The authors extend their thanks to Mr. T. Hattori and to Miss T. Kawano for carrying out the elemental analyses.

Experimental*

S-(*p*-Nitrobenzyl)-thiuronium Chloride (I)—To a solution of 17.1 g. of *p*-nitrobenzyl chloride and 50 cc. of alcohol, 7.6 g. of thiourea was added and refluxed for 1 hour. The separated prismatic crystals were collected after cooling, washed with alcohol, and recrystallized from 10% hydrochloric acid, m.p. 223°. *Anal.* Calcd. for $C_8H_{10}O_2N_3ClS$: N, 16.97. Found: N, 16.83.

S-(2,4-Dinitrobenzyl)-thiuronium Chloride (II)—26.6 g. of 2,4-dinitrobenzyl chloride, 7.6 g. of thiourea, and 80 cc. of alcohol were refluxed for 1 hour and the pale yellow plate crystals were recrystallized from 5% hydrochloric acid, m.p. 202°. *Anal.* Calcd. for $C_8H_9O_4N_4ClS$: N, 19.16. Found: N, 19.26.

General Preparation of the Thiuronium Salts of Carboxylic Acids—0.002 mole of carboxylic acid was dissolved in a few cc. of alcohol, neutralized with 1*N* sodium hydroxide, acidified with a small amount of the acid used, then 0.002 mole of reagent (I) or (II) was added. Dissolved by heating a short time on a water bath, it was chilled and the separated salt was recrystallized from diluted alcohol.

Summary

S-(*p*-Nitrobenzyl)- and S-(2,4-dinitrobenzyl)-thiuronium chloride may be used for identification and separation of carboxylic acids, amino acids, and sulfonic acids. The thiuronium salts of these acids are readily prepared and have distinct melting points. The carboxylic acids can easily be regenerated from the thiuronium salts.

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* All melting points are uncorrected.

Tsutomu Momose, Yosuke Ohkura, and Hiroko Tanaka: Organic Qualitative Analysis. V.* Paper Chromatography of Aromatic Hydrocarbons and Ethers.

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The paper chromatography of aromatic hydrocarbons and ethers was carried out leading to their derivatives in the following two methods.

First, aromatic hydrocarbon or ether is condensed with succinic anhydride by the Friedel-Crafts method converting to β-aroylpropionic acid, and developed with butanol-ammonia. β-Aroylpropionic acid, which has an active methylene, can be colored by successively spraying aqueous solution of sodium nitroprusside and of sodium hydroxide.

Naphthalene shows two spots on the paper chromatogram, which indicates that the condensation occurs at α- and β-positions[1]; anisole, also, shows two spots as one methyl

* Part IV: This Bulletin, 2, 152 (1954).

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1) Haworth: J. Chem. Soc., 1932, 1950.

group is partially eliminated in the reaction[2]. *p*-Dichlorobenzene has the same Rf-value as chlorobenzene. The reason is that one chlorine atom is eliminated in the Friedel-Crafts reaction as chlorine, and the condensation occurs at the same position as that in chlorobenzene.

The yielded acid is different from β-(*p*-chlorobenzoyl)-propionic acid, which is produced by the same method without using nitrobenzene[3], but is recognized as *o*-derivative converting to *o*-chlorobenzoic acid by potassium permanganate oxidation.

Secondarily, it is led to barium salt of phenylsulfonic acid by sulfonation with chlorosulfonic acid, and successively heating with water and barium carbonate. The barium salt is developed by the same solvent as above. The paper chromatograms of *p*-toluenesulfonic acid and some naphthalenesulfonic acids were detected by spraying the universal indicator[4] but it is found that methyl red is more distinctive in general, which turns to red upon the sulfonic acids on pale yellow background. *p*-Dichlorobenzene does not react with chlorosulfonic acid. The Rf-values are shown in the table.

	Rf-values of	
	β-Aroylpropionic acid	Phenylsulfonic acid
Benzene	0.19	0.33
Toluene	0.37	0.45
m-Xylene	0.50	0.57
Naphthalene	α:0.26, β:0.47	0.47
Tetralin	0.65	0.63
Anisole	0.29 (demethylated: 0.19)	0.30
Veratrole	0.17	0.23
Resorcinol dimethyl ether	0.30	—
Hydroquinone dimethyl ether	0.35	0.26
2-Methyl-1,4-hydroquinone dimethyl ether	0.47	—
Chlorobenzene	0.25	0.54
p-Dichlorobenzene	(0.25)	—

Experimantal

As β-Aroylpropionic Acids—One drop of liquid sample or about 30 mg. of solid was placed in a microtest tube, added with about 30 mg. of succinic anhydride, 5 drops of nitrobenzene, and about 0.1 g. of anhydrous aluminum chloride, corked tightly, and stood 24 hours, mixing occasionally. The solution was decomposed with 1 cc. of water and extracted with 2 cc. of ether. The ethereal layer was washed with two successive 1-cc. portions of 5% hydrochloric acid and at last 1 cc. of water, then extracted with 0.5 cc. of 10% aqueous sodium carbonate solution. The yielded solution of sodium β-aroylpropionate was spotted on a strip of filter paper, and developed with butanol saturated with 10% ammonia. The chromatogram was dried 10 minutes at 80°, and 2% aqueous solution of sodium nitroprusside and next 2% solution of sodium hydroxide sprayed. Brown red color appeared immediately, which was deepened by heating 5 minutes at 80°.

