Notes

A department for short papers of immediate interest.

Corn Plant Resistance Factor

Edward E. Smissman, Jules B. LaPidus,
and Stanley D. Beck

Received November 8, 1956

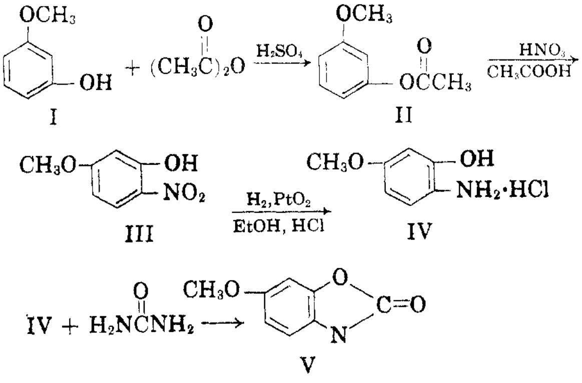
We have isolated a compound from the corn plant which appears to be partially responsible for the resistance of the plant to attack by the European corn borer. Virtanen and Hietala[1] previously reported a compound to be present in the rye plant which is benzoxazolinone. They found this compound prevented the growth of *Fusarium nivale*, a rye plant rot. After corresponding with a former member of our group Virtanen assumed a product he isolated from wheat and maize plants to be 6-methoxy-2(3)-benzoxazolinone[2] but never confirmed this assignment.

We have synthesized 6-methoxy-2(3)-benzoxazolinone and have shown it to be identical with the natural product by infrared spectra comparison and by mixed melting point. In our isolation procedure we designated the naturally occurring compound as *factor A* and found it to have the following constants: m.p. 154–155°; $\lambda_{\text{max}}^{H_2O}$ 230, 287 (E_{max} 10,000, 4,500); benzoyl derivative m.p. 161–163°; benzene sulfonyl derivative m.p. 163–164°.

Anal. Calcd. for $C_8H_7O_3N$: C, 58.18; H, 4.27; N, 8.48; CH_3O-, 18.75; Mol. Wt., 165. Found C, 58.41; H, 4.29; N, 8.40; CH_3O-, 18.46; Mol. Wt., 171 (ebulloscopic).

The material was readily recrystallized from water and was found to be soluble in dilute sodium hydroxide. On reviewing our infrared spectra, our analysis, the chemical nature of the compound and its degradation products, we decided to synthesize a methoxy-2(3)-benzoxazolinone. The 5-methoxy-2(3)-benzoxazolinone was previously synthesized,[3] m.p. 172°. On the basis of our absorption spectra we synthesized the 6-methoxy-2(3)-benzoxazolinone which had been postulated by Virtanen, *et al.*[2]

The procedure we followed involved the acetylation of monomethyl resorcinol, I, to give acetoxy methyl resorcinol, II, b.p. 135–136°/23 mm. Mononitration using nitric acid in glacial acetic acid gave 2-hydroxy-4-methoxynitrobenzene, (III), m.p. 94–95°, which on catalytic reduction gave the corresponding amino compound, IV. This compound on fusion with urea afforded 6-methoxybenzoxazolinone, V.



The product, V, obtained from the synthesis gave no depression in melting point when mixed with factor A and their infrared spectra were superimposable.

Division of Pharmaceutical Chemistry
School of Pharmacy
Department of Entomology
University of Wisconsin
Madison, Wis.

---

(1) A. I. Virtanen and P. K. Hietala, *Suomen Kemistilehti*, **28B**, 165 (1955); *Acta Chem. Scand.*, **9**, 1543 (1955).

(2) A. I. Virtanen, P. K. Hietala, and O. Wahlroos, *Suomen Kemistilehti*, **29B**, 143 (1956).

(3) W. J. Close, B. D. Tiffany, and M. A. Spielman, *J. Am. Chem. Soc.*, **71**, 1265 (1949).

Rearrangement of Dihydroquercetin Tetramethylether with Alkali

Carl Enebäck and Jarl Gripenberg

Received September 12, 1956

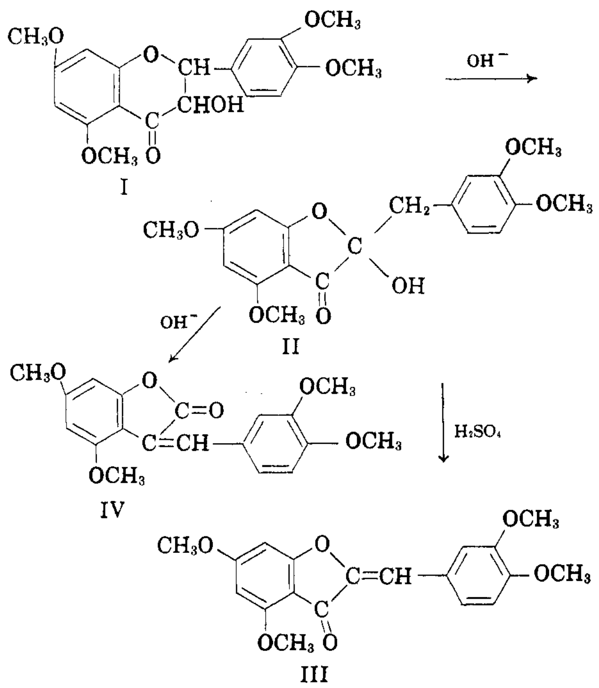
In a recent paper dealing with the methylation of dihydroquercetin (taxifolin) Hergert, Coad and Logan[1] found that methylation under certain conditions led to the formation of 2-(3,4-dimethoxybenzyl)-2-hydroxy-4,6-dimethoxycoumaran-3-one (II). The same compound could also be obtained by treatment of dihydroquercetin-3′,4′,5,7-tetramethylether (I) (Hergert, Coad and Logan[1] use the incorrect name 3′,4′,5,7-tetramethoxydihydroquercetin for this compound) for a few minutes with alkali. When treated with concentrated sulfuric acid II was converted into 2-(3,4-dimethoxybenzylidene)-4,6-dimethoxycoumaran-3-one (III). This is all in accordance with expectations.[2] However, their further statement that prolonged treatment of I or

---

(1) Hergert, Coad and Logan, *J. Org. Chem.*, **21**, 304 (1956).

