UDC 547.659.3

79. **Tsutomu Momose and Yosuke Ohkura:** Organic Analysis. X.* Reaction Mechanism of 5-Hydroxytetralone with Glucose.

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In the previous paper1) of this series, 5-hydroxy-1-tetralone was shown to give a sensitive fluorescence reaction with hexoses, oligosaccharides, and polysaccharides which contain hexose units in their molecule, and could be used as a new reagent for their detection. This paper describes the structure of the fluorescent compound and the mechanism of this reaction.

Isolation of the Fluorescent Compound

5-Hydroxytetralone was heated in a water bath with the same weight of glucose in 80% by volume of sulfuric acid. In this reaction, when excess of glucose was used, a large quantity of humin substance was formed and separation of the fluorescent compound became more difficult. The mixture was poured into ice water, the separated brown substance was collected, and extracted with ethyl acetate. The extract was passed through a short column of alumina to remove resinous substance and was dissolved in benzene.

Chromatographic separation of the benzene solution on alumina gave several fractions which were divided by their absorption color on alumina. The first fraction gave a small amount of colorless needles, which gave no fluorescence when dissolved in sulfuric acid. The second and main fraction which showed an orange band on alumina gave yellow needles when the solvent was concentrated. This substance gave a strong green fluorescence in sulfuric acid and was recognized as the main fluorescent compound of the reaction. The third and fourth fractions gave a small amount of oily substance which had no fluorescence in sulfuric acid. Several other fractions were seen on alumina, but they were so small and could not be treated successfully.

The fluorescent compound was recrystallized from benzene to crystals of m.p. 212.5°, which decomposed gradually by light, turning to a dark green-colored substance. It also changed to dark green when heated in alcoholic alkali. Therefore, chromatographic separation of the compound should be carried out carefully in a dark room with neutralized alumina. The green fluorescence of the compound dissolved in sulfuric acid faded away after about 10 days at a room temperature. Paper chromatography of the compound with petroleum ether (b.p. 65~70°) and benzene (9 : 1) gave one spot, which was detected by alkali and had an Rf value of 0.75.

Structure of the Fluorescent Compound and Reaction Mechanism

The molecular weight of the fluorescent compound determined by the Rast method was about 230, but this value might not be so accurate because the compound partly decomposed in camphor turning yellowish green. Elementary analysis of the compound agreed with the formula $C_{13}H_8O_2$. The infrared spectrum suggested that the molecule might have an extended quinoid carbonyl ($6.07\,\mu$ or $1647\,cm^{-1}$) and had no hydroxyl linkage. Reduction of the compound with zinc dust and acetic anhydride gave a leucoacetate as faint yellowish green prisms, m.p. 145°, which had the formula $C_{17}H_{14}O_4$. The infrared spectrum of the leucoacetate had an ester carbonyl band at $5.68\,\mu$ ($1761\,cm^{-1}$) instead of

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* Part IX: Yakugaku Zasshi, **78**(1958), in press.

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1) T. Momose, Y. Ohkura: This Bulletin, **4**, 209(1956).

the former quinoid carbonyl. The ultraviolet spectra of the fluorescent compound and its leucoacetate are shown in Fig. 1.

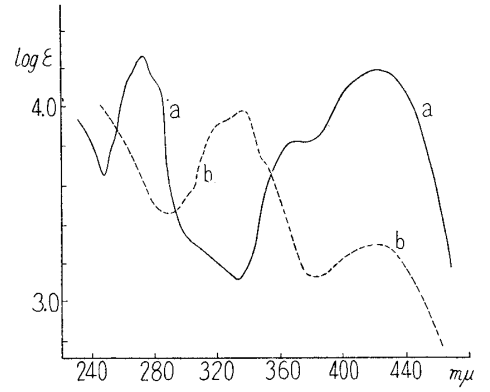
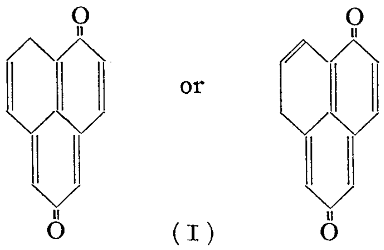


