

sponding to that of the three trans 1,4-dihalogenocyclohexanes. A detailed X-ray study of the whole series of isomorphous compounds (including *N,N'*-dichloropiperazine⁴) is in progress. Part of a Fourier projection along the *b* axis of the bromine compound worked out by Bergskoug is reproduced in Fig. 1.⁵

In the case of the chloro-bromocompound the conclusion had to be drawn that the chlorine and bromine atoms are indeed crystallographically equivalent. No sign of a transition into a second modification could be observed in this case. It is therefore very probable that dichloro- and chloro-bromocyclohexane have different crystal structures at their melting points.

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Preparation of Carboxylated Oleic Acid*

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The above-mentioned labelled acid, which was required for metabolic studies, was prepared from erythro-9,10-dihydroxystearic acid.

The acid (m.p. 129°) was acetylated and subjected to the silver salt bromine degradation. The diacetoxylbromide was deacetylated to erythro-8,9-dihydroxy-1-bromo-heptadecane m.p. 102–103°. A nitrile synthesis using labelled potassium

cyanide, followed by alkaline hydrolysis, yielded carboxylated erythro-9,10-dihydroxystearic acid.

This labeled acid was then transformed into the dibromo acid with hydrogen bromide in acetic acid-sulphuric acid according to Ames and Bowman¹. By following their procedure of debrominating the esterified dibromo acid, sterically pure oleic acid was obtained.

If the low melting threo-9,10-dihydroxystearic acid is used as starting material elaidic acid should be obtained by the same method².

EXPERIMENTAL. Dihydroxystearic acid (m.p. 129°) was prepared from oleic acid by oxidation with permanganate³.

Silver salt of erythro-9,10-diacetoxy octadecanoic acid. 4.5 g of 9,10-dihydroxystearic acid was dissolved in a mixture of acetic anhydride (5 ml) and pyridine (10 ml) and heated on the steam bath for one hour. After concentration *in vacuo* to a syrup, ice and ether were added. The ether solution was washed with *N* hydrochloric acid and water, dried over sodium sulfate and evaporated to dryness. The crude product was dissolved in 50 ml ethanol and neutralized with sodium hydroxide (phenolphthalein). A solution of 2 g silver nitrate in 30 ml 60 per cent ethanol was added with rapid stirring. The resulting sticky mass of the precipitated silver salt was filtered off, washed with a little water and dried overnight in a vacuum oven at 60°. The silver salt forms a brown gum which is soluble in hot carbon tetrachloride.

1-Bromo-8,9-dihydroxyheptadecane. 65.5 g of crude oven-dried silver salt was dissolved in a mixture of 1 l of carbon tetrachloride and 200 ml of methylene chloride and the solvents distilled until the b.p. was 76.5° and water no longer appeared in the condenser. The residual solution was mixed with dry silver acetate (10 g) according to a procedure described earlier⁴ and treated with bromine (11 ml).

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The precipitated silver bromide was removed by filtration and the filtrate was washed successively with solutions of potassium iodide, sodium thiosulphate and sodium carbonate. After washing with water and drying, the solvent was removed yielding an amber-coloured oil (36.9 g). 5 g of this material was dissolved in 25 ml absolute methanol containing 4 milli-equiv. HCl-gas and refluxed for 3 hours. After dilution with water and extraction with ether, the dihydroxybromide was crystallized from heptane or methanol. M.p. 102–103°.

$C_{17}H_{35}O_2Br$ (351.37)

Calc. C 58.1 H 10.0 Br 22.8

Found » 59.1 » 10.1 » 22.6; 22.9

Isotopic dihydroxystearic acid. 2.8 millimoles of bromide and 2.8 millimoles of $K^{13}CN$ were refluxed in a mixture of 10 ml of ethanol and one ml of water for 48 hours. 2 g of potassium hydroxide was added and the refluxing continued for a further 48 hours. Dihydroxystearic acid-1- ^{13}C (m.p. 126–127°) was obtained in a yield of 85 per cent. Similar yields have been obtained with $K^{14}CN$ under the same conditions except that an excess of bromide was used.

Oleic acid. Treatment of 5 g of labelled dihydroxystearic acid with hydrogen bromide-acetic acid-sulphuric acid and subsequent debromination as described by Ames and Bowman¹ yielded 2.5 g oleic acid-1- ^{14}C m.p. 12°.

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Crystalline Modifications of D-Mannitol

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The crystallographic data of two modifications of D-mannitol are quoted by Groth¹ i.e. α -mannitol and β -mannitol, both orthorhombic, the former with $a:b:c = 0.4718 : 1 : 0.5200$, the latter $a:b:c = 0.5121 : 1 : 0.6577$. According to Groth, β -mannitol crystallizes from aqueous or alcoholic solutions, but it is not stated when α -mannitol is formed, though it is said sometimes to occur in mixture with the β -form. Becker and Rose² determined the unit cell for mannitol (not stating from which solvent) as $a = 10.36$ A, $b = 8.1$ A, $c = 4.55$ A and $a:b:c = 1.275 : 1 : 0.562$. Marwick³ reported for β -mannitol: $a = 8.65$ A, $b = 16.90$ A, $c = 5.56$ A and $a:b:c = 0.511 : 1 : 0.329$. She also suggested that β -mannitol belongs to the space group V^4 , and that the molecule is parallel to [100]. Our determinations for β -mannitol are in agreement with the latter data, whereas those of B. & R. have not been verified. Calculated density from B. & R.'s values, with $Z = 2$, is 1.587, which differs from the actual sp. density of 1.49.

It has been found in the present work that two other forms of mannitol may be obtained by recrystallization from water-alcohol 1 : 1 or alcohol-aceton:water 5:5:2 (volume). In the first case, however, the result depends upon the rate of crystallization. Thus, rapid cooling produces the new form (γ), while slow cooling gives a mixture of α - and β -forms (see below). Powder photographs of the new γ -form can be indexed by assuming orthorhombic symmetry and $a = 9.33$ A, $b = 17.36$ A, $c = 4.99$ A and $a:b:c = 0.537:1:0.287$, giving $V = 808.2$ A³, $Z = 4$ and $d_x = 1.496$ g/cm³. Reflexions $h00$ and $0k0$ are absent