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Amino Acid Studies. Part II.* Structure and Synthesis of Albizziine (L-2-Amino-3-ureidopropionic Acid), an Amino Acid from Higher Plants**

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Albizziine is an amino acid, recently isolated from various species of the botanical family *Mimosaceae*. The suggested structure, L-2-amino-3-ureidopropionic acid (I), has now been unequivocally established by comparison of N-benzoylalbizziine methyl ester with a synthetic specimen of methyl L-2-benzamido-3-ureidopropionate (III).

A simple and satisfactory synthesis of L-albizziine from L-2,3-diaminopropionic acid has been developed, based on temporary masking with cupric ions of the 2-amino-grouping during carbamylation at the desired 3N-position. The same procedure has been applied in the preparation of DL-albizziine. L-2-Ureido-3-aminopropionic acid (II), the positional isomeride of L-albizziine, has been synthesized for comparison purposes.

Various observations relating to the acid hydrolysis and biogenesis of albizziine are briefly discussed.

Albizziine constitutes a recent addition to the rapidly increasing class of free amino acids occurring in higher plants (for a summary *cf. e.g.* Ref.[1]). It was discovered in and isolated from seeds of the botanical species *Albizzia julibrissin* Durazz. by Gmelin *et al.*[2]. The same authors demonstrated commercially available seed material of the species *Albizzia lophantha* Benth. to be an alternative and satisfactory source of albizziine and provided paper-chromatographic evidence for the presence of the new amino acid in several other species of the same or related genera, all belonging to the family *Mimosaceae* [2]. Still more recently, Gmelin *et al.*[3] listed additional sources of albizziine and mentioned *Enterolobium cyclocarpum* as a particularly rich source. The elementary composition [2,3], positive reaction with ninhydrin and Ehrlich's reagent [2], and the products formed upon acid hydrolysis [3], suggested that

* The communication which appeared in *Experientia* 15 (1959) 253 should be regarded as Part I of this series.

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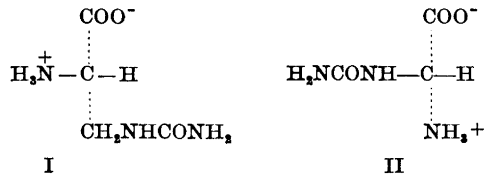
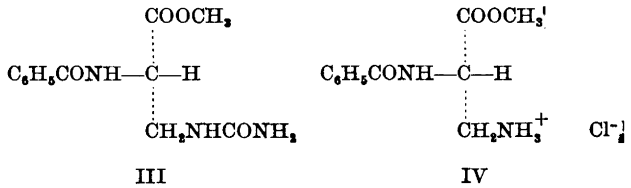
albizziine was L-2-amino-3-ureidopropionic acid (I), although the isomeric structure (II) was not incompatible with the available evidence [3].



I II

In a preliminary communication from this laboratory [4], (I) has been unequivocally established as the correct structure for albizziine. It is the purpose of the present paper to expand on the structure determination, as well as to describe a single-step synthesis of albizziine from L-2,3-diaminopropionic acid. Furthermore, various observations in connexion with the acid hydrolysis of the latter will be discussed.

Upon benzoylation in aqueous carbonate solution, albizziine yielded an oily derivative which, however, could be transformed into a crystalline methyl ester on treatment with diazomethane. The identity of the ester as methyl L-2-benzamido-3-ureidopropionate (III) was established upon critical comparison with an unambiguously synthesized specimen.



III IV

The latter was produced by interaction at pH 7 of potassium cyanate and *levo*rotatory methyl 2-benzamido-3-aminopropionate hydrochloride (IV). Synthesis of this was achieved essentially as described by Schneider [5] through a series of reactions departing from configurationally known L-asparagine and involving the preparation of L-2,3-diaminopropionic acid. Additional and independent corroboration of the L-configuration of (IV) was available through its experimentally established relationship with L-serine [5]. The above transformations unequivocally established the projection formula (I) as the correct expression for albizziine.

