for the measurements using the No. 1554 Leeds and Northrup shielded capacitance and conductance bridge with a thousand cycle oscillator. The acid was purified by fractional crystallization, and the material had a melting point of −15.25 ± 0.05°. All manipulation of the pure sample was performed in a vacuum system and without contact of waxes and greases. The values obtained with a probable error of 2% are

Temp., °C.		$g_x \times 10^3$ l./ohms
−11	26.2	1.28
− 6.2	27.2	1.38
− 2.3	28.7	1.49
0	29.5	1.55
12.8	36.1	1.68
14.2	36.0	1.72
21.5	40.2	2.03
27.7	43.4	2.33

The third column of the above table gives the determined conductances. The cell constant was approximately 0.007 cm.$^{-1}$. A slightly impure sample of the acid with a higher conductance was measured at 0°. The dielectric constant found was 26.9 and the conductance in the above units 1.69 showing that in the method of making the measurements an increase in conductivity resulted in a lower determined number for the dielectric constant. The same technique was employed using the same bridge and cell with nitrobenzene, and values were obtained which agreed with those recorded in the literature to better than 1%.

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RECEIVED JANUARY 18, 1950

STUDIES ON LIGNIN AND RELATED PRODUCTS. II.[1] 5-CARBOXYVANILLIC ACID IN THE BISULFITE-SOLUBLE FRACTION FROM THE SILVER OXIDE OXIDATION OF FERMENTED SULFITE SPENT LIQUOR[2]

Sir:

In a recent paper on the silver oxide oxidation of basic calcium lignosulfonate[1] the isolation of substantial amounts of a 21% sodium bisulfite-soluble fraction which contained only small percentages of vanillin was noted. The bisulfite-soluble fraction from a similar silver oxide oxidation of a *Torulopsis utilis* fermented sulfite spent liquor has been found to contain at least 50% 5-carboxyvanillic acid.

The light brown crystalline bisulfite-soluble fraction (6.8 g.) was covered with 100 ml. of dry ether, heated to boiling, and filtered. The clear solution was treated with 50 ml. of dioxane and distilled slowly from a water-bath until all the ether was removed. After cooling and standing, the crystals were filtered, washed with cold dioxane, and dried. The yield of almost colorless crystals melting at 276–277° was 2.8 g. Concentration of the combined dioxane filtrate and washings yielded 0.6 g. of similar crystals. Repeated recrystallization from water raised the melting point to 281°. The product was identical with 5-carboxyvanillic acid reported by Freudenberg, Klink, Flickinger and Sobek,[3] who obtained it by partially hydrolyzing either 5-cyanoveratric acid or 5-carboxyveratric acid with hydrochloric acid.

Anal. Calcd. for $C_9H_8O_6$: C, 50.93; H, 3.80; CH_3O, 14.63. Found: C, 50.80; H, 3.88; CH_3O, 14.65.

The synthesis, degradation, derivatives, and significance to the structure of lignin of 5-carboxyvanillic acid will be discussed in forthcoming papers.

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[1] For Part I of this series, see THIS JOURNAL, **71**, 2196 (1949).

[2] This paper represents a portion of the results obtained in the research program sponsored by the Sulphite Pulp Manufacturers' Research League and conducted for the League by The Institute of Paper Chemistry. Acknowledgment is made by the Institute for permission on the part of the League to publish these results.

[3] Freudenberg, Klink, Flickinger and Sobek, *Ber.*, **72**, 224 (1939).

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN IRWIN A. PEARL

RECEIVED JANUARY 16, 1950

ACID DEGRADATION OF AMYLOPECTIN TO ISOMALTOSE

Sir:

Considerable indirect evidence exists for C6 as the point of branching in amylopectin but it is desirable to place this on a more definitive basis through degradative experiments involving the isolation of crystalline products of known structure. Action of the α- and β-amylases of malt on amylopectin does not yield isomaltose,[1] although levoglucosan is found in the hydrolyzate[2] (on subsequent treatment with the mold enzyme mentioned below). Isomaltose is isolable in crystalline form, and as the crystalline β-D-octaacetate, in the hydrolysis of amylopectin with an enzyme system of mold origin (a Takadiastase type from *Aspergillus oryzae*).[3] We report herein the isolation of isomaltose, as its crystalline β-D-octaacetate, from the acid hydrolyzate of amylopectin. Evidence is cited that this disaccharide is not an acid reversion product.

Following the procedure employed with glycogen,[4] amylopectin (waxy maize starch, 20.0 g.) in 0.4% concentration was hydrolyzed at 100° in 0.08 *N* hydrochloric acid for ten hours (degree of hydrolysis *ca.* 85%). After ion removal with exchange resins (Duolite C-3 and A-4), the amorphous solid obtained on solvent removal was acetylated with hot acetic anhydride and sodium acetate. A portion (5.9 g.) of the resultant sugar acetate mixture (39.0 g.) was chromatographed[5]

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[1] M. L. Wolfrom, L. W. Georges, A. Thompson and I. L. Miller, THIS JOURNAL, **69**, 473 (1947); **71**, 2873 (1949).

[2] Edna M. Montgomery and G. E. Hilbert, *ibid.*, **68**, 916 (1946).

[3] Edna M. Montgomery, F. B. Weakley and G. E. Hilbert, *ibid.*, **69**, 2249 (1947); **71**, 1682 (1949).

[4] M. L. Wolfrom and A. N. O'Neill, *ibid.*, **71**, 3857 (1949).

