Furthermore, intermediate between the most simple aromatic monomers and the final, highly complex, polymerized lignin, it is possible that some preliminary stage of lignification could occur. In this stage, a dimerization or trimerization has already occurred, and the final product, lignin, is formed as a result of an eventual polymerization of these intermediary 'secondary building stones'.

Our present knowledge of the process of lignification may then be expressed as follows: by the process of photosynthesis, the carbon dioxide of the atmosphere is converted by plants into glucose. The straight chain of carbon atoms of the sugar molecule is then cyclized into shikimic acid. This compound is then aromatized into compounds of the type of p-hydroxyphenylpyruvic acid. These latter compounds then become the first, or 'primary', lignin building stones. They then undergo dimerization, or other changes, and are thereby converted into the 'secondary' lignin building stones. These latter then eventually undergo the final polymerization which results in the enigmatic substance we call lignin [22].

Additional insight into the mechanism of lignification may be had from a study of the metabolism of a species of wood-destroying mold, namely, *Lentinus lepideus*. This fungus has the capacity to produce methyl p-methoxycinnamate from glucose-containing media [23]. The parallel between the two biochemical processes is apparent from the similarity of the structure of this aromatic ester with the structures of the lignin building stones [19,20]. Thus, the biogenesis of this ester has likewise been found to proceed by a pathway involving shikimic acid [24].

[22] W. J. SCHUBERT and F. F. NORD, Adv. Enzymol. *18*, 349 (1957).
[23] F. F. NORD and J. C. VITUCCI, Arch. Biochem. *14*, 243 (1947); *15*, 465 (1947).
[24] H. SHIMAZONO, W. J. SCHUBERT, and F. F. NORD, J. Amer. chem. Soc. *80*, 1992 (1958).

Recently, it has been found that methyl p-coumarate may be regarded as an intermediate in the metabolism of methyl p-methoxy cinnamate by *L. lepideus*, and also possibly in the biosynthesis of that compound [25]. It is therefore possible that, in the first step of the metabolism of methyl p-methoxycinnamate, this compound may be demethylated to methyl p-coumarate, and then, this latter compound may be further oxidized by a phenolase enzyme, possibly tyrosinase [26]. Such methylation and demethylation of phenolic compounds could have an important bearing on the mechanism of the biogenesis of lignin, and also on the metabolism of that substance by wood-destroying fungi.

Of course, this outline does not represent a complete scheme, since there are still some gaps in it which must be filled in. However, what is of transcendent importance is that now, finally, with the availability of present-day enzymological techniques, and even more recently, of the radioactive tracer technique, biochemists can now look forward with confidence to a complete clarification of the mechanism of this important natural process which occurs in certain plants and makes them 'woody', which process has mystified plant chemists now for over a century.

Zusammenfassung

Lignin kann in seiner ursprünglichen Form durch Abbau von Holz mit Hilfe von Zellulose-zerstörenden Pilzen und darauffolgender Extraktion mit kaltem Alkohol isoliert werden. Die Verbindung stellt enzymatisch freigesetztes Lignin dar. Im verholzenden Gewebe entsteht das Lignin aus photosynthetisch gebildeter Glukose über Shikimisäure und *p*-Hydroxyphenyl-Brenztraubensäure.

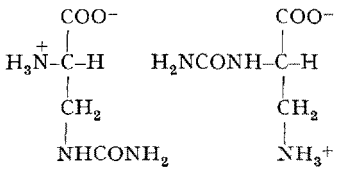
[25] H. SHIMAZONO and F. F. NORD, Arch. Biochem. Biophys. *78*, 263 (1958).
[26] H. SHIMAZONO, Arch. Biochem. Biophys. *83* (in press), 1959.

