>	999.7	-79.8	80.3	248.3
	<i>iso</i> -C <sub>5</sub>	1099.7	-83.8	79.3	249.3
3-Methyl-2-butenoates	<i>n</i> -C <sub>1</sub>	799.7	31.3	218.3	396.3
	<i>n</i> -C <sub>2</sub>	899.7	2.3	188.3	354.3
	<i>n</i> -C <sub>3</sub>	999.7	-4.7	177.3	344.3
	<i>n</i> -C <sub>4</sub>	1099.7	-11.7	170.3	335.3
	<i>n</i> -C <sub>5</sub>	1199.7	-20.7	162.3	322.3
	<i>n</i> -C <sub>6</sub>	1299.7	-28.7	152.3	313.3
	<i>iso</i> -C <sub>3</sub>	999.7	-59.7	111.3	259.3
	<i>iso</i> -C <sub>4</sub>	1099.7	-49.7	120.3	279.3
	<i>iso</i> -C <sub>5</sub>	1199.7	-53.7	119.3	279.3

(Continued on p. 222)

TABLE I (continued)

Series	Compound	$I_M$	$I^*$		
			SE-30	OV-25	SILAR 5CP
<i>trans</i> -2-Hexenyl esters	Formate	899.7	4.3	157.3	373.3
	Acetate	999.7	-16.7	148.3	331.3
	Propionate	1099.7	-29.7	132.3	305.3
	Butyrate	1199.7	-46.0	111.3	277.3
	Pentanoate	1299.7	-56.0	102.3	265.3
	Hexanoate	1399.7	-62.0	91.3	235.3
<i>cis</i> -2-Hexenyl esters	Formate	899.7	3.3	168.3	378.3
	Acetate	999.7	-17.7	156.3	330.3
	Propionate	1099.7	-30.7	142.3	303.3
	Butyrate	1199.7	-47.7	119.3	275.3
	Pentanoate	1299.7	-56.7	110.3	264.3
	Hexanoate	1399.7	-66.7	99.3	250.3
Alk-1-ene-3-yl acetates	Pentyl	876.7	-58.7	76.4	264.4
	Hexyl	976.7	-79.7	65.4	249.4
	Heptyl	1076.7	-87.7	55.4	232.4
	Octyl	1176.7	-93.7	42.4	213.4
	Nonyl	1276.7	-101.7	29.4	201.4
	Decyl	1376.7	-109.7	15.4	184.4
2-Alkanones	Propanone	399.7	59.3	174.3 <sup>a</sup>	507.3
	Butanone	499.7	69.3	190.3	394.3
	Pentanone	599.7	73.3	186.3	378.3
	Hexanone	699.7	78.3	192.3	387.3
	Heptanone	799.7	75.3	198.3	388.3
	Octanone	899.7	77.3	206.3	388.3
Diketones	2,3-Butanedione	599.2	-44.2	90.8 <sup>a</sup>	405.8
	2,3-Pentanedione	699.2	-32.2	98.8	418.8
	2,4-Pentanedione	699.2	79.2	231.8	740.8
	2,3-Hexanedione	799.2	-35.2	85.8	394.8
	2,5-Hexanedione	799.2	106.8	310.8	800.8
	3,5-Heptanedione	899.2	77.8	213.8	689.8
	2,3-Octanedione	999.2	-31.2	85.8	395.8
4,6-Nonanedione	1099.2	52.8	168.8	547.8	
Pyruvates	<i>n</i> -C <sub>1</sub>	713.5	-12.5	159.5 <sup>a</sup>	574.5
	<i>n</i> -C <sub>2</sub>	813.5	-39.5	127.5	527.5
	<i>n</i> -C <sub>3</sub>	913.5	-43.5	114.5	511.5
	<i>n</i> -C <sub>4</sub>	1013.5	-45.5	106.5	507.5
	<i>n</i> -C <sub>5</sub>	1113.5	-46.5	98.5	503.5
	<i>n</i> -C <sub>6</sub>	1213.5	-49.5	90.5	497.5

<sup>a</sup> Stationary phase DC-710.

alkyl or alcohol chain (R<sup>1</sup>) length increases and as the acyl or acid chain (R) length increases. Both effects are due to increasing methylene content of the compounds, the reduced polar character tending towards the behaviour of hydrocarbons.

All of the values are higher than those obtained on low polarity SE-30, on OV-25 with accepted donor character and on Silar 5CP with acceptor characteristics. The

increased values of  $I^*$  with the alkyl esters are largely due, however, to the increased general polarity of the phases rather than the effects of particular interactions.

