CHROM. 4941

SEPARATION AND DETECTION OF CARBAMATES AND RELATED COMPOUNDS ON POLYAMIDE LAYERS

KINZO NAGASAWA, HISAE YOSHIDOME AND FUMIKO KAMATA
Faculty of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo (Japan)

(Received July 3rd, 1970)

SUMMARY

The separation and detection of 22 carbamates and related compounds including insecticidal or herbicidal materials, in current use, were investigated on polyamide layers. Suitable solvent systems and the R_F data obtained were reported.

A new spray reagent, Pinacryptol Yellow, was examined for the detection of these compounds and its usability was ascertained. A comparison was also made between the detection limits by UV absorption on polyamide and silica gel layers, and the superiority of the polyamide layers was confirmed.

INTRODUCTION

Polyamide has been used as a chromatographic substrate by a number of workers[1-6]. Recent developments include its use for the separation and identification of many kinds of substances containing hydroxyl groups such as phenolic compounds[2,3]. Substances containing of carbamate, urea, and anilide groups constitute a number of insecticidal or herbicidal materials and pharmaceuticals, and most of them contain a fundamental linkage $\begin{matrix} H & O \\ | & \| \\ -N- & -C- \end{matrix}$ in the molecules. Each hydrogen and oxygen atom in this linkage could be concerned in hydrogen bonding with the $\begin{matrix} H & O \\ | & \| \\ -N- & -C- \end{matrix}$ groups in the polyamide molecules.

This paper deals with the separation and detection of carbamates and related compounds including eighteen insecticidal or herbicidal materials in practical use and four synthesized materials for comparison, by thin-layer chromatography using polyamide.

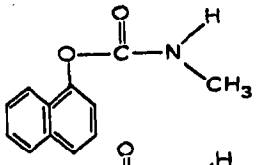
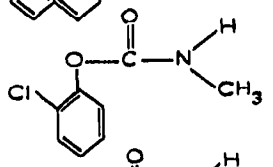
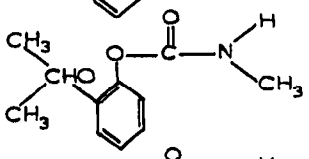
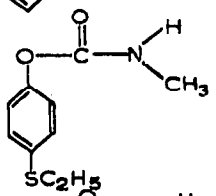
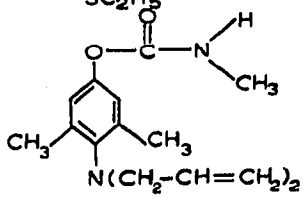
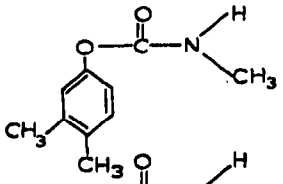
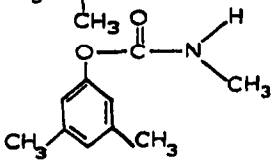
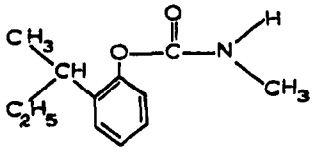
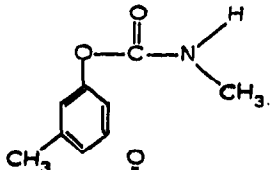
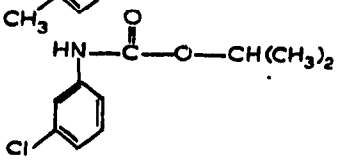
EXPERIMENTAL

