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39. **Tsutomu Momose and Yosuke Ohkura**: Organic Analysis. VII.[*] New Fluorescence Reaction of Hexose by 5-Hydroxytetralone.

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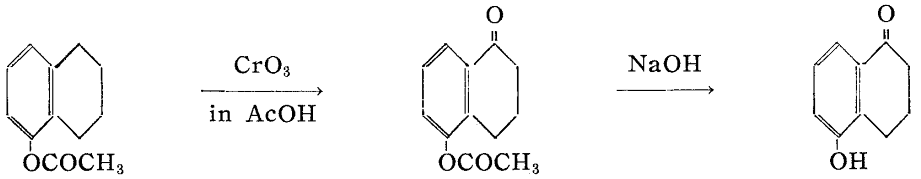
It has been found that several phenols give a specific coloration when heated with sugars in a strong mineral acid. Resorcinol, orcinol,1) α-naphthol, phloroglucinol,2) naphthoresorcinol,3) thymol,4) and catechol5) are recommended in the detection and estimation of sugars. This paper describes a fluorescence reaction of hexoses by a new phenolic reagent, 5-hydroxytetralone-(1).

5-Hydroxyteteralone-(1) had been already synthesized by another method6) but it was conveniently prepared in higher yield by the oxidation of *ar*-α-acetoxytetralin with chromium trioxide and deacetylation of the resulting ketone with sodium hydroxide.



When an aqueous solution of a hexose was heated with the reagent in sulfuric acid, faint brown color with fluorescence appeared. On dilution of the mixture with a large quantity of water, the green fluorescence was distinctly observed in daylight, as the brown color became so faint as to be almost colorless. This fluorescence was specific for hexoses, oligosaccharides, and polysaccharides which contain hexose units in their molecule. The limit of their quantity in one drop of water detected by this method is shown in Table I. Pentoses gave a yellow fluorescence under the ultraviolet light by this reaction, but they were evidently distinguished from hexoses as the fluorescence was invisible in the daylight.

TABLE I. Limit of Detection of Hexoses, Oligosaccharides, and Polysaccharides with Hexose Units (in one drop of water)

	γ		γ
Glucose	2	Saccharose	2.5
Mannose	2.5	Starch (soluble)	2
Galactose	3	Dextrin	2
Fructose	2	Inulin	2
Maltose	3	Agar-agar	3.5
Lactose	2	Cellulose	3

The fluorescence reaction is more sensitive than other methods in the detection of glucose. Two γ of the sugar gave positive result by 5-hydroxytetralone-(1), whereas it needed 7.5γ with α-naphthol, 5γ with anthrone, and 250γ with 3,5-dinitrosalicylic acid. The blank test solution of 5-hydroxytetralone-(1) was colorless, but those produced by other reagents had some coloration.

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A few substances interfered with this reaction. A large amount of most aldehydes gave a greenish yellow fluorescence, but a small amount of them had no effect upon the reaction. Glycerol gave the same fluoresence when it was present in over 1 mg. per drop, and a few γ of glyceraldehyde also showed a positive result. Other substances tested, involving amino acids, alcohols, polyhydric alcohols, ascorbic acid, glucuronic acid, galacturonic acid, ethers, organic acids, ketones, and proteins, gave no interference in this reaction.

Other phenolic derivatives of tetralin and tetralone tested gave neither fluorescence nor color reaction with sugars in sulfuric acid. Those involved *ar*-α-hydroxy-,⁷⁾ *ar*-β-hydroxy-,⁸⁾ *ar*-1,3-dihydroxy-,⁹⁾ *ar*-2,3-dihydroxy-,¹⁰⁾ *ar*-1,4-dihydroxytetralin,¹¹⁾ 6-hydroxy-,¹²⁾ 7-hydroxy-,¹³⁾ 5,8-dihydroxy-,¹⁰⁾ and 5-methoxy-8-hydroxytetralone-(1).¹⁰⁾ Therefore, it is more probable that the reaction requires the carbonyl group of tetralone, the hydroxyl group at 5-position, and the unsubstituted 8-position. Works on the mechanism of the reaction are in progress.

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Experimental

ar-α-**Acetoxytetralin**—When prepared by the catalytic hydrogenation of α-acetoxynaphthalene, it was described in the literature¹⁴⁾ to melt at 75°, but it showed much lower m.p. when it was prepared by the acetylation of *ar*-α-hydroxytetralin with Ac_2O and H_2SO_4 as given below.

To a solutioh of 30 g. of *ar*-α-hydroxytetralin⁷⁾ in 100 cc. of Ac_2O, 1 cc. of H_2SO_4 was added and allowed to stand over night. After decomposing the excess anhydride with ice water, the separated oily substance was repeatedly extracted with ether. The combined ethereal solution was washed successively with aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated. The residue was distilled *in vacuo*, b.p$_{2.5}$ 119~121°, and recrystallized from MeOH to plates of m.p. 40~40.5°. *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found : C, 75.81; H, 7.48.