The formally simple structure of albizziine rendered the development of a synthesis of this lower homologue of L-citrulline a logic extension of the structure determination. L-2,3-Diaminopropionic acid offered itself as a suitable starting material, and attempts were consequently directed towards selective carbamylation of its terminal amino-grouping. From analogous cases it appeared natural to proceed *via* selective protection of the 2N-grouping, carbamylation at the 3N-position and, eventually, removal of the protecting group under mild conditions. Apart from its circumstantial character this approach, however, suffered from the disadvantage that no 2N-monoacylated derivatives of

diaminopropionic acid had ever been prepared by direct acylation *. From theoretical considerations this should, in principle, be possible by direct acylation under controlled conditions [6]; steric factors may, however, be responsible for the failure in effecting the process as desired.

An alternative approach, based on Hofmann-degradation of a suitable N-acyl-L-asparagine and introduction of the carbamido-grouping into the 3-amino-substituent of the 2N-acylated intermediate, ultimately followed by removal of the acyl-group, constitutes a variant of a method formerly employed in the synthesis of L-2,3-diaminopropionic acid [8,5]. Though this approach seemed promising in principle **, a route involving fewer steps still appeared desirable. Hence, attention was directed towards the possibility of introducing a carbamido-grouping into L-2,3-diaminopropionic acid selectively and in a single reaction step.

First, the diamino-acid was subjected to reaction with potassium cyanate in a series of experiments in which the relative amounts of reactants, as well as the pH-value of the solutions, were varied. As estimated from paper chromatography ***, mixtures of the isomerides, (I) and (II), were consistently obtained, accompanied by varying amounts of the 2,3-diureido-derivative; the latter appeared on the chromatograms as Ehrlich-positive, ninhydrin-negative spots possessing higher R_F-values than the monosubstituted products. Clearly, masking of the 2-amino-grouping was required to secure a homogeneous reaction product.

In the synthesis of ω-acylated derivatives of 2,ω-diaminocarboxylic acids, copper complexes have often proved very useful. Thus, Kurtz [10] prepared DL-citrulline from urea and the copper complex of ornithine, a procedure subsequently extended by the same author [11] to include syntheses of L-citrulline, DL- and L-2-amino-6-ureidohexanoic acid, as well as DL- and L-2-amino-4-ureidobutyric acid. More recently, Smith [12] modified the synthesis of L-2-amino-4-ureidobutyric acid, L-citrulline and L-2-amino-6-hexanoic acid from urea or cyanate and the appropriate 2,ω-diamino acids. In the 2,4-diaminobutyric acids, the two amino groupings are sufficiently close to form an alternative site of complex formation, as evident from the strong complexing action between cupric ions and 1,3-diaminopropane. Still, however, the 1,2-complex must be present, in view of the successful preparation of the 4-ureido-

* Several years ago, one of us (A.K.) demonstrated monocarbobenzoxylation of DL-diaminopropionic acid to take place exclusively at the 3N-position [6]. However, recent reinvestigation of the mono-derivative has revealed its content of a slight amount of the 2N-isomeride. The alternative course, leading predominantly to the latter and suggested as prevalent in a less alkaline environment, has not since been experimentally verified [6]. Lately, Poduška *et al.* [7] demonstrated that DL-diaminopropionic acid upon treatment with tosylglycyl chloride afforded the 3N-tosyl-glycyl-derivative.

** After the conclusion of the present work, we were privately informed that Dr. J. Rudinger, Institute of Chemistry, Czechoslovakian Academy of Science, Prague, has, in actuality, synthesized L-2-amino-3-ureidopropionic acid (I) along similar lines, utilizing the tosyl-derivative of L-asparagine. Specimens of his synthetic material, natural albizziine, and a sample synthesized in this laboratory as described below, were all found to possess coinciding infra-red spectra.

*** For the present purpose a general paperchromatographic method was devised [9], according to which 2-monoaminocarboxylic acids can be distinguished from other ninhydrin-positive compounds. Thus, the isomeric aminoureidopropionic acids, (I) and (II), can be individually recognized by this procedure.

