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Keichiro Hayashi and Yohei Hashimoto : Studies on the Microanalysis of Essential Oil Components. II. The Paper Chromatography of Essential Oil Components by Silicone-treated Paper.

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As to the method of paper chromatography of essential oils, Kirchner *et al.*[1] reported a chromatobar in which a concreted calcium sulfate bar makes it possible to spray corrosive spray reagent, such as a solution containing concentrated sulfuric acid, revealing spots of essential oil components on chromatograms.

Recently, a method of silicone-treated paper was tried in our laboratory, by which these components were separated on paper, forming clearly outlined spots after spraying several color reagents which contain some corrosive components. The filter paper strip (Toyo Roshi No. 50, 1.5×18 cm.) was immersed in 2% benzene solution of "Dow-Corning Silicone 1107" and excess solution was removed by pressing it between two sheets of dry filter paper. After evaporating the solvent from the filter paper, it was heated to 150° for half an hour.

The sample or its solution was spotted at the start line drawn 3 cm. from the end of paper strip and then developed by mixed organic solvents. The spots were revealed by spraying the reagents listed in the Table.

This procedure may offer a wide application of paper chromatography for a group of water-insoluble organic substances including mono- and polyterpenoids, or some essential oil components. The procedure has already been used successfully in the paper chromatography of steroids by Kritchevsky *et al.*[2] The Rf values thus obtained are listed in the accompanying Table.

Rf Value of Essential Oil Components by Silicone-treated Paper

	(a)	(b)	(c)	(d)	(e)	(f)	Color reagent used
Anethol	.86	.78	.84	.74	.72	.68	A
Cinnamic alcohol	.75	.64	.68	.54	.78	.54	B
Citronellol	.78	.76	.86	.68	.68	.72	B
Eugenol	.75	.86	.78	.70	.62	.76	A
Geraniol	.84	.70	.74	.64	.70	.68	B
Heliotropin	.82	.80	.76	.72	.64	.70	C
Hydroxycitronellal	.82	.88	.81	.76	.76	.80	C
α-Ionone	.74	.66	.80	.78	.76	.74	C
Linalool	.80	.84	.82	.74	.74	.78	B
Nerol	.74	.74	.84	.70	.72	.76	B
Terpineol	.76	.80	.84	.72	.72	.84	B
Vanillin	.58	.74	.70	.44	.48	.40	C

a) 15% Ethyl acetate in hexane
b) 10% Benzene in methanol
c) 15% Cyclohexane in methanol
d) 5% Ether in ligroine (b.p. 80~100°)
e) 5% Ether in ligroine (b.p. 100~115°)
f) Ligroine (b.p. 80~100°)-benzene (5:1)

Color Reagents :
(A) For phenol compounds : 1) Fluorescein-bromine[1]
2) Phloroglucinol-conc. HCl[3]

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(B) For terpene alcohols: 1) conc. H_2SO_4-conc. H_3PO_4(1:9)
  2) Ehrlich-Müller's reagent (alternative spraying of 5% AcOH solution of *p*-dimethylaminobenzaldehyde and conc. H_3PO_4)4)
  3) Fluorescein-bromine reagent1)
  4) Phosphomolybdic acid-conc. H_3PO_4(1:1)
(C) For carbonyl compounds: 1) 0.1% Solution of 2,4-dinitrophenylhydrazine reagent
  2) Fluorescein-bromine reagent1)
  3) Ehrlich-Müller's reagent4)

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Tsukasa Kuraishi: 4,5-Substituted Pyridazines. I.

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In a previous paper,1) the author reported the synthesis of 4-aminopyridazine and 4-amino-3,6-dichloropyridazine by heating 3,4,6-trichloropyridazine with dehyd. ethanolic ammonia solution. In order to carry out the synthesis of 4,5-substituted pyridazines, the reaction of mucochloric acid with hydrazine sulfate was attempted. Mowry2) carried out the condensation of mucochloric acid with semicarbazide hydrochloride in the presence of potassium carbonate in 50% ethanol solution and heating in glacial acetic acid to give 4,5-dichloro-3-pyridazone. Mucobromic acid was condensed with hydrazine sulfate in aq. solution with use of sodium acetate by Grundmann.3) These results have been extended to the preparation of similar 4,5-substituted pyridazines.

The present work was prompted by a desire to obtain 4,5-substituted pyridazines from 4,5-dichloropyridazone, which is obtained by the Grundmann's method, and derive them to 4-aminopyridazines.

Although the condensation of α-hydroxy- and -phenoxy-β-chloro-β-formylacylic acid (mucoxy- and mucophenoxy-chloric acid) were attempted, the desired products were not obtained by the Grundmann's method.

4,5-Dichloro-3-pyridazone was led to 3,4,5-trichloropyridazine by heating with phosphoryl chloride by the usual method. Replacement of chlorine in the trichloropyridazine with an amino group was attempted with a saturated ethanolic ammonia solution but only one chlorine was substituted even when heated at 130∼140° for eight hours. 3-Amino-4,5-dichloropyridazine was not obtained but two isomers of another monoaminodichloropyridazine having m.p. 151°(Ⅲ) and 178°(Ⅳ). These monoaminodichloropyridazines were derived to 4-aminopyridazines by catalytic reduction. The structures of the 4- or 5-aminodichloropyridazines (Ⅲ and Ⅳ) are still in question.

Ultraviolet spectra of these aminodichloropyridazines in ethanol are given in Fig. 1. 4-Amino-3,6-dichloropyridazine shows the large shift of the weak bands at ca. 300 mμ to a longer wave length side from that of 4-aminopyridazine. The shift of the bands

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