

Table 1. Molecular weight, sedimentation (S) and diffusion coefficients (D) of sucrose, determined from pairs of co-ordinates taken from five exposures. Allowance was made in the exposure time for the period of acceleration to 50,740 r.p.m.; $r_0 = 6.074$ cm

Corrected exposure time (sec)	r_1 (cm)	r_2	$(dn/dr)_1^*$	$(dn/dr)_2^*$	Mol wt.	S/D (cm ⁻¹)	S ($\times 10^{13}$) (sec)	D ($\times 10^6$) (cm sec ⁻¹)
665	6.094	6.162	0.897	0.462	322.8	5.26	0.47	8.9
1,625	6.100	6.160	0.930	0.759	386.0	6.29	0.58	9.2
2,590	6.100	6.232	0.869	0.424	320.5	5.22	0.36	6.9
2,590	6.100	6.144	0.869	0.660	322.2	5.25	0.23	4.3
3,065	6.100	6.208	0.945	0.528	349.1	5.69	0.31	5.4
4,025	6.110	6.224	0.885	0.451	341.0	5.55	0.22	3.9
				Mean	340.3	5.54	0.36	6.4
				S.E. \pm	9.4	0.13	0.05	0.85

* dn/dr = refractive index gradient $\times \tan \theta$, where θ = angle of schlieren phase-plate.

It is essential in this method of molecular weight assessment to measure co-ordinates with a high degree of precision. Thus the frequently used procedure of tracing an enlarged image on to graph paper is insufficiently accurate, and a micrometer method must be used. In the present experiment the parameters were measured using a digital scanner ('Oscar', Benson and Lehner, England) which automatically prints the data in a form suitable for immediate insertion into the computer. The use of this device greatly reduces the time required for accurate measurement, and in the present case each exposure required only about 1 min for measurement. The digital computation took an average of 6 sec on a Ferranti Atlas computer.

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Asymmetric Synthesis of α -Amino-acids by the Strecker Synthesis

THE non-enzymatic asymmetric synthesis of α -amino-acids has long been of considerable stereochemical interest. However, the method of catalytic hydrogenation is the only one appearing in the literature¹⁻⁸. In this communication, a new method of asymmetric synthesis of α -amino-acids in solution is described.

The method involves: (a) the reaction of an aldehyde with hydrogen cyanide and D-(-)- α -methylbenzylamine ($[\alpha]_D^{25} = -40.6^\circ$ in benzene) in methanol; (b) hydrolysis of the resulting amino nitrile to the *N*-(α -methylbenzyl) amino-acid; (c) catalytic hydrogenolysis to remove the methylbenzyl group. A typical example of the asymmetric synthesis is as follows: sodium cyanide, 1.47 g (0.03 mole), and D-(-)- α -methylbenzylamine hydrochloride, 4.73 g (0.03 mole), were dissolved in 5 ml. of cold water. To this, 20 ml. of methanol and 1.0 g of free D-(-)- α -methylbenzylamine were added. Then, acetaldehyde, 1.32 g (0.03 mole), was added to the cold methanolic solution. The clear solution was kept at room temperature for five days. The solvent was evaporated *in vacuo*. The residue was dissolved in 50 ml. of 1 N hydrochloric acid and the solution was extracted twice with ether. To the aqueous solution was added 12 N hydrochloric acid to adjust the normality of the acid to approximately 5 N. The solution was then refluxed for 6 h. The hydrochloric acid was evaporated *in vacuo* and the residue was dried over sodium hydroxide under reduced pressure. The crude *N*-(α -methylbenzyl) alanine hydrochloride was dissolved in 200

ml. of 50 per cent alcohol and the pH was adjusted to 6.0 with sodium bicarbonate. To this solution, 3.5 g of palladium hydroxide catalyst⁹ was added. Hydrogenolysis was carried out for 10 h to remove the methylbenzyl group. The catalyst was filtered and washed with hot water. The combined filtrate was evaporated to about one-third volume and acidified with dilute hydrochloric acid to about pH 1. The solution was evaporated to dryness and the alanine hydrochloride was extracted from the dry residue with absolute ethanol three times (total 50 ml.). The solution was kept at -5° C overnight to precipitate the contaminated salt. After filtration, pyridine was added to the alcoholic solution to precipitate crude alanine. Yield, 0.71 g $[\alpha]_D^{25} = +10.01^\circ$ in 6 N hydrochloric acid $c. = 2.18$; m.p. 235° – 243° dec. A single spot was observed following paper chromatography. The crude alanine which contains salt was dissolved in 2.5 ml. of water, the pH was adjusted with pyridine to 5.5–6.0, and 10 ml. of absolute ethanol was added. A yield of 0.45 g of L-alanine was obtained (17 per cent) $[\alpha]_D^{25} = +13.13^\circ$, in 6 N hydrochloric acid, $c. = 2.32$; asymmetric yield, 90 per cent; m.p. 290° dec. Anal. calcd. for $C_5H_7NO_2$: C, 40.44; H, 7.92; N, 15.72. Found: C, 40.53; H, 8.07; N, 15.78.

The intermediate *N*-(α -methylbenzyl)alanine was isolated using the reaction conditions here. After hydrolysis and evaporation of the hydrochloric acid, the residue was extracted with absolute ethanol. Pyridine was added to the solution and the ethanolic solution was kept at 5° C for 2 days to complete the precipitation of *N*-(α -methylbenzyl) alanine. A yield of 0.85 g (15 per cent) of material was obtained. m.p. 277° dec., $[\alpha]_D^{25} = -41.96^\circ$ in 6 N hydrochloric acid, $c. = 1.91$. The product was purified by sublimation⁸ (0.1 mm mercury at 200° C); 0.68 g of pure *N*-(α -methylbenzyl) alanine was obtained. m.p. 281° dec., $[\alpha]_D^{25} = -43.9^\circ$ in 6 N hydrochloric acid $c. = 2.15$; anal. calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25; found: C, 68.21; H, 7.81; N, 7.26. Hydrogenolysis of this gave L-alanine, $[\alpha]_D^{25} = +13.99^\circ$ (95 per cent optically active).

The mechanism of the asymmetric synthesis has not been clarified. However, the synthesis may involve several sterically controlled reactions⁹.

The Strecker synthesis of amino-acids has been considered as one of the modes of formation of amino-acids in the primordial Earth¹⁰⁻¹². The asymmetric synthesis described here is therefore interesting in connexion with the formation of optically active amino-acids on the primitive Earth. This type of asymmetric synthesis is under further investigation.

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