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CHROMATOGRAPHIC BEHAVIOUR OF DIASTEREOMERS

IV. PATTERNS OF ADSORPTION OF SOME RELATED ACYCLIC AND CYCLIC DIASTEREOMERS IN THIN-LAYER CHROMATOGRAPHY ON SILICA GEL

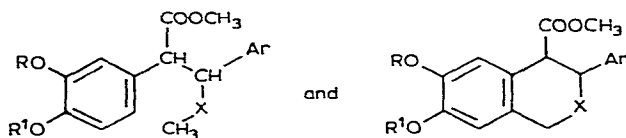
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SUMMARY

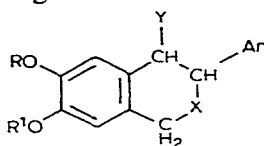
For diastereomers of the types



R_M values on silica gel are investigated as a function of the mole fraction of the more polar solvent in binary solvent systems, according to Soczewiński's method. The correlation between R_F and pK_a is discussed, and thin-layer chromatographic comparison between acyclic and cyclic compounds is made. The data are consistent with two-point adsorption by the X and COOCH_3 groups for the compounds where X is NCH_3 or O and with one-point adsorption by X, where it is the NH group, via definite conformations. Thus, the semi-empirical postulates, made earlier on the basis of Snyder's theory, about the relative order of such diastereomers in thin-layer chromatography on silica gel, are both confirmed and specified.

INTRODUCTION

In the previous papers of this series¹⁻³ the following correlations were reported concerning the relative retentions of diastereomers of types 1 and 2 in thin-layer chromatography (TLC) on silica gel:



Ar-CH(X)-CH(Y)-Ar'
 type 1 (*erythro* and *threo*)
 X and Y = NH_2 , OH, COOH
 or their derivatives

$R_F(\text{erythro}) > R_F(\text{threo})$

type 2 (*cis* and *trans*)
 group 2a
 X = NCH_3 , Y = COOCH_3 or
 CH_2OH
 X = O, Y = COOCH_3
 $R_F(\text{trans}) > R_F(\text{cis})$

group 2b
 X = NH, Y = COOCH_3 or
 CH_2OH
 X = O, Y = CH_2OH
 $R_F(\text{cis}) > R_F(\text{trans})$

On the basis of Snyder's theory⁴⁻¹⁰ the relationship $R_F(\text{erythro}) > R_F(\text{threo})$ was attributed to one-point or two-point adsorption, via suitable conformations, whereas the difference in the relative retentions of the diastereomers of type 2 compared with those of the acyclic compounds arises from the different pattern of adsorption^{2,3}. Namely, via definite conformations, two-point adsorption was postulated for the compounds of the group 2a, where $R_F(\text{trans}) > R_F(\text{cis})$. In group 2b, compounds showing $R_F(\text{cis}) > R_F(\text{trans})$, one-point adsorption should occur. These semi-empirical treatments permitted the outlining of the scope and limitation of the above correlations which is of importance in using TLC for assignment of the relative configurations of other diastereomers of types 1 and 2. In this connection, data concerning the pattern of adsorption were lacking. The present paper deals with this problem. The sets of compounds of types 1 and 2 studied differ by two hydrogen atoms only (see Tables I and II below). Here Soczewiński's method of dilution¹¹⁻²⁴ was applied. The correlation between R_F and pK_a , and TLC comparison of the acyclic and cyclic compounds, were used as well.

Separations of diastereomeric pairs of acyclic and cyclic compounds by TLC and high-performance liquid chromatography (HPLC) have been reported²⁵⁻⁵³. The separation orders are attributed to the difference in solute-adsorbent interactions within the diastereomers^{25-28,31,36,40,42,53}. Helmchen *et al.*^{26,40}, Daisley and Walker²⁸ and Maurette *et al.*³¹ support the idea of using TLC as a method for the assignment of the relative configurations of some diastereomers. According to Bergot *et al.*,⁴⁴ this problem requires further investigation in the isoprenoid amide series.

EXPERIMENTAL

Silica gel DG (Riedel-de Haën, Hannover, G.F.R.) was used for TLC as previously¹⁻³. Coating of the plates, application of the samples and visualization of the zones was performed as indicated in ref. 1. Layers 0.5 mm thick were used. No preliminary saturation of the tank with vapours of the solvent system was carried out. The solvent systems used were: A, benzene-diethyl ether (1:1); B, hexane-diethyl ether (1:2); C, diethyl ether; D, hexane-ethyl acetate (1:1); E, benzene-methanol (10:1); F, hexane-acetone (2:1); G, hexane-tetrahydrofuran (2:1); H, hexane-diethyl ether-methanol-ethanol-ammonia (25:25:1:1:1); I, heptane-benzene-diethyl ether (2:5:5); J, methylene chloride; K, heptane-diethyl ether-methanol-ethanol-ammonia (25:25:1:1:1).

