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Optical Resolution of DL-Aspartic Acid Copper Complex by the Use of Biopolymers

ASYMMETRIC adsorption of organic compounds on biopolymers such as polysaccharides[1–7], wool[8,9] and casein[9] has been reported, but the resulting optical activities of these were usually very low and the capacity for adsorption was very small. On the other hand, several studies of optical resolution by preferential crystallization have been reported (reviewed in ref. 10). Recently, DL-aspartic acid copper complex[11], DL-aspartic acid, DL-glutamic acid, DL-asparagine and DL-glutamine[12] have been resolved almost completely by the preferential crystallization method in our laboratory.

In this communication, the partial optical resolution of DL-aspartic acid copper complex from its supersaturated solution by seeding with biopolymers, such as wool and cotton, is described.

A hot solution of DL-aspartic acid (0·01 mole) ($[\alpha]_D^{25}$ = 0·0° 6 N HCl) in 100 ml. of water was mixed with copper acetate (0·005 mole) in 40 ml. of water containing 2·0 ml. of acetic acid. The solution of DL-aspartic acid copper complex was filtered through a 'Millipore' filter. The solution was cooled to about 40° C, and 0·5 g of absorbent cotton was added to the solution. Crystallization of the aspartic acid copper complex began after 30 min. After standing for 3 h at room temperature without agitation, the copper complex–cotton mixture was isolated by filtration, and washed thoroughly with water and then with acetone. A total of 1·02 g of mixture was obtained. The copper complex mixture was dissolved in 60 ml. of 5 per cent acetic acid by heating, and hydrogen sulphide was passed through to precipitate the copper. The solution was filtered and evaporated to dryness. A total of 0·30 g of free DL-aspartic acid was obtained. Optical activity was with the Rudolph model 80 polarimeter with *PEC*-101 photometer, $[\alpha]_D^{25} = -11{\cdot}0°$ ($c = 2{\cdot}3$, 6 N HCl). Optical resolution using wool was carried out in the same way as with cotton, but crystallization took longer (3–7 h) compared with the resolution by cotton (1–4 h). Results are summarized in Table 1.

To examine the possibility of the presence of optically active impurities derived from the wool or cotton during the process, DL-aspartic acid (0·4 g) ($[\alpha]_D^{25} = 0{\cdot}0°$, 6 N HCl) was heated with cotton (0·5 g) or wool (0·5 g) in 5 per cent acetic acid in the same conditions employed in the isolation of D-aspartic acid. Isolated DL-aspartic acid showed no optical rotation in either case: $[\alpha]_D^{25} = 0{\cdot}0°$ ($c = 5{\cdot}0$, 6 N HCl). To confirm this result, D-aspartic acids obtained by seeding of wool (No. 1, optical purity 18 per cent) and by cotton (No. 15, optical purity 45 per cent) were each treated with 2,4-dinitrofluorobenzene to convert them to the DNP-derivatives. The extracted crude DNP-aspartic acids were purified by column chromatography of 'Celite'[14,15] without fractionation of the optical isomer[16,17]. Resultant optical purities were: No. 1, $[\alpha]_D^{25} = -17{\cdot}4°$ (1 N NaOH), optical purity 19 per cent; No. 15, $[\alpha]_D^{25} = -37{\cdot}4°$ (1 N NaOH), optical purity 41 per cent. These experiments showed that contamination of the product by optically active material extracted from the cotton or wool used was very small or non-existent. As Table 1 shows, it is difficult to reproduce the same amount of optical activity in each experiment. The sign of optical rotation of the resulting amino-acid is, however, always consistent.

This resolution method can be regarded as a combination of asymmetric adsorption of organic molecules on the biopolymers and a preferential crystallization of optically active compounds from the supersaturated solution by seeding. The biopolymers might be assumed to adsorb D-aspartic acid copper complex selectively from the supersaturated solution of DL-aspartic acid copper complex. Because of the supersaturation of the solution, asymmetrically adsorbed D-aspartic acid copper complex might form microcrystals on the biopolymer for subsequent crystallization. If this is so, the preferential crystallization which takes place magnifies the stereoselective adsorption activity of the D-aspartic acid copper complex on the wool or cotton so that optically active aspartic acid copper complex in quantity results. This kind of resolution method throws light on new practical resolution of organic compounds and on concepts of development of optical activity in the prebiological world. In the latter, the resulting optically active organic compounds, including biopolymers, may act as seeds for further development of optical activity of the biochemical substances.

Table 1. OPTICAL RESOLUTION OF DL-ASPARTIC ACID COPPER COMPLEX BY THE USE OF BIOPOLYMERS

		H_2O (ml.)	AcOH (ml.)	Cu Complex (g)	D-Aspartic acid $[\alpha]_D^{25}$	Optical purity (per cent)
Wool I	1	80	1	0·92	−4·4	18
	2	110	1·5	0·64	−3·7	15
	3	140	2	0·90	−*A*	—
Wool I	4	80	1	0·70	−1·4	5·7
	5	110	1·5	0·63	−0·5	2·1
	6	140	2	0·53	0	—
Wool II	7	80	1	0·76	−0·4	1·8
	8	110	1·5	0·72	−0·8	3·1
	9	140	2	0·59	−2·3	9·4
Wool III	10	80	1	0·62	−*A*	—
	11	110	1·5	0·62	−*A*	—
	12	140	2	0·51	−1·9	7·7
Cotton I	13	80	1	0·83	−3·3	14
	14	110	1·5	0·54	−6·2	25
	15	140	2	0·52	−11·0	45
Cotton II	16	80	1	0·55	0	—
	17	110	1·5	0·38	0	—
	18	140	2	0·35	−2·2	8·9

DL-Aspartic acid (0·01 mole) was converted to its copper complex in 80, 110 and 140 ml. of hot aqueous solution which contained 1, 1·5 and 2 ml. of glacial acetic acid respectively. The hot copper complex solution was filtered through a 'Millipore' filter. The filtrate was seeded with 0·5 g each of cotton or wool at varying temperatures (40°–60° C). −*A*, These products show slight minus rotation.

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