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.

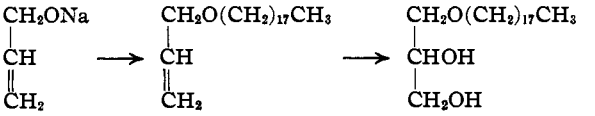
An explanation as to why the enzyme normally produces no greater yield of dextrins from whole corn starch might be that the more linear chains, which are probably coils in water solution, become enmeshed or oriented, thus blocking the approach of the enzyme to the individual molecules and possibly inhibiting 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).

solution maintained at 70–80° for 20–22 hours. When cold, the mixture was rendered alkaline with dilute ammonium hydroxide, extracted with ether and the ether distilled off. The residue obtained upon removal of the ethyl ether was treated at 60° for seven hours with a solution containing 220 g. of potassium hydroxide, 660 ml. of water and 2500 ml. of ethanol. The solution was then concentrated to approximatley 750 ml. at 40° under reduced pressure. The resulting mixture was extracted with ether, the extracts washed with water and the ether removed. The product was purified by two recrystallizations from ethanol; white crystals, which sinter at 69° and melt 70–71° (cor.); yield 30–37 g. (55–67%). Hydroxylation of 50 g. of allyl *n*-octadecyl ether according to the procedure described by Davies, Heilbron and Owens[4] gave only 19 g. (34%) of pure glyceryl ether.

Allyl Alcohol and Sodium Allyl Oxide.—A solution of sodium (45 g.) in allyl alcohol (700 cc., Eastman Kodak Co. white label quality) was protected by a soda-lime guard tube while it was refluxed gently for forty-eight hours. The turbid mixture was cooled, diluted with water and extracted thoroughly with ether. The aqueous alkaline solution was then acidified with sirupy phosphoric acid and again extracted with ether. In this way the product was separated into a neutral (A) and an acidic (B) fraction. The ether solutions were washed with water, dried and distilled at 2 mm. From (A) was obtained 66 g. of material boiling at 63–140° with $n^{25}D$ ranging from 1.4696 to 1.5148. (B) gave 90 g. of material boiling at 73–155° with $n^{25}D$ ranging from 1.4673 to 1.5021. In each instance the first portion of the distillate was colorless and very fluid; with rising boiling point the distillate gradually becomes light yellow and quite viscous. Both (A) and (B) were insoluble in water, but soluble in ethanol, and both gave negative fuchsin tests. Both absorbed hydrogen over Adams catalyst and gave positive tests for unsaturation with bromine in carbon tetrachloride. (A) reacted with sodium, evolving a gas.

This experiment was repeated several times with substantially the same results. In one run allyl alcohol which had been dried over Drierite was employed and the reaction carried out in an atmosphere of nitrogen with results essentially the same as those described above. Conversion of allyl alcohol to high boiling products under these conditions has apparently not been reported previously.

The neutral and acidic fractions were not investigated further.

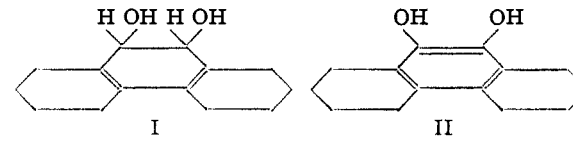
OBERLIN COLLEGE
OBERLIN, OHIO

RECEIVED SEPTEMBER 30, 1942

The Structure of Skita's "Decahydro-9,10-dihydroxyphenanthrene"

BY PHILIP LEVINE[1]

In a previous article,[2] reference was made to the preparation of a compound identical with that described by Skita[3] as decahydro-9,10-dihydroxyphenanthrene (I). Further investigation of this substance has now shown that the meso positions have not been hydrogenated and that the compound in question is *s*-octahydro-9,10-dihydroxyphenanthrene (II).



I II

The reasons for questioning the structure proposed by Skita were the resistance of the compound to hydrogenation over Raney nickel at 120°, the failure to undergo dehydration to *s*-octahydro-9-phenanthrol, and the readiness with which the compound is oxidized by the atmosphere. Also Skita's only evidence for the glycol structure (I) was the analytical data for the compound itself and for its diacetate. A comparison of Skita's figures with the calculated values for (II) and its derivative shows that the analytical data do not suffice to distinguish between (I) and (II).

Oxidation of the compound to the octahydroquinone requires only one equivalent of lead tetraacetate. Assuming Skita's formula, one might expect either normal cleavage to the dialdehyde or the consumption of *two* equivalents of lead tetraacetate for oxidation to the quinone.

The question was unequivocally settled in favor of the hydroquinone structure (II) by reductive acetylation of the quinone obtained by oxidizing the compound. The diacetate thus obtained was identical in appearance and melting point with the diacetate from the original compound and no depression of the melting point was observed on mixing the two samples. The method used for the reductive acetylation of the quinone was that which normally converts a quinone into the diacetate of the corresponding hydroquinone without effecting any further reduction.

Experimental[4]

Lead Tetraacetate Oxidation of Octahydrophenanthrenehydroquinone.—To 0.7 g. of the hydroquinone in 15 cc. of benzene was added in small portions 1.4 g. (one equivalent) of lead tetraacetate. The solution became deep red. Additional lead tetraacetate was unreacted as shown by tests with starch–iodide paper. A small amount of glycerol was added to remove excess oxidizing agent. The benzene solution was washed twice with water, dried over magnesium sulfate, and evaporated almost to dryness. The brilliant red crystals, melting at 139–141°, were evi-

(1) Present address, The Squibb Institute for Medical Research, New Brunswick, New Jersey.

(2) Linstead and Levine, THIS JOURNAL, 64, 2022 (1942).

(3) Skita, *Ber.*, 58, 2685 (1925).

(4) All melting points are corrected.