min., yielding a colorless precipitate (1.01 g., 0.0068 mole, 34%), m.p. 97–98.5°. After recrystallization from ether the sample melted at 99.5–100.5°, mixed m.p. 100.5–101.5° with a sample of *N*-methylacetanilide prepared[13] from Eastman Kodak Co. White Label *N*-methylaniline. The infrared spectra of the two samples in Nujol were identical. ν_{NH} none; $\nu_{C=O}$ 1672 cm.$^{-1}$ in Nujol.

Decarboxylation of 9-methylcarbazole-1-carboxylic acid (IV), 9-Methylcarbazole-1-carboxylic acid[5] (0.50 g., 0.00221 mole) was mixed thoroughly with powdered soda-lime (2.5 g.) and the mixture decarboxylated as described previously. The white sublimate (0.23 g., 0.00127 mole, 58%), m.p. 87.5–89.0°, did not depress the melting point of authentic 9-methylcarbazole,[5] and the infrared spectra in Nujol were identical. ν_{NH} none.

Decarboxylation of 9-methylcarbazole-1,8-dicarboxylic acid (V). 9-Methylcarbazole-1,8-dicarboxylic acid[5] (0.50 g., 0.00186 mole) was decarboxylated as described previously. The white sublimate (0.17 g., 0.00094 mole, 50%), m.p. 84–86°, did not depress the melting point of authentic 9-methylcarbazole[5] (it is interesting to note, however, that the mixed melting point of equal quantities of carbazole and 9-methylcarbazole is 83–87°) and the infrared spectra in Nujol were essentially identical, except for the presence of a medium weak NH or OH band at 3500 cm.$^{-1}$, suggesting contamination by a small amount of carbazole, the *N*-demethylation product.

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A New Synthesis of Benzothiazoline

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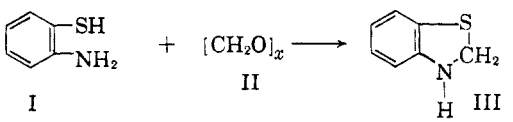
Although a number of syntheses for benzothiazoline have been reported in the literature,[1–4] none offers the convenience of the method which we report here.

We found that benzothiazoline (III) was formed in good yields by refluxing 2-aminobenzenethiol (I) with paraformaldehyde (II) followed by distillation under reduced pressure.



I II III

EXPERIMENTAL

To 12.5 g. (0.1 mole) of 2-aminobenzenethiol (American Cyanamid, tech. grade) dissolved in 20 ml. of anhydrous methyl alcohol was added a mixture of 4 g. of paraformaldehyde (Eastman Kodak, pract. grade) suspended in 10 ml. of anhydrous methyl alcohol. The mixture was refluxed until the original yellow color disappeared (about 12 hr.).

Upon cooling to room temperature, two distinct layers formed. The bottom layer was withdrawn and distilled. The fraction collected at 146–149°/18 mm. was identified as benzothiazoline. The yield was 75–80% based on 2-aminobenzenethiol.

Identification of the product was accomplished as follows: (a) The infrared spectrum showed an intense nitrogen-hydrogen stretching band at 3.0 μ. (b) The boiling point was identical with that reported,[1,5] in the literature (b.p. 270°). (c) The phenylisocyanate derivative melted at 161–162°. The literature[5] value was 162°.

Acknowledgment. The authors are grateful to the American Cyanamid Co. for graciously supplying 2-aminobenzenethiol.

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(1) M. Claaz, *Ber.*, **45**, 1031 (1912); **49**, 1141 (1916).
(2) M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **47**, 3078 (1925).
(3) H. P. Lankelma and P. X. Sharnoff, *J. Am. Chem. Soc.*, **53**, 2654 (1931).
(4) K. Baker, *Helv. Chim. Acta*, **33**, 2011 (1950).
(5) R. A. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, 71, 2297 (1949).

