propanespirohydantoin (prepared according to the procedure of Ingold, Sako and Thorpe[8]) and 15 cc. of 66% hydrobromic acid was heated in an oil-bath at 120° for one hour. After removal of the hydrobromic acid by distillation at 20 mm. the solid residue was recrystallized from ethanol. The total weight of 5-(β-bromoethyl)-hydantoin was 7.3 g., m. p. 141–142°; yield 87%.

5-(β-Methylmercaptoethyl)-hydantoin, V.—To a solution of 10.35 g. (0.05 mole) of 5-(β-bromoethyl)-hydantoin in 75 cc. of absolute ethanol was added a solution of sodium methylmercaptide (prepared by bubbling 2.5 g. (0.05 mole) of methyl mercaptan[9] from a cylinder into a solution of 2.8 g. (0.05 mole) of sodium methylate in 50 cc. of absolute ethanol. The mixture was heated under reflux for one hour, most of the alcohol removed by evaporation, and the residue diluted with water. Acidification to the neutral point with 6 *N* hydrochloric acid gave a copious precipitate, which after recrystallization from water melted at 105–106° (lit.[3], 117°); weight 6.4 g.; yield 73.5%.

Anal. Calcd. for $C_6H_{10}N_2O_2S$: N, 16.09; S, 18.39. Found: N, 15.11; S, 18.81.

dl-Methionine, VI.—A mixture of 17.4 g. (0.1 mole) of 5-(β-methylmercaptoethyl)-hydantoin, 50.5 g. (0.16 mole) of barium hydroxide octahydrate and 300 cc. of water was charged into a 450-cc. rotating iron autoclave and heated at 155° for fifteen minutes. After removal of the barium carbonate, the filtrate was shaken with 9.1 g. (0.08 mole) of ammonium carbonate monohydrate, the barium carbonate removed by filtration and the filtrate evaporated under water pump vacuum to dryness. The residue was slurried with ethanol and suction filtered to yield 14.2 g. of *dl*-methionine; m. p. 268–270° (dec.); yield 95%.

Anal. Calcd. for $C_5H_{11}NO_2S$: N, 9.40; S, 21.48. Found: N, 9.30; S, 21.41.

Summary

A convenient synthesis of *dl*-methionine is described. γ-Butyrolactone is brominated, the α-bromo-γ-butyrolactone thus obtained is aminated to yield α-amino-γ-hydroxybutyric acid, which, with potassium cyanate, gives γ-hydroxy-α-ureidobutyric acid. Treatment of the ureido acid with concentrated hydrobromic acid gives 5-(β-bromoethyl)-hydantoin, which, with sodium methylmercaptide, is converted to 5-(β-methylmercaptoethyl)-hydantoin, from which *dl*-methionine is obtained by alkaline hydrolysis.

MIDLAND, MICH. RECEIVED AUGUST 13, 1945

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[9] Pure methyl mercaptan is commercially available from the Union Oil Company.

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY, NEW ORLEANS, LOUISIANA[1]]

The Organic Acid Content of Raw Cotton Fiber. Isolation of *l*-Malic Acid and Citric Acid from Cotton Fiber

BY ELIZABETH R. MCCALL AND JOHN D. GUTHRIE

A typical sample of oven-dry raw cotton fiber contains about 94% cellulose, 1.3% protein, 1.2% pectic substances, 1.2% ash, 0.6% wax and 0.3% sugars.[2] Even on this crude basis, about 1.4% of the fiber is unaccounted for. A consideration of some of the properties of raw cotton fiber, especially its high content of alkaline ash, indicates that it probably contains considerable quantities of the organic acids commonly found in plants. These acids probably occur in the fiber as potassium, calcium, magnesium and sodium salts. Four samples of raw cotton fiber were analyzed for malic acid, citric acid, oxalic acid and total organic acids. Since these analyses showed about 0.5% malic acid and 0.07% citric acid, it seemed feasible to isolate these acids from raw cotton fiber and thus remove any doubt as to their occurrence in the fiber.

Experimental

Description of Samples.—The following samples of cleaned raw cotton roving were analyzed:

Sample No. 1. Variety: Unknown. Source: U. S. Dry Land Field Station, Big Springs, Texas. Grade: Strict low middling. Staple: 1 inch.

Sample No. 2. Variety: Wilds. Grade: Strict middling. Staple: $1^5/_{16}$ inch.

Sample No. 3. Variety: Stoneville. Grade: Middling. Staple: $1^3/_{32}$ inch.