Brèves communications - Kurze Mitteilungen Brevi comunicazioni - Brief Reports

Structure of Albizziine [L(—)-2-Amino-3-ureidopropionic Acid], an Amino Acid from Higher Plants *(Mimosaceae)*

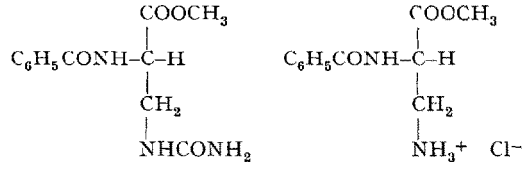
Albizziine is a new plant amino acid, recognized by GMELIN *et al.* [1] as a constituent of several species belonging to the family *Mimosaceae*. Its elementary composition, $C_4H_9N_3O_3$, infra-red spectrum and colour reactions with ninhydrin and Ehrlich's reagent [1], together with its degradation upon acid hydrolysis to carbon dioxide, ammonia and partially racemized L-2,3-diaminopropionic acid [2] strongly suggest the structure (I) or (II) for albizziine. Evidence is now available in this laboratory in support of the expression (I), which is formally analogous to L-citrulline.

[1] R. GMELIN, G. STRAUSS, and G. HASENMAIER, Z. Naturforsch. *13b*, 252 (1958).
[2] R. GMELIN, G. STRAUSS, and G. HASENMAIER, Hoppe-Seyler's Z. *314*, 28 (1959).



I II

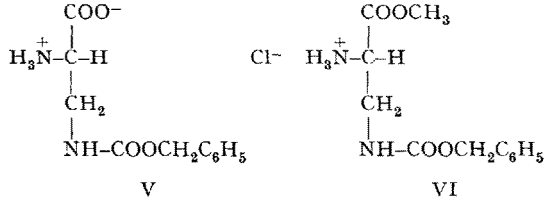
Upon benzoylation, albizziine[1,2] ($[\alpha]_D^{23}$: −67°C [c = 2·1 in H_2O]) afforded an oily N-benzoyl-derivative which was, in turn, esterified with diazomethane to yield the crystalline, *laevo*rotatory *N-benzoylalbizziine methyl ester* [m.p.[3] 171–174°C (from H_2O); Found: C 54·40; H 5·68; N 15·89. $C_{12}H_{15}N_3O_4$ requires C 54·33; H 5·70; N 15·84]. On critical comparison, this compound proved to be identical with a synthetic specimen of *methyl* L-*2-benzamido-3-ureidopropionate* (III) ($[\alpha]_D^{28}$: −32·5°C [c = 1·2 in CH_3OH]), prepared by reaction of methyl L-2-benzamido-3-aminopropionate hydrochloride[4] (IV) ($[\alpha]_D^{30}$: −48·3°C [c = 1·0 in CH_3OH][5]) with excess potassium cyanate in aqueous solution (pH 7) at 30°C.



III IV

The latter salt was synthesized according to SCHNEIDER[4], who further established its spatial relationship with the L-series by degradation to L-serine.

In course of the present studies, the albizziine-isomeride (II) was synthesized for comparison. L-2,3-Diaminopropionic acid hydrochloride ($[\alpha]_D^{24}$: +24·8°C [c = 4·7 in 1 N HCl]), isolated from seeds of *Mimosa Palmeri*[2], was treated with one equivalent of carbobenzoxy chloride in a phosphate buffer at pH 7 to give a 78% yield of a monosubstituted acid (V), separating from water in needles, m.p. 226–231°C (dec.) [Found: C 55·45; H 5·80; N 11·89. $C_{11}H_{14}N_2O_4$ requires C 55·45; H 5·92; N 11·76); ($[\alpha]_D^{21}$: −18·7°C (c = 1·0 in 1 N HCl), $[\alpha]_D^{18}$: −4·0°C (c = 1·1 in 0·1 N NaOH)]. The identity of the latter as L-*2-amino-3-carbobenzoxyamidopropionic acid* appeared from its transformation by means of diazomethane into a methyl ester hydrochloride, indistinguishable on basis of undepressed mixed melting point and coinciding infra-red spectra from an authentic sample of methyl L-2-amino-3-carbobenzoxyamidopropionate hydrochloride[4] ($[\alpha]_D^{21}$: −4·2°C [c = 2·1 in H_2O][5]).

