Claisen flask. At the end of this time the mixture was distilled under reduced pressure. Water came over first and then 31.4 g. (71%) of *m*-bromopropenylbenzene boiling at 108–114° at 16 mm. was obtained. This was dissolved in 100 cc. of ethanol and reduced in a Burgess–Parr reducing outfit with hydrogen and 0.1 g. of platinum oxide catalyst.[1] The reduction was complete in two and one-half hours. The mixture was filtered and distilled. There was thus obtained 27 g. (85%) of *m*-bromo-*n*-propylbenzene boiling at 96–100° at 17 mm.; $n^{20}D$ 1.5354.

Anal. Calcd. for $C_9H_{11}Br$: Br, 40.15. Found: Br, 40.19.

m-Bromo-n-butylbenzene.—Using the same general procedure 74 g. of *n*-propyl bromide and 92.5 g. of *m*-bromobenzaldehyde gave 71 g. of *m*-bromobutenylbenzene boiling at 126–130° at 22 mm.; which on reduction yielded 59 g. of *m*-bromo-*n*-butylbenzene, b. p. 113–116° at 18 mm.; $n^{20}D$ 1.5330.

Anal. Calcd. for $C_{10}H_{13}Br$: Br, 37.51. Found: Br, 37.50.

(1) Adams, Vorhees and Shriner, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1929, p. 452.

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RECEIVED MARCH 19, 1941

n-Heptylsulfonylacetic Acid

The reaction of sodium chloroacetate with the sodium mercaptide from 25 g. (0.17 mole) of *n*-heptyl mercaptan was carried out in the same way as described[1] for the reaction of butyl mercaptan. The α-(*n*-heptylthio)-acetic acid was liberated by the addition of a solution prepared by dissolving 40 ml. of concentrated sulfuric acid in 180 ml. of water. The oil was separated and the aqueous layer extracted with ether. The combined water-insoluble layers were dried over anhydrous sodium sulfate and the ether removed by distillation. The residue was dissolved in 90 ml. of a mixture of glacial acetic acid-acetic anhydride (1:1) and oxidized with 43 g. (0.38 mole) of 30% hydrogen peroxide under the conditions previously[1] described. After removal of the solvent under reduced pressure the residue was crystallized from ether. The yield was 35 g. (83%) m. p. 90–91°. Recrystallization from water gave large glistening laminae of *n*-heptylsulfonylacetic acid, m. p. 95.5–96° (cor.).

Anal. Calcd. for $C_9H_{18}O_4S$: S, 14.42. Found: S, 14.54, 14.59.

(1) Pomerantz and Connor, THIS JOURNAL, **61**, 3144 (1939).

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING
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PHILADELPHIA, PENNA. RALPH CONNOR

RECEIVED MARCH 11, 1941

COMMUNICATIONS TO THE EDITOR

THE CARBOHYDRATE IN COLLAGEN

Sir:

It has been reported by Grassmann and Schleich [*Biochem. Z.*, **277**, 320 (1935)] that the carbohydrate complex of collagen contains glucose and galactose in equimolecular proportions. In connection with a determination of the amount of carbohydrate in samples of collagen that were being investigated, an attempt was made to destroy the sugar in hydrolyzed collagen by fermentation with yeast. It was found that the sugar was not fermentable with a galactose-active yeast. When *d*-galactose and yeast were added to samples of the hydrolyzate, the added sugar was destroyed and the sugar from the collagen remained. These experiments give conclusive proof that neither *d*-glucose nor *d*-galactose forms a considerable part of the carbohydrate in collagen. The presumption is that the sugar is a mixture of *l*-glucose and *l*-galactose, but it has not been established that this is the case. It is significant in this regard that Bell and Baldwin [*Nature*, **146**, 559 (1940)] recently found *l*-galactose as a component of a polysaccharide of animal origin.

NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C. JOHN BEEK, JR.

RECEIVED APRIL 8, 1941

THE ISOLATION OF PURE LINOLEIC ACID BY CRYSTALLIZATION

Sir:

The only method previously available for the preparation of linoleic acid which is pure as evaluated from its iodine number is that of debromination of pure tetrabromostearic acid. However, Matthews, Brode and Brown[1] have shown that the debromination acid may contain 12% of an isomeric linoleic acid. When this contaminating acid is removed by repeated low temperature crystallization, the resultant product melts nearly 2° higher than any specimen of linoleic acid so far reported.

(1) Matthews, Brode and Brown, THIS JOURNAL, **63**, 1064 (1941).

In previous reports from this Laboratory[2,3] the preparation of several specimens of linoleic acid from cottonseed and corn oils by fractional low temperature crystallization was described. The highest purity was about 93%. We have just succeeded in isolating pure linoleic acid from corn oil by a modification of the crystallization procedure.