Sample No. 4. Variety: SXP. Staple: $1^1/_8$ inch.

Analysis of Raw Cotton for Organic Acids.—Samples weighing about 20 g. were placed in desiccators over concentrated hydrochloric acid for forty-eight hours and extracted in Soxhlet extractors for forty-eight hours with ethyl ether purified according to Pucher and Vickery.[3] The ether extracts were neutralized with 5 *N* sodium hydroxide solution free of carbonates, transferred to 100-ml. volumetric flasks, made to volume with carbon dioxide-free water and filtered through dry filter paper. Aliquots of the filtrate were analyzed for malic acid, citric acid, oxalic acid and total organic acids by the methods of Pucher, Wakeman and Vickery.[4] All determinations were made in duplicate but averages are reported in Table I.

TABLE I

ORGANIC ACID CONTENT OF RAW COTTON FIBER IN PER CENT. OF THE DRY WEIGHT

Sample no.	Malic acid	Citric acid	Oxalic acid	Unidentified organic acids[a]	Total organic acids[a]
1	0.49	0.05	0.004	0.33	0.87
2	.57	.10	.005	.24	.91
3	.48	.07	.005	.27	.82
4	.32	.05	.002	.40	.77

[a] Calculated in terms of an acid with an equivalent weight of 67.

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[1] One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] John D. Guthrie, Carroll L. Hoffpauir, Edward T. Steiner and Mack F. Stansbury, Mimeographed Circular AIC-61 (1944), Bureau of Agricultural and Industrial Chemistry.

[3] G. W. Pucher, H. B. Vickery and A. J. Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **6**, 140–143 (1934).

[4] (a) G. W. Pucher, *J. Biol. Chem.*, **153**, 133–137 (1944); (b) G. W. Pucher, A. J. Wakeman and H. B. Vickery, *Ind. Eng. Chem., Anal. Ed.*, **13**, 244–246 (1941).

Isolation of *l*-Malic Acid and Citric Acid from Raw Cotton Fiber.—Citric acid and *l*-malic acid were isolated in crystalline form from 5.2 kg. of sample no. 1. The raw cotton was extracted in small portions by boiling five minutes with a total of 20.9 liters of water. It was pressed out in a screw press and then in a hydraulic press. About 19.2 liters of extract was obtained. About 345 ml. of saturated neutral lead acetate was added, the precipitate was separated by decantation and centrifugation, and washed once with water. The supernatant and washings (A) were saved for further work to be described later. The lead precipitate was suspended in water, decomposed with hydrogen sulfide, the lead sulfide filtered out and the hydrogen sulfide removed from the filtrate by aeration with nitrogen.

The filtrate was mixed with 30 ml. of 0.3 *N* barium hydroxide to bring down a small precipitate which was centrifuged out and discarded. The supernatant and washings were made faintly alkaline to litmus with hot, saturated barium hydroxide. The resulting precipitate was centrifuged out and the supernatant liquid (B) saved for further work to be described later. The precipitate was partially dissolved with 10% hydrochloric acid, centrifuged, washed with water and the small precipitate discarded. The supernatant and washings were made faintly basic with hot, saturated barium hydroxide and the precipitate washed with water, alcohol and ethyl ether. It weighed 8.7 g. Barium was removed by suspending the precipitate in water, adding the amount of sulfuric acid calculated from the barium content of the precipitate and allowing to stand overnight. The filtrate was evaporated *in vacuo* at less than 50° to yield 3 g. of sirup. This was crystallized from ethyl ether to yield 0.7 g. of crystalline material. After recrystallization from ethyl ether and drying at 103° it weighed 0.3 g. and melted at 149 to 150°. Anhydrous citric acid melts at 153°. The material crystallized from water on a microscope slide to give elongated, six-sided plates, showing parallel extinction. The angle adjacent to the long side was about 117°. In these respects the material was identical with a known sample of citric acid. The acid equivalent was 64.9; calculated for citric acid, 64.0. The *p*-bromophenacyl ester melted at 150° (cor.); mixed melting point 151°.

Anal. Calcd. for $C_6H_8O_7$: C, 37.4; H, 4.2. Found: C, 37.4; H, 4.3.