Table II shows representative esters of the same molecular weight, *i.e.*,  $C_7H_{14}O_2$ , where it is apparent that  $I^*$  decreases as  $R^1$  decreases and  $R$  increases, and also as  $R^1$  increases and  $R$  decreases. The effect is common with other series as shown previously<sup>2</sup> and demonstrates that the addition of a methylene group has a greater effect on retention when introduced into the alcohol ( $R^1$ ) than the acyl ( $R$ ) chain. The effect is due to the lone pair of electrons on the ethereal oxygen atom.

TABLE II  
SELECTIVITY INDICES OF ESTERS OF EMPIRICAL FORMULA  $C_7H_{14}O_2$

Ester	Chain length		Selectivity index		
	$R$	$R^1$	SE-30	OV-25	Silar 5CP
Hexyl formate	0	6	-6.8	133.2	340.2
Pentyl acetate	1	5	-22.8	130.2	298.2
Butyl propanoate	2	4	-27.8	118.2	281.2
Propyl butanoate	3	3	-38.8	108.2	265.2
Ethyl pentanoate	4	2	-37.8	100.2	265.2
Methyl hexanoate	5	1	-11.8	142.2	311.2
Isopentyl acetate	1	5	-54.8	78.2	258.2
Isobutyl propanoate	2	4	-65.8	71.2	229.2
Isopropyl butanoate	3	3	-93.8	41.2	177.2

It is evident from Table II that the value for methyl hexanoate is atypical and from Table I it is observed that the  $I^*$  values for the methyl esters are much higher than those for the other homologues owing to their higher retention. This methyl effect is well known, with the methyl group having a greater effect on the carbonyl group.

With branched-chain alkyl groups,  $I^*$  is decreased relative to the *n*-alkyl group, with the effect being most apparent with the isopropyl group and being progressively reduced with the isobutyl and isopentyl groups. The effect of branching on the carbonyl group, which is essentially responsible for  $I^*$ , is reduced as the pendant group becomes more distant from the carbonyl group.

When branching is introduced into the acyl chain similar effects are observed. By examination of the series of alkyl isobutanoates and isobutylalkanoates and of the alkyl isopentanoates and isopentylalkanoates, shown in Table III, it is evident that the presence of the branched-chain group in the alkyl chain has a greater effect on retention than when it is in the acid chain.

The effect of branching in other than the terminal position is shown by the homologous 2-methyl pentanoates and 2-ethyl butanoate esters. The first series show  $I^*$  values which are much lower than those of both the normal and the isoesters, the effect of a methyl substituent at the 2- rather than the 4-position having a profound effect on the carbonyl group. The ester of the same molecular weight having an ethyl group at the 2-position has a slightly greater effect with reduced retention and reduced  $I^*$ .

TABLE III  
INFLUENCE OF BRANCHING OF ALKYL AND ACYL CHAINS

<i>Isoalkanoate esters</i>	<i>I*</i>		<i>Isoalkyl esters</i>	<i>I*</i>	
	<i>OV-25</i>	<i>Silar 5CP</i>		<i>OV-25</i>	<i>Silar 5CP</i>
<i>Isobutanoates</i>			<i>Isobutyl esters</i>		
Ethyl	61	202	Acetate	84	249
Propyl	54	193	Propanoate	71	227
Butyl	45	187	Butanoate	51	203
Pentyl	41	180	Pentanoate	42	193
Hexyl	24	169	Hexanoate	32	183
<i>Isopentanoates</i>			<i>Isopentyl esters</i>		
Ethyl	53	200	Acetate	87	258
Propyl	45	192	Propanoate	72	229
Butyl	35	182	Butanoate	49	202
Pentyl	24	172	Pentanoate	39	191
Hexyl	22	100	Hexanoate	28	180

The effect of chain branching is further evident with the pivalate esters, where on all stationary phases substantially lower  $I^*$  values are evident than with the *n*-acyl esters and with branched alkyl chain esters. With the pivalate esters further shielding of the carbonyl occurs with branching in the alcohol chain, and further reductions in  $I^*$  occur.

The effect of introducing unsaturation into the esters is considered at several positions along the acyl chain. The homologous series of 2-propenoates show only slightly greater values of  $I^*$  than the corresponding propanoates. A greater enhancement of  $I^*$  might have been expected owing to the conjugated type of structure. The values of  $I^*$  are only slightly reduced by the presence of a methyl group adjacent to the carbonyl, but the enhancement of  $I^*$  is considerable relative to the saturated counterparts, *i.e.* alkyl isobutanoates, as shown in Table IV.

