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	λ_{max}, mμ	λ_{min}, 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°).

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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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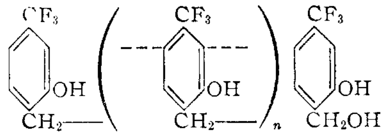
This report records in part the transformation of 4-trifluoromethylsalicylic acid[1] (I) into the corresponding amide, anilide, hydrazide, hydroxamic acid and *o*-hydroxybenzyl alcohol. These compounds are to be tested for chemotherapeutic or fungicidal activity. 4-Trifluoromethyl-2-hydroxybenzyl alcohol (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.

out success. A reaction did occur when the solvent was ethylene glycol. The product, however, was β-hydroxyethyl 4-trifluoromethylsalicylate, formed possibly by a transesterification mechanism as indicated later.

Experimental

Silver 4-Trifluoromethylsalicylate.—4-Trifluoromethylsalicylic acid[1] was neutralized with aqueous ammonia, and allowed to react with silver nitrate solution to give a quantitative yield of silver 4-trifluoromethylsalicylate.

Anal. Calcd. for $C_8H_4O_3F_3Ag$: Ag, 34.47. Found: Ag, 34.27.

4-Trifluoromethylsalicylamide.—Ten grams of methyl 4-trifluoromethylsalicylate,[1] b.p. 97° (10 mm.), was introduced slowly into a three-necked flask containing 100 g. of concentrated ammonia and 0.4 g. of powdered aluminum[6] and heated with stirring at 70° for 2.5 hours. Upon neutralization with a slight excess of concentrated hydrochloric acid, 9 g. (97%) of crude 4-trifluoromethylsalicylamide (m.p. 140–144°) was isolated. The solid was washed with dilute sodium bicarbonate to remove possible traces of organic acid. The precipitate was then redissolved in dilute sodium hydroxide and reprecipitated upon acidification. Upon decolorization with charcoal and repeated crystallization from aqueous alcohol, slightly pink needles of m.p. 149–151° were obtained.

Anal.[7] Calcd. for $C_8H_6O_2NF_3$: C, 46.84; H, 2.95; N, 6.83. Found: C, 47.04; H, 2.93; N, 6.58.

4-Trifluoromethylsalicylanilide.—A mixture of 10.3 g. of I, 5.12 g. of aniline and 15 cc. of dimethylaniline was heated at 100° until the acid dissolved, and 5 cc. of phosphorus trichloride was added dropwise with stirring during ten minutes. The mixture was heated at 100–105° for an additional half-hour and then poured (while hot) into a warm solution of 50 ml. of concentrated hydrochloric acid and 200 ml. of water with vigorous stirring. The crude solid (10 g., 71%) was washed with bicarbonate, dissolved in alkali and reprecipitated with acid. After several recrystallizations from 50% aqueous alcohol (and decolorization with charcoal) pure 4-trifluoromethylsalicylanilide, m.p. 189–190° (white powder), was obtained.

Anal. Calcd. for $C_{14}H_{10}O_2NF_3$: C, 59.79; H, 3.58; N, 4.98. Found: C, 59.69; H, 3.72; N, 4.94.

4-Trifluoromethylsalicylic Acid Hydrazide.—Eleven grams of methyl 4-trifluoromethylsalicylate was added dropwise to a refluxing solution of 3 ml. of 85% hydrazine hydrate and 10 ml. of absolute ethanol. After the addition of water, there was found 10.5 g. of crude material consisting of the desired hydrazide and a product melting at *ca.* 325° which is believed to be di-(4-trifluoromethylsalicylic acid) hydrazide. After several recrystallizations from ethanol, there was isolated 3.5 g. of white, crystalline, 4-trifluoromethylsalicylic acid hydrazide, m.p. 170.5–171.5°.

Anal. Calcd. for $C_8H_7O_2N_2F_3$: C, 43.64; H, 3.21; N, 12.73. Found: C, 43.93; H, 3.36; N, 12.74.

The pure hydrazide which melted to a clear colorless liquid at 171°, upon continued heating formed a new solid at 180–181° with liberation of a gas, which finally melted, with some decomposition, at 319–321°. This is thought to be due to diacyl hydrazide formation.

4-Trifluoromethylsalicylhydroxamic Acid.—Ten grams of methyl 4-trifluoromethylsalicylate was added with stirring to a mixture of 6.95 g. of hydroxylamine hydrochloride, 11.8 g. of potassium hydroxide, 160 ml. of water and 100 ml. of ethanol. The reaction mixture was allowed to stand at room temperature for one day. After addition of hydrochloric acid and recrystallization from ethanol, 8.5 g. of pale pink, almost white, 4-trifluoromethylsalicylhydroxamic acid, m.p. 185.5–186.0°, was obtained.