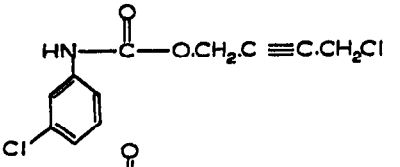
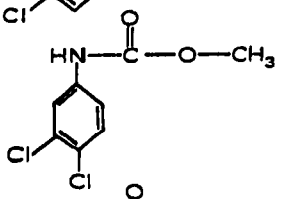
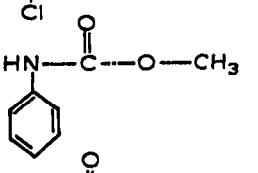
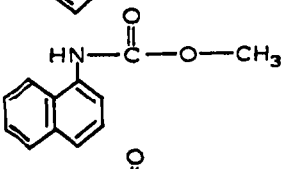
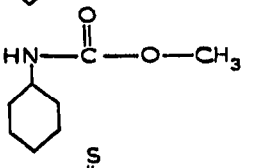
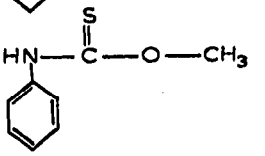
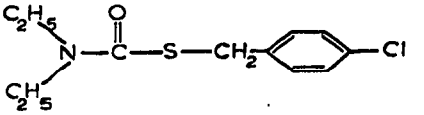
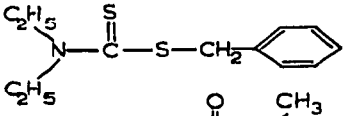
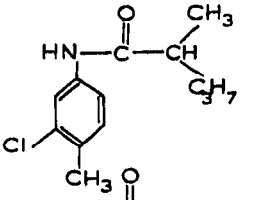
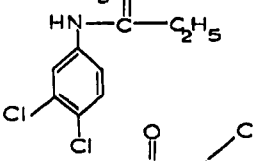
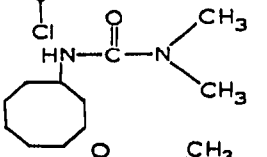
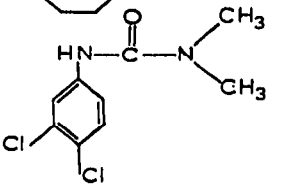
Materials

Wakō Polyamide B-10 which contains 10% anhydrous calcium sulfate (w/w)

TABLE I

CARBAMATES AND RELATED COMPOUNDS

Sample No.	*Chemical name*	*Chemical structure*	*Commercial name*
1	1-Naphthyl N-methylcarbamate		Denapon, Carbaryl Sevin, NAC
2	2-Chlorophenyl N-methylcarbamate		CPMC
3	2-Isopropoxyphenyl N-methylcarbamate		Bayer 39,007, Suncide, Baycon
4	4-Ethylmercaptophenyl N-methylcarbamate		EMPC, Tokisameito
5	4-Diallylamino-3,5-dimethylphenyl N-methylcarbamate		APC, Hydrole
6	3,4-Dimethylphenyl N-methylcarbamate		MPMC, Meobal
7	3,5-Dimethylphenyl N-methylcarbamate		Cosban, XMC
8	2-*sec.*-Butylphenyl N-methylcarbamate		Osbac, BPMC
9	3-Methylphenyl N-methylcarbamate		Tsumacide, MTMC
10	Isopropyl N-(3-chlorophenyl) carbamate		Chloro-IPC

11	4-Chloro-2-butynyl N-(3-chlorophenyl) carbamate		Carbyne, CBN
12	Methyl N-(3,4-dichlorophenyl) carbamate		Swep, MCC
13	Methyl N-phenylcarbamate		
14	Methyl N-α-naphthylcarbamate		
15	Methyl N-cyclohexylcarbamate		
16	Methyl N-phenylthiocarbamate		
17	S-p-Chlorobenzyl-N-diethyl thiolcarbamate		Saturn
18	S-Benzyl-N-diethyl dithiocarbamate		Cabac, TDW-39
19	N-(3′-Chloro-4′-methylphenyl)-2-methylpentaneamide		Solan, Dakuron
20	N-(3′,4′-Dichlorophenyl) propionamide		Stam, DCPA
21	3-Cyclooctyl-1,1-dimethylurea		Cycluron, Alipur-O
22	3-(3′,4′-Dichlorophenyl)-1,1-dimethylurea		Karmex, Diuron

as a binder (Wakō Pure Chemical Ind. Ltd., Tokyo) was used for the thin-layer chromatography.

The reagents and solvents used in this investigation are of a specially refined grade.

The carbamates and related compounds used are as listed in Table I. Sample Nos. 1–12 and 17–22 were the commercial products of technical grade which were supplied with domestic manufacturers. If necessary, the samples were purified by conventional methods such as column chromatography and recrystallization.