derivatives. The copper complexes of 2,3-diaminopropionic acid have been studied by Ley and Hegge [13]. Visually these authors noticed a red-violet colour of the copper complex of this acid, deviating from that given by ordinary 2-amino-acids and hence attributed to participation of the 3-amino-grouping. On acidification, the colour changed to a bluish-purple, characteristic for the ordinary 2-amino-acids. From the comprehensive studies of Albert [14,15] on copper complexes of amino acids it can be inferred that the deviating properties exhibited by 2,3-diaminopropionic and 2,4-diaminobutyric acid must be ascribed to their contents of terminal amino-groups, in sufficient proximity to the other active site to permit additional complex formation of a different type. Calculations, based on the quantitative treatment of Albert (*l.c.*), suggested that in the pH-range 3—5, ionic species containing a positively charged amino group in 3-position should be predominant and, hence, selective carbamylation feasible. Explorative experiments indicated that this was, in fact, the case. The individual runs were controlled by paper chromatography in acid solvent systems, in which the copper complexes are sufficiently dissociated to permit the free amino acids to migrate (*cf.* Ref.[16]). Development of the chromatograms were performed with Ehrlich's reagent as well as with ninhydrin according to the modification devised in this laboratory [9]. Best results were obtained when a solution of L-2,3-diaminopropionic acid hydrochloride and half a molecular proportion of cupric sulphate was maintained at pH 5 and 58° during the slow addition of a large excess of potassium cyanate. The soluble copper complex of the reaction product was then decomposed by hydrogen sulphide, the resulting amino acids absorbed on an acid exchange resin, and finally isolated by elution with ammonia. On addition of ethanol, albizziine, uncontaminated with the isomeride (II), separated in about 50 % yield. The usual procedure for the preparation of copper complexes of 2-amino acids consists in boiling the latter with excess cupric oxide or carbonate. In the present case, however, it was observed that considerable quantities of the desired complex was lost by adherence to the excess of solid reagents, and it was found advantageous and convenient to form the complex simply by adding a soluble copper salt to the amino acid solution. Most likely, this modification could be employed also in other, analogous cases. On critical comparison, the pure, synthetic compound proved indistinguishable from natural albizziine. The infra-red spectrum is presented in Fig. 1.

The new plant amino acid possessed a surprisingly high *levo*rotation in water ($[\alpha]_D^{22} - 67°$), yet displaced towards more *dextro*rotatory values on acidification in accordance with the Lutz-Jirgenson rule for L-2-amino acids [17]. Table 1 presents a collection of rotatory values for the next higher homologues, measured under identical conditions. The numerically high rotation of albizziine probably reflects a strong vicinal influence from the carbamido-grouping.* The isomeride (II) is seen to deviate principally from the 2-amino-acid derivatives in its rotatory pattern.

* Through the courtesy of Dr. W. Klyne, Postgraduate Medical School, London, the rotatory dispersion curves of L-albizziine and the higher homologues of the same configurational series have been determined over the wave-length range 290—600 mμ. Whereas in aqueous solution the latter all possess similar, plain and positive curves, L-albizziine exhi-