[5] M. L. Wolfrom, L. W. Georges and I. L. Miller, *ibid.*, **71**, 125 (1949).

on Magnesol–Celite under such developmental conditions that monosaccharide derivatives were removed from the column. β-D-Glucose pentaacetate was identified in the effluent and β-D-maltose octaacetate in the bottom zone (identifications by melting point, mixed melting point and rotation). The next higher zone was twice rechromatographed in the same manner and the eluent which crystallized from ethanol was identified as β-D-isomaltose octaacetate (m. p. 144–145°, unchanged on admixture with an authentic specimen; $[\alpha]^{25}_{D}$ +96°, c 2.0, chloroform); yield 50 mg.

Repetition of the previously described procedure[4] with the substitution of corn amylose for animal glycogen, failed to yield any β-D-isomaltose octaacetate by chromatography.

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RECEIVED FEBRUARY 7, 1950

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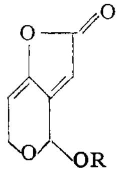
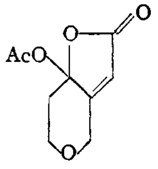
THE SYNTHESIS OF PATULIN

Sir:

We have reported elsewhere[1,2] the considerations which led us to propose the structure (I, R = H) for patulin. The evidence now available[1,2,3,4] in favor of that expression may be regarded as conclusive. A partial synthesis of the antibiotic has already been achieved.[4] We now wish to record the total synthesis of patulin.



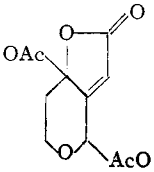
I



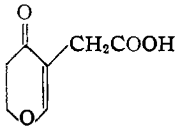
II

The lactol acetate (II)[1] in carbon tetrachloride in the presence of a trace of benzoyl peroxide rapidly consumed one mole of N-bromosuccinimide. When the crude bromination product was taken up in acetic acid and treated with silver acetate, the diacetate (III) m. p. 142–143° (Calcd. for $C_{11}H_{12}O_7$: C, 51.56; H, 4.69. Found: C, 51.91; H, 4.80), was formed. The structure of the diacetate was confirmed through its conversion, by hydrogenation over reduced platinum oxide in pure dioxane followed by hydrolysis with warm hydrochloric acid, to **desoxypatulinic acid (IV)**.[4]

Treatment of the pure diacetate (III) for a short time with warm acetic anhydride–acetic acid–sulfuric acid[1] gave a complex mixture of substances from which patulin acetate (I, R = Ac) was read-



III



IV

ily isolated in 1–2% yield by taking advantage of the fact that in ethereal solution it traveled more rapidly through a column of Brockmann alumina than its congeners. The pure synthetic acetate melted at 114–116°, alone or in admixture with the acetate (m. p. 115–116.5°) from natural patulin. The ultraviolet ($\lambda_{max.}$ 277 mμ) and infrared spectra of the synthetic and natural samples were identical. The ready hydrolysis of patulin acetate to patulin is well known.[5]

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[1] Woodward and Singh, THIS JOURNAL, **71**, 758 (1949).

[2] Woodward and Singh, *Experientia*, in press.

[3] Dauben and Weisenborn, THIS JOURNAL, **71**, 3853 (1949).

[4] Woodward and Singh, *Nature*, in press.

[5] *Cf.* Bergel, Morrison, Moss and Rinderknecht, *J. Chem. Soc.*, 418 (1944).

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RECEIVED FEBRUARY 6, 1950

ON THE MECHANISM OF OXIDATION OF INDOLE COMPOUNDS[1,2]

Sir:

Perbenzoic acid cleaves indole compounds[3] in the same way as ozone,[4] or, in some cases, peracetic acid.[5] It was possible to isolate as an intermediate in these reactions derivatives of β-hydroxyindolenines in the case of some natural products in which internal addition to the reactive C=N bond blocked further oxidation.[6]

In accordance with this view 11-hydroxytetrahydrocarbazolenine (I)[7] reacted smoothly with perbenzoic acid to yield the 9-membered cyclic lactam II (magnificent, slightly yellow prisms from ethyl acetate, m. p. 157°. *Anal.* Calcd. for $C_{12}H_{13}O_2N$: C, 70.94; H, 6.40; N, 6.9. Found: C, 71.05; H, 6.76; N, 6.8). II was also obtained from 11-hydroperoxytetrahydrocarbazolenine[8] (III) by a rearrangement that was almost quantitative under neutral or slightly acidic conditions. The change in the latter case seems to be analogous to some peroxide rearrangements involving intermediate cationoid oxygen.[9,10] The kinetic evaluation of this interesting rearrangement is in progress. Under the action of cold 2 *N* aqueous alkali on II, the initially yellow solution (salt of the enol of II) became slightly warm and then decolorized.

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[1] This investigation was supported by a grant-in-aid from Research Corporation, New York.

[2] Directed Oxidations in the Indole Series. IV.

[3] Witkop and Fiedler, *Ann.*, **558**, 91 (1947).

[4] Witkop, *ibid.*, **556**, 103 (1944).

[5] Witkop, *ibid.*, **558**, 98 (1947).

[6] Witkop, in preparation.

[7] Patrick and Witkop, THIS JOURNAL, **72**, 633 (1950).

[8] *Cf.* Beer, McGrath, Robertson and Woodier, *Nature*, **164**, 362 (1949).

[9] Criegee, *Ann.*, **560**, 127 (1948).

[10] Leffler, *Chem. Reviews*, **45**, 385 (1949).