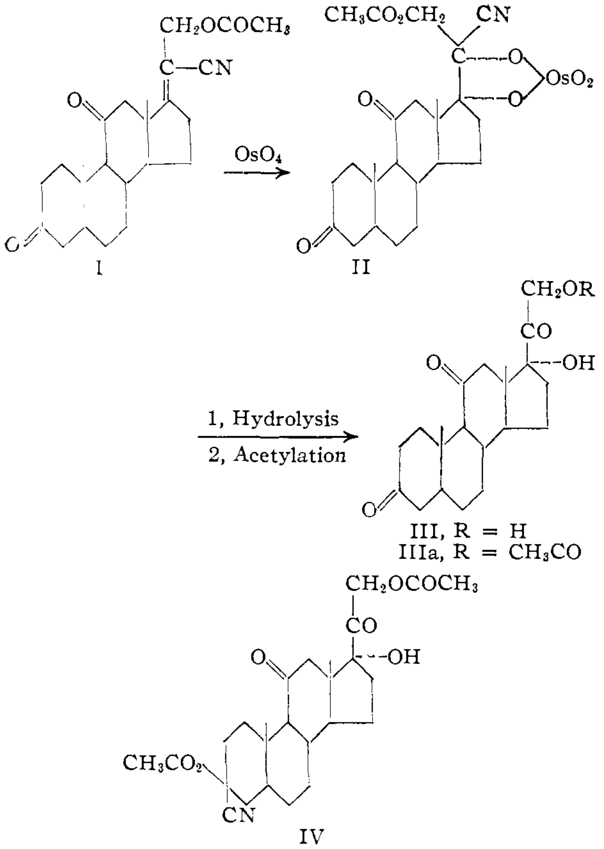

I

II

III, R = H
IIIa, R = CH$_3$CO

IV

conditions. This observation made it virtually certain that the 3-keto group of the by-product was masked in the form of a cyanohydrin acetate and could be represented by structure IV. This structure was confirmed by submitting the by-product to hot bicarbonate hydrolysis whereby it was converted to III. The formation of IV during the decomposition of the osmium complex II is an interesting example of hydrogen cyanide transfer within a polycarbonyl system.

Experimental

By-product (IV).—Isolated by chromatography of the mother liquors obtained from the crystallization of IIIa; microprisms from methanol m.p. 226.5–228.5°; infrared $\lambda_{\max}^{\mathrm{CHCl_3}}$ 2.83 μ (-OH), 5.73 μ (-OAc) and 5.85 μ (C=O).

Anal. Calcd. for $C_{26}H_{35}O_7N$: C, 65.94; H, 7.45; N, 2.96; CH$_3$CO, 18.2. Found: C, 66.13; H, 7.46; N, 2.88; CH$_3$CO, 18.9.

Treatment of IV in methanol with 2,4-dinitrophenylhydrazine reagent[3] at room temperature failed to give a derivative.

Hydrolysis of By-product (IV).—A suspension of 15 g. of the by-product IV in 380 cc. of methanol and 190 cc. of 1 *N* aqueous potassium bicarbonate was refluxed for 30 minutes. During this period the reaction mixture became homogeneous. The methanol was evaporated *in vacuo* at 35° and the product extracted with ethyl acetate. The ethyl acetate extracts were combined, washed with water, dried over anhydrous sodium sulfate and concentrated to dryness to give 11.1 g. of crude III. Recrystallization from acetone gave a first crop of 5.98 g. of III, m.p. 225–228°, not depressed on admixture with authentic III. **Acetate IIIa** obtained by the acetylation of the hydrolyzed by-product with acetic anhydride in pyridine melted at 226.5–230° and showed no depression on admixture with authentic IIIa; the infrared spectrum was identical with an authentic specimen of IIIa.

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[3] R. C. Fuson and R. L. Shriner, "The Systematic Identification of Organic Compounds," 3rd edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

Anthochlor Pigments. IX. The Structure of the Aurone Pigment of *Cosmos sulfureus*, "Orange Flare" and "Yellow Flare"

BY T. A. GEISSMAN AND LEONARD JURD

RECEIVED APRIL 20, 1954

Nordström and Swain[1] recently observed that synthetic 6,3′,4′-trihydroxyaurone[2] (I) appeared to be different from sulfuretin, the aurone pigment isolated from *Cosmos sulfureus* by Shimokoriyama and Hattori and assigned the structure I.[3] Our own observations on the pigments of the orange and yellow color forms of *C. sulfureus* had found us in complete agreement with the conclusion of Shimokoriyama and Hattori as to the structure of sulfuretin, since (a) the absorption spectrum (Fig. 1) of sulfurein (II) (sulfuretin glucoside) is very similar to that of leptosin (III); (b) the co-occurrence[3] of coreopsin and sulfurein (see Fig. 1) suggests a biogenetic relationship paralleling that existing between leptosin and lanceolin in *Coreopsis grandiflora*[3] and *Coreopsis lanceolata*[3]; (c) the purple color given by sulfurein in alkali is virtually identical with that given by leptosin; and (d) the R_f values of sulfurein and sulfuretin on paper chromatograms are entirely consistent with the structures I and II.