As Phenylsulfonic Acids—One drop of liquid sample or about 30 mg. of solid was added to two drops of chlorosulfonic acid and stood two hours. The yielded phenylsulfonic chloride was converted to sulfonic acid by adding 1 cc. of water and excess of barium carbonate, and heating on a steam bath until no more carbon dioxide evolved. The solution was filtered still hot, spotted on a strip of filter paper, and developed with the same solvent. The chromatogram was dried, and sprayed with methyl red solution, which was prepared by dissolving 0.1 g. of the reagent in 4 cc. of 4% sodium hydroxide and adding sufficient water to make 50 cc.

β-(*o*-Chlorobenzoyl)-propionic Acid—To a solution of 5 g. of chlorobenzene and 25 cc. of nitrobenzene was added 9 g. of anhydrous aluminum chloride and stood overnight at 15°. The complex was decomposed with ice and extracted with ether. The propionic acid was extracted again from

2) Berliner: Org. Reactions, V, 234; Perkin, Robinson: J. Chem. Soc., 1908, 489.
3) Skraup, Schwamberger: Ann., 462, 135 (1928).
4) Long, Quayle, Stedman: J. Chem. Soc., 1951, 2197.

the ethereal layer with 10% sodium carbonate solution, precipitated by adding hydrochloric acid, and recrystallized from benzene forming needles of m.p. 159° (uncorr.). *Anal.* Calcd. for $C_{10}H_9O_3Cl$: C, 56.48; H, 4.27. Found: C, 56.43; H, 4.61.

The same condensation was carried out with *p*-dichlorobenzene, evolving some quantities of chlorine, which could be recognized with a filter paper moistend with aqueous solution of fluorescein and potassium bromide. The solution was treated as above, and yielded propionic acid of m.p. 159°, showing no depression by fusion with the above acid.

Oxidation of β-(*o*-Chlorobenzoyl)-propionic Acid—A solution of 0.5 g. of β-(*o*-chlorobenzoyl)-propionic acid, 20 cc. of 2% sodium hydroxide, and 2 g. of potassium permanganate was heated at 80° for 3 hours and filtered. The filtrate was evaporated *in vacuo*, acidified with hydrochloric acid, and extracted with ether. The extract was freed from the solvent and the residue was recrystallized from benzene to m.p. 138~139°, undepressed by admixture with *o*-chlorobenzoic acid.

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Yujiro Hara and Sin-ichiro Fujise: The Synthesis of some Thiazole Derivatives from Levulinic Acid.

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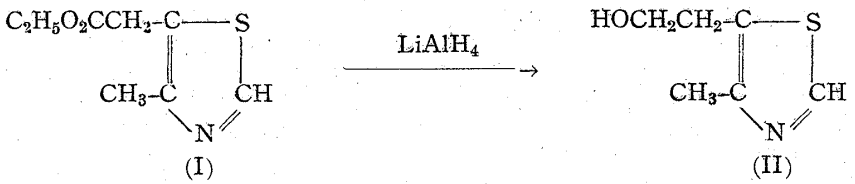
The present series of experiments were performed as the preliminary synthesis of the thiazole fragment of vitamin B_1. After completing this work, we read a similar report[1], but have decided to publish our deta. Ethyl 2-mercapto-4-methylthiazole-5-acetate (V) and some of its derivatives were obtained by the condensation of ethyl β-bromolevulinate and ammonium dithiocarbamate. The thiazole moiety of vitamin B_1 was obtained from ethyl 4-methylthiazole-5-acetate (I) by its reduction with lithium aluminum hydride. The synthesis of some thiazole derivatives from ethyl β-bromolevulinate which was derived from levulinic acid has been reported previously by Cerecedo and Tolpin[2] and Gregory and Wiggins[3]. Cerecedo and Tolpin failed in the attempted reduction of ethyl 4-methylthiazole-5-acetate (I) to obtain the thiazole fragment of vitamin B_1, 4-methyl-5-β-hydroxyethylthiazole (II). However, they suggested the possibility of obtaining the alcohol (II) from the ester (I) by some reductive agent.



In the present series of experiments, reduction of the ester (I) was attempted first by the use of lithium aluminum hydride as the mildest agent. and this proved to be successful. The results obtained thereby are described. The studies are being continued in search of a more economical method for reduction of the ester (I).

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* Katahira-cho, Sendai (原 雄次郎, 藤瀬新一郎).

1) Dornow, Petsch: Ber., 86, 1404 (1953).
2) Cerecedo, Tolpin: J. Am. Chem. Soc., 59, 1660 (1937).
3) Gregory, Wiggins: J. Chem. Soc., 1947, 590.