

The ester, after purification by distillation, was subjected to thermal decomposition between 110 and 130°. Traces of carbon dioxide were removed from the carbon monoxide formed, and the carbon monoxide was burned to carbon dioxide, absorbed in 1 *N* sodium hydroxide, and precipitated as barium carbonate. The radioactivity of the α -carbon atom in the pyruvate was 3180 counts/min./mg. C (12.9 disintegrations per cent). There was no detectable activity in the carbon monoxide formed in 90% yield, or in the trace of carbon dioxide formed. It is found in the acid obtained by hydrolysis of the pyrolytic residue. Without further kinetic studies, it is difficult to suggest a detailed mechanism, but it is clear that the evolved carbon monoxide comes from the carboxyl group of the α -keto-ester.

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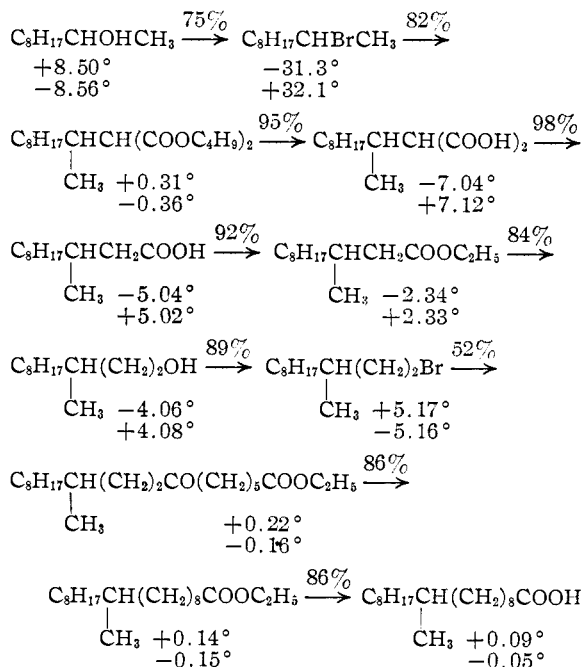
THE SYNTHESIS OF TUBERCULOSTEARIC ACID

Sir:

Tuberculostearic acid is one of the branched-chain acids isolated by Anderson¹ and co-workers from acid-fast bacteria. From oxidation experiments Spielman² concluded that the acid was 10-methyloctadecanoic acid and prepared the *dl*-form of this acid for comparison. The synthetic acid melted at 20–21°; the natural acid at 10–11°. The amides and tribromoanilides of the two acids had closely similar melting points. The natural acid was reported as optically inactive, but Spielman suggested that it might nevertheless be an active form having a faint rotation and a lower melting point than the corresponding *dl*-form.

In order to test this suggestion we have again synthesized *dl*-10-methyloctadecanoic acid by another method and have also synthesized pure *d*- and *l*-10-methyloctadecanoic acids. These acids were purified by repeated crystallization: *dl*-form, m. p. 25.4–26.1°; *d*- and *l*-forms, m. p. 13.0–13.5°, $[\alpha]_D$ ca. 0.05°. These data strongly indicate that tuberculostearic acid is one of the active isomers of 10-methyloctadecanoic acid. This conclusion was tested further by means of mixture melting point experiments using our active acids and their derivatives and samples of tuberculostearic acid and its derivatives kindly

furnished by Dr. Anderson. The mixture of once-crystallized tuberculostearic acid (m. p. 10.3–11.7°) with approximately an equal amount of the synthetic *l*-acid melted at 11.0–12.4°, while a similar mixture with the *d*-acid melted at 19.4–20.1°. A mixture of the two synthetic acids melted at 21.0–25.8°. Melting points were determined also for the amides and the tribromoanilides of our *l*-acid and tuberculostearic acid, singly and as mixtures. The respective values were 75.1–76.3°, 71.5–75.6° and 72.5–76.3° for the amides, and 94.0–95.3°, 94.5–95.4° and 93.9–95.5° for the tribromoanilides. It thus appears to be established that tuberculostearic acid is the levorotatory isomer of 10-methyloctadecanoic acid.



The scheme of synthesis is outlined in the accompanying chart. The first rotation value, $[\alpha]_D$, in each instance refers to the isomer derived from (+)-2-decanol. Configurational inversion and slight racemization occurred in the formation of the 2-bromodecanes and the dibutyl 2-decylmalonates. Rigorous purification by fractional crystallization of the less soluble active 2-decylmalonic acids, however, assured the antipodal purity of all succeeding compounds in both series.

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(1) Anderson and Chergaff, *J. Biol. Chem.*, **85**, 77, (1929).

(2) Spielman, *ibid.*, **106**, 87 (1934).