Schiff Bases from 4-(4-Aminostyryl)quinoline and Aldose Sugars[1]

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4-(4-Aminostyryl)quinoline (I) reacted readily with 4-dimethylaminobenzaldehyde to form a Schiff base that was less toxic than I.[2] It seemed that aldose sugars might produce similar products and that the sugar moiety might cause the compounds to be water soluble. The use of a small amount of dimethylformamide made it possible to bring the reactants into a homogeneous liquid reaction mixture at the desired temperature, 120–130°. Glyceraldehyde, ribose, galactose(II), glucose(III), lactose, and maltose all seemed to react smoothly under these conditions, but only II formed crystals that were purified readily by recrystallization. The other products tended to precipitate as gels or amorphous solids.

EXPERIMENTAL

Galactose Schiff base of 4-(4-aminostyryl)quinoline. A mixture of 30.0 g. of I and 15.0 ml. of dimethylformamide was heated to 130° to produce a clear solution. This solution was cooled to 110°, 21.6 g. of II was added slowly with stirring, and the mixture was heated 10 min. at 120–130°. The resulting solid mass was washed with benzene and with water to remove excess starting materials. One gram of solid was dissolved in 30 ml. of dimethylformamide, 20 ml. of the solvent was removed by distillation at 60° at 2.5 mm. The bright yellow crystals which formed were recrystallized

(1) This research was supported by a grant from the National Cancer Institute.
(2) Carl T. Bahner, Clarence Cook, John Dale, John Fain, Fred Hannan, Patricia Smith, and Joan Wilson, *J. Org. Chem.*, **23**, 1060 (1958).

four times in this way, darkening at 209°, melting with decomposition at 216–217°; yield 60%.

Anal. Calcd. for $C_{23}H_{23}N_2O_5$: C, 67.71; H 5.92. Found: C, 67.48–67.75; H, 5.85, 6.06.[3]

Dextrose Schiff base of 4-(4-aminostyryl)quinoline. To a solution formed by heating 9.8 g. of I and 5 ml. of dimethylformamide to 130°, 13.8 g. of III was added slowly, with stirring, at 110°. The mixture was then heated to 120–130° for 30 min., until it solidified. The product was washed with benzene and with water and recrystallized four times from isopropyl alcohol, using a Soxhlet extractor, and three times from methanol; m.p. 189.7–191.7° (dec.).

Anal. Calcd. for $C_{23}H_{23}N_2O_5$: C 67.71; H, 5.92. Found: C, 67.48, 67.75; H, 5.85, 6.06.[3]

These compounds were not readily soluble in water but dissolved readily in hot propyleneglycol and in dimethylformamide.

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(3) Analyses by Galbraith Microanalytical Laboratories.

Methyl Ethers of Quercetin in Tobacco Flowers[1]

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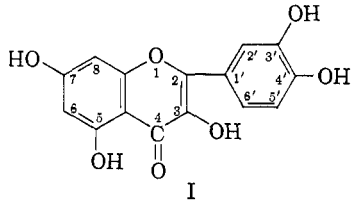
Monomethyl and dimethyl ethers of quercetin (3,3′,4′,5,7-pentahydroxyflavone, I) having no methoxyl group at the 3-position, such as rhamnetin (quercetin-7-methyl ether), isorhamnetin (quercetin-3′-methyl ether), quercetin-4′-methyl ether, and rhamnazin (quercetin-3′,7-dimethyl ether) have been found previously in natural products, usually as glycosides. A 3,7,4′-trimethyl ether of quercetin, ayanin, has been isolated from the heartwood of the tree *Distemonanthus Benthamianus* by King, *et al.*[2] However, monomethyl and dimethyl ethers of quercetin that contain a methoxyl group at the 3-position have been obtained only by laboratory synthesis.[3–5] This note describes the isolation and identification of quercetin-3,3′-dimethyl ether from tobacco flowers. We have also found other related flavonol ethers in these flowers. One of these other compounds has been tentatively identified as quercetin-3-methyl ether.