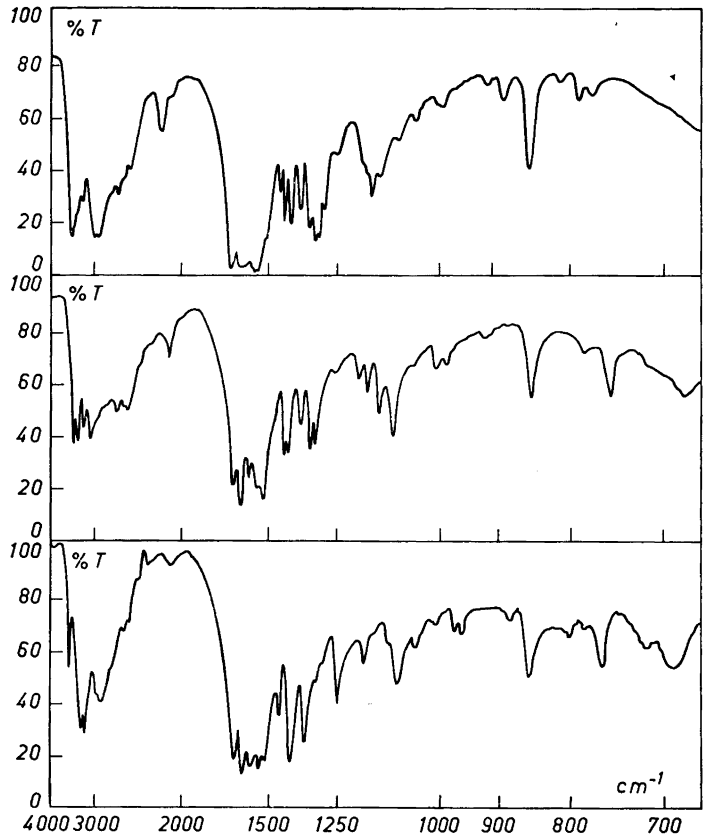


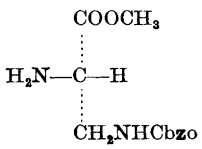
Fig. 1. Infra-red spectra, determined in potassium bromide discs. Upper curve: natural L-albizziine (I); middle curve: racemic albizziine; lower curve: the L-albizziine-isomeride (II) (L-2-ureido-3-aminopropionic acid).

The synthesis of DL-2-amino-3-ureidopropionic acid (DL-albizziine) from DL-2,3-diaminopropionic acid hydrobromide was achieved as described above for the L-series, with the sole exception that the intermediate copper complex was slightly soluble and therefore separated during preparation. Again, racemic albizziine was considerably less soluble in water than the natural isomeride and possessed a distinctly different infra-red spectrum in the solid state (Fig. 1).

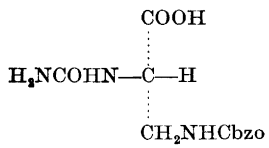
During the present studies it became of interest to synthesize L-2-ureido-3-aminopropionic acid (II), the positional isomeride of albizziine. Carbobenz-

bits an almost mirror image-formed, negative curve. This pattern is a telling illustration of the frequently observed, dramatic influence of chromophores in positions adjacent to an optically active centre and of the caution required in interpreting dispersion curves devoid of Cotton effect. In acid and alkali the deviations are less conspicuous.

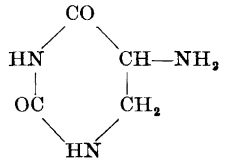
oxylation of the hydrochloride of L-2,3-diaminopropionic acid at pH 7 proceeded to give a homogeneous mono-derivative, transformed by diazomethane into an ester, which was proved to be methyl L-2-amino-3-benzyloxycarbamido-propionate (V, Cbzo = $C_6H_5CH_2OCO$) upon comparison with an authentic specimen, synthesized as described by Schneider [5]. Hence, the monocarbobenzoxylated L-diaminopropionic acid carried the acyl-grouping in 3N-position.



V



VI



VII

Reaction of the latter acid with potassium cyanate afforded crystalline L-2-ureido-3-benzyloxycarbamidopropionic acid (VI, Cbzo = $C_6H_5CH_2OCO$) which, on hydrogenolysis, yielded (II). On paper chromatograms, run in several solvent systems, this albizziine-isomeride migrated at virtually the same rate as albizziine but could be distinguished from the latter by its much weaker and slower ninhydrin-reaction or, still better, by its deviating behaviour when treated with copper salt and ninhydrin according to the method developed in this laboratory [9]. Both albizziine and (II) yielded, as expected, the same positive Ehrlich-reaction, but clearly deviated in their rotations (Table 1) and infra-red spectra (Fig. 1).

Table 1. Molecular rotation of L-albizziine and various homologues, determined in this laboratory.

Compound	Water			2 N HCl			0.11 N NaOH		
	$[M]_D$	g/100 ml	t°C	$[M]_D$	g/100 ml	t°C	$[M]_D$	g/100 ml	t°C
L-2-Amino-6-ureidohexanoic acid	+ 7.6°	2.1	24	+37.4°	3.8	24	+18.9°	1.0	26
L-Citrulline	+ 6.1°[a]	5		+37.1°	3.8	24	+18.9°	1.1	25
L-2-Amino-4-ureidobutyric acid	− 1.0°	2.1	24	+42.3°	3.2	24	+14.5°	1.0	26
L-Albizziine	−98.5°	2.1	23	−32.2°	2.1	22	− 8.2°	1.0	26
L-2-Ureido-3-aminopropionic acid	+ 4.7°	1.0	25	−63.2°[b]	1.0	25	+36.2°	1.0	27

[a] Gornall, A. G. and Hunter, A. *Biochem. J.* **33** (1939) 170. [b] In 0.1 N HCl.

