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SHORT COMMUNICATIONS

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*Syntheses of New Phenylfluorone Derivatives  
and their Reaction with Metal Ions*

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Although numerous investigations have been published on the colorimetric determinations of germanium, tin, titanium and zirconium with phenylfluorone (abbr. of 2,3,7-trihydroxy-9-phenylfluorone), researches for phenylfluorone derivatives are insufficient. Only 2,3,7-trihydroxy-9-(4'-dimethylaminophenyl)-fluorone has been synthesized by the author and his coworkers<sup>1)</sup>. Subsequently, some derivatives were synthesized by a similar procedure. 2,3,7-Trihydroxy-9-(3'-nitrophenyl)-fluorone, 2,3,7-trihydroxy-9-(4'-nitrophenyl)-fluorone and 2,3,7-trihydroxy-9-(2'-sulfophenyl)-fluorone were obtained. These compounds have never been described in the literature of the subject except the 3'-nitro derivative<sup>2)</sup>.

**Procedure for Synthesis.**—Twenty g. of the benzaldehyde derivative concerned was dissolved in 300 ml. of 20 % ethanol. To the solution were added 100 ml. of ethanolic solutions, containing 70 g. of hydroxyhydroquinone triacetate and 10 ml. of concentrated sulfuric acid or 30 ml. of concentrated hydrochloric acid. The solution was heated on a steam bath for about three hours, and allowed to stand for a week. The yellow or red crystalline precipitate was filtered and suspended in water at pH 4. The hydrolyzed precipitate was filtered, washed and dried in a vacuum desiccator. The yields of 3'-nitro, 4'-nitro, and 2'-sulfo derivative are 21, 30, and 28 %

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1) K. Kimura, H. Sano and M. Asada, This Bulletin, **29**, 640(1956).2) E. Heintschel, *Ber.*, **38**, 2878 (1905).

of the theoretical, respectively.

*Anal. of the 4'-nitro derivative.* Found: C, 60.25; H, 3.27. Calcd. for  $C_{19}H_{11}O_7N$ : C, 62.47; H, 3.04 %.

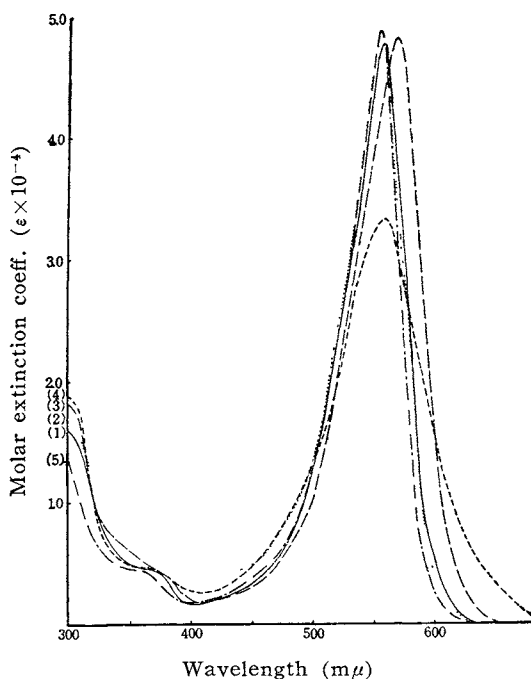


Fig. 1. Absorption spectra of products in alkaline media.

- Curve (1) — Phenylfluorone.  
 Curve (2) ..... 4'-Dimethylaminophenylfluorone.  
 Curve (3) --- 3'-Nitrophenylfluorone.  
 Curve (4) -.- 4'-Nitrophenylfluorone.  
 Curve (5) --- 2'-Sulfophenylfluorone.

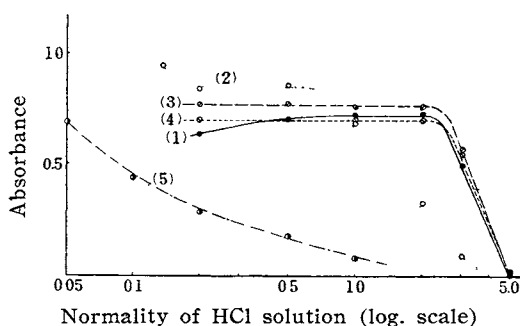


Fig. 2. Effect of acidity on germanium-fluoronates with germanium concentration fixed.

- Curve (1) Phenylfluorone (510 mμ).  
 Curve (2) 4'-Dimethylaminophenylfluorone (510 mμ).  
 Curve (3) 3'-Nitrophenylfluorone (520 mμ).  
 Curve (4) 4'-Nitrophenylfluorone (520 mμ).  
 Curve (5) 2'-Sulfophenylfluorone (500 mμ).

*Anal. of the 2-sulfo derivative.* Found: C, 56.03; H, 3.35. Calcd. for  $C_{16}H_{12}O_3S$ : C, 57.01; H, 3.02 %.

**Properties of the Products.**—The products do not melt below 270°C. The colors of 3'-nitro, 4'-nitro and 2'-sulfo derivative, are red, brownish red, and orange respectively. 3'-Nitro and 4'-nitro derivative are difficultly soluble in water but slightly soluble in ethanol. 2'-Sulfo derivative is slightly soluble both in water and in ethanol. Addition of acid or base to the ethanolic solution increases the solubility. The absorption spectra in strongly alkaline solutions are analogous to that of phenylfluorone or 4'-dimethylaminophenylfluorone as shown in Fig. 1. The absorption maxima shift toward longer wavelength in the cases of 4'- and 3'-nitro derivative, as is expected from the *I*- or *E*- effect of the nitro group. On the other hand the absorption maximum shifts toward shorter side in the case of 2'-sulfo derivative, suggesting that the effect of the phenyl group is reduced by the steric hindrance of the sulfo group. These facts convince the author that the products correspond to the compounds named.

**Reactions with Metal Ions.**—These compounds react with metal ions such as germanium, tin, titanium and zirconium, in adequate conditions. For instance the reactivities of the compounds with germanium at various acidities are illustrated in Fig. 2, including those of the phenylfluorone and the 4'-dimethylaminophenylfluorone for the comparison. The reactivity increases with increasing *I*- or *E*-effect of the substituent. The germanium complexes of 4'- or 3'-nitrophenylfluorone are slightly soluble in ethanolic solution, whereas that of 2'-sulfophenylfluorone is soluble to the same extent as the 4'-dimethylaminophenylfluorone chelate. These suggest that the compounds are useful for the colorimetric determinations of germanium. The complexes with other metals show a similar tendency in the reactions. The other derivatives such as 3',5'-dinitro, 3'-amino, or 4'-sulfophenylfluorone are under investigation. Detailed information on the compounds and their metal chelates will be published before long.

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