When Soczewiński's method¹¹⁻²⁴ was applied, the tank was pre-saturated for 30 min with vapours of the solvent system. The silica gel layers were not activated but dried overnight at room temperature, as in refs. 1-3. The solvents were dried and distilled. The developing distance was 18 cm. The reproducibility of R_F values was usually ± 0.02 . The experimental points of the graphs in Figs. 1-5 (see below) are arithmetic means of three separate measurements.

RESULTS AND DISCUSSION

The compounds studied are 10 diastereomeric pairs of aminoesters or ether-esters of types 1 and 2, where Y is COOCH_3 , without intramolecular hydrogen bonds. The preparations are given in refs. 2 and 54-59. The data of chromatograms No. 1 and

No. 9 (see Table II) are published in ref. 2 for the acyclic compounds and in ref. 3 for the cyclic compounds.

Application of Soczewiński's method: R_M versus X_S correlations

Investigations of R_M as a function of the composition of binary solvent systems are of great importance in liquid-solid chromatography (see refs. 11-24, 60-63 and papers cited therein).

The basic equation in the dilution method of Soczewiński and collaborators¹¹⁻²⁴ is the following:

$$R_M \left[= \log \left(\frac{1}{\xi R_F} - 1 \right) \right] = \text{const} - n \log X_S \quad (1)$$

where ξ is a constant depending on the chromatographic conditions and X_S is the mole fraction of the more polar solvent in a binary solvent system. The parameter n is the number of solvent molecules displaced by a solute molecule from the adsorbent surface and thus corresponds to the number of the adsorbing groups. The absolute values of n derived from the linear slopes of R_M versus $\log X_S$ plots generally correspond to the number of the adsorbing groups in aromatic compounds containing one or more polar groups. The measurements are done on different adsorbents by TLC in the usual manner or in a sandwich tank operated in a quasi-column manner and by HPLC.

Competition between solute and solvent molecules for adsorption on the adsorbent surface has been adopted in Soczewiński's and in Snyder's⁴⁻¹⁰ adsorption models (for comparison see ref. 8). According to Snyder's model the parameter n of eqn. 1 is expressed by the ratio of the areas occupied at the surface of the adsorbent by the solute molecule (A_s) and the polar solvent molecule (n_b)^{13,23}:

$$n = \frac{A_s}{n_b} \quad (2)$$

The diastereomeric acyclic and cyclic compounds 1-8 are weak bases ($\text{p}K_A = 4.64-6.30$, see Table I below). This allows application of Soczewiński's method, because hydrogen bond formation between solutes and adsorbent is expected (*cf.* ref. 14). TLC was chosen for the measurements because this technique was used previously¹⁻³ in estimating the separation order of the diastereomers.

R_M versus $\log X_S$ correlations for compounds 1-8 in five binary solvent systems were investigated. The polar solvent was ether, ethyl acetate or tetrahydrofuran. The diluting non-polar solvent was benzene, cyclohexane or hexane. The latter widely used previously and tetrahydrofuran were not applied in the original method¹¹⁻²⁴. The polar solvent concentration was varied within the range of 0.1-0.9 mole fraction. The value $\xi = 1.1$ was used in R_F - R_M conversions, as usually in the original method. The data obtained are shown in Figs. 1-5. The slopes of the plots corresponding to the absolute values of n are given in Table I.

In the cases studied the relationship of R_M to X_S was also linear and can be used in the elucidation of the adsorption pattern.

The tertiary aminoesters 1-4 show absolute values of n of about two units and therefore they have two-point adsorption, with the two most strongly adsorbing groups being the tertiary amino group and the COOCH_3 group (see refs. 2 and 3).

