no ferric coloration in ethanol, m.p. and mixed m.p. 149–150°.

Band D on crystallization from ethanol furnished 3'-hydroxy-3,4',5,7-tetramethoxyflavone in yellow prisms (190m g.), m.p. 223–224.5° (lit.[11] m.p. 220–222°) $\lambda_{max}^{C_2H_5OH}$ 343 mμ, $\lambda_{max}^{0.002M\ NaOC_2H_5\ in\ C_2H_5OH}$ 380, 333 mμ, giving no ferric coloration in ethanol.

Anal. Calcd. for $C_{15}H_6O_2(OCH_3)_4$: C, 63.7; H, 5.1; OCH_3, 35.0. Found: C, 63.9; H, 5.0; OCH_3, 34.1.

The *acetate* of this compound separated from ethanol in colorless needles, m.p. 214–216°.

Anal. Calcd. for $C_{21}H_{20}O_8$: C, 63.0; H, 5.0; Found: C, 63.2; H, 5.1.

On ethylation with excess of ethyl iodide and potassium carbonate in boiling acetone during 4 hr. it furnished 3-ethoxy-3,4',5,7-tetramethoxyflavone in cream colored needles, m.p. 156.5–158° undepressed on admixture with an authentic sample.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.0; H, 5.5.

The benzene insoluble fraction of the methylation product of quercetin pentaacetate was repeatedly crystallized from aqueous ethanol, furnishing rhamnetin in yellow needles (340 mg.) m.p. 291–294°, undepressed on admixture with authentic amaterial. Paper chromatography of the mother liquors showed the presence of quercetin.

3'-Ethoxy-5,7-dihydroxy-3,4'-dimethoxyflavone. A mixture of ω-methoxyphloracetophenone[13] (3 g.), sodium 3-ethoxy-4-methoxybenzoate (3 g.) and 3,3'-diethoxy-4,4'-dimethoxybenzoic anhydride[14] was heated *in vacuo* to 180° for 4 hr. and the product hydrolyzed in boiling alcoholic sodium hydroxide (10%, 200 ml.) during 20 min. The solution was then evaporated to one-third bulk, diluted with water (2 l.) and neutralized by the addition of solid carbon dioxide. The resulting solid was crystallized from aqueous acetic acid and then from ethanol, furnishing the flavone in yellow needles (5.0 g.) m.p. 217.5–218.5°.

Anal. Calcd. for $C_{19}H_{18}O_7$: C, 63.7; H, 5.1. Found: C, 63.5; H, 5.0.

Its *diacetate* formed colorless needles, m.p. 167–168.5°.

Anal. Calcd. for $C_{23}H_{22}O_9$: C, 62.4; H, 5.0. Found: C, 62.4; H, 5.3.

3'-Ethoxy-3,4',5,7-tetramethoxyflavone. A mixture of the foregoing compound (500 mg.) methyl sulfate (2 ml.) and potassium carbonate in acetone (40 ml.) was refluxed for 4 hr., filtered, and the combined filtrate and washings evaporated to low bulk. The remaining solid was dissolved in benzene, washed with water, dried, and chromatographed on alumina. Elution with benzene-ethanol (99.5:0.5) and crystallization from ethanol furnished cream colored needles, m.p. 158°.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.3; H, 5.8.

3'-Ethoxy-5-hydroxy-3,4',7-trimethoxyflavone. 3'-Ethoxy-5,7-dihydroxy-3,4'-dimethoxyflavone (900 mg.) was methylated with 1.1 equivalents of methyl sulfate (0.35 g.) and the product isolated by the above method. After purification by elution from silicic acid–Celite (2:1) with benzene-ethanol (99.5:0.5) and crystallization from ethanol, yellow needles (690 mg.), m.p. 138–139°, were obtained, giving a brown ethanolic ferric reaction.

Anal. Calcd. for $C_{22}H_{22}O_7$: C, 64.5; H, 5.4. Found: C, 64.4; H, 5.4.