TABLE IV  
EFFECT OF UNSATURATION IN PROPANOIC AND ISOBUTANOIC ACIDS

<i>Alkyl group</i>	<i>I*</i>							
	<i>Propanoates</i>		<i>2-Propenoates</i>		<i>Isobutanoates</i>		<i>2-Methyl-2-propenoates</i>	
	<i>SE-30</i>	<i>Silar 5CP</i>	<i>SE-30</i>	<i>Silar 5CP</i>	<i>SE-30</i>	<i>Silar 5CP</i>	<i>SE-30</i>	<i>Silar 5CP</i>
Methyl	161	333	177	352	98	243	160	326
Ethyl	130	284	136	314	61	202	121	272
Propyl	120	284	144	312	54	193	115	273
Butyl	118	281	137	309	45	187	108	264
Pentyl	111	275	131	302	41	180	99	256
Hexyl	101	274	121	292	24	169	88	245
Isopropyl	57	187	57	227	-25	200	32	182
Isobutyl	71	227	87	250	-7	135	56	110
Isopentyl	72	229	89	256	-6	135	57	113



The 2-butenates show much higher values of  $I^*$  (50%) than the corresponding saturated esters, the only difference from the 2-propenoates being the terminal methyl group. The influence of the conjugated type of structure is evident particularly as the 3-butenates show only slightly greater values of  $I^*$  than the saturated homologues.

The alkyl-1-enyl-3-yl acetates show reduced values of  $I^*$  in the isolated examples where comparison with normal esters is possible and with the branched-chain structure, and this is to be expected.

Pyruvate esters with a double carbonyl group show the same effect as esters with a single carbonyl group in that decreased values of  $I^*$  are observed as the methylene content is increased. The absolute values of  $I^*$  on the non-polar and phenyl phases are slightly lower than for the corresponding acetate, but a considerable enhancement is experienced on the Silar 5CP phase.

The simple ketones, *i.e.*, 2-alkanones, show higher values of  $I^*$  than the almost comparable acetate esters on both the low-polarity and the phenyl phase; the values for the ketones increase slightly with increasing methylene content whereas the esters show a much more pronounced decrease. The values of  $I^*$  for the ketones on the highly polar phase are increased considerably and the values tend to be relatively stable with increasing number of methylene groups. Here the effects are due principally to polar interactions of the carbonyl group and the polar groups of the stationary phase. The overall increases in the  $I^*$  values of the ketones are not unexpected as the dipole moments of the ketones are substantially higher than those of the esters.

The 2,3-diketones on SE-30 and the phenyl phase surprisingly show lower  $I^*$  values than for the simple ketones and slightly higher values on Silar 5CP. Variation of the position of the carbonyl group, however, has a profound effect on the  $I^*$  values. On Silar 5CP the carbonyl groups at the 2,4- rather than the 2,3-position cause a 75%

TABLE V  
SELECTIVITY INDICES OF ALIPHATIC DIKETONES

Structure	Selectivity index	
	SE-30	Silar 5CP
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	98.8	418.8
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	231.8	740.8
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	310.8	800.8
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	213.8	689.8
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	168.8	547.8

increase, whereas on increasing the chain length to maintain the  $\text{CH}_3\text{CO}$ - end groups and to increase the distance between the carbonyl groups to two methylene groups a further increase in  $I^*$  occurs. Similarly, maintaining a single methylene group between the carbonyl groups and with  $\text{CH}_3\text{CH}_2\text{CO}$ - and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}$ - end groups progressive decreases in  $I^*$  occur, as shown in Table V.

The values of  $I^*$  may in part be explained by enolization and the inductive effect of the methyl groups, where dipole moment studies show an increased polarity of the carbonyl bond adjacent to a methyl group. However, such inductive effects are not transmitted greatly along an alkyl chain.

The propyl effect, *i.e.* the intramolecular interaction between a propyl group and a  $\pi$ -electron system of the solute, has been shown to have a pronounced effect on retention<sup>6</sup>. The low values for 2-pentanone (Table I) and the diketones (Table V) may be due to steric hindrance. Steric hindrance has previously been shown to affect the reactivity of various ketones in studies involving on-column chemical reactions<sup>7</sup>.

As the selectivity and dispersion indices are determined from the retention indices, no contribution or allowance is made for adsorption effects, which in certain circumstances are significant. The same limitation applies in the Rohrschneider and McReynolds systems. If allowances are to be made for adsorption effects it is likely that a primary reference series other than the *n*-alkanes is necessary. Despite many reports over several decades, it is apparent that no alternative standards have been universally acceptable.

#### ACKNOWLEDGEMENT

The authors acknowledge the care taken by Jane Fordham in the preparation of the manuscript.

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