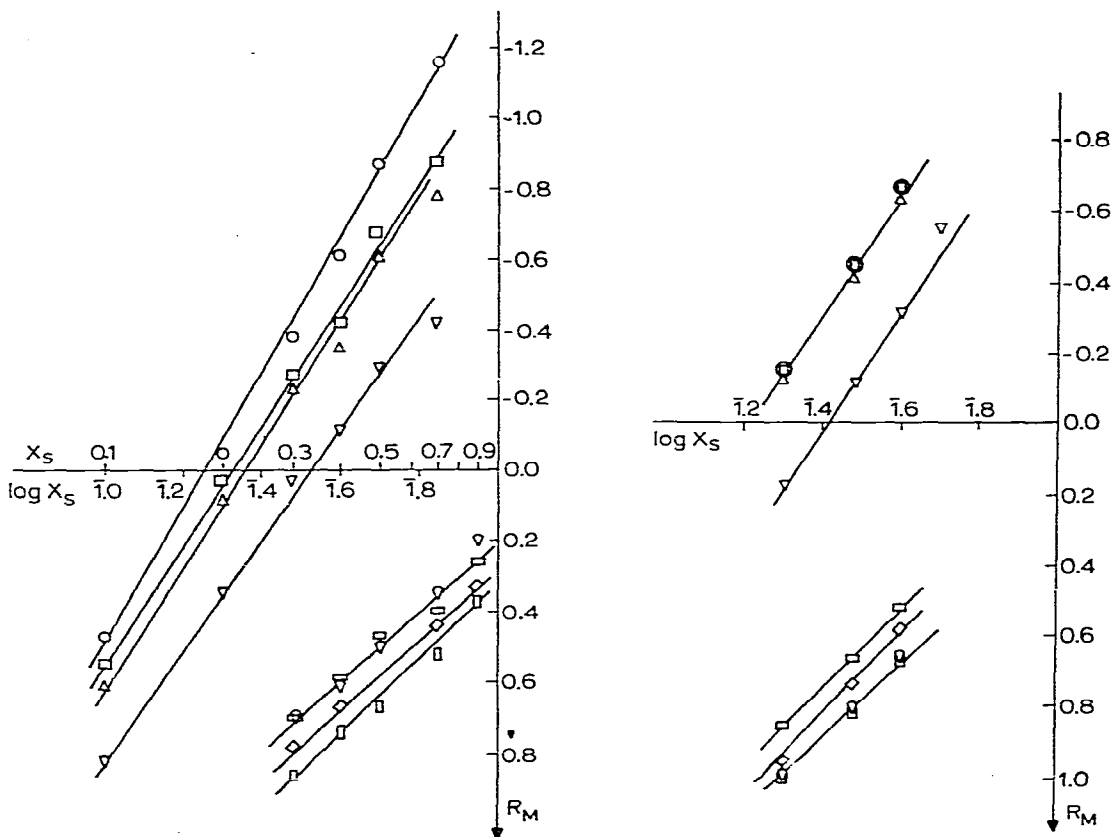


Fig. 1. R_M versus $\log X_S$ plots of the compounds 1 (Δ), 2 (\circ), 3 (∇), 4 (\square), 5 (\square), 6 (\diamond), 7 (\equiv) and 8 (\odot). See Table I for the structures of the solutes. Solvent system: benzene-diethyl ether (polar solvent).

Fig. 2. As Fig. 1, except solvent system: benzene-ethyl acetate (polar solvent).

Referring to eqn. 2, the areas under adsorption, A_s , of compounds 1–4 are approximately equal in any of those cases where n_b has definite value (see Table 8-1 in ref. 5). Then, the position of the X and COOCH_3 groups under adsorption should be nearly the same since A_s is given by the sum of the areas of the adsorbing groups (ref. 5, p. 199). Thus, *erythro-A'* (or *A''*), *trans-C'*, *threo-B* and *cis-D'* (see the formulae in Scheme 1) are the adsorbing conformations having the X and COOCH_3 groups in close proximity.

The absolute values of n for the secondary aminoesters 5–8 are about one unit in the first three solvent systems of Table I and about three units in the remaining two solvent systems where the diluent is hexane. It is clear that replacement of cyclohexane by hexane in the mixtures with ethyl acetate results in increasing values of n from about 1 to 3 units. From a theoretical point of view this replacement cannot change the adsorption pattern since hexane and cyclohexane have a relative solvent strength ϵ° of approximately zero (see Table 8-1 in ref. 5). The abnormally high values of $n \approx 3$ require additional investigation. Consequently, the R_M versus $\log X_S$ plots of the compounds 5–8 indicate one-point adsorption through the group X. As a second-