The supernatant liquid and washings (A) from the first lead precipitation of the cotton fiber extract was mixed with 50 ml. of 10% sodium hydroxide and a second lead precipitate separated by decantation and centrifugation. The supernatant liquid (C) was saved for further work. The precipitate was decomposed with hydrogen sulfide in the usual manner and the lead-free filtrate was made alkaline with hot, saturated barium hydroxide. After standing overnight the supernatant liquid was separated by decantation and centrifugation. The supernatant and washings were mixed with 3 volumes of 95% ethyl alcohol. The precipitate was separated and partially dissolved in water. A small amount of insoluble material was separated by centrifuging and the supernatant mixed with 3 volumes of alcohol. The precipitate was redissolved in water, again precipitated with 3 volumes of alcohol, washed with alcohol, with ethyl ether and dried. It weighed 10 g. It was suspended in water and barium removed with the calculated amount of sulfuric acid. The filtrate was concentrated to dryness *in vacuo* to yield 4.9 g. of crude material. This was crystallized twice from anhydrous ethyl ether to yield 1.2 g. of crystalline material in the first fraction. The material melted at 103° (cor.). Three known samples of *l*-malic acid after recrystallization from ethyl ether melted at 103° (cor.). The melting point of 100° given in the literature for *l*-malic acid may be in error. Mixed melting point was 103°. The acid equivalent was 67.2; calculated for *l*-malic acid, 67.0. The *p*-bromophenacyl ester melted at 179° (cor.); mixed melting point 179° (cor.). When 87.6 mg. was neutralized and dissolved in 50 ml. of 0.04 *M* uranyl acetate and polarized according to the directions of Andrews,[5] the levorotation was 1.62°. The calculated rotation for *l*-malic acid is 1.66°. The value found with 87.6 mg. of known *l*-malic acid was 1.65°.

Anal. Calcd. for $C_4H_6O_5$: C, 35.8; H, 4.5. Found: C, 35.8; H, 4.5.

The supernatant liquid (C) from the second lead precipitation was mixed with an additional 50 ml. of 10% sodium hydroxide. The precipitate was separated by decantation and centrifugation and washed once with water. The precipitate was decomposed with hydrogen sulfide, the lead sulfide was filtered out and the filtrate was aerated with nitrogen to remove hydrogen sulfide. The filtrate was made faintly alkaline with hot, saturated barium hydroxide. The precipitate was centrifuged, washed once with water, and the supernatant and washings mixed with 3 volumes of 95% alcohol to bring down a precipitate. This was redissolved in water and precipitated again with 3 volumes of alcohol to yield 8.7 g. of barium salts. Working these over in the manner previously described yielded 4.3 g. of crystalline material. Two recrystallizations from ethyl ether yielded 0.8 g. of a product that melted at 104 to 106° (cor.). The acid equivalent was 67.5. The *p*-bromophenacyl ester melted at 179° (cor.). Mixed melting point with the *p*-bromophenacyl ester of *l*-malic acid was 180°. The rotation when dissolved in 0.04 *M* uranyl acetate showed the material to be 90% *l*-malic acid.

The supernatant liquid and washings (B) from the barium hydroxide precipitation from the first lead precipitate (see above) were mixed with 3 volumes of alcohol to bring down a precipitate, which was redissolved in water and reprecipitated with alcohol two times. The yield of barium salts in this fraction was 12 g. Working this over in the manner previously described yielded 2.3 g. of crystalline material. This was recrystallized from anhydrous ethyl ether to give 0.8 g. in the first fraction. This material melted at 105° (cor.); mixed melting point with *l*-malic acid was 105.5°. Acid equivalent was 66.2. The levorotation when 87.6 mg. was neutralized and dissolved in 50 ml. of 0.04 *M* uranyl acetate was 1.56. The *p*-bromophenacyl ester melted at 181° (cor.); mixed melting point 181°. Although less pure than the best fraction, it is at least 94% *l*-malic acid.

Anal. Calcd. for $C_4H_6O_5$: C, 35.8; H, 4.5. Found: C, 36.0; H, 4.6.

Small amounts of *l*-malic acid of various degrees of purity based on rotation in 0.04 *M* uranyl acetate and formation of the *p*-bromophenacyl ester of *l*-malic acid were obtained from the mother liquors of the various recrystallizations.

Acknowledgment.—The authors wish to thank Lawrence E. Brown for the micro carbon and hydrogen determinations.

Summary

Raw cotton fiber contains about 0.5% *l*-malic acid and 0.07% citric acid. The presence of both of these acids in raw cotton fiber has been definitely established by isolating them in crystalline form.

New Orleans, La. Received October 29, 1945

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[5] Launcelot W. Andrews, *Proc. Iowa Acad. of Sci.*, **32**, 299–320 (1925).