2. Sulfur in the *para* position has a decided auxochrome effect on the color and the shift is toward the blue. Sulfur in the *ortho* position has a similar effect but to a less degree. Increasing the molecular weight of the alkyl groups results in a loss of some of the auxochrome effect. In general the auxochrome effect of the various groups is in the order $—SCH_3 > —OCH_3 > —CH_3$.

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[Contribution from the Chemical Laboratory of the John Hopkins University]

THE EFFECT OF SULFUR ON THE COLOR OF CERTAIN PHTHALEINS[1]

By H. S. Holt and E. Emmet Reid

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Introductory and Historical

It has been shown[2] that the introduction of sulfur into triphenylmethane dyes causes a decided shift in color, this change being toward the shorter wave length. This idea has been extended into the field of phthaleins, the problem in general being the synthesis of a series of phthaleins containing alkyl-linked sulfur and observation of the auxochrome effect.

No mention of phthaleins containing alkyl sulfur could be found in the literature although compounds such as phenolsulfonephthalein and its derivatives have been known for some time.[3]

The Present Investigation

The method of attack first suggesting itself was the fusion of phthalic anhydride with phenols containing sulfur substituents, $RS.C_6H_4.OH$, the procedure being similar to that used in the preparation of phenolphthalein. These phenols were made from the corresponding amines[4] by the diazo reaction: $RS.C_6H_4.NH_2 \longrightarrow RS.C_6H_4.OH$.

It was found, however, that when one mole of phthalic anhydride is fused with two moles of *o*-hydroxyphenyl methyl sulfide at 180° in the presence of fused zinc chloride, hydroxymethyl-mercapto-anthraquinone is formed. That is, although two moles of thio-ether were used only one reacted: $C_6H_4(CO_2)O + RS.C_6H_4.OH \longrightarrow C_6H_4(CO)_2C_6H_2(OH)SR$. No attempt was made to determine the position of the hydroxyl or methyl mercapto groups.

o-Hydroxyphenyl-thiophenol, $HO.C_6H_4.SC_6H_5$, does not react with phthalic anhydride under similar conditions.

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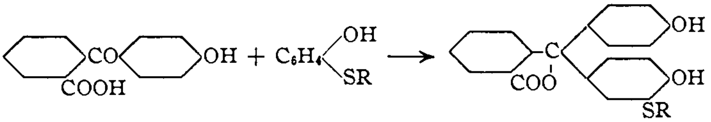
[1] From the dissertation of H. S. Holt, 1924.

[2] This Journal, **46**, 2329 (1924).

[3] Remsen, *Am. Chem. J.*, **20**, 263 (1898).

[4] Foster, This Journal, **46**, 1936 (1924).

Orndorff and Murray[5] and Moir[6] have shown that *p*-hydroxybenzoyl-*o*-benzoic acid has the power of condensing with a great variety of phenols to give mixed phthaleins. It has been found that this acid will condense with such compounds as thiophenol, *o*-nitro-thiophenol, *p*-nitro-thio-anisole, *o*-nitro-thio-anisole and the *o*-hydroxyphenyl thio-ethers. The present work was confined almost entirely to the hydroxy thio-ethers and by this reaction it is possible to prepare phthaleins containing alkyl-linked sulfur.



The procedure consisted in heating *p*-hydroxybenzoyl-*o*-benzoic acid with an excess of the hydroxy thio-ether in the presence of fused zinc chloride. The products so formed are true phthaleins; they form acetates, benzoates and oximes and in alkaline solution are deeply colored. Neither the acetates nor benzoates could be crystallized from the common solvents. Analyses were made on the oximes which could be obtained quite pure.

Table I contains the new hydroxyphenyl thio-ethers which were prepared and fused with *p*-hydroxybenzoyl-*o*-benzoic acid, their properties and analyses.

TABLE I

HYDROXYPHENYL THIO-ETHERS AND METHYLSULFONE

Compound	B. p. or m. p. °C.	Density 25/25	Sulfur Calcd.	Sulfur Found	Yield %
o-$HO.C_6H_4SCH_3$	b. p., 105 (22 mm.)	1.168	22.85	22.60	52
o-$HO.C_6H_4SC_4H_9$	b. p., 125 (10 mm.)	1.061	17.58	17.73	45
o-$HO.C_6H_4SC_6H_5$	m. p., 44	...	15.84	15.53	50
o-$HO.C_6H_4.SO_2CH_3$	m. p., above 220	...	18.60	18.41	..

