520 mμ.[1] When a chloroform solution of the orange-colored pigment is treated with concentrated hydrochloric acid and then with antimony trichloride, the solution exhibits the absorption spectrum characteristic of the gossypol–antimony trichloride reaction product. This observation indicates that the final reaction products of both pigments are the same and that concentrated hydrochloric acid converts the orange-colored pigment into gossypol.

The absorption spectra curves of chloroform extracts of some raw cottonseeds and cottonseed meals, as well as those of their reaction products with antimony trichloride, have maxima which indicate the presence of the orange-colored pigment.[2] The production of a characteristic gossypol reaction when such extracts are treated with concentrated hydrochloric acid prior to their reaction with antimony trichloride[2] confirms the presence of the orange-colored pigment in the seeds and meals. The occurrence of this pigment in high concentration in certain cottonseed meals may account, at least in part, for the frequently observed lack of correlation[3] of gossypol content with toxicity of these meals when the gossypol is determined as the dianilino compound.

---

(2) Boatner, Caravella and Kyame, in press.

(3) Gallup, *Ind. Eng. Chem.*, **20**, 59–63 (1928).

BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
SOUTHERN REGIONAL RESEARCH LABORATORY
2100 ROBERT E. LEE BOULEVARD
NEW ORLEANS, LOUISIANA RECEIVED FEBRUARY 16, 1944

The Preparation of Ethyl ε-Bromocaproate

BY GEORGE BOSWORTH BROWN AND C. W. H. PARTRIDGE

Ethyl ε-bromocaproate may be prepared conveniently and inexpensively from cyclohexanone. The crude mixed lactones of ε-hydroxycaproic acid, obtained by the procedure of Robinson and Smith,[1] may be treated directly with hydrobromic and sulfuric acids, thus obviating the losses involved in the use[2] of ethyl ε-hydroxycaproate as an intermediate.

The oxidation of 174 g. of cyclohexanone was carried out between 10 and 15° as described[1] in the preparation under the heading of ethyl 6-hydroxyhexoate using an oxidizing mixture prepared from 919 g. of potassium persulfate.

The 200 g. of crude lactones was then treated with a cooled mixture of 1 liter of 48% hydrobromic acid and 240 cc. of concentrated sulfuric acid. After standing for two hours at room temperature, this was heated for four hours on the steam cone, was cooled and poured into 2 liters of water. The organic layer was separated and the water solution was saturated with ammonium sulfate and was extracted four times with ether. The combined organic layer and extract were washed three times with saturated ammonium sulfate, and were dried and concentrated.

The 250 g. of crude bromo acid was esterified by refluxing for eight hours with 600 cc. of absolute alcohol and 15 cc. of sulfuric acid. After concentrating *in vacuo*, the residue was taken up in ether and was washed with water and with 5% sodium carbonate. The ether solution was dried over sodium sulfate and was distilled yielding 178 to 218 g. of the product distilling at 120–125° at 14 mm., $n^{21}\text{D}$ 1.4566, d^{23}_{23} 1.241, $MR\text{D}$ 48.92 (calcd. 48.57). This represents an over-all yield from cyclohexanone of 45–55%. No evidence of the inhomogeneity noted once by Barger, Robinson and Smith[2] has been observed. The product has been used satisfactorily in the preparation of η-ketopelargonic acid.[2]

---

(1) R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937).

(2) G. Barger, R. Robinson and L. H. Smith, *ibid.*, 718 (1937).

DEPARTMENT OF BIOCHEMISTRY
CORNELL UNIVERSITY MEDICAL COLLEGE
NEW YORK, N. Y. RECEIVED FEBRUARY 19, 1944

Polymerization of Undecylenic Acid in the Presence of Boron Fluoride

BY JOHN R. CANN[1] AND E. D. AMSTUTZ

It has been found that when undecylenic acid is treated with gaseous boron fluoride at room temperature much heat is evolved and the acid polymerizes to a dark heavy oily material. This polymer, after having been freed of catalyst, exhibits the characteristic properties of an acid and also those of an ester. Thus it shows some tendency to dissolve in dilute aqueous caustic and regenerates carboxyl groups on refluxing in alkaline solutions.

The loss in carboxyl function has been found to be directly related to the fall in iodine value which indicates that one of the processes of polymerization is the esterification of the carboxyl group by means of the unsaturated linkage. (It had been previously demonstrated that the same treatment of stearic acid did not cause decarboxylation.) Since the fall in iodine value was stoichiometrically greater than the loss of carboxyl function it appeared that some double bond polymerization also took place. The analytical data show that this is a reaction of secondary importance with esterification assuming the major role.

The oil resulting from saponification of the polymer gave a positive iodoform test which indicates the hydroxy acid produced had the methylcarbinol structure. This proves the orientation of at least part of the polymerization process.

This type of polymerization[2] of undecylenic

---

(1) Raybestos-Manhattan Research Fellow in Chemistry 1942–1943. Present address, Frick Chemical Laboratory, Princeton, New Jersey.

(2) Unpublished results obtained in this Laboratory by Cann and by H. R. Nace indicate that this behavior is also shown by the fatty acids from drying oils and also by crotonic acid. The latter requires somewhat more strenuous conditions, however, due to its conjugated structure.