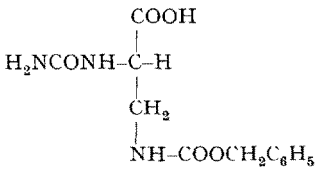


V VI

[3] Melting points are uncorrected and determined in an electrically heated block. Infra-red spectra (in KBr) have been determined of all the compounds discussed. Microanalyses were performed by Mr. P. HANSEN at the Chemical Laboratory of the University of Copenhagen.

[4] F. SCHNEIDER, Liebigs Ann. *529*, 1 (1937).

[5] No rotation data have formerly been published.



VII

Upon reaction with potassium cyanate, the acid (V) was transformed into the corresponding L-*2-ureido-3-carbobenzoxyamidopropionic acid* (VII), m.p 188–190°C (dec.) (from H_2O) [Found: C 51·10; H 5·58; N 15·01. $C_{12}H_{15}N_3O_5$ requires C 51·24; H 5·38; N 14·94]; ($[\alpha]_D^{17}$: −1·5°C [c = 1·0 in 0·1 N NaOH]), which on hydrogenolysis with Pd-black afforded L-*2-ureido-3-aminopropionic acid* (II), separating from aqueous ethanol in colourless needles, m.p. 204–210°C (dec.) [Found: C 32·75; H 6·24; N 28·70. $C_4H_9N_3O_3$ requires C 32·65; H 6·17; N 28·56]; ($[\alpha]_D^{25}$: +3·2°C [c = 1·0 in H_2O], $[\alpha]_D^{25}$: −43·0°C [c = 1·0 in 0·1 N HCl], $[\alpha]_D^{27}$: +24·6°C [c = 1·0 in 0·1 N NaOH]). Like albizziine, the isomeride (II) produces normal colour reactions with Ehrlich's reagent and ninhydrin, but differs from the former in other respects, notably in its infra-red spectrum and rotatory data.

Further results in connexion with studies of the degradation and synthesis of albizziine will form the subject of a forthcoming communication elsewhere.

A. KJÆR, P. OLESEN LARSEN, and R. GMELIN

Organic Chemical Laboratory of the Royal Veterinary and Agricultural College, Copenhagen (Denmark), March 12, 1959.

Zusammenfassung

Eine neue Aminosäure, Albizziin, wurde durch chemische Verknüpfung zwischen N-Benzoylalbizziinmethylester und L-2-Benzamido-3-ureidopropionsäuremethylester (III) als L-2-Amino-3-ureidopropionsäure (I) identifiziert. Die Synthese von L-2-Ureido-3-aminopropionsäure (II) wird beschrieben.

The Metabolism of 3-Hydroxytyramine-1-C^{14} in Brain Tissue Homogenates[1]

Recently it was reported that the distribution of 3-hydroxytyramine in the brain is different from that of norepinephrine[2]. This finding suggests that 3-hydroxytyramine may have an independent role in brain function in addition to being a precursor of norepinephrine. While we have previously reported the metabolites of 3-hydroxytyramine in rats urine[3], to our knowledge no data on the metabolites of this compound recovered from brain tissue has been reported. We, therefore, investigated the metabolism of 3-hydroxytyramine in brain homogenates by the following procedure:

Fresh cow brain obtained from the slaughter house was homogenized in a Waring blender with ice cold phosphor

[1] This study was supported in part by United States Public Health Service Grant M 2717.

The authors are grateful to R. J. FLOODY, M. D. of Hoffmann-La Roche Inc., for providing us with iproniazid.

[2] A. BERTLER and E. ROSENGREN, Exper. *15*, 10 (1959).

[3] M. GOLDSTEIN, A. J. FRIEDHOFF, and C. SIMMONS, Biochem. Biophys. Acta (in press).