TABLE I

MORPHOLINE IN WATER

$C \times 10^3$	Λ	$C \times 10^3$	Λ
8.45	4.11	10.15	3.811
5.60	4.98	33.80	2.182
2.559	7.40	16.03	3.172
1.221	10.04	7.34	4.63
191.6	0.849	3.560	5.98
108.6	1.164	2.133	8.14
68.9	1.477	1.063	11.02
27.65	2.342		

TABLE II

MORPHOLINIUM CHLORIDE IN WATER

$C \times 10^3$	Λ	$C \times 10^3$	Λ
56.25	98.6	0.861	111.8
22.49	103.7	48.1	99.6
8.47	108.2	22.02	104.1
4.56	109.9	6.55	108.0
2.341	111.0		

line and Λ against $\sqrt{c}$ for morpholinium chloride indicate, by their deviations from the expected curves,[5] that the values of Λ for the most dilute points have been somewhat over-corrected for solvent conductance. The extrapolation to Λ_0 for morpholinium chloride takes this into account, but may be a few per cent. in error because of hydrolysis. This determination seems to be the source of greatest error. However, it seems unlikely that it can be more than two or three per cent. Assuming it to be 3% the error in K would be slightly less, about 2.8%. The value of Λ_0 was taken as 115.

Using this value and 261.5[6] for NaOH and 126.4[7] for NaCl, Λ_0 for morpholinium hydroxide is 250. Plotting the straight line form of the Arrhenius conductance ratio equation for the ionization constant, $1/\Lambda = c\Lambda/K\Lambda_0^2 + 1/\Lambda_0$, the graphically determined slope $1/K\Lambda_0^2$ gives a value of 2.44×10^{-6} for K.

(5) The ionization constant of morpholine is low enough so that in view of the two sources of error previously mentioned, it was considered unnecessary to use the more accurate forms of the $1/\Lambda - c\Lambda$ plot proposed by Fuoss (THIS JOURNAL, **57**, 488 (1935)) and Shedlovsky (*J. Franklin Inst.*, **225**, 739 (1938)).

(6) H. Jeffery and A. I. Vogel, *Phil. Mag.*, **16**, 395 (1933).

(7) D. A. MacInnes, T. Shedlovsky and L. G. Longsworth, THIS JOURNAL, **54**, 2758 (1932).

HAYDEN MEMORIAL LABORATORIES
NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS RECEIVED OCTOBER 24, 1942

Action of Macerans Enzyme on a Component of Corn Starch

BY RALPH W. KERR

The origin of the Schardinger dextrins, when starch is treated in the presence of *B. Macerans* or the enzyme prepared from this bacillus[1] has been a matter of speculation for many years. In another paper[2] the writer sought to show that, in procedures which might ordinarily be used to convert corn starch with this enzyme, the yield of Schardinger dextrins, precipitable with trichloroethylene, arose almost entirely from a degradation of the most permanently dispersed fraction of the starch, which latter amounts to approximately 55% of the total starch. It was concluded that these dextrins were probably formed by synthesis from the more simple configurations in this product.

We are now able to elaborate on these conclusions. In another communication[3] we discussed the isolation of an amylose in yields of 5 to 6% of starch, by crystallizing the product from a warm water extract of corn starch with butanol. The amylose quickly changes to an insoluble form, however, in concentrations over 1 g. per 100 cc. in water solution. In this condition it might be expected to be rather inert in the presence of starch splitting enzymes. It may, however, be held in a relatively stable solution at *p*H 6.0 at lesser concentrations, *e. g.*, 0.30 g. per 100 cc.

A conversion of such a solution of the amylose was attempted adding 40 cc. of a *Macerans* enzyme preparation of 0.3 unit activity[2] to 2 l. of water containing 6 g. of the amylose in its soluble form. The conversion was made at *p*H 6.0 and 45° for forty-eight hours. The liquors were then concentrated by vacuum distillation to 400 cc. at 45° and allowed to stand at this temperature for another twenty-four hours at *p*H 6.0. Practically no insolubles were in evidence. The liquors were concentrated to 130 cc., a small amount of floc filtered off and 130 cc. of trichloroethylene added. The mixture was allowed to stand for forty-eight hours at room temperature, with intermittent stirring, and then for forty-eight hours in the refrigerator. The dextrins were filtered off, washed with ice water, then with methanol, dried and weighed: 4.2 g. of mixed dextrins, precipitable with trichloroethylene resulted, a yield of 70%. Further quantities precipitated when the mother liquors were concentrated.

Inasmuch as the crystalline amylose gives a conversion limit[3,4] of 93% maltose with β-amylase

(1) E. B. Tilden and C. S. Hudson, THIS JOURNAL, **61**, 2900 (1939).

(2) R. W. Kerr, "On the Significance of the Degradation of Starch by Macerans Enzyme," presented at the 102nd meeting of the American Chemical Society, September, 1941.

(3) R. W. Kerr and G. M. Severson, "The Isolation of an Amylose in Crystalline Form," in press.