Methyl N-phenylcarbamate (No. 13) and methyl N-α-naphthyl carbamate (No. 14) were synthesized from the corresponding isocyanate and methanol, respectively[7,8]. Methyl N-phenylthiocarbamate (No. 16) was synthesized from an equimolar amount of phenyl isothiocyanate and methanol by reacting them together at 120° for 5 h, and was purified by column chromatography and recrystallization to give needles, m.p. 88.0°. Methyl N-cyclohexylcarbamate (No. 15) was prepared by reacting an equimolar amount of cyclohexyl isocyanate and methanol at 50° for 2 h, and purified by recrystallization to give needles, m.p. 70.5°.

Preparation of the polyamide chromatoplates

Fourteen grams of Wakō Polyamide B-10 were mixed in a flask with 60 ml of distilled water and shaken for 30 sec to give a homogeneous suspension. This suspension was spread evenly on 5 glass plates (20 × 20 cm) with a suitable applicator, pre-set to give an 0.25-mm thick layer. The coated plates were kept horizontal and dried at 60–70° for 1 h and stored in a desiccator containing silica gel.

Application of the samples and development of chromatoplates

For the determination of R_F values, samples (1 μl of 1% solution in ethanol except for Nos. 3, 6, 7, 8, 9, 14, 16 and 22 which are each 2% solution) were spotted on the starting line 2.5 cm from the edge of the plate. The plate was developed in the ascending manner at 24–26° in a closed tank until the length of run was 12 cm.

Detection of spots on the chromatoplates

The following methods 1–6 were used according to the properties of the compounds.

(1) p-Nitrobenzenediazonium fluoroborate–KOH[9]. The plate is sprayed with 1 *N* KOH solution in ethanol, followed by spraying with a 10% ethanolic solution of ethylene glycol saturated with *p*-nitrobenzenediazonium fluoroborate. Only N-methylcarbamates with an O-aryl substitution give a blue-reddish violet spot against a whitish yellow background with this reagent.

(2) Bromine–fluorescein. After exposure to bromine vapor for about 15 sec, the plate is sprayed with an 0.2% (w/v) ethanolic solution of fluorescein. All of the compounds give a yellow spot against an orange-pink background in transmitted UV light.

(3) Rhodamine B–ultraviolet[10]. The plate is sprayed with Rhodamine B reagent which is prepared by dissolving Rhodamine B (0.2 g) in a mixture of 0.02 *N* $AgNO_3$ (50 ml) and 1 *N* HCl (50 ml) and filtering the resultant suspension. When the sprayed plate is irradiated with UV light for 30 min, most of the compounds give a violet spot against an orange background in transmitted UV light.

TABLE II

SOLVENT SYSTEMS FOR CHROMATOGRAPHY OF CARBAMATES AND RELATED COMPOUNDS ON POLYAMIDE LAYERS

Symbol	*Components*	*Ratio (v/v)*
A	H_2O–MeOH	5:5
B	H_2O–AcOH–MeOH	5:1:4
C	H_2O–acetone	6:4
D	H_2O–AcOH	6:4
E	H_2O–HCOOH–MeOH	4:1:5
F	H_2O–conc. NH_3–MeOH	3:1:6
G	H_2O–DMF	6:4
H	Petroleum ether–toluene–AcOH	7:2:1
I	Petroleum ether–xylene–AcOH	8:1:1
J	Cyclohexane–acetone	8:2

(4) UV absorption. The compounds having UV absorbing group(s) in their molecules are detectable as dark spots in transmitted UV light. For the sensitive detection of spots, a quick operation is necessary because most of the compounds are easily decomposed by UV irradiation.