Fig. 1. Ultraviolet Absorption Spectra (in EtOH)

a : Fluorescent compound
b : Leucoacetate of the fluorescent compound

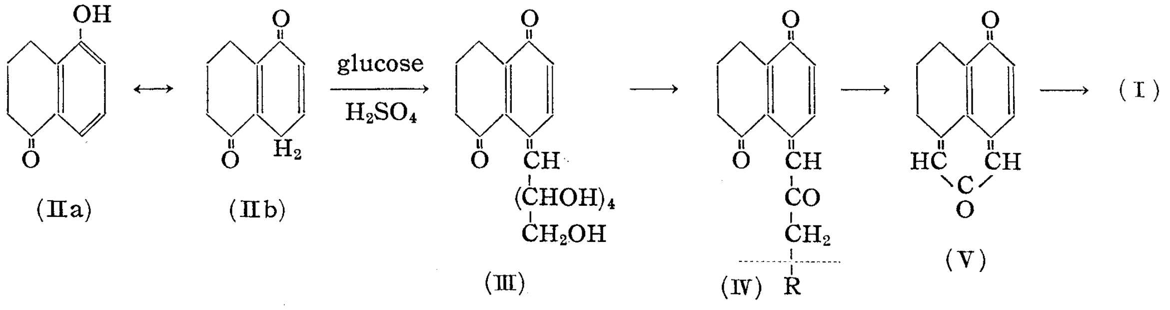
Above data indicate that the fluorescent compound might be a quinone formed by the addition of three carbons to tetralone skeleton.

On the other hand, chemical behavior of the compound in sulfuric acid and alkali is very similar to that of benzanthrone[2] and benzonaphthenone.[3] Therefore, the probable structure of the compound might be benzonaphthenedione (I).



(I)

5-Hydroxytetralone may be written in resonance structures (IIa↔IIb) and may first combine by its activated methylene with the aldehyde group of glucose (III). Then dehydration may occur to produce an active methylene in the 3-position of bonded glucose (IV), which may combine with the carbonyl group of tetralone. This ring closure partly resembles that of 1,8-diacetoxynaphthalene which gives 3-methylbenzonaphthen-1-one by piperidine.[4] Three carbons (R) of glucose may be eliminated before or after the ring closure, and resulting dihydrobenzonaphthenedione (V) may be oxidized to benzonaphthenedione (I), similarly as dihydrobenzonaphthenone is easily oxidized to benzonaphthenone.[3]



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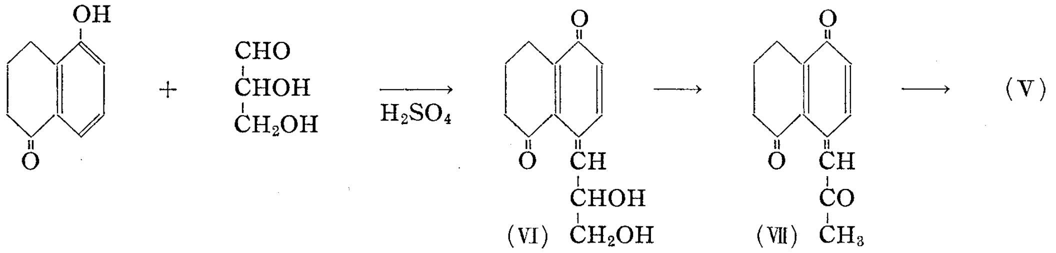
[2] L. Macleod, C. Allen : Org. Syntheses, **14**, 4(1934); Merck Index, 124(1956).
[3] J. Cook, C. Hewett : J. Chem. Soc., **1934**, 368.
[4] R. Criegee, *et al.* : Ann., **507**, 159(1933).

Above assumption is confirmed by the fact that the same fluorescent compound was isolated from the reaction mixture of 5-hydroxytetralone with glyceraldehyde, which was already shown to give a weak positive reaction with the reagent.[1] Glyceraldehyde might be decomposed at a higher temperature, and therefore it was heated with the reagent in sulfuric acid at 65～70° for 10 hours. The mixture was treated as above and chromatographic separation gave a small amount of yellow needles, m.p. 212°. This substance was identified with the fluorescent compound obtained from glucose by the melting point of admixture, Rf value of paper chromatography, and infrared spectra.

Glyceraldehyde may combine with 5-hydroxytetralone by its aldehyde group (VI) and dehydration may produce a ketone (VII), which would give dihydrobenzonaphthenedione (V) by ring closure.



In addition, the same fluorescent compound was also isolated from the reaction mixture of 5-hydroxytetralone with mannose, galactose, or fructose, and identified by the melting point of admixture and Rf value of paper chromatography.

The authors are indebted to Messrs. T. Hattori, T. Horai, and K. Funakoshi for the microanalyses.

Experimental

Isolation of the Fluorescent Compound—To a solution of 10 g. of 5-hydroxy-1-tetralone in 500 cc. of 90% (v/v) H_2SO_4, 10 g. of glucose dissolved in 50 cc. of water was added under cooling and heated on a water bath for 20 mins. The mixture was poured into ice water and separated brown substance was collected, washed with water, and dried. It was extracted with 300 cc. of hot AcOEt and the extract was passed through a short alumina column to remove resinous matter. The solvent was distilled off and the residue was dissolved in hot benzene. After cool, about 4 g. of 5-hydroxytetralone was recovered.