Its *acetate* formed colorless needles, m.p. 164–165° from ethanol.

Anal. Calcd. for $C_{24}H_{24}O_8$: C, 63.8; H, 5.4. Found: C, 63.8; H, 5.5.

3',5-Diethoxy-3,4',7-trimethoxyflavone. The foregoing hydroxyflavone (250 mg.) was ethylated with excess ethyl sulfate and potassium carbonate in acetone and the product isolated and purified by elution from neutral alumina with benzene-chloroform (1:1). Crystallization from ethanol furnished colorless needles (250 mg.) m.p. 162.5–164°.

Anal. Calcd. for $C_{23}H_{24}O_7$: C, 66.0; H, 6.0. Found: C, 65.8; H, 5.8.

3,3'-Diethoxy-5-hydroxy-4',7-dimethoxyflavone. 3,3'-Diethoxy-5,7-dihydroxy-4'-methoxyflavone[14] (1.3 g.) was monomethylated and the product purified as in the previous partial methylation experiment, furnishing yellow prisms (1.1 g.), m.p. 130–131° giving a dark brown ferric coloration.

Anal. Calcd. for $C_{21}H_{22}O_7$: C, 65.3; H, 5.7. Found: C, 65.4; H, 5.9.

Its *acetate* formed colorless needles, m.p. 153–154.5° from ethanol.

Anal. Calcd. for $C_{23}H_{24}O_8$: C, 64.5; H, 5.7. Found: C, 64.1; H, 5.5.

3,3',5-Triethoxy-4',7-dimethoxyflavone. The foregoing compound (800 mg.) was alkylated with excess ethyl sulfate and the product isolated by the standard method. Elution from neutral alumina with benzene-chloroform (1:1) and crystallization from benzene–petroleum ether (b.p. 80–100°) furnished colorless needles (600 mg.), m.p. 138–139°.

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The Sulfonation of 2-6-Dinitronaphthalene

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In a previous report,[1] the sulfonation of 1,3-dinitronaphthalene was described. The present work is concerned with the sulfonation of the 2,6-isomer.

This reaction proceeded at room temperature with oleum as the sulfonating agent, and was complete in less than seven hours. Conventional orientation rules[2] would indicate that the 4-sulfonic acid should be formed (3,7-dinitronaphthalene-1-sulfonic acid, I), and this was found to be the case. Reaction of the sodium salt of I with phosphorus pentachloride at moderate temperatures gave the sulfonyl chloride, while at higher temperatures, 1,3,7-trichloronaphthalene was formed. The infrared spectrum of the latter was identical to that of an authentic specimen, and provides evidence for the assigned structure.

Contrary to expectation, the sulfonic acid I did not appear to be formed in the nitration of 7-nitronaphthalene 1-sulfonic acid,[3] other isomers

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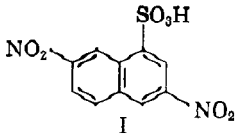
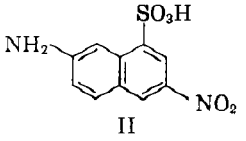


I

being produced.

Reduction of I furnished the corresponding diaminosulfonic acid, isolated as the monohydrochloride salt. This substance was also prepared by reduction of 7-amino-3-nitronaphthalene-1-sulfonic acid (II), obtained as described by Blangey.[4]



II

The infrared spectra of the two diaminosulfonic acids obtained by reduction were the same, thus providing further proof of structure.

Attempts to sulfonate 6-nitro-2-naphthylamine under several reaction conditions failed, dark tars being formed.

EXPERIMENTAL

The yields are not given as each product or its precursor was contaminated unavoidably by sodium chloride.

3,7-Dinitronaphthalene-1-sulfonic acid, sodium salt. 2,6-Dinitronaphthalene (0.2 g.) was treated with 5.2 ml. of 30% oleum at room temperature, and left sealed with occasional shaking for 7 hr. The mixture was then poured on ice, the solution filtered and the filtrate saturated with sodium chloride. The crystalline deposit of sodium salt was filtered and washed twice with brine, yield, 0.22 g. For spectral tests, the light yellow salt was redissolved in water and resalted with sodium chloride to eliminate any sodium sulfate.

