

## Thin-layer chromatography of isomeric chlorophenyl *m*-fluorosulfonylbenzoic acid esters

Isomeric chlorophenols and their esters have extensive utility as nematocides<sup>1,2</sup>, germicides<sup>3</sup>, herbicides<sup>4,5</sup>, growth regulators<sup>6,7</sup>, and insecticides<sup>8</sup>.

An earlier paper<sup>9</sup> described the detection and thin-layer chromatography of isomeric chlorophenols and their derivatives, *e.g.* *N*-(trichloroacetyl) carbamates. In a continuation of the elaboration of the TLC behavior of the isomeric chlorophenols, a number of chlorophenyl *m*-fluorosulfonylbenzoic acid esters were prepared and analyzed.

### Experimental

*Thin-layer chromatography.* The silicic acid chromatoplates were prepared according to the method of MORLEY AND CHIBA<sup>10</sup>. Silica Gel DF-5\* was applied on 8 × 8 in. plates to a thickness of 280 μ. After air-drying, the plates were activated in an oven for 30 min. Acetone solutions (1–2 μl containing 1–10 μg/μl) of test substance were applied along a line 2.5 cm from the lower end of the plate and developed by the ascending method (30 min, *ca.* 15 cm). After evaporation of the solvent, the spots were located by U.V. detection, then sprayed with one of the chromogenic reagents and the initial color development as well as subsequent color changes noted with the results described in Table I.

The developing solvent systems utilized in this work were:

- (A) 2.5 % acetone in benzene.
- (B) Isoamyl alcohol–ammonia–water (30:15:5).
- (C) Chloroform–acetic acid (5:1).

### Detecting reagents

- (1) DDQ reagent: 2 % 2,3-dichloro-5,6-dicyano-1,4-benzoquinoneimine in benzene.
- (2) TCNE reagent: 2 % tetracyanoethylene in benzene.
- (3) Rhodamine B reagent: 0.5 % Rhodamine B in acetone.

### Materials

*m*-Fluorosulfonylbenzoyl chloride was obtained from the Aldrich Chemical Company, Milwaukee, Wis., U.S.A. The isomeric chlorophenyl *m*-fluorosulfonylbenzoic acid esters were prepared via the reaction of *m*-fluorosulfonylbenzoyl chloride with the appropriate chlorophenol in the presence of pyridine.

### Results and discussion

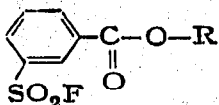
All of the derivatives tested yielded orange-crimson spots with the DDQ and TCNE detectors and magenta spots with the Rhodamine B reagent that fluoresced orange under U.V. illumination. The DDQ reagent was found to be the most useful of the detectors tested.

Table I depicts the  $R_F$  values obtained for the benzoate esters on Silica Gel DF-5 plates with the three solvent systems. The isomeric monochlorophenyl derivatives

\* Obtained from Camag, Muttenz, Switzerland.

TABLE I.

$R_F$  VALUES OF ISOMERIC CHLOROPHENYL *m*-FLUOROSULFONYLBENZOIC ACID ESTERS ON SILICA GEL DF-5 CHROMATOPLATES



Solvent systems: (A) 2.5% acetone in benzene; (B) isoamyl alcohol-ammonia-water (30:15:5); (C) chloroform-acetic acid (5:1).

<i>R</i>	<i>M.p.</i> (°C)	$R_F$ value in solvent system		
		<i>A</i>	<i>B</i>	<i>C</i>
<i>o</i> -Chlorophenyl	68-69	0.54	0.76	0.82
<i>m</i> -Chlorophenyl	47-48	0.47	0.71	0.77
<i>p</i> -Chlorophenyl	78-79	0.43	0.68	0.73
2,3-Dichlorophenyl	101-102	0.47	0.69	0.72
2,4-Dichlorophenyl	68-69	0.48	0.68	0.71
2,5-Dichlorophenyl	85-86	0.44	0.65	0.66
2,6-Dichlorophenyl	129-130	0.40	0.61	0.62
3,4-Dichlorophenyl	74-75	0.35	0.53	0.54
3,5-Dichlorophenyl	110-111	0.38	0.57	0.59
2,4,5-Trichlorophenyl	79-81	0.48	0.63	0.67
2,4,6-Trichlorophenyl	118-119	0.53	0.67	0.72

were found to be separable in all of the solvent systems employed with the acetone-benzene system being the solvent of choice. The order of  $R_F$  values for the monochlorophenyl derivatives in all of the solvent systems was  $o > m > p$ . Separation of the isomeric dichlorophenyl derivatives was best achieved utilizing solvent B, isoamyl alcohol-ammonia-water. For all the systems tested, the order of  $R_F$  values was 2,3; 2,4 > 2,5; 2,6 > 3,5 > 3,4. The preferred solvent system for the separation of trichlorophenyl derivatives was solvent A (2.5% acetone-benzene) with the order of  $R_F$  values being 2,4,6 > 2,4,5 in all three solvents.

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