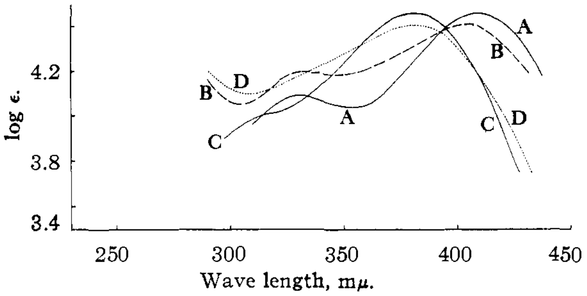
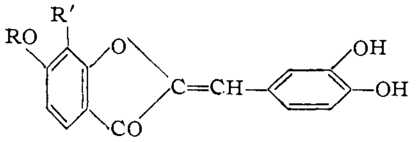


Fig. 1.—Absorption spectra (in EtOH) of: A, leptosin; B, R_f 0.66 component of *Cosmos sulfureus;* C, butein; D, R_f 0.71 component of *Cosmos sulfureus.* R_f values are for butanol–acetic acid–water, on Whatman No. 1 paper.

The report of Nordström and Swain that the triacetate of synthetic I has a m.p. about 25° lower than sulfuretin acetate[3] suggested that sulfuretin was actually different from I or that the substance isolated from *C. sulfureus* was not a pure compound.



I, sulfuretin, R = R′ = H
II, sulfurein, R = glucosyl; R′ = H
III, leptosin, R = glucosyl; R′ = OCH$_3$

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[1] C. G. Nordström and T. Swain, *Chemistry and Industry*, 823 (1953).

[2] E. C. Bate-Smith and T. A. Geissman, *Nature*, **167**, 688 (1951).

[3] M. Shimokoriyama and S. Hattori, THIS JOURNAL, **75**, 1900 (1952).

The possibility that sulfuretin was 4,3′,4′-trihydroxyaurone (IV) was disposed of by a comparison of the absorption spectra of the trimethyl ether of IV and sulfuretin trimethyl ether. The compounds are clearly different, as the values in Table I show. On the other hand, synthetic 6,3′,4′-trimethoxyaurone and sulfuretin trimethyl ether show identical absorption spectra. Thus sulfuretin is indeed I, and the purple color of alkaline solutions of sulfurein show that the latter is II, as Shimokoriyama and Hattori[3] suggested.

It is of interest to note that the deep orange ("Orange Flare") and lemon yellow ("Yellow Flare") varieties of *Cosmos sulfureus* contain approximately equal amounts of sulfurein and coreopsin. The color of the orange flower is due in part to a red pigment which appears not to be a chalcone, aurone, anthocyanin or carotenoid. Its structure is now under investigation.

TABLE I

Compound	λmax. mμ	λmin. mμ
4,3′,4′-Trimethoxyaurone	413, 313, 272	322, 295, 248
6,3′,4′-Trimethoxyaurone	392, 257	294, 240
Sulfuretin trimethyl ether	392, 257	294, 240
Sulfurein 3′,4′-dimethyl ether	400	306
Sulfuretin 3′,4′-dimethyl ether	401, 270 (infl.)	292

Sulfurein Dimethyl Ether.—A solution of 4 mg. of sulfurein in 5 ml. of dry acetone was treated with 0.2 ml. of dimethyl sulfate and an excess of dry potassium carbonate and heated under reflux for four hours. The filtered solution was evaporated to dryness and the residue taken up in chloroform. The chloroform solution was dried over sodium sulfate and a sample removed for the determination of the absorption spectrum (evaporated and the residue dissolved in ethanol). The bulk of the solution was used for the preparation of sulfuretin di- and trimethyl ethers.

Sulfuretin 3′,4′-dimethyl ether was prepared by hydrolyzing the residue from the above-described chloroform solution by heating it under reflux with 2 ml. of 1.0 *N* hydrochloric acid for 1.5 hours. The solution was neutralized with sodium bicarbonate and extracted with chloroform. A portion of the chloroform solution was set aside for absorption spectrum measurement and the remainder used directly in the following experiment.