(5) Silver nitrate–ultraviolet[11]. Silver nitrate (0.1 g) is dissolved in a mixture of 2-phenoxyethanol (10 ml) and water (1 ml), and the solution is diluted with acetone to 200 ml. The plate is sprayed with this reagent and irradiated with UV light for 15

TABLE III

R_F VALUES OF CARBAMATES AND RELATED COMPOUNDS ON POLYAMIDE LAYERS

Sample No.	*Solvent system*									
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*
1	0.42	0.52	0.57	0.46	0.63	0.61	0.62	0.44	0.34	0.51
2	0.62	0.68	0.67	0.61	0.75	0.82	0.72	0.49	0.40	0.54
3	0.73	0.78	0.74	0.70	0.81	0.82	0.80	0.55	0.48	0.60
4	0.52	0.61	0.59	0.54	0.70	0.72	0.61	0.54	0.46	0.60
5	0.32	0.71	0.40	0.89	0.90	0.62	0.35	0.75	0.70	0.78
6	0.60	0.70	0.65	0.63	0.74	0.74	0.71	0.58	0.49	0.61
7	0.58	0.69	0.65	0.63	0.74	0.73	0.70	0.60	0.52	0.67
8	0.58	0.67	0.59	0.58	0.73	0.73	0.60	0.66	0.59	0.74
9	0.67	0.76	0.70	0.68	0.78	0.76	0.74	0.56	0.47	0.63
10	0.28	0.39	0.40	0.33	0.50	0.54	0.39	0.70	0.65	0.79
11	0.22	0.33	0.35	0.30	0.47	0.50	0.36	0.54	0.47	0.67
12	0.20	0.29	0.34	0.29	0.41	0.44	0.30	0.52	0.44	0.60
13	0.56	0.66	0.64	0.60	0.71	0.70	0.69	0.57	0.48	0.61
14	0.39	0.51	0.53	0.44	0.58	0.59	0.59	0.60	0.52	0.58
15	0.81	0.88	0.70	0.68	0.73	0.87	0.74	0.98	0.89	0.91
16	0.35	0.41	0.41	0.34	0.48	0.58	0.48	0.65	0.57	0.65
17	0.34	0.40	0.36	0.32	0.53	0.62	0.39	0.96	0.86	0.95
18	0.19	0.24	0.27	0.18	0.38	0.49	0.28	0.96	0.84	0.93
19	0.21	0.33	0.32	0.28	0.48	0.50	0.30	0.52	0.44	0.72
20	0.23	0.33	0.36	0.33	0.47	0.47	0.33	0.28	0.21	0.50
21	0.71	0.77	0.72	0.69	0.80	0.81	0.71	0.57	0.48	0.61
22	0.33	0.45	—[a]	0.44	0.56	—	—	0.26	—	0.45

[a]Symbol — means that no experiment was performed.

min. The compounds having a phenyl group substituted with chlorine atom(s) are detectable by this method as a yellowish brown spot against a light brown background.

(6) Pinacryptol Yellow–ultraviolet[12]. The plate is sprayed with 0.1% (w/v) solution of Pinacryptol Yellow in 95% ethanol and air-dried in the dark. All of the compounds appear as dark greyish spots on a light blue background in transmitted UV light.

RESULTS AND DISCUSSION

The solvent systems suitable for the separation of the carbamates and related compounds on polyamide layers are summarized in Table II. They are roughly classified into two types, solvents A–G and H–J, according to the polarity of the constituent solvents. These solvents resolved all the compounds on the layers and the R_F values

TABLE IV

DETECTION LIMITS OF CARBAMATES AND RELATED COMPOUNDS ON POLYAMIDE LAYERS AND SILICA GEL LAYERS

Method 1 = *p*-Nitrobenzenediazonium fluoroborate–KOH;
Method 2 = Br_2–fluorescein;
Method 3 = Rhodamine B–UV;
Method 4 = UV absorption or fluorescence;
Method 5 = $AgNO_3$–UV;
Method 6 = Pinacryptol Yellow–UV.