In course of their degradation studies on albizziine, Gmelin *et al.*[3] isolated 2,3-diaminopropionic acid hydrohalides of lower specific rotation than previously recorded, subsequent to hydrolysis with strong mineral acid. The authors suggested acid-induced racemization of L-diaminopropionic acid as a likely explanation, an assumption which has now been confirmed in this laboratory. Upon heating at 125° the specific rotation of a solution of L-2,3-diaminopropionic acid hydrochloride in 48 % hydrobromic acid decreased from an initial value of 19.3° to 1.2° in the course of 6 h. Paper chromatography confirmed that no extensive decomposition was responsible for the loss in rotatory power. On the other hand, paperchromatographic analysis of an acid hydrolysis mixture of albizziine as a function of time suggested the concomitant or intermediate formation of a ninhydrin-positive product with higher R_F-values, possibly one of the unknown 5-aminodihydrouracils (VII). The obviously limited formation of this cyclized product is in marked contrast to the customary, and usually very facile cyclodehydration of 3-ureido-substituted carboxylic acids [18,19]. Possible explanations for this fact, supplemented by a detailed investigation of the albizziine hydrolysis, will be presented in a forthcoming communication.

A possible relationship between albizziine and a hydrouracil derivative merits further consideration in connexion with reflections on the biogenesis of the former. Formally, it recalls the well-established biosynthesis in animals and microorganisms of the uracil ring from ureidosuccinic acid *via* dihydroorotic and orotic acid. In lack of evidence to the contrary, however, albizziine may equally well, if at all, be on the pathway of reductive pyrimidine degradation [20]. A different biochemical perspective in connexion with the occurrence of albizziine is suggested by its formal similarity with citrulline, a key compound in the formation of arginine and urea, or decomposition products of the latter, in mammalian tissues and certain microorganisms. In this connexion, the recent establishment by Gmelin *et al.*[3] of the occurrence of free L-2,3-diaminopropionic acid, a formal analogue to L-ornithine, in seeds of *Mimosa Palmeri* and *M. hemiendyta* of the family *Mimosaceae*, appears particularly interesting. Botanically, these species are close allies of the known albizziine-producing plants and it may well be that the new amino acids within this family are results of a particular and interesting enzymic mechanism.

EXPERIMENTAL

Melting points are uncorrected and determined in an electrically heated block. Rotations are measured in a 1 dm tube at the D-line. Infra-red spectra of all the compounds described have been determined in potassium bromide pellets on a Perkin-Elmer "Infracord"-instrument.

N-Benzoylalbizziine methyl ester. To a cooled and stirred aqueous solution of albizziine* (149 mg) and anhydrous soda (285 mg), a total of 0.175 ml of benzoyl chloride was added in small portions. Extraction with ether, acidification, extraction with pentane, and treatment of the aqueous phase with Norite gave a solution from which the reaction product was removed by extraction with ethyl acetate. The colourless, glassy product was

* The specimen employed was isolated from seeds of *Albizzia lophantha* Benth. according to the procedure of Gmelin *et al.* [2] and had an $[\alpha]_D^{23}$ of —67.0° (*c* 2.1, H_2O).

dissolved in anhydrous methanol and treated with excess diazomethane. Evaporation of the solvent and trituration of the residue with pentane yielded the crystalline ester (78 mg) which was recrystallized twice from water before analysis (15 mg), m. p. 171—174° (decomp.). (Found: C 54.40; H 5.68; N 15.89. Calc. for $C_{12}H_{15}N_3O_4$: C 54.33; H 5.70; N 15.84.) A slightly impure specimen, isolated from the mother liqour, had the rotation value $[\alpha]_D^{21}$ −30° (*c* 1.0, CH_3OH). The infra-red spectrum of the pure product was indistinguishable from that of the synthetic specimen described in the sequel.

