as fast as 20° as at 25°, but upon addition of chloroform to prevent freezing and cooling with solid carbon dioxide it appeared to be instantaneous.

The only hypothesis that seems to accord with all of these results is the one suggested by Liebhafsky,[1] that the reactive halogen is in the form of hydrate. If these hydrates contain a number of molecules of water, like the solid $Cl_2 \cdot 6H_2O$, they could involve the large heat of formation required to explain the large negative temperature coefficient of the reaction. There is, of course, ample evidence that the number of "icebergs" in water falls off rapidly from 0° to room temperature.

It has been difficult to secure sufficient reproducibility to give satisfactory quantitative data, and since this may take some time, it seems appropriate to publish the above preliminary results.

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[1] H. A. Liebhafsky, *Chem. Rev.*, **17**, 89 (1935).

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RECEIVED APRIL 15, 1946

THE ISOLATION OF LEVOGLUCOSAN FROM THE ENZYMIC HYDROLYSATES OF WAXY CORN STARCH

Sir:

Waxy corn starch[1,2,3] has been subjected to the consecutive action of β-amylase, α-amylase, β-amylase, and an amylase prepared from *Aspergillus oryzae* in order to obtain information on its structure.

The starch, pasted at 80°, was first treated with β-wheat amylase[4] free from α-amylase and maltase. Dextrin A[5] and maltose, the end-products of this hydrolysis, were isolated in yields of 49 and 48%, respectively.

Dextrin A was then subjected to the action of α-malt-amylase,[6] free from β-amylase and maltase, until no further increase in the reducing power of the hydrolysate occurred. From this hydrolysate, dextrin B-1 was separated by the addition of ethanol to a concentration of 85% by volume; after two reprecipitations the new dextrin was dialyzed continuously against distilled water for nine hours. The liquor remaining after dialysis was concentrated and the dextrin B-1a was recovered by precipitation with ethanol; yield, 44% of the weight of dextrin A; $[\alpha]^{25}\mathrm{D}$ +160.2° in water; reducing power 3.8 and 8.0% of that of glucose by Shaffer–Hartmann and Gore–Steele methods, respectively.

Dextrin B-1a was next submitted to the action of β-amylase until the rotation and reducing power were constant. The products of this hydrolysis were dextrin B-1a$_1$ and maltose, the yields being 62 and 30% of the weight of dextrin B-1a, respectively. Dextrin B-1a$_1$ rotated +146.0° in water and had a reducing power by the Gore–Steele method equivalent to 12% of that of glucose. On treatment with the amylase of *Aspergillus oryzae*, the reducing power of dextrin B-1a$_1$ increased about sixfold and the rotation decreased to +38°. This hydrolysate after fermentation with yeast did not reduce Fehling solution and was levorotatory. After removal of the yeast and concentration of the solution, a solid was obtained by addition of ethanol; $[\alpha]^{25}\mathrm{D}$ −32° in water; yield, 4.2% of the weight of dextrin A. This solid was acetylated and from the resulting product levoglucosan triacetate was isolated; yield, 0.6% of that calculated for levoglucosan on the basis of waxy corn starch; $[\alpha]^{25}\mathrm{D}$ −65.5° in $CHCl_3$ (*c*, 1); m. p. 110–111°,[7] (mixed m. p. unchanged). On deacetylation, levoglucosan was obtained in pure crystalline form and characterized. Levoglucosan was also obtained from the hydrolysate resulting from the action of the amylase from *Aspergillus oryzae* on dextrin B-1a without prior fermentation. Isolation was effected both by distillation and by fractional crystallization after acetylation. Further work will have to be carried out to determine whether the 1,6-anhydro linkage is formed during enzymic fission of the substrate or actually occurs in waxy starch.

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[1] Hixon and Sprague, *Ind. Eng. Chem.*, **34**, 959 (1942).

[2] MacMasters and Hilbert, *ibid.*, **36**, 958 (1944).

[3] Schopmeyer, Felton and Ford, *ibid.*, **35**, 1168 (1943).

[4] Hanes, *Biochem. J.*, **30**, 174 (1936).

[5] *Cf.* Haworth, Kitchen and Peat, *J. Chem. Soc.*, 619–625 (1943).

[6] Hanes, *Can. J. Research*, **13B**, 185–208 (1935).

[7] Zemplén, Gerecs and Valatin, *Ber.*, **73**, 576 (1940).

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RECEIVED MARCH 4, 1946

6-CHLOROVANILLIN FROM THE CHLORITE OXIDATION OF LIGNIN

Sir:

In a fundamental study of the reaction of lignin with sodium chlorite in acid solution, the original filtrate from the preparation of holocellulose from black spruce (*Picea mariana*) by means of sodium chlorite in dilute acetic acid according to Wise and co-workers[1,2] was investigated. The filtrate was further acidified with sulfuric acid and fractionated. The steam non-volatile aldehyde fraction was identified as 6-chlorovanillin, colorless plates from ethanol melting at 167–168°. (*Anal.* Calcd. for $C_8H_7O_3Cl$: C, 51.49; H, 3.78; Cl, 19.00; CH_3O, 16.63. Found: C, 51.34; H, 3.76; Cl, 19.19; CH_3O, 16.70.) The oxime, prepared by heating with a solution of hydroxylamine hy-

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[1] Wise, *Ind. Eng. Chem., Anal. Ed.*, **17**, 63–64 (1945).

[2] Wise, Murphy and D'Addieco, *Paper Trade J.*, **122**, No. 2, 35 (1946).