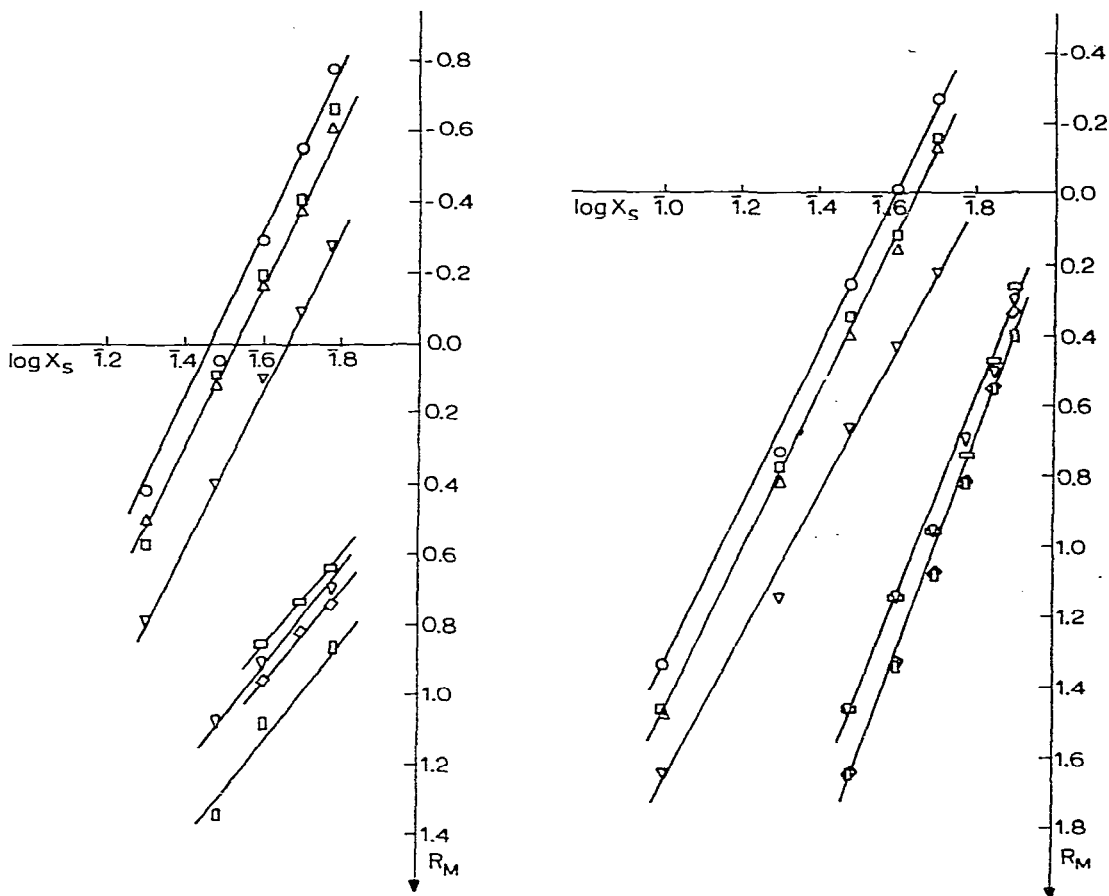


Fig. 3. As Fig. 1, except solvent system: cyclohexane-ethyl acetate (polar solvent).

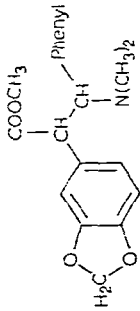
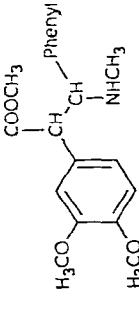
Fig. 4. As Fig. 1, except solvent system: hexane-ethyl acetate (polar solvent).

ary amino group it has a greater free energy of adsorption than the COOCH_3 group (see ref. 3). The areas of adsorption A_s of compounds 5-8 should be approximately equal in any of the binary solvent systems where $n \approx 1$ and n_b is a constant. This means that in these cases the adsorbing NH group occurs in nearly the same environment. Thus, the adsorbing conformations are *erythro-A''*, *trans-C*, *threo-B* and *cis-D'* where NH is in the most favoured steric position.

R_F/pK_a correlations

R_F values of all the acyclic and cyclic diastereomers studied are shown in Table II. The TLC behaviour of compounds 1-8 was investigated in eight solvent systems. Comparison with their pK_a values (Table I) reveals the usual correlation, namely the more basic secondary aminoesters 5-8 ($pK_a = 5.66-6.30$) have lower R_F values than the weaker bases of tertiary aminoesters 1-4 ($pK_a = 4.66-5.77$). The higher pK_a values of 5-8 support the greater free energy of adsorption, Q° , of the

TABLE I
 pK_a VALUES AND ABSOLUTE VALUES OF THE SLOPES (n) OF R_M VERSUS $\log X_S$ PLOTS OF THE COMPOUNDS 1-8

Formula	Configu- ration	Compound No.	pK_a^*	Absolute values of the slopes (n) of $R_M/\log X_S$ plots using binary solvent systems of**				
				Benzene- ether	Benzene- ethyl acetate	Cyclohexane- ethyl acetate	Hexane-ethyl acetate	Hexane-tetra- hydrofuran
	<i>threo</i>	1	5.05	1.7	1.7	2.1	2.2	2.3
	<i>erythro</i>	2	5.57	1.9	1.7	2.2	2.2	2.2
	<i>cis</i>	3	4.98	1.6	1.7	2.1	2.0	2.4
	<i>trans</i>	4	4.64	1.7	1.7	2.1	2.2	2.4
	<i>threo</i>	5	6.28	1.0	1.0	1.4	2.9	3.2
	<i>erythro</i>	6	6.30	1.0	1.0	1.4	2.7	3.3
	<i>cis</i>	7	5.66	1.0	1.1	1.3	2.7	3.2
	<i>trans</i>	8	5.83	1.0	1.1	1.3	2.9	3.0

* pK_a values are determined (see ref. 55) by Simon's method⁶⁴ in 80% methyl cellulose.