Sample No.	*Method of detection*						
	1	*2*	*3*	*4*	*5*	*6*	*4*
	Polyamide						*Silica gel*[a]
				(in μg)			
1	0.02	0.3	3	0.1[c]	10	0.25	5
2	0.05	5	5	1	0.5	5	5
3	0.05	1	—	5	—	1	1
4	0.5	0.5	0.5	0.1	0.5	0.5	5
5	—[b]	0.5	—	0.5	5	0.5	1
6	0.5	0.5	30	5	—	1	5
7	0.05	0.5	30	10	—	5	10
8	0.05	5	30	1	—	5	5
9	0.05	0.5	50	5[c]	—	1	5
10	—	0.5	0.5	0.05	0.1	0.1	1
11	—	0.5	0.5	0.1	0.1	0.5	1
12	—	1	0.5	0.05	0.1	0.1	0.5
13	—	0.5	—	0.1	—	0.25	5
14	—	1	1	0.5[c]	1	0.5	5
15	—	0.5	80	—	—	20	100
16	—	0.5	1	0.05	1	0.05	0.1
17	—	0.5	1	0.5	50	5	20
18	—	0.5	0.1	0.05	1	0.5	0.5
19	—	0.5	0.5	0.01	0.1	0.01	10
20	—	5	0.5	0.05	0.1	0.05	20
21	—	0.5	50	—	—	5	20
22	—	3	0.5	0.01	0.05	0.05	5

[a] SilicAR TLC-7G (Mallinckrodt Chemical Works) was used.
[b] Symbol — means that no spot was observed even at 100 μg.
[c] These spots are fluorescent.

obtained are listed in Table III. Examination of the R_F values of the following pairs of samples, *viz.*, Nos. 1 and 14, Nos. 13 and 15, and Nos. 13 and 16 implies that the hydrogen bonding forces between both the $-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-$ groups in the carbamates and the polyamide molecules are feeble.

One of the characteristics of polyamide layers is to give a bright background in transmitted UV light, and this phenomenon provides a highly sensitive method of detecting UV absorbing substances on the chromatoplate[13].

A comparison is made between the detection limit of the spots by UV absorption (method 4) on polyamide layers and on silica gel layers. It can be seen from Table IV that the detection of the compounds containing UV absorbing groups in their molecules is more sensitive on polyamide layers than on silica gel layers.

With regard to other methods of detection, methods 1–3, and 5 can be used on the polyamide layers as well as on silica gel layers (see Table IV and EXPERIMENTAL).

The Pinacryptol Yellow reagent (method 6) which has been used by us for the detection of synthetic sweetners was here again applied to the detection of spots of carbamates and related compounds. By spraying with this reagent, all of the compounds gave a dark greyish spot against a light (fluorescent) blue background in transmitted UV light. The results shown in Table IV indicate that the applicability and sensitivity of the method are comparable to those of the bromine–fluorescein (method 2) or the UV absorption (method 4).

REFERENCES

1 E. STAHL AND P. J. SCHORN, in E. STAHL (Editor), *Dünnschicht Chromatographie*, Springer, Berlin, 1962, p. 383.
2 H. ENDRES AND H. HÖRMANN, *Angew. Chem.*, 75 (1963) 288.
3 L. HÖRHAMMER, H. WAGNER AND K. MACEK, *Chromatog. Rev.*, 9 (1967) 103.
4 K. EGGER AND M. KEIL, *Z. Anal. Chem.*, 210 (1965) 201.
5 J. W. COPIUS-PEEREBOOM AND H. W. BEEKES, *J. Chromatog.*, 20 (1965) 43.
6 K. EGGER, *Z. Anal. Chem.*, 182 (1961) 161.
7 A. W. HOFMANN, *Ber.*, 18 (1885) 518.
8 V. T. BICKEL AND H. E. FRENCH, *J. Am. Chem. Soc.*, 48 (1926) 747.
9 J. M. FINOCCHIARO AND W. R. BENSON, *J. Assoc. Offic. Agr. Chemists*, 50 (1967) 888.
10 D. O. EBERLE AND F. A. GUNTHER, *J. Assoc. Offic. Agr. Chemists*, 48 (1965) 927.
11 L. C. MITCHELL, *J. Assoc. Offic. Agr. Chemists*, 44 (1961) 643.
12 K. NAGASAWA, H. YOSHIDOME AND K. ANRYU, *J. Chromatog.*, 52 (1970) 173
13 K. NAGASAWA AND H. YOSHIDOME, *J. Chromatog.*, 43 (1969) 473.