Synthetic methyl L-*2-benzamido-3-ureidopropionate* (III). A sample of methyl L-2-amino-3-benzyloxycarbamidopropionate hydrochloride * (488 mg) was benzoylated according to Schneider [5] to give *methyl* L-*2-benzamido-3-benzyloxycarbamidopropionate* (480 mg). An analytical specimen separated from chloroform as colourless needles, m. p. 98.5—99.5°, $[\alpha]_D^{28}$ −17.3° (*c* 1.2, CH_3OH). (Found: C 63.85; H 5.67; N 7.74. Calc. for $C_{19}H_{20}N_3O_5$: C 64.04; H 5.66, N 7.86.) Literature value [5]: m. p. 102°, (no rotation reported). Again, decarbobenzoxylation was performed with hydrogen and palladium black as described [5]. It was found advantageous, however, to run the reaction at 40°. *Methyl* L-*2-benzamido-3-aminopropionate hydrochloride* (IV) was obtained in 80 % yield as colourless crystals, m. p. 171—174° (decomp.), $[\alpha]_D^{30}$ −48.3° (*c* 1.0, CH_3OH). (Found: C 51.10; H 5.87; N 10.67. Calc. for $C_{11}H_{15}N_3O_3$, HCl: C 51.06; H 5.84; N 10.83.) Literature value [5]: m. p. 179° (decomp.), (no rotation reported).

A solution of (IV) (130 mg) and potassium cyanate (113 mg) in water (3 ml) deposited, in the course of 3 h, a crystalline product the amount of which was increased (to 92 mg) upon concentration. A pure specimen of *methyl* L-*2-benzamido-3-ureidopropionate* (III) (69 mg) separated from water as clusters of colourless needles, m. p. 172—173.5° (decomp.), alone or in admixture with the methyl ester of N-benzoylalbizziine described above. $[\alpha]_D^{28}$ −32.5° (*c* 1.2, CH_3OH). The infra-red spectra of the two specimens were identical and possessed all the bands expected.

Synthesis of L-*albizziine* (I). A solution of L-2,3-diaminopropionic acid hydrochloride ** (300 mg) and cupric sulphate (2.2 ml of a 0.5 M solution) in water (28 ml) was brought to pH 5 by addition of 2 N NaOH. The stirred solution was kept at 58° and placed in a pH-stat, preset to maintain a constant pH of 5 by automatic addition of 4 N HCl during the introduction of a solution of potassium cyanate (430 mg in 4.8 ml) in the course of 100 min. At the end of another 100 min, the colour had changed from an initial reddish-violet to a bluish-purple and the HCl-consumption was very slow. The solution was then treated with hydrogen sulphide and filtered. The combined filtrate and washings (200 ml) were percolated through a column containing a cation exchange resin (Zeokarb 215, packing volume: 100 ml) in the acid form. The column was washed with water, and the amino acids eluted by means of 2 % ammonia. Evaporation of the eluate afforded crystalline needles (255 mg), consisting of reasonably pure albizziine. Two recrystallizations from aqueous ethanol afforded pure L-albizziine (150 mg), m. p. 206—211° (decomp.), alone or when mixed with a natural specimen, $[\alpha]_D^{26}$ −66.0° (*c* 2.0, H_2O). The infra-red spectrum was identical with that of a natural sample of albizziine [3] (Fig. 1).

Synthesis of DL-*albizziine.* When a solution of DL-2,3-diaminopropionic acid hydrobromide (555 mg) was processed as described for the corresponding L-isomeride, the light-blue copper complex (273 mg) separated and was filtered off. After decomposition with hydrogen sulphide and evaporation of the resulting solution, a crystalline residue (239 mg) was obtained. It was recrystallized twice from aqueous ethanol to give prisms of pure DL-albizziine (138 mg), m. p. 210—216° (decomp.). (Found: C 32.30; H 6.29; N 28.28. Calc. for $C_4H_9N_3O_3$: C 32.65; H 6.17; N 28.56.) The infrared spectrum (Fig. 1) deviates distinctly from that of the optical isomeride.

L-*2-Amino-3-benzyloxycarbamidopropionic acid.* To a cooled and stirred solution of L-2,3 diaminopropionic acid hydrochloride (1.41 g) in a phosphate buffer of pH 7 (15 ml, 1/15 M) and water (10 ml), a toluene solution (1.9 ml) containing 11 mequiv. of carbo-

* The sample employed was prepared as formerly described [5] and had the rotation $[\alpha]_D^{21}$ —4.2° (*c* 2.0, H_2O); (no rotation was previously recorded).