Sulfuretin 6,3′,4′-trimethyl ether was prepared by methylation with methyl sulfate and potassium carbonate (in acetone) of the residue obtained by evaporation of the chloroform solution of the dimethyl ether. The filtered acetone solution was evaporated and the residue taken up in ether. The ether solution was washed with 20% aqueous sodium hydroxide and with water, dried, and diluted with low-boiling petroleum ether. The solution was evaporated to 1 ml. and, upon cooling, tiny yellow needles separated. These were dissolved in ethanol for the determination of the absorption spectrum.

2′-Hydroxy-3,4,6′-trimethoxychalcone.—A suspension of 0.54 g. of 2-hydroxy-6-methoxyacetophenone and 0.6 g. of veratraldehyde in 0.5 ml. of methanol was treated with 1.25 ml. of 60% aqueous potassium hydroxide. After 20 minutes an orange oil had separated. This was dissolved by the addition of more methanol and the solution was poured into iced, dilute hydrochloric acid. The crystalline yellow solid (0.87 g.) that formed when a little ether was added was collected and recrystallized from chloroform–petroleum ether. The compound formed bright yellow needles, m.p. 125°.

Anal. Calcd. for $C_{18}H_{18}O_5$: C, 68.79; H, 5.77. Found: C, 68.46; H, 5.72.

4,3′,4′-Trimethoxybenzalcoumaranone.—The method of Geissman and Fukushima[4] was used. To a suspension of 0.6 g. of 2′-hydroxy-3,4,6′-trimethoxychalcone in 3 ml. of methanol was added 3 ml. of 20% aqueous sodium hydroxide and 1.2 ml. of 30% hydrogen peroxide. A vigorous reaction ensued and a yellow solid separated. This was collected, washed with water and methanol, and recrystallized from methanol. The aurone formed bright yellow needles, m.p. 187.5°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.20; H, 5.16. Found: C, 68.81; H, 5.18.

6,3′,4′-Trimethoxybenzalcoumaranone was prepared from 6-methoxycoumaranone and veratraldehyde. It had m.p. 183° (reported[5] m.p. 183–184°).

Acknowledgment.—This work was aided by a grant from the U. S. Public Health Service, Department of Health, Education and Welfare, for which the authors express their thanks.

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(4) T. A. Geissman and D. K. Fukushima, THIS JOURNAL, **70**, 1686 (1948).

(5) K. von Auwers and P. Pohl, *Ann.*, **405**, 243 (1914).

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Some Reactions of Trifluoromethylsalicyclic Acid

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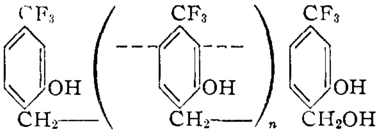
RECEIVED APRIL 3, 1954

This report records in part the transformation of 4-trifluoromethylsalicylic acid[1] (I) into the corresponding amide, anilide, hydrazide, hydroxamic acid and *o*-hydroxybenzyl alcohol. These compounds are to be tested for chemotherapeutic or fungicidal activity. 4-Trifluoromethyl-2-hydroxybenzyl alcohol (II) prepared by the reaction of lithium aluminum hydride with I was not esterified by *n*-perfluorobutyric acid. Instead a resin of probable structure



was formed due to the self-condensation of II.

During the course of this work an attempt to esterify I with 1,1-di-H-perfluoroethanol failed. The usual method for preparing esters of 1,1-di-H-perfluoro alcohols (*i.e.*, *via* the acid chloride or anhydride[2,3]) did not appear to be promising in this case. It was noted, however, that salicylic acid is converted into the methyl or ethyl ester by boiling a 10% sodium carbonate solution of the acid with the corresponding alkyl *p*-toluenesulfonate.[4] Under these conditions I and 1,1-di-H-perfluoroethyl *p*-toluenesulfonate[5] failed to react. Attempted reactions of the tosyl ester with sodium 4-trifluoromethylsalicylate in the presence of high-boiling solvents, including Diethyl Carbitol, Dibutoxy Tetraglycol and N-dimethylformamide were with-

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(1) M. Hauptschein, E. A. Nodiff and A. J. Saggiomo, THIS JOURNAL, **76**, 1051 (1954).

(2) M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, *ibid.*, **75**, 87 (1953).

(3) R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien and M. Hauptschein, *ibid.*, **75**, 2693 (1953).

(4) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 534.

(5) G. V. D. Tiers, H. A. Brown and T. S. Reid, THIS JOURNAL, **75**, 5978 (1953) reported the preparation of *p*-toluenesulfonyl (tosyl) esters of 1,1-di-H-perfluoro alcohols and their conversion to the corresponding halides.