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Note

Separation of some azo-pigments from their diazo- and coupling components by chromatography on Sephadex LH-20 with N,N-dimethylformamide as eluent

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In two previous papers[1,2] we discussed the elution behaviour of some derivatives of 2-(4-hydroxyphenyl)-2-phenylpropane (cumylphenol) on Sephadex LH-20 using different solvents. Some pairs of these compounds were separated with N,N-dimethylformamide (DMFA) as eluent. Besides the elution parameters of the other cumylphenol derivatives, those of 2-(4-amino-3,5-dinitrophenyl)-2-phenylpropane and 2-(4-amino-3,5-dinitrophenyl)-2-(4'-nitrophenyl)propane were also determined. Meanwhile, some new azo-pigments were synthesized[3] with these two amines as diazo-components and some commercial naphthols as coupling components.

The present work was undertaken to examine the possibility of separating these azo-pigments from their diazo- and coupling components by the same gel–eluent system: Sephadex LH-20–DMFA. It was first necessary to study the elution behaviour of these pigments and of their coupling components. The elution parameters of their diazo-components were available from the previous work[1].

EXPERIMENTAL

Apparatus and chromatographic procedures were as described previously[1]. The naphthols were commercial products (Hoechst, Frankfurt/M, G.F.R.) and were used without further purification. The pigments were repeatedly recrystallized.

The main characteristics of the gel bed and the experimental conditions are given in Table I.

TABLE I

COLUMN CHARACTERISTICS AND EXPERIMENTAL CONDITIONS

Column diameter (cm)	2.7
Height of gel bed (cm)	48.5
Dry weight of gel (g)	66.6
Total volume of gel bed, V_t (ml)	278
Void volume, V_0 (ml)	92
Inner volume, V_i (ml)	145
Sample size (mg)	3
Sample volume (ml)	0.7
Flow-rate (ml/h)	60

RESULTS AND DISCUSSION

Distribution ratios (K_D) of azo-pigments and of naphthols used as their coupling components are listed in Tables II and III. In Table II the azo-pigments are represented as their diazo- and coupling components. In both tables the molecular weights (M) of the compounds are given to allow an approximate comparison of their molecular size.

TABLE II

ELUTION PARAMETERS OF SOME AZO-PIGMENTS ON SEPHADEX LH-20 WITH N,N-DIMETHYLFORMAMIDE

	Pigment		M	K_D
	Diazo-component	*Coupling component*		
I	2-(4-Amino-3,5-dinitrophenyl)-2-phenylpropane	β-naphthol	456	0.44
II	2-(4-Amino-3,5-dinitrophenyl)-2-phenylpropane	naphthol AS	575	0.28
III	2-(4-Amino-3,5-dinitrophenyl)-2-phenylpropane	naphthol AS-BR	1208	0.14
IV	2-(4-Amino-3,5-dinitrophenyl)-2-(4′-nitrophenyl)propane	β-naphthol	501	0.38
V	2-(4-Amino-3,5-dinitrophenyl)-2-(4′-nitrophenyl)propane	naphthol AS	660	0.25
VI	2-(4-Amino-3,5-dinitrophenyl)-2-(4′-nitrophenyl)propane	naphthol AS-BS	665	0.19
VII	2-(4-Amino-3,5-dinitrophenyl)-2-(4′-nitrophenyl)propane	naphthol AS-LT	664	0.20
VIII	2-(4-Amino-3,5-dinitrophenyl)-2-(4′-nitrophenyl)propane	naphthol AS-BR	1298	0.12

The results show that the K_D values of all compounds are within the limits $0 < K_D < 1$, which indicates that none of the compounds is strongly adsorbed on the gel. In spite of their considerable molecular dimensions, azo-pigments are not excluded from the gel phase. They partially permeate the gel and are eluted in order of decreasing molecular weight according to the sieving mechanism. This is seen very clearly from the comparison of K_D values for pigments I, II and III as well as for pigments IV, V, VI, VII and VIII (Table II). In each of these two groups the azo-pigments have the same diazo-component but different coupling components, whose size regularly increases. A slight sieving effect is also evident from the comparison of K_D values for pigments I and IV, II and V as well as for pigments III and VIII, which have the same coupling components but different diazo-components. A molecular sieving mechanism also appears to govern the elution behaviour of the naphthols used as coupling components for these pigments (Table III).

TABLE III

ELUTION PARAMETERS OF SOME NAPHTHOLS ON SEPHADEX LH-20 WITH N,N-DIMETHYLFORMAMIDE AS ELUENT

Naphthol	M	K_D
β-Naphthol	144	0.66
Naphthol AS	263	0.54
Naphthol AS-LT	307	0.48
Naphthol AS-BS	308	0.49
Naphthol AS-BR	584	0.41

In Table IV the separation volumes (V_s) and the sum of the half-widths ($w'/2 + w''/2$) of the two chromatographic peaks for each of the pairs, pigment–diazo-component and pigment–coupling component, are compared. It can be seen that all the pigments are separated from their coupling components. Pigments II, III, V, VI, VII and VIII can be also separated from their diazo-components. Only pigments I and IV are not completely separated from their diazo-components.

TABLE IV

SEPARATION PARAMETERS OF SOME AZO-PIGMENTS FROM THEIR DIAZO- AND COUPLING COMPONENTS

Pairs of components	$\frac{w'}{2} + \frac{w''}{2}$ *(ml)*	V_s *(ml)*
Pigment I –coupling component	22	32
Pigment I –diazo-component	20	14
Pigment II –coupling component	17	37
Pigment II –diazo-component	16	37
Pigment III –coupling component	19	39
Pigment III –diazo-component	18	57
Pigment IV –coupling component	21	41
Pigment IV –diazo-component	19	13
Pigment V –coupling component	17	42
Pigment V –diazo-component	16	33
Pigment VI –coupling component	16	44
Pigment VI –diazo-component	15	41
Pigment VII –coupling component	17	40
Pigment VII –diazo-component	17	39
Pigment VIII–coupling component	16	42
Pigment VIII–diazo-component	15	52

Obviously, chromatography on Sephadex LH-20 with N,N-dimethylformamide as eluent offers a good method of separating some azo-pigments from their diazo- and coupling components.

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