Sulfonation of the dinitronaphthalene with 100% sulfuric acid did not occur during 3 days in the cold.

Other salts. The aqueous acid is readily salted out by potassium chloride giving a product resembling the sodium salt, but the ammonium salt is formed with more difficulty.

A cobaltammine salt is formed as a pink crystalline deposit from solutions of chloropentaminocobaltic chloride and the sodium salt. The complex ammine salts of copper, nickel and zinc are produced from ammoniacal solutions of the respective ions as heavy crystalline precipitates.

3,7-Dinitronaphthalene-1-sulfonyl chloride. A mixture of 0.9 g. of the sodium salt and 3.5 g. of phosphorus pentachloride was ground together and 0.1 ml. of phosphorus oxychloride added. After heating in a bath at 120–125° for 2.5 hr., the product was cooled, hydrolyzed by ice, and the solids filtered off and washed. The filtered acetone solution was diluted slowly with ice water to obtain a crystalline product free of inorganic impurities. It was recrystallized from aqueous acetone at 0–10°, and then from chloroform-hexane, yielding light yellow crystals, m.p. 126–127.5°.

Anal. Calcd. for $C_{10}H_5N_2SO_6Cl$: S, 10.1. Found: S, 10.2.

Conversion of the sulfonyl chloride to 1,3,7-trichloronaphthalene. The sulfonyl chloride was mixed with five times its weight of phosphorus pentachloride and heated to 175–180° for 2 hr. It was then cooled, hydrolyzed, and the semisolid material steam distilled for several hours. The solid product in the distillate was filtered, washed, and dried and the infrared spectrum taken and compared with that of authentic 1,3,7-trichloronaphthalene. These were found to be the same.

3,7-Diaminonaphthalene 1-sulfonic acid monohydrochloride (from the dinitrosulfonic acid I). The sodium salt of I was dissolved in hot 1*N* hydrochloric acid and three times its weight of stannous chloride added. The solution was boiled for 1 hr. with concentration to one-third of the original volume. On cooling, a paste of crystalline product formed, which was filtered and washed with 9*N* hydrochloric acid. After recrystallization from 9*N* hydrochloric acid, it formed a white crystalline powder.

From 7-amino-3-nitronaphthalene-1-sulfonic acid (II). The starting material (II) was prepared and separated from its isomers as Blangey describes.[4] It was reduced by stannous chloride as outlined above for the dinitro acid. The sparingly soluble nitroamino acid slowly dissolved as the reduction proceeded and the diamino acid hydrochloride was isolated as before.

Anal. Calcd. for $C_{10}H_{11}N_2SO_3Cl$: Cl, 12.9. Found: Cl, 13.1. The infrared spectra of the two samples were identical.

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The Synthesis of Some Pyridylpyridazines and -pyrimidines[1]

WALTER A. BUTTE AND FRANCIS H. CASE

A previous report from this laboratory[2] described the preparation of 2,4,6-tris(2′-pyridyl)-*s*-triazine (I). The arrangement of nitrogen atoms in this molecule resembles that in 2,6-bis(2′-pyridyl)-pyridine (II) and other workers[3] have demonstrated that like the latter it forms stable coordination compounds with transition metal ions. This analogy can be extended to ring systems containing two nitrogens. Goodwin and Lions[4] have prepared the structurally related 2,3,5,6-tetrakis(2′-pyridyl)pyridine (III) and studied its chelate salts. This paper describes the synthesis of pyrimidines and pyridazines which are similarly substituted with 2-pyridyl groupings on the carbons adjacent to the nitrogen atoms.

The condensation of amidines with β-ketonic esters, which is perhaps the most general route to substituted pyrimidines, was adapted to the preparation of pyridyl-substituted pyrimidines.

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