5-Acetoxytetralone-(1)—To a solution of 30 g. of *ar*-α-acetoxytetralin dissolved in a mixture of 120 cc. of AcOH and 90 cc. of Ac_2O, solution of 43 g. of CrO_3 dissolved in 150 cc. of 90% AcOH was added with stirring during 1 hr. at 35~40°, stirred for additional 5 hrs., and allowed to stand over night. The mixture was diluted with H_2O and extracted repeatedly with ether. The combined ethereal solution was washed successively with Na_2CO_3 solution and H_2O and dried over Na_2SO_4. After removal of the solvent, the separated crystals were recrystallized from MeOH to colorless needles, m.p. 127°. Yield, 18 g. *Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.25; H, 5.80.

5-Hydroxytetralone-(1)—A solution of 29 g. of 5-acetoxytetralone-(1) dissolved in a mixture of 70 cc. of EtOH, 15 cc. of H_2O, and 12 g. of NaOH, was refluxed for 15 mins. in H_2 atmosphere. After distillation of EtOH, the mixture was acidified with 10% HCl and the separated crystals were recrystallized from MeOH to colorless plates, m.p. 204~205°, showing no depression of m.p. on admixture with 5-hydroxytetralone-(1), prepared according to the method in the literature.⁶⁾

Fluorescence Reaction of Hexose—The reagent solution was prepared by dissolving 1 g. of 5-hydroxytetralone-(1) in 100 cc. of 95% EtOH. It was coloress and was stable at room temperature.

To 1 drop of aqueous solution of hexose, 2 drops of the reagent solution and 0.5 cc. of 98% H_2SO_4 were added, and heated on a boiling water bath for 10 mins. After cooling, the mixture was diluted with 5 cc. of H_2O, and its green fluorescence was observed in the daylight. When the sugar was in excess against the reagent, the mixture gave a contaminated brown color. In this case, it was necessary to repeat the reaction with a diluted sample solution.

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Summary

5-Hydroxytetralone-(1) gave a green fluorescence when heated in sulfuric acid with hexoses, oligosaccharides, or polysaccharides which contains hexose units in their molecule. The reaction was sensitive and specific for hexose, and interfered by only a few substances. The limit of the detection of hexoses, oligosaccharides, and polysaccharides was tabulated, and a new syntheses of the reagent was described.

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40. **Ikuo Suzuki** : Rearrangement Reaction of Picolyl Ethers with Sodium Amide. I.

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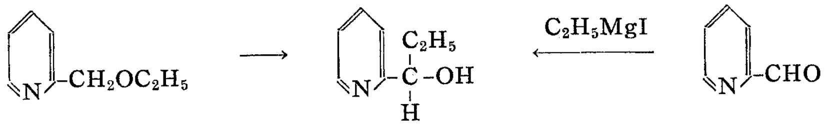
It has been found that α- or γ-ethers of picolyl compounds (Table I) undergo interesting rearrangement reaction by sodium amide in Decalin, xylene, or benzene, details of which are set in the present paper.

Table I. Properties of Picolyl Ethers used as the Starting Material

	Methyl (α)	Methyl (γ)	Ethyl (α)	Ethyl (γ)	Ethyl (β)
b.p. (°C/mm.)	45~55/4	62~65/4	63~64/5	75~80/5	77~78/5
Picrate, m.p. (°C)	81~83	107~109	119~121	112~114	108~109
Yield (%)	69.1	76.2	86.5	81.6	79.8

	sec-Butyl (α)	*sec*-Butyl (γ)	Phenyl (α)	Phenyl (γ)	Benzyl (α)	Benzyl (γ)
b.p. (°C/mm.)	73~75/5	81~83/5	140~143/5	145~150/3	150~160/7	153~158/6
Picrate, m.p. (°C)	101~103	107~109	170~171	171~172	117~119	145~146
Yield (%)	44.0	63.3	72.4	47.0	85.2	82.5

Reaction of ethyl α-picolyl ether and ethyl γ-picolyl ether with equivalent amount of sodium amide, in Decalin or benzene, respectively yields a viscous oil of b.p$_4$ 66~77°(picrate, m.p. 98~100°) and of b.p$_6$ 125~126°(picrate, m.p. 113~115°). These oily products were found to be respectively identical with ethyl-α-pyridylcarbinol and ethyl-γ-pyridylcarbinol, obtained from α- and γ-pyridylaldehydes by the application of ethylmagnesium iodide in ether.



(and the same with 4-position)

The same reactions were carried out with the α- and γ-substituted compounds of benzyl, *sec*-butyl, methyl, and phenyl picolyl ethers, and ethyl β-picolyl ether, and the results listed in Table II were obtained.

As can be seen from these tables, benzyl ether underwent rearrangement to the pyridylcarbinol with a slightly better yield than the ethyl ether, while *sec*-butyl ether gave a poor yield. Further, ethyl β-picolyl ether and the methyl and phenyl ethers failed to yield the rearrangement products (cf. Table III).

It should be noted from the foregoing experimental results that picolyl ethers undergo rearrangement only when they are α- or γ-substituents, and no such reac-

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