I

EXPERIMENTAL

Separation of quercetin ethers. Samples each containing 100 g. of powdered, oven-dried flowers from tobacco plants, *Nicotiana tabacum*, one-sucker variety, grown in the greenhouse at Argonne National Laboratory during 1958, were extracted with 500 ml. of the following solvents in the order named: *n*-pentane, benzene, chloroform, ethyl acetate (anhydrous), and acetone. Each 500-ml. extract was concentrated *in vacuo* to 5 ml. and studied by paper chromatography. The flavonol ethers were mostly in the chloroform fraction, although at least two such compounds were present in small amounts in the ethyl acetate extract.

Each 5-ml. chloroform concentrate was streaked onto eight sheets of Whatman No. 3 MM chromatography paper (approx. 7″ × 22½″), and the chromatograms were developed by descending chromatography in 15% acetic acid–water for about 24 hr. The upper part of each chromatogram, containing the methylated flavonol compounds which moved only a relatively short distance in this solvent, was cut out and sewn onto a new sheet of S & S chromatography paper, No. 589, Red Ribbon. Each sheet was next developed in *n*-butyl alcohol–acetic acid–water (6:1:2 v./v.). After drying, the papers were viewed under long wave-length ultraviolet light (3660 Å). A dark brown zone was seen near the solvent front; it was poorly separated from some blue-fluorescing material. The broad, dark brown zone containing the mixture of methylated flavonols was cut from each chromatogram, eluted with methanol, and then subjected to further extended chromatography, first in 15% acetic acid for 36–48 hours, then on fresh sheets in 60% acetic acid–water. The latter effected separation of the quercetin dimethyl ether from a trace amount of another brown fluorescing substance which had the same mobility as authentic quercetin-3-methyl ether on chromatograms. The yield of this latter compound from the 1958 tobacco flowers was insufficient to confirm its identity. After elution of the brown fluorescing zone containing the quercetin dimethyl ether, the methanol eluates were subjected to further chromatography on S & S No. 589 paper, using four different solvent systems in the order: 15% acetic acid–water: ethyl acetate–formic acid–water (10:2:3 v./v., upper layer); *n*-butyl alcohol–acetic acid–water (6:1:2 v./v.); and finally 60% acetic acid–water. The quercetin dimethyl ether zone of each final chromatogram was then pure enough for identification studies.

Identification of quercetin-3,3′-dimethyl ether. On paper chromatograms, the quercetin dimethyl ether exhibited a dark brown fluorescence under ultraviolet light, but after the compound had been sprayed with a 1% solution of aluminum chloride in ethanol, it gave a yellow fluorescence. Flavone aglycones such as apigenin (4′,5,7-trihydroxyflavone); flavonol glycosides such as isoquercitrin (quercetin-3-glucoside); and certain 3-methyl ethers of flavonols, such as quercetin-3-methyl ether and quercetin-3,7-dimethyl ether exhibit this fluorescent behavior.

After the isolated tobacco quercetin dimethyl ether was refluxed with hydriodic acid, sp. gr. 1.7, for 4 hr., a product was obtained which proved to be quercetin. Identity was established by comparison of color tests, fluorescence, ultraviolet absorption spectra, and co-chromatography with authentic quercetin.

After the tobacco quercetin dimethyl ether was refluxed with dimethyl sulfate and sodium carbonate in acetone for 6 hr., the product showed a blue fluorescence under ultraviolet light and was identified as quercetin-3,3′,4′,5,7-pentamethyl ether by paper chromatographic comparison with an authentic sample. Thus, the unknown was definitely a methyl ether

(1) This work was performed in part under the auspices of the U. S. Atomic Energy Commission.

(2) F. E. King, T. J. King, and K. Sellars, *J. Chem. Soc.*, **155**, 92 (1952).

(3) R. Kuhn and I. Löw, *Ber.*, **77B**, 211 (1944).

(4) A. C. Jain, K. S. Pankajamani, and T. R. Seshadri, *J. Sci. Ind. Res. (India)*, **12B**, 127 (1953).

(5) T. R. Seshadri, *Tetrahedron*, **6**, 196 (1959).