The indicators prepared are all derivatives of phenolphthalein containing the —SR or —SO_2R group adjacent to one of the hydroxyls. The indi-

TABLE II

SUBSTITUTED PHENOLPHTHALEINS, THEIR SÖRENSEN (*P*H) RANGE[a] AND COLOR IN ALKALI WITH MELTING POINTS AND ANALYSES OF THEIR OXIMES

Group	*P*H values	Color in alkali	M. p. °C.		Sulfur Calcd. %	Sulfur Found %
—SCH	8.4–10	violet	189	decomp.	8.44	8.54
—SC_4H_9	8.6– 9.8	violet	175–176	decomp.	7.60	7.56
—SC_6H_5	9.0–10	violet-pink	190	decomp.	7.25	6.98
—SO_2CH_3	9.6	orange	165–167	decomp.	7.78	7.50

[a] Thanks are due the LaMotte Chemical Products Co. for the determination of the *P*H values.

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[5] Orndorff and Murray, THIS JOURNAL, **39**, 678 (1917).

[6] Moir, *Trans. So. African Acad.*, **1917–1922.**

cators could not be obtained in a condition pure enough for analysis, the sulfur determinations running 0.7 to 1.2% low, but they are readily converted into oximes. These are easily obtained pure by recrystallization and may be relied on for characterization. Analyses of the oximes are given.

Under similar conditions, *p*-hydroxybenzoyl-*o*-benzoic acid condenses with thiophenol, *o*-nitro-thiophenol, *p*-nitro-thio-anisole and *o*-nitro-thioanisole. The products dissolved in alkali forming deep red or red-violet solutions but proved difficult to purify and were not further studied.

Discussion of Results

The effect of the alkyl mercapto groups on the color was observed by adding 1 cc. of a 0.02% indicator solution in alcohol to 20 cc. of a buffer solution of *P*H 12. A similar solution of phenolphthalein was used for comparison.

In general the results agree with those obtained by us on triphenylmethane dyes.[2] The introduction of the— SCH_3 group results in a purple color, that is, a shift toward the blue. As the molecular weight of the alkyl group increases, much of the purple is lost until finally with the indicator containing the —S—C_6H_5 group, it has almost disappeared and a violet-pink results. Oxidation to the sulfone destroys whatever auxochrome effect the sulfur had, and the color is orange and of low tinctorial power. The usefulness of this indicator is diminished for this reason.

The alkyl mercapto groups have little effect on the *P*H values of the indicators. An examination of the tables will show them all to have nearly the same range as phenolphthalein, turning a little further on the alkaline side.

Experimental Part

The Preparation of the *o*-Hydroxyphenyl Thio-ethers.—A solution of 25 g. of the corresponding amine hydrochloride in about 250 cc. of water containing 40 g. of concd. hydrochloric acid was cooled to zero degrees and diazotized with a slight excess over the calculated amount of sodium nitrite. The diazo solution was then warmed, the thio-ether distilled with steam and extracted from the distillate with benzene. The benzene solution was dried with sodium sulfate, the solvent evaporated and the thio-ether distilled under reduced pressure. In the case of the phenylthio-ether which is not volatile with steam, the reaction mixture was dried and the residue distilled in a vacuum.

***o*-Hydroxyphenyl Methylsulfone.**—Thirty-four g. of *o*-aminophenyl methylsulfone was diazotized and the diazo solution decomposed by boiling. The material came out of solution as a tarry mass which was separated and dissolved in sodium hydroxide solution. This was filtered and the filtrate diluted to about 800 cc. and acidified with acetic acid. The solid which precipitated could not be crystallized but was dissolved in alcohol and reprecipitated by the addition of ether.

p-Hydroxybenzoyl-*o*-benzoic acid was made by boiling phenolphthalein oxime with dil. sulfuric acid (1:8) as described by Orndorff and Murray.[5]

The Condensation of Phthalic Anhydride with *o*-Hydroxyphenyl Methyl Sulfide

A mixture of 5 g. of phthalic anhydride and 9.4 g. of thio-ether was heated to 180° for several hours in the presence of fused zinc chloride; it became viscous and solidified on cooling. The solid was powdered and boiled with dil. hydrochloric acid to remove basic zinc salts. This treatment converted the solid to a black, tarry substance which again solidified on cooling. It was dissolved in sodium hydroxide solution, the solution filtered and reprecipitated with strong acetic acid. It was a dark solid dissolving in alkalies forming a reddish-purple solution. Attempts to crystallize it from the usual solvents were unsuccessful. A partially purified product was obtained by dissolving in ether and filtering into petroleum ether in which it is insoluble. Under these conditions it was precipitated as a salmon-colored amorphous solid that melted at 188° with decomposition.