** The solvents are given as follows: diluting solvent-polar solvent.

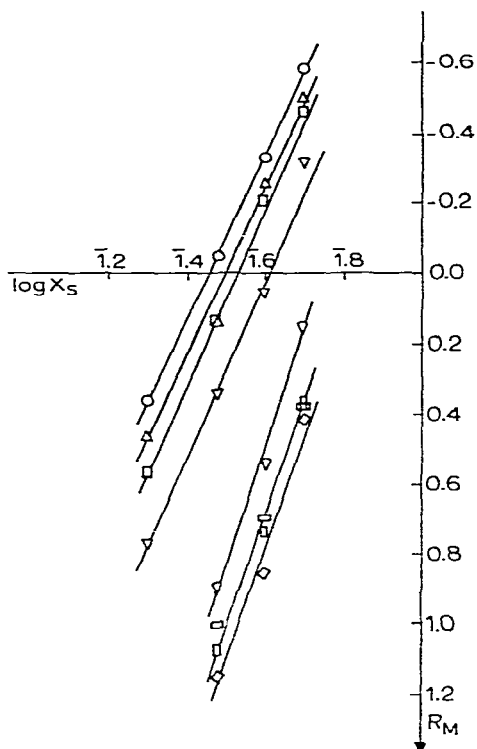


Fig. 5. As Fig. 1, except solvent system: hexane-tetrahydrofuran (polar solvent).

secondary amino group relative to that of a tertiary one (as was assumed in ref. 3), and thus these values are consistent with one-point adsorption in these cases.

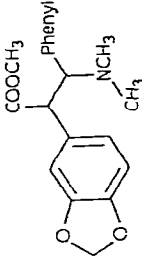
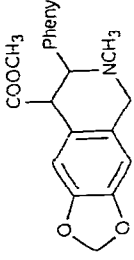
For the acyclic diastereomers 1 and 2 the *erythro*-isomer, 2, having a greater basicity, shows higher R_F values than the *threo*-isomer. This anomalous behaviour is considered additional evidence for the two-point adsorption of 1 and 2 since not only the basic group is responsible for their adsorptivity. Two-point adsorption should occur within the related cyclic diastereomers 3 and 4 having lower basicity. pK_a values of the acyclic diastereomers 5 and 6 are equal within experimental error, as the relation $R_F(\textit{erythro}) > R_F(\textit{threo})$ is kept.

In the case of the cyclic diastereomers, 3 and 4 and 7 and 8, the more basic isomers of *cis*-3 and *trans*-8 have greater adsorption than their diastereomers. Linear R_M versus pK_a plots were obtained for the four cyclic diastereomers independent from the two-point adsorption of 3 and 4 and the one-point adsorption of 7 and 8. The plots in three solvent systems are shown in Fig. 6.

TLC comparison of the acyclic and cyclic diastereomers

TLC comparison of the acyclic and cyclic diastereomers is given in Table II, the diastereomers of a given steric series are in a vertical line. The configurational relationships between the acyclic diastereomers of type 1 and the cyclic diastereomers of type 2 follow from the stereospecific cyclization of the acyclic compounds. *Threo*-

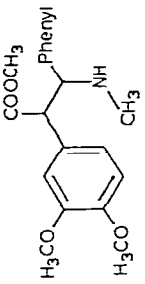
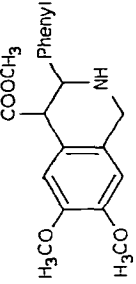
TABLE II
THIN-LAYER CHROMATOGRAPHIC COMPARISON OF ACYCLIC COMPOUNDS OF TYPE 1 AND CYCLIC COMPOUNDS OF TYPE 2

Chromatogram No.	Solvent system	Configuration	Compound No.	R_F	Formula	Configuration	Compound No.	R_F	ΔR_F
Group <i>a</i> where R_F (erythro) $\geq R_F$ (threo) and R_F (trans) $\geq R_F$ (cis)									
1	A	threo	1	0.76		erythro	2	0.83	0.08
2	B**	cis	3	0.62 $\Delta = 0.14$		trans	4	0.77 $\Delta = 0.06$	0.10
3	C		1	1.00			2	1.00	0.05
			3	0.95 $\Delta = 0.05$			4	1.00 $\Delta = 0.00$	
4	D		1	0.70			2	0.76	0.10
			3	0.55 $\Delta = 0.15$			4	0.71 $\Delta = 0.05$	
5	E**		1	0.61			2	0.66	0.05
			3	0.51 $\Delta = 0.10$			4	0.61 $\Delta = 0.05$	

