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).

through the fact that the galactosan, but not the glucosan, condenses easily with acetone. Acetone-D-galactosan yields D-galactosan (m. p. 223–224 cor., $[\alpha]^{20}D$ −22.0 in water, agreeing with Micheel's[4] data) by the hydrolytic conditions that were used in making D-mannosan from its acetone compound.[2] Periodate oxidation shows that the ring configurations for D-galactosan are $<1,5>\beta$-$<1,6>$. Acetone-D-galactosan $<1,5>\beta<1,6>$ possesses only one free hydroxyl group, the position of which is limited to one of three carbon atoms (2, 3 and 4).[5] The substance, now so readily available,[6] offers possibilities for syntheses, especially of disaccharides. The work is being continued.

(5) The recent research of McGreath and Smith, *J. Chem. Soc.*, 387 (1939), indicates that the free hydroxyl group is one carbon atom 2, the acetone having condensed on the *cis* hydroxyls of carbon atoms 3 and 4, as originally supposed by Micheel.

(6) Micheel's synthesis of D-galactosan starts from acetobromogalactose and trimethylamine.

NATIONAL INSTITUTE OF HEALTH
U. S. PUBLIC HEALTH SERVICE RAYMOND M. HANN
WASHINGTON, D. C. C. S. HUDSON

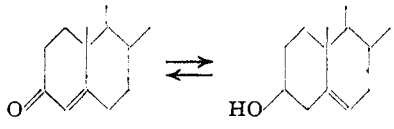
RECEIVED MARCH 25, 1941

STEROLS. CXXII

Sir:

Recently, Wolfe, Fieser and Friedgood [THIS JOURNAL, **63,** 583, 1941] raised a question as to our hypothesis on the formation of the Δ^5-3-hydroxysteroids as reduction products of a Δ^4-3-ketosteroid as lacking any foundation of analogy and as unlikely because "the process would require the migration of the double bond at 4,5, presumably after reduction of the carbonyl group, away from its position of conjugation with the oxygen atom."

We wish to point out that this type of reduction in the animal has been accomplished by Schoenheimer, Rittenberg and Graff [*J. Biol. Chem.*, **111,** 183 (1935)]. These authors fed coprostenone, a Δ^4-3-ketosteroid to a dog and found that it was eliminated as cholesterol, a Δ^5-3-hydroxysterol in which reduction of the ketone group had taken place with a migration of the double bond at 4,5.



They concluded that the formation of cholestenone from cholesterol is a biologically reversible process. Their work was discussed in our article on the theory of the formation of the various steroids [THIS JOURNAL, **60,** 1725 (1938)]. Although it is possible that the above reduction may be bacterial, it should be noted that it has never been proven that the various urinary steroidal reduction products are formed by glandular reduction and not by bacterial reduction.

In addition, it should be pointed out that according to our hypothesis of the formation of the various steroids, dehydroisoandrosterone need not be a transformation product of testosterone, or of androstenedione, but can arise directly as a degradation product of many of the numerous cortical steroids, by mechanisms described in our paper, without going through testosterone as an intermediate. The same is true for isoandrosterone, androsterone, etiocholanolones, etc. The numerous routes through which these products could be formed from the cortical compounds were omitted from our original paper, for the sake of brevity.

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STATE COLLEGE, PENNA. RUSSELL E. MARKER

RECEIVED FEBRUARY 21, 1941

ORIGIN OF DEHYDROISOANDROSTERONE IN URINE

Sir:

The observation of Schoenheimer, Rittenberg and Graff cited by Marker in the accompanying communication does not seem to us to constitute a valid reason for believing that the dehydroisoandrosterone secreted in urine arises from a Δ^4-3-ketosteroid precursor. The feeding of cholestone to a dog on a biscuit diet resulted in an increase in the fecal cholesterol over that noted in control periods; when the dog was put on a meat diet, cholestenone feeding increased the output of the principal fecal sterol, which in this case was coprosterol. The cholestenone used carried no indicator element, and no proof was adduced that the excess excretory sterols were transformation products of the material administered. Over 80% of the administered material remained unaccounted for, even on the supposition of a conversion, and the ketone may have stimulated normal sterol excretion, supplanted a normal transformation product of cholesterol, or influenced the sterol excretion in some other indirect manner. The experiment, therefore, cannot be considered to have established that cholestenone is capable of undergoing reduction to cholesterol