Anal. Calcd. for $C_8H_6O_3NF_3$: C, 43.45; H, 2.74; N, 6.34. Found: C, 43.74; H, 2.70; N, 6.45.

4-Trifluoromethyl-2-hydroxybenzyl Alcohol.—4-Trifluoromethylsalicylic acid (41.2 g.), dissolved in 150 ml. of ethyl ether was added drop by drop to 7.6 g. of lithium aluminum hydride in 200 ml. of anhydrous ethyl ether over a period of 4 hours.[8] The reaction mixture was worked up in the usual manner. 4-Trifluoromethyl-2-hydroxybenzyl alcohol (36 g., 94%) was isolated. After recrystallization from benzene the white solid, which gave a wine-red ferric chloride reaction, melted at 66–66.5°.

Anal. Calcd. for $C_8H_7O_2F_3$: C, 50.01; H, 3.67. Found: C, 49.92; H, 3.73.

4-Trifluoromethyl-2-hydroxybenzyl alcohol (1.92 g.), *n*-perfluorobutyric acid (2.35 g.) and benzene (20 ml.) were refluxed together for 6 hours. Upon washing the reaction mixture with sodium bicarbonate solution, essentially all of the perfluorobutyric acid was recovered as the sodium salt. After all of the benzene was distilled out of the previously dried organic layer, the product was heated *in vacuo* to 250°. The residue consisted of *ca.* 1 g. of a fluorine-containing resin, m.p. *ca.* 85°, probably resulting from the self-condensation of the 4-trifluoromethyl "saliginen."[9]

Attempted Reaction of I with 1,1-Di-H-perfluoroethanol.—1,1-Di-H-perfluoroethanol (4.05 g.), I (8.7 g.) and 2 ml. of fuming sulfuric acid were refluxed in benzene for 8 hours. Upon washing the mixture with dilute sodium bicarbonate, almost all of I was recovered as the sodium salt, indicating that no reaction occurred.

The Reaction of I with 1,1-Di-H-perfluoroethyl *p*-Toluenesulfonate.—A mixture of 10.3 g. of I, 4.3 g. of sodium bicarbonate in 43 ml. of water and 12.45 g. of 1,1-di-H-perfluoroethyl *p*-toluenesulfonate was refluxed for 8 hours with vigorous stirring. No reaction occurred.

The following modification was then tried. Sodium 4-trifluoromethylsalicylate was prepared by dissolving I in 10% sodium carbonate solution, cooling in ice, and collecting the salt formed. To 7.5 g. of this salt, 8.12 g. of the tosyl ester and 34 ml. of ethylene glycol were added. The mixture was refluxed for six hours. The bottom layer solidified on cooling and the crude product weighed 7.6 g. Upon recrystallization from heptane, a white solid melting at 55.5–57° was obtained. This ester is hydrolyzed easily in cold 10% sodium hydroxide solution to give sodium 4-trifluoromethylsalicylate. Elemental analysis indicated that the ester was not the expected 1,1-di-H-perfluoroethyl 4-trifluoromethylsalicylate, but was rather β-hydroxyethyl 4-trifluoromethylsalicylate.

Anal. Calcd. for $C_{10}H_9O_4F_3$: C, 48.01; H, 3.63. Found: C, 48.35, 48.40; H, 3.66, 3.96.

Since essentially none of the original tosyl ester was recovered, it is possible that the trifluoroethyl ester was indeed first formed but that at the temperature of boiling glycol transesterification occurred. A large excess of glycol and the low boiling point of trifluoroethanol (74°) would displace the equilibrium to the right.

Several other attempts to prepare 1,1-di-H-perfluoroethyl 4-trifluoromethylsalicylate utilizing as solvents Diethyl Carbitol, Dibutoxy Tetraglycol and N-dimethylformamide, failed.

Acknowledgment.—The financial support of the Research Corporation is gratefully acknowledged.

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(6) M. Maeda, *et al.*, Japan Patent 5365 (Dec. 17, 1952).

(7) Microanalyses by Clark Microanalytical Laboratory.

(8) R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947), prepared *o*-hydroxybenzyl alcohol, similarly, in 99% yield.

(9) For a discussion of the condensation polymerization of *o*-hydroxybenzyl alcohol, see M. M. Sprung and M. T. Gladstone, THIS JOURNAL, **71**, 2907 (1949).

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Direction of Addition of the Nitrate Ion to an Unsymmetrical Oxide[1]

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In a previous publication[3] the nitrate ion was

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(1) This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.

(2) To whom inquiries regarding this article should be sent.

(3) P. L. Nichols, Jr., A. B. Magnusson and J. D. Ingham, THIS JOURNAL, **75**, 4255 (1953).