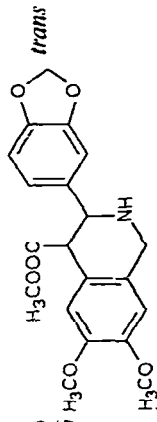
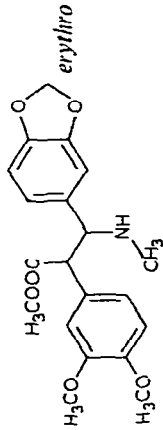
6	F***	1	0.53	2	0.54	0.05
		3	0.48	4	$\frac{0.54}{\Delta = 0.00}$	
7	G**	1	0.84	2	0.88	0.07
		3	0.72	4	$\frac{0.83}{\Delta = 0.05}$	
8	H†	1	0.85	2	0.90	0.07
		3	0.70	4	$\frac{0.82}{\Delta = 0.08}$	
9	I	9	0.39	10	0.48	0.08
		11	0.26	12	$\frac{0.43}{\Delta = 0.05}$	
10	J**	13	0.21	14	0.21	0.09
		15	0.10	16	$\frac{0.19}{\Delta = 0.02}$	

<i>threo</i>		<i>erythro</i>
<i>cis</i>		<i>trans</i>
<i>threo</i>		<i>erythro</i>
<i>cis</i>		<i>trans</i>

TABLE II (continued)

Chromatogram No.	Solvent system	Configuration	Compound No.	R_F	Formula	Configuration	Compound No.	R_F	ΔR_F
Group b where $R_F(\text{erythro}) > R_F(\text{threo})$ and $R_F(\text{cis}) > R_F(\text{trans})$									
11	A	threo	5	0.23		erythro	6	0.31	-0.11
12	B**	cis	7	0.29 $\Delta = -0.06$		trans	8	0.26 $\Delta = 0.05$	-0.13
13	C		5	0.37			6	0.47	-0.16
			7	0.45 $\Delta = -0.05$			8	0.39 $\Delta = 0.08$	
14	D		5	0.17			6	0.21	-0.08
			7	0.21 $\Delta = -0.04$			8	0.17 $\Delta = 0.04$	
15	E**		5	0.43			6	0.45	-0.06
			7	0.49 $\Delta = -0.06$			8	0.45 $\Delta = 0.00$	

16	F ^{***}	5	0.32	6	0.38	-0.06
		7	$\frac{0.32}{\Delta = 0.00}$	8	$\frac{0.32}{\Delta = 0.06}$	
17	G ^{**}	5	0.33	6	0.45	-0.16
		7	$\frac{0.35}{\Delta = -0.02}$	8	$\frac{0.31}{\Delta = 0.14}$	
18	H [†]	5	0.43	6	0.47	-0.08
		7	$\frac{0.39}{\Delta = 0.04}$	8	$\frac{0.35}{\Delta = 0.12}$	
19	K [†]	17	0.40	18	0.45	-0.09
		19	$\frac{0.33}{\Delta = 0.07}$	20	$\frac{0.29}{\Delta = 0.16}$	



