

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 milliequiv. 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 Bowman<sup>1</sup> 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 Groth<sup>1</sup> i.e.  $\alpha$ -mannitol and  $\beta$ -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,  $\beta$ -mannitol crystallizes from aqueous or alcoholic solutions, but it is not stated when  $\alpha$ -mannitol is formed, though it is said sometimes to occur in mixture with the  $\beta$ -form. Becker and Rose<sup>2</sup> 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  $a:b:c = 1.275 : 1 : 0.562$ . Marwick<sup>3</sup> reported for  $\beta$ -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  $\beta$ -mannitol belongs to the space group  $V^4$ , and that the molecule is parallel to [100]. Our determinations for  $\beta$ -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 ( $\gamma$ ), while slow cooling gives a mixture of  $\alpha$ - and  $\beta$ -forms (see below). Powder photographs of the new  $\gamma$ -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  $V = 808.2$  A<sup>3</sup>,  $Z = 4$  and  $d_x = 1.496$  g/cm<sup>3</sup>. Reflexions  $h00$  and  $0k0$  are absent

when  $h$  resp.  $k$  is odd, suggesting that the space group may be  $V^3-P2_12_12$ , but absences cannot be stated with certainty from powder patterns alone, and the crystals were too small for single crystal methods.

A powder photograph of mannitol from alcohol-aceton-water is identical with that of mannitol prepared from the triethylidene compound (see Meunier<sup>4</sup>). Purified by the latter method, followed by slow crystallization from 96 % alcohol, good crystals for X-ray investigations were obtained. Unit cell dimensions of the orthorhombic crystals were determined from oscillation and Weissenberg photographs:  $a = 8.94$  A,  $b = 18.41$  A,  $c = 4.92$  A,  $a:b:c = 0.486 : 1 : 0.267$ ,  $V = 809.7$  A<sup>3</sup>,  $Z = 4$  and  $d_x = 1.494$  g/cm<sup>3</sup>. Many absences are recorded, thus,  $h00$  when  $h$  odd,  $0k0$  when  $k$  odd,  $00l$  when  $l$  odd,  $0kl$  when  $l$  odd,  $h0l$  when  $h+l$  odd and  $hk0$  when  $h$  odd. No orthorhombic space group has all these absences, and some of them must, therefore, be due to pseudosymmetry. By re-examination of the photographs a few exceedingly weak reflexions  $0k0$  were found for which  $k$  is odd, thus  $[010]$  is no true screw axis. The remaining absences would suggest the space group  $V_h^4-Pcna$ , but no reasonable arrangement of the molecules could be found. On the assumption that absences of  $0kl$  for  $l$  odd are also due to pseudosymmetry (these absences being less certain since reflexions  $0kl$  for  $l$  even are also very weak), the others correspond to the space group  $C_{2v}^6-Pmna$ . A satisfactory arrangement of the molecules can be found such that the direction of their carbon chains is parallel to  $[010]$  and their approximate centers are located close to the positions  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ ,  $\frac{3}{4}\frac{1}{4}\frac{1}{4}$ ,  $\frac{1}{4}\frac{3}{4}\frac{1}{4}$ ,  $\frac{3}{4}\frac{3}{4}\frac{1}{4}$ . This arrangement would also account for the systematic weaknesses.

The axial ratio of this form agrees roughly with that quoted by Groth for  $\alpha$ -mannitol (with  $c$ -axis doubled), and this

form may, therefore, possibly correspond to  $\alpha$ -mannitol.

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## The Presence of Djencolic Acid in Hydrolysates of Mammalian Tissues

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Djencolic acid was first isolated from urine of natives of Java who had eaten the djencolic bean and were suffering from djencolic poisoning. Later on Van Veen and Hyman isolated the compound from alkaline extracts of the bean<sup>1,2</sup>. Consden *et al.*<sup>3</sup> found the amino acid in hydrolysates of reduced wool treated with methylene bromide or formaldehyde. To our knowledge the amino acid has not been isolated from common protein hydrolysates of mammalian tissues.

In connection with microbiological and chemical analysis of a peptide fraction isolated from calf plasma<sup>4</sup> we found that the two-dimensional chromatograms of the acid-hydrolyzed material (3 N HCl, 16 hours at 120°) showed a spot close to the known positions of ethanolamine-phosphoric acid, djencolic acid and diamino-pimelic acid<sup>5-7</sup>.

The substance was eluted with HCl together with the leucine-isoleucine fraction from a Dowex 50 columns according to the method of Stein and Moore<sup>8</sup>. The dry mixture was packed on a small column and eluted with *tert.* - amyl alcohol where