(4) R. W. Kerr, O. R. Trubell and G. M. Severson, *Cereal Chemistry*, **19**, 64 (1942).

and hence is essentially linear in configuration, and inasmuch as β-amylase produces no reducing sugars whatsoever from the Schardinger dextrins,[2] it would seem evident that the *Macerans* enzyme was able to synthesize the cyclo amyloses from linear arrangements of glucopyranose units.

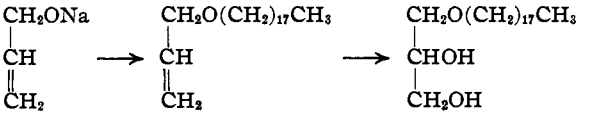
An explanation as to why the enzyme normally produces no greater yield of dextrins from whole corn starch might be that the more linear chains, which are probably coils in water solution, become enmeshed or oriented, thus blocking the approach of the enzyme to the individual molecules and possibly inhibiting the closing of the cycle to form the dextrin; whereas the linear configurations in our highly branched fraction,[3] which are principally the side branches in this case, are held more or less rigidly into space, thus greatly reducing the number that become enmeshed, one with the other. This condition would favor the production of large yields of the Schardinger dextrins from this latter component according to this viewpoint, and would, incidentally, account for the greater colloidal stability of solutions of this constituent, which we have called, provisionally, the more alcohol-soluble fraction.

CORN PRODUCTS REFINING CO.
ARGO, ILLINOIS RECEIVED FEBRUARY 2, 1942

Batyl Alcohol[1]

BY N. KORNBLUM[2] AND HARRY N. HOLMES

An earlier communication from this Laboratory described the isolation and identification of batyl alcohol $CH_2OH\text{-}CHOH\text{-}CH_2O(CH_2)_{17}\text{-}CH_3$, from the non-saponifiable fraction of yellow bone marrow.[3] Preliminary tests carried out by Dr. Roy Kracke of Emory University with a crystalline product obtained by us from yellow bone marrow indicated that batyl alcohol might be of value in the treatment of agranulocytosis. In order to permit of an extended program of physiological testing, a substantial quantity of pure batyl alcohol was needed. The synthesis employed here is that of Davies, Heilbron and Owens,[4] modified to give better yields of pure products.



Substitution of octadecyl iodide for the chloride (used by Davies, *et al.*) and a reaction temperature of 60–65° instead of reflux conditions resulted in a significant increase in the yield of pure allyl octadecyl ether. This is a consequence of the fact that the lower operating temperature minimizes the conversion of allyl alcohol to high boiling products which contaminate the desired allyl octadecyl ether. This auto-condensation of allyl alcohol containing sodium allyl oxide, which apparently has not been hitherto reported, proceeds in the presence or absence of oxygen and gives a complex series of unsaturated neutral and acidic compounds.

Conversion of the allyl ether to the glycerol derivative was best effected by the improved hydroxylation procedure of Scanlan and Swern,[5] except that it was found necessary to heat the reaction mixture in batches of the size employed here.

Experimental

Octadecyl Iodide.—This substance was prepared by the procedure of Bleyberg and Ulrich.[6] The product was purified by distillation *in vacuo;* b. p. 194–197° (2 min.); yield 70–75%. Upon recrystallization from acetone white plates melting at 33–34° were obtained.

Allyl *n*-Octadecyl Ether.—To a solution of 31 g. of sodium in 450 g. of allyl alcohol was added 150 g. of *n*-octadecyl iodide. The mixture was maintained at 60–65° for twenty hours and when cold was diluted with water and, *without* being acidified, extracted with ether. After washing the extracts with water the major portion of the solvent was distilled, approximately 25 ml. of benzene added, and the residual ethyl ether, benzene and entrained moisture then removed by distillation. A final bath temperature of about 160° was required. The yellow oil which remained was fractionally distilled *in vacuo* through a Widmer column. After an appreciable forerun which separated into two layers, there was obtained 85–96 g. (70–79%) of a colorless liquid, b. p. 150–152° (2 mm.); m. p. 28.5–29° (thermometer in melt); $n^{32}D$ 1.4441. Recrystallization from ethanol did not alter the refractive index. Davies, Heilbron and Owens[4] reported m. p. 27.5–28.5°.

Octadecyl Glyceryl Ether (Batyl Alcohol).—A mixture of 41.7 g. of 30% hydrogen peroxide solution and 500 ml. of glacial acetic acid was heated at 80–85° for one hour, at which point 49.5 g. of allyl *n*-octadecyl ether dissolved in 420 ml. of glacial acetic acid was added and the resulting

(1) Presented in part before the division of Biological Chemistry of the American Chemical Society, St. Louis meeting, April, 1941. At this same meeting Erich Baer and H. O. L. Fischer announced an alternate synthesis of batyl alcohol and subsequently published the details in *J. Biol. Chem.*, **140**, 397 (1941).

(2) Present address: Converse Memorial Laboratory, Harvard University, Cambridge, Mass.

(3) Holmes, Corbet, Geiger, Kornblum and Alexander, THIS JOURNAL, **63**, 2607 (1941).

(4) Davies, Heilbron and Owens, *J. Chem. Soc.*, 2542 (1930).

(5) Scanlan and Swern, THIS JOURNAL, **62**, 2305 (1940).

(6) Bleyberg and Ulrich, *Ber.*, **64**, 2510 (1931).