** The diamino-acid employed was isolated from seeds of *Mimosa Palmeri* as described by Gmelin *et al.*[3] and had the rotation value $[\alpha]_D^{24}$ + 24.8° (*c* 4.7, 1 N HCl).

benzoxy chloride was gradually added in the course of 1 h. Intermittent addition of 1 N NaOH served to maintain the pH-value at 6.5—7. After standing for 2.5 h at room temperature the solution was cooled. The crystalline precipitate was filtered off and washed with ice-cold water and ether. The carbobenzoxy-derivative (1.85 g) separated from water in colourless needles, m. p. 227—229° (decomp.), $[\alpha]_D^{21}$ −18.7° (*c* 1.0, 1 N HCl); $[\alpha]_D^{18}$ −4° (*c* 1.1, 0.1 N NaOH). (Found: C 55.45; H 5.80; N 11.80. Calc. for $C_{11}H_{12}N_2O_4$: C 55.45; H 5.92; N 11.76.) The specimen proved to be uncontaminated with the 2N-acylated isomer when tested by our spot test technique [9].

That the carbobenzoxy-group had entered the L-2,3-diaminopropionic acid in 3N-position appeared from the transformation of the above carbobenzoxyacid into the corresponding methyl ester hydrochloride. The acid (96 mg) was suspended in anhydrous methanol (2 ml) and treated with an excess of ethereal diazomethane. After filtration and evaporation an oil was obtained which upon solution in methanol and addition of methanolic HCl yielded an ester hydrochloride (36 mg) which was recrystallized from methanol and ether; m. p. 161—162° (decomp.), alone or in admixture with a specimen of *methyl* L-*2-amino-3-benzyloxycarbamidopropionate hydrochloride* (V) prepared as described by Schneider [5], who reported the m. p. 164°. Furthermore, the infra-red spectra of the two preparations were completely identical.

L-*2-Ureido-3-benzyloxycarbamidopropionic acid* (VI). A solution of the above described L-2-amino-3-benzyloxycarbamidopropionic acid (875 mg) and potassium cyanate (1 440 mg) in water (100 ml) was boiled under reflux for 20 min. After concentration to 30 ml and ether extraction, acidification with conc. HCl to pH 3 and cooling caused the ureido-acid to separate in crystalline form (721 mg), m. p. 181—182° (decomp.), $[\alpha]_D^{17}$ −1.5° (*c* 1.0, 0.1 N NaOH). A specimen was recrystallized twice from water before analysis, m. p. 188—190° (decomp.). (Found: C 51.10; H 5.58; N 15.01. Calc. for $C_{12}H_{15}N_3O_5$: C 51.24; H 5.38; N 14.94.)

L-*2-Ureido-3-aminopropionic acid* (II). A suspension of palladium black (90 mg) in a solution of the carbobenzoxy-acid (VI) (500 mg) in 50 % methanol (50 ml) was kept at 50° while a stream of hydrogen was passed through, until the production of CO_2 ceased. After filtration and concentration of the filtrate, the latter was treated with Norite, and ethanol was cautiously added, resulting in separation of needles of the colourless ureido-acid (II) (225 mg). A sample for analysis was recrystallized twice from water by addition of ethanol, m. p. 204—210° (decomp.); $[\alpha]_D^{25}$ +3.2° (*c* 1.0, H_2O), $[\alpha]_D^{25}$ −43.0° (*c* 1.0, 0.1 N HCl), $[\alpha]_D^{27}$ +24.6° (*c* 1.0, 0.1 N NaOH). (Found: C 32.75; H 6.24; N 28.70. Calc. for $C_4H_9N_3O_3$: C 32.65; H 6.17; N 28.56.) The infra-red spectrum of this albizziine-isomeride is reproduced in Fig. 1.

Racemization of L-*2,3-diaminopropionic acid.* A solution in constantly boiling hydrobromic acid of L-2,3-diaminopropionic acid hydrochloride, with an initial rotation of $[\alpha]_D^{20}$ +19.3° (*c* 1.6), was heated at 125° in a closed vessel. After 4 h, the rotation had decreased to $[\alpha]_D^{23}$ +4.6° (*c* 1.6) and at the end of 6 h a rotation of $[\alpha]_D^{21}$ +2° (*c* 1.6) indicated almost complete racemization. Upon paper chromatography only one spot was observed, *viz.* that of 2,3-diaminopropionic acid.

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