The mixed fatty acids are dissolved in acetone (75 g./l.) and fractions are taken off at −20 and −50°. The filtrate is cooled to −70°. The crystal fraction at this temperature is about 90% linoleic. This product (232 g.) is dissolved in petroleum ether (65 g./l.) and cooled to −48°. The crystal fraction (103 g.) has an iodine number of 176.4 (95%). The remaining impurity is largely oleic acid. It can be removed by taking advantage of the fact that while the composition of the mixture is about 19–1 in favor of linoleic acid, the solubility of the linoleic acid is only about 4–5 times that of the oleic acid at −60°. Thus, when a quantity of the 95% acid is dissolved in sufficient petroleum ether to hold all of the oleic acid in solution at −60° and the solution is cooled to that temperature, practically pure linoleic acid crystallizes out with apparently very little mixed crystal formation. From three runs, in each of which 50 g. of the 95% acid in 8 liters of petroleum ether was cooled to −60°, the combined crystal fractions amounted to 66 g., iodine number, 179.9. This product was twice crystallized from 500 cc. of petroleum ether at −62°, the two filtrates amounting to 1.5 and 2.5 g. of iodine numbers 186 and 178, respectively. (The former value, 186, suggests the presence of a trace of linolenic acid in the oil.) The product, 62 g., before distillation was faintly colored; iodine number, 179.8; n^{20} 1.4699; m. p. −5.0 to −4.5°; tetrabromide number, 100.7. The distilled product was colorless; iodine number 180.8; n^{20} 1.4699; m. p. −5.4° (sharp); tetrabromide number 100.6. Data on the twelve-times crystallized debromination acid[1] were: iodine number, 181.0; n^{20} 1.4699; m. p. −5.2 to −5.0°; tetrabromide number, 102.3. The mixed melting point of the latter two preparations was −5.2°. We believe these data indicate that the acid prepared by direct crystallization from corn oil is essentially identical with the repeatedly crystallized debromination acid. The former acid, however, on the basis of its slightly lower tetrabromide number, may contain 1–2% of an isomeric linoleic acid.

By the procedure described above it has been possible to prepare for the first time a specimen of pure linoleic acid from a seed oil by a simple physical method. We are using this method in attempts to prepare natural linoleic acid from a number of different oils.

LABORATORY OF PHYSIOLOGICAL CHEMISTRY
THE OHIO STATE UNIVERSITY JEROME FRANKEL
COLUMBUS, OHIO J. B. BROWN

RECEIVED APRIL 3, 1941

(2) Brown and Stoner, THIS JOURNAL, **59**, 3 (1937).

(3) Brown and Frankel, *ibid.*, **60**, 54 (1938).

D-GLUCOSAN<1,5>β<1,6> AND D-GALACTOSAN-<1,5>β<1,6> FROM THE PYROLYSIS OF LACTOSE[1]

Sir:

The ease with which acetone-D-mannosan can now be made[2] from the products of pyrolysis of vegetable ivory, and used as an intermediate in the preparation of D-mannosan<1,5>β<1,6>, has led us to apply this procedure to an investigation of the pyrolysis products from other naturally occurring carbohydrates. Since the agar of commerce is known to contain polysaccharides which are hydrolyzable by acid to yield much galactose,[3] it was thought that a D-galactosan might be obtainable from this source. The pyrolysis of agar in the apparatus previously described,[2] and the condensation of the sirupy distillate with acetone in the customary way, led to a crystalline acetone-D-galactosan (m. p. 151–152, $[\alpha]^{20}D$ −72.9 in chloroform) which is identical with the product that Micheel[4] has synthesized. The yield from four commercial brands of agar varied from 0.2 to 1.4%; its lowness and its uncertainty led to the search for a better material. The galactan gum of the Western larch seems a possibility and it will be tested as soon as a supply is procured. In the meantime the pyrolysis of ordinary milk-sugar (α-lactose monohydrate) has given such good yields of D-galactosan<1,5>β<1,6> and D-glucosan<1,5>β<1,6> (6.5 g. of each from 100 g. lactose) that the problem of a satisfactory source for the galactosan may be regarded as solved. The two anhydrides are readily separable

(1) Publication authorized by the Surgeon General, U. S. Public Health Service.

(2) See the accompanying article by Knauf, Hann and Hudson, THIS JOURNAL, **63**, 1447 (1941).

(3) Pirie [*Biochem. J.*, **30**, 369 (1936)] estimates a galactose content of 28–30%; Percival and Somerville (*J. Chem. Soc.*, 1937, p. 1615) estimate 55%.

(4) Micheel, *Ber.*, **62**, 687 (1929).