From the reaction mixture it was found that the volatile amine fraction accounted for 85% or more of the total nitrogen of the proteins and model compounds subjected to hydrogenolysis with copper chromite at 250°. The exception was the case of acetyl zein in which the linkages appear to be partly protected. Less was produced from zein II upon Raney nickel hydrogenolysis at 185°. In every instance of hydrogenolysis the volatile amine fraction gave a negative Nessler test for ammonia; instead the reagent produced a white, chalky precipitate. All of this base in each case was identified as tri-*n*-butylamine which was isolated and purified as the picrate. All samples melted from 103–105° with no depression when mixed with authentic sample. The nitrogen content by modified micro-Kjeldahl was 12.9%, the calculated value is 13.5%. However, a value of 12.9% was also obtained on an authentic sample of tri-*n*-butylamine picrate. No primary amine nitrogen was found; such would be expected since the conditions of hydrogenolysis favor alkylation, as has been shown by Adkins.[3] During hydrogenolysis the amide and peptide linkages of the compounds appear to be attacked to the same extent with conversion of their nitrogen to the fully alkylated base.

During butanolysis, primary amino nitrogen was liberated and ammonia appeared in all products except from nylon and butyl hippurate. No alkylated nitrogen product was detected. Peptide nitrogen is markedly more resistant to butanolysis than hydrogenolysis; this is particularly evident with butyl hippurate and nylon. Furthermore, the peptide linkages are more resistant to hydrogenolysis than the primary amide bonds of acetamide and polyacrylamide.

Hydrogenolysis produced marked changes in the forms of nitrogen as revealed by the Van Slyke nitrogen analyses summarized in Table II. Most striking is the enormous increase in the "ammonia" fraction which was all identified as tri-*n*-butylamine. After butanolysis the "phosphotungstic acid bases" and the "non-amino" nitrogen in the filtrate are increased at the expense of the "soluble amino" nitrogen. Similar but less drastic changes are produced upon zein II by hydrogenolysis with Raney nickel at 185°; as may also be seen with acetyl zein.

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## A Novel Acetylation of Quercetin 3,3′,4′,7-Tetramethyl Ether (5-Hydroxy-3,3′,4′,7-tetramethoxyflavone)

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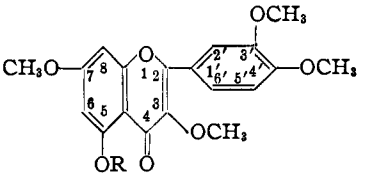
In an investigation of the methanesulfonation of quercetin and its derivatives,[1] we have observed that quercetin 3,3′,4′,7-tetramethyl ether (I) cannot be methanesulfonated by the action of methanesulfonyl chloride in pyridine. Several modifications of the usual procedure were then employed, one of which involved the action on I of a mixture of methanesulfonyl chloride and acetic acid in pyridine at room temperature. Instead of the methanesulfonate there was obtained a colorless, sulfur-free product, identified as 5-acetoxy-3,3′,4′,7-tetramethoxyflavone (II).



I, R = H
II, R = $COCH_3$

The difficulty encountered in attempting to methanesulfonate I is not surprising, since the 5-hydroxyl of I is known to be also difficult to methylate,[2,3] and acetylation has been reported only when the vigorous conditions of boiling acetic anhydride and anhydrous sodium acetate were used.[4] Our acetylation procedure accordingly seems remarkable, employing as it does very mild conditions.

### Experimental

**Quercetin 3,3′,4′,7-Tetramethyl Ether** (I).—Quercetin was methylated by the method of Waliaschko,[5] with retention of the product, m.p. 155–157°, considered by Waliaschko to be a trimethyl ether, but subsequently shown[3] to be I, thus confirming Herzig's contention.[2]

**5-Acetoxy-3,3′,4′,7-tetramethoxyflavone.**—To 0.1 g. of quercetin 3,3′,4′,7-tetramethyl ether, dissolved in 11 ml. of reagent pyridine, was added first 0.7 ml. of glacial acetic acid, then 0.6 g. of methanesulfonyl chloride. Heat was evolved, and crystalline material (water-soluble) separated in approx. 30 seconds. The pyridine solution was decanted from solid material after 40 minutes, and the pyridine decantate permitted to stand at room temperature an additional 42 hours. The crude acetate was isolated by pouring the reaction mixture into 90 ml. of water, and permitting the aqueous suspension to stand for three hours. The crude, crystalline solid deposited was collected by filtration, washed with water and air-dried for several days; m.p. 165–170°. After sodium fusion, the crude product gave negative tests for sulfur both with lead acetate and sodium nitroprusside. The crude acetate was recrystallized twice from absolute ethanol to give colorless, silken needles, m.p. 169–171° (lit. m.p. 167–169°,[4] 171–172°[6]), no depression upon admixture with authentic 5-acetoxy-3,3′,4′,7-tetramethoxyflavone (m.p. 169–170.5°), prepared by the method of Herzig.[4]

(1) J. H. Looker and A. L. Krieger, unpublished observations.

(2) J. Herzig, *Sitzungsber.*, **121**, 333 (1912).

(3) Methylation of the 5-hydroxyl of I has been achieved, however, by employment of dimethyl sulfate and solid potassium hydroxide [A. S. Gomm and M. Nierenstein, THIS JOURNAL, **53**, 4408 (1931)].

(4) J. Herzig, *Monatsh.*, **5**, 86 (1884).

(5) N. Waliaschko, *Ber.*, **42**, 727 (1909).

(6) N. Krassowski, *Chem. Centr.*, **80**, [I] 772 (1909).

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## Chlorotetranitronaphthalenes

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Although two isomeric bromotetranitronaphthalenes were described seventy years ago, no mention has been found in the literature of chlorotetranitronaphthalenes.

The two chlorotetranitronaphthalenes described here were prepared mainly for trial as colorimetric