Anal. Calc. for $C_6H_4(CO)_2C_6H_2(OH)SCH_3$: S, 11.88. Found: 12.30.

The Condensation of *p*-Hydroxybenzoyl-*o*-benzoic Acid with *o*-Hydroxyphenyl Thio-ethers

The following procedure was used in the preparation of each indicator. About 10 g. of acid and a slight excess of thio-ether were heated to 180° in a porcelain or metal dish for several hours. A little fused zinc chloride was added to speed the reaction. The mixture became dark and viscous and solidified on cooling. After it had been pulverized it was dissolved in water, the solution made acid with hydrochloric acid and the excess of thio-ether removed by steam distillation. The solid material was filtered off, dissolved in 10% sodium hydroxide solution and this solution again filtered to remove any zinc salts. The alkaline filtrate was diluted to a considerable volume and made acid with acetic acid, precipitating the free indicator. The yields are practically quantitative.

Acetylation and Benzoylation

Acetates were prepared by boiling with acetic anhydride for three hours and pouring into water. The resulting products were pasty and could not be made to crystallize. The benzoyl derivatives were prepared according to the directions of Bistrzycki and Nencki[7] but could not be purified.

Conversion of the Indicators to their Oximes

The procedure followed was similar to that described by Orndorff and Murray. These oximes were pure enough for analysis.

Summary

1. A number of new indicators have been prepared by fusing *p*-hydroxybenzoyl-*o*-benzoic acid with *o*-hydroxyphenyl thio-ethers, and by comparison with phenolphthalein the auxochrome effect of the alkyl mercapto groups has been studied.

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[7] Bistrzycki and Nencki, *Ber.*, **29**, 132 (1896).

2. Sulfur in the *ortho* position has a decided auxochrome effect, the shift being toward the blue. As the molecular weight of the alkyl group increases, much of this effect is lost. Oxidation of sulfide to sulfone destroys whatever auxochrome effect the sulfur had.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE NON-VOLATILE ACIDS OF THE PEACH

BY E. K. NELSON

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According to Kunz and Adam,[1] the peach contains citric acid but no malic or tartaric acid. Bigelow and Dunbar[2] state that their analyses showed that the peach probably contains only malic acid and that the question of the acids of peaches must be left open, the widespread assumption that this fruit contains malic acid as the predominating acid being shaken by the researches of Kunz and Adam.

As the nature of the acids in peaches remained in doubt, an investigation was conducted in the Bureau of Chemistry to determine just what acids are present.[3]

Water-packed sliced peaches (18 kg.) were boiled with water and pressed and the juice was concentrated. The pectin precipitated by alcohol was removed by filtration and the filtrate was treated with lead acetate in slight excess. The precipitate of lead salts was collected on a filter, washed with water and decomposed with sulfuric acid, the excess of sulfuric acid being removed with barium hydroxide.

The filtrate from barium sulfate was concentrated, water was removed by repeated evaporation with alcohol, and the residue of acids was esterified by refluxing for five hours with absolute alcohol containing 2.5% of hydrogen chloride.

After removing the alcohol by distillation, the operation was repeated with a fresh quantity of alcoholic hydrogen chloride, the alcohol was again removed, and the esters were purified by solution in ether and washing with a solution of sodium hydroxide.

The ether was evaporated and the esters were submitted to distillation at 10mm. pressure when the following fractions were collected.

Fraction	1	2	3	4
Temp., °C.	97–120	120–140	140–160	160–165
Yield, g.	1.91	4.80	3.63	8.30

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[1] Kunz and Adam, *Z. Nahr. Genussm.*, **12**, 670 (1906).

[2] Bigelow and Dunbar, *J. Ind. Eng. Chem.*, **9**, 762 (1917).

[3] The volatile acids of the peach have been fully investigated by Power and Chesnut, THIS JOURNAL, **43**, 1725 (1921).