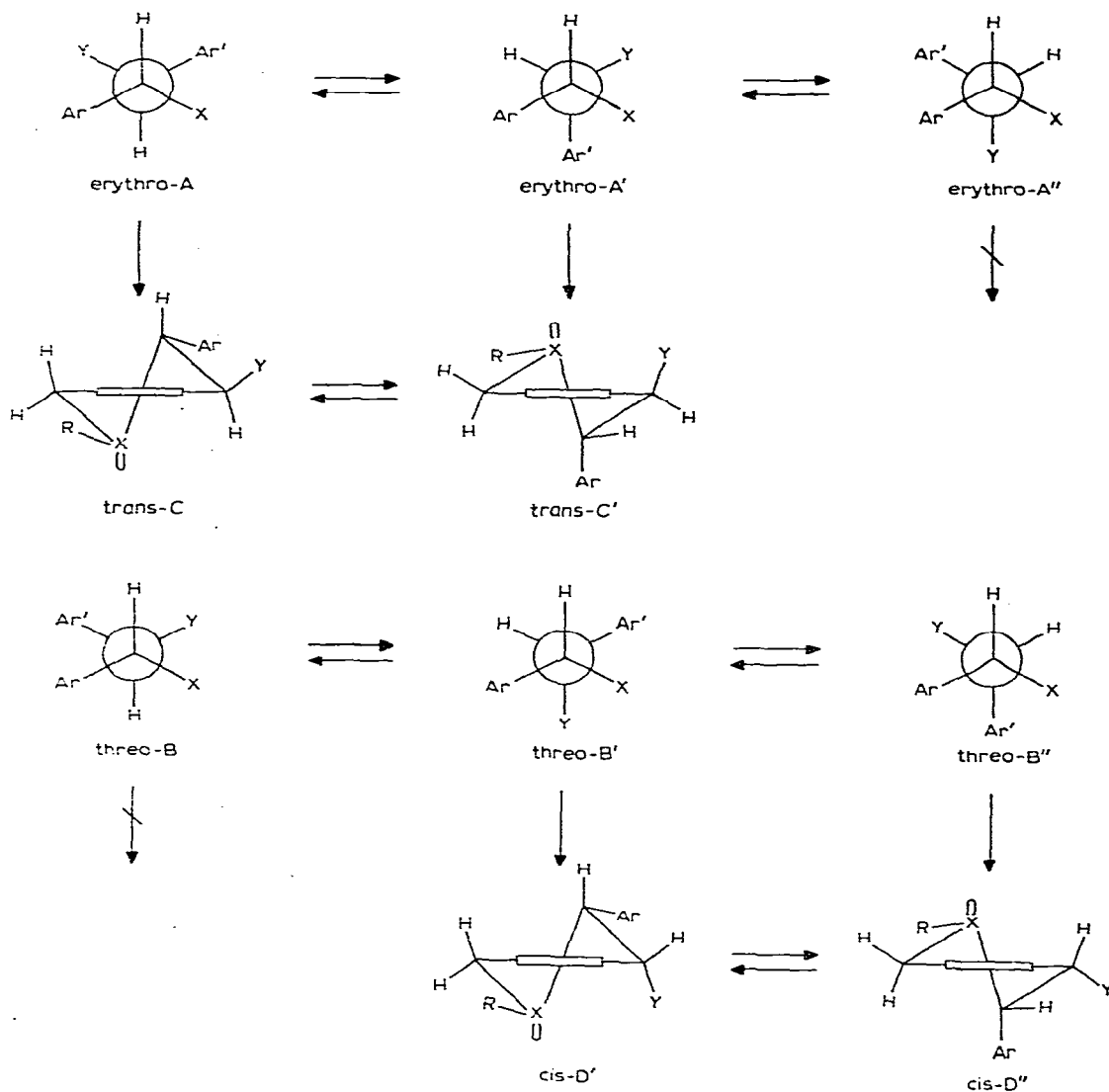
* $\Delta\Delta = [R_F(\text{thireo}) - R_F(\text{cis})] - [R_F(\text{erythro}) - R_F(\text{trans})]$.

** Developed twice.

*** Developing distance, 18 cm.

† Developed three times.

isomers give *cis*-compounds and *erythro*-isomers yield *trans*-compounds^{54,56-59}. Scheme I represents the possibilities for cyclization between the groups X and Ar' in terms of conformational equilibria.



Scheme I.

The data of Table II show $R_F(\text{erythro}) > R_F(\text{threo})$ for all the acyclic compounds, $R_F(\text{trans}) > R_F(\text{cis})$ for the cyclic compounds of group *a* and $R_F(\text{cis}) > R_F(\text{trans})$ for the cyclic compounds of group *b*. In the case of all the compounds of group *a* the difference, Δ , in R_F values within the *threo-cis* steric series is always greater than the same difference within the *erythro-trans* series. Conversely, the greater difference, Δ , in R_F show the compounds of group *b* in the *erythro-trans* series. Thus, the parameter $\Delta\Delta = [R_F(\text{threo}) - R_F(\text{cis})] - [R_F(\text{erythro}) - R_F(\text{trans})]$ has positive