(2) Gripenberg, *Acta Chem. Scand.*, **7**, 1323 (1953).

II with alkali also gives III is contrary to expectations. One would expect that such a treatment should, through a benzilic acid rearrangement, finally lead to 3-(3,4-dimethoxybenzylidene)-4,6-dimethoxycoumaran-2-one (IV), isomeric with III.[3,4,5]



As a matter of fact we synthesized the compound IV, making thereby the remark, that it should be formed from taxifolintetramethylether upon treatment with alkali.[5]

That it is indeed IV that is formed when II, and hence also I, is boiled with alkali has now been confirmed by a direct comparison of the product with synthetic IV, thereby establishing their identity. II was prepared by the method of Kimura[6] and gave, in agreement with Hergert, Coad and Logan,[1] upon treatment with concentrated sulfuric acid, III, identified by comparison with an authentic sample prepared according to Geissman and Fukushima.[7]

The isomeric compounds III and IV have nearly the same melting points, 171.5–172° and 173.5–174°, respectively, but they give a definite depression of melting point in a mixture test. They further differ in their color reactions with concentrated sulfuric acid. III gives a stable crimson-magenta color,[7] whereas IV in sufficient dilution gives a green color, which upon standing turns brown.

EXPERIMENTAL

2-(3,4-Dimethoxybenzyl)-2-hydroxy-4,6-dimethoxycoumaran-3-one (II). 2′-Hydroxy-3,4,4′,6′,α-pentamethoxychalcone[6] (1 g.) was dissolved in ethanol (100 ml.). To this was added 2*N* sulfuric acid (20 ml.) and the solution was refluxed for 24 hours. After removing the ethanol the product was taken up in ether. The ether solution was extracted with 1*N* sodium hydroxide. Acidification gave a precipitate, which was taken up in chloroform. Removal of the chloroform and recrystallization once from light petroleum-chloroform and once from methanol gave 0.6 g. white crystals, m.p. 176.5°. (Reported, 176°.[1,6])

3-(3,4-Dimethoxybenzylidene)-4,6-dimethoxycoumaran-2-one (IV). 2-(3,4-Dimethoxybenzyl)-2-hydroxy-4,6-dimethoxycoumaran-2-one (II) (0.5 g.) was dissolved in 48% ethanol (14 ml.) containing potassium hydroxide (0.5 g.). The solution was refluxed for one hour, acidified, and extracted with ether. The ether was removed and the residue recrystallized from ethanol giving 0.07 g. of yellow crystals, m.p. 173.5–174°, undepressed when mixed with an authentic sample.[5] It dissolved in concentrated sulfuric acid with a green color, slowly turning brown.

DEPARTMENT OF CHEMISTRY
INSTITUTE OF TECHNOLOGY
HELSINGFORS, FINLAND

---

[3] Oyamada, *Ann.*, **538**, 44 (1939).

[4] Kotake and Kubota, *Ann.*, **544**, 253 (1940).

[5] Gripenberg and Juselius, *Acta Chem. Scand.*, **8**, 734 (1954).

[6] Kimura, *J. Pharm. Soc. Japan*, **58**, 415 (1938).

[7] Geissman and Fukushima, *J. Am. Chem. Soc.*, **70**, 1686 (1948).

Some 4(or 5)-(2′-Aminopropyl)imidazoles

GORDON A. ALLES,[1] BURNETT B. WISEGARVER,[1] N. B. CHAPMAN,[2] AND A. J. TOMPSETT[2]

Received August 17, 1956

The substitution of a 2-aminopropyl group in place of the 2-aminoethyl side chain of phenethylamines was found by Alles[3] to produce but little change in the intensity of their peripheral sympathomimetic activities though the duration of such actions is much prolonged. The effects of corresponding substitution of the 2-aminoethyl side chain of histamine and of its 5(or 4)-methyl derivative that has similar physiological activities was of interest.

It was found that a synthesis of histamine itself could be accomplished from 1,4-diaminobutanone-2, and this synthesis has been recently reported by Fraser and Raphael.[4] The success of this method suggested the possibility of using it for preparing the corresponding 2-aminopropyl imidazole from 1,4-diaminopentanone-2. The preparation of this intermediate from 2-phthalimidobutyryl chloride has been improved over that described by Erne, Ramirez, and Burger.[5] Condensation of the so derived 1,4-diaminopentanone-2 with potassium thiocyanate gave 4(or 5)-(2′-aminopropyl)-2-thiolimid-

---

[1] Laboratories of Gordon A. Alles, Pasadena, Calif.

[2] University Chemical Laboratory, Southampton, England.

[3] G. A. Alles, *J. Pharmacol.*, **47**, 337 (1933).

[4] M. M. Fraser and R. A. Raphael, *J. Chem. Soc.*, 226 (1952).

[5] M. Erne, F. Ramirez, and A. Burger, *Helv. Chim. Acta*, **34**, 143 (1951).