The benzene solution was poured onto a neutralized and activated alumina column of 2～3 cm. in diameter and 30 cm. in height, and eluted with benzene. The second main fraction gave crystals when the solvent was concentrated. Recrystallization from benzene gave yellow needles, m.p. 212.5° (microscopic determination). Yield, 150 mg. The filtrate from the brown substance still had a strong fluorescence and was extracted with benzene. The extract was also added to the column. *Anal.* Calcd. for $C_{13}H_8O_2$: C, 79.58; H, 4.11; mol. wt., 196.3. Found: C, 80.02; H, 4.06; mol. wt., 230.

In the case of glyceraldehyde, 1 g. of it dissolved in 5 cc. of water was added to a solution of 1 g. of 5-hydroxytetralone in 50 cc. of 90% (v/v) H_2SO_4 under cooling, and heated at 65～70° for 10 hrs. The mixture was treated as above. Most of 5-hydroxytetralone used was recovered and the reaction was repeated several times. Chromatographic separation of the combined benzene solution and recrystallization from benzene gave yellow needles, m.p. 212°, which showed no depression on admixture with the fluorescent compound obtained from glucose.

Leucoacetate—100 mg. of the fluorescent compound was dissolved in 5 cc. of Ac_2O and boiled about 20 mins. with 1 g. of Zn dust. Excess of Zn was removed while hot and washed with AcOH. To the filtrate 80 cc. of water was added and separated crystals were collected. Recrystallization from dil. EtOH gave faint yellowish green needles, m.p. 145° (microscopic determination). Yield, 30 mg. *Anal.* Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.45; H, 4.90.

Absorption Spectra—Infrared spectra were measured in Nujol mull in about 0.01-mm. thickness by a Koken Model DS-201 infrared spectrophotometer. Ultraviolet spectra were measured in 10-mm. thickness by a Beckman DK-2 ratio recording spectrophotometer.

Summary

A fluorescent compound produced in the reaction of 5-hydroxy-1-tetralone with glucose in sulfuric acid was separated in crystalline form and its probable structure was forwarded as benzonaphthenedione. The same compound was also isolated from the reaction mixture of glyceraldehyde with the same reagent. The mechanism of these reactions was discussed.

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80. **Tsutomu Momose, Yo Ueda, and Tatsuo Shōji** : Organic Analysis. XI.* Infrared Spectra of Phenylsulfonyl Derivatives. (1). The SO_2 Stretching Frequencies.

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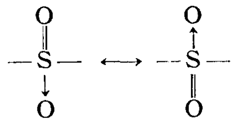
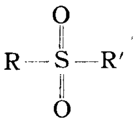
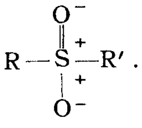
Several infrared spectral studies on phenylsulfonyl derivatives were reported by Schreiber,[1] Amstutz, *et al.*,[2] and by Barnard, *et al.*[3] concerning mainly with the hydrogen-bond formation of sulfonyl group. Bellamy,[4] quoting the data of Haszeldine,[5] Barnard,[3] and Baxter,[6] and their co-workers, concluded that the substituent effect of a sulfonyl group was much smaller than that of a carbonyl group, because sulfonyl group has a tetrahedral structure.

However, since sulfonyl group has decet electronic structure in its resonance state of  $-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\downarrow}}{S}}- \longleftrightarrow -\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle O}{\|}}{S}}-$, and has a double bond-like character, some substituent effect of this group may be expected. Thus, Amstutz, *et al.* already found a shift of 3 cm^{-1} between 4-hydroxydiphenyl and 4-hydroxy-2-methoxydiphenyl sulfones, and Vogl-Högler[7] recognized some constitutive influence upon the SO frequencies. Szmant, *et al.*[8] assumed from the study of ultraviolet spectra that when a phenylsulfonyl compound had an electron-accepting radical it might take a structure of  $R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-R'$, and when it had an electron-donating radical it might take a structure of  $R-\overset{\overset{\displaystyle O^-}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{S}}\overset{+}{\underset{+}{}}-R'$.

In this paper, infrared spectra of 50 phenylsulfonyl derivatives that were measured and substituent effect on the sulfonyl group are discussed.

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* Part X : This Bulletin, **6**, 412(1958).

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3) D. Barnard, J.M. Fabian, H.P. Koch : J. Chem. Soc., **1949**, 2442.

4) L.J. Bellamy, R.L. Williams : *Ibid.*, **1957**, 863.

5) R.N. Haszeldine, J.M. Kidd : *Ibid.*, **1955**, 2901.

6) J.N. Baxter, J. Cymerman-Craig, J.B. Willis : *Ibid.*, **1955**, 669.

7) R. Vogl-Högler : Acta Phys. Austriaca, **1**, 323(1948) (C.A., **42**, 6663(1948)).

8) H.H. Szmant, G. Suld : J. Am. Chem. Soc., **78**, 3400(1956); H.H. Szmant, J. Dixon : *Ibid.*, **78**, 4384(1956).