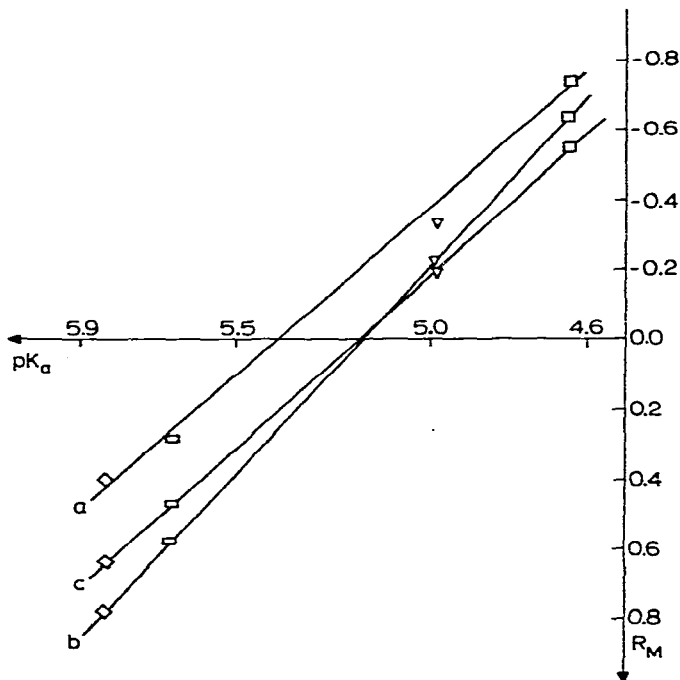


Fig. 6. R_M versus pK_a plots of the cyclic compounds 3 (∇), 4 (\square), 7 (\square) and 8 (\diamond). See Table I for the formulae of the compounds. (a) Solvent system A, R_M values correspond to R_F values of chromatograms No. 1 and 11, Table II. (b) Solvent system B, developed twice, R_M values correspond to R_F values of chromatograms No. 2 and 12, Table II. (c) Solvent system D, R_M values correspond to R_F values of chromatograms No. 4 and 14, Table II.

values in the compounds of group *a* and negative values in the compounds of group *b*. This difference in the sign of $\Delta\Delta$ is attributed to the different pattern of adsorption in the two groups of compounds, namely two-point adsorption of the compounds of group *a* and one-point adsorption of the compounds of group *b*. In the discussions below the conformations preferred in solution are referred to as energetically favoured. Nuclear magnetic resonance studies, including the principles of conformational analysis, have assessed the preferred conformations of the diastereomers of the type 1⁶⁵ and of the type 2^{54,56-59}.

Conformations *erythro-A'* (or *A''*), *trans-C'*, *threo-B* and *cis-D'* are suitable for two-point adsorption since the X and COOCH_3 groups are sterically close. Conformations *threo-B* and *cis-D'* only are favoured. For instance the difference in pK_a values of *threo-1* and *cis-3* is insignificant (see Table I). The adsorption of the more flexible acyclic compounds is expected to occur with greater entropy loss than that of the structurally similar cyclic compounds. This is the main reason, together with the additional two hydrogen atoms in the acyclic compounds, for the greater difference $\Delta = R_F(\textit{threo}) - R_F(\textit{cis})$ found for the compounds of group *a*. Here, the smaller differences $\Delta = R_F(\textit{erythro}) - R_F(\textit{trans})$ is to be attributed to the unfavoured conformation *trans-C'* (the equilibrium $\textit{trans-C} \rightleftharpoons \textit{trans-C}'$ is directed strongly to the left). The low basicity of 4 also contributes to the smaller differences in R_F .

Conformations *erythro-A''*, *trans-C*, *threo-B* and *cis-D''*, with the least hindered

lone electron pairs of NH group, are suitable for one-point adsorption. Conformation *erythro-A''* is unfavoured, while *trans-C* is favoured. This probably determines the greater differences $\Delta = R_F(\textit{erythro}) - R_F(\textit{trans})$ within the compounds of group *b*. Here, in the *threo-cis* series, *threo-B* is favoured and the stability of *cis-D''* is not much lower than that of *cis-D'*. Therefore the differences $\Delta = R_F(\textit{threo}) - R_F(\textit{cis})$ are smaller. The greater basicity of the *trans*-isomer 8 relative to that of the *cis*-isomer 7 when the basicity of the acyclic compounds 5 and 6 is equal, leads to the same conclusion.

Hence, the data for the parameter $\Delta\Delta$ of Table II fit the pattern of adsorption of all the compounds studied.

CONCLUSIONS

Soczewiński's method for the number of the adsorbing groups on the basis of the plots of R_{M} versus $\log X_S$ is applicable to the study of diastereomers of types 1 and 2.

The correlation of R_F and pK_a is indicative of two-point adsorption when the more basic diastereomer shows a lower adsorption on the acidic adsorbent.

TLC comparison of related acyclic and cyclic diastereomers, together with conformational equilibria and basicity, leads to a parameter which is considered to reflect the pattern of adsorption. This comparison demonstrates that the separation order of diastereomers in TLC is determined directly by conformational factors. This requires a careful analysis in using TLC as a method for assignment of the relative configurations.

Data obtained are consistent with two-point adsorption by the X and Y groups of the diastereomers studied of types 1 and 2, via conformations *erythro-A'* (or *A''*), *trans-C'*, *threo-B* and *cis-D'*, where X(NCH₃ or O) and Y(COOCH₃) are in close proximity. One-point adsorption by X is established in the case of the acyclic and cyclic diastereomers, with X being the NH group and Y the COOCH₃ group, via conformations *erythro-A''*, *trans-C*, *threo-B* and *cis-D''* where the adsorbing group is least sterically hindered. Thus, the semi-empirical postulates made earlier^{2,3} on the basis of Snyder's theory about the relative order of such diastereomers in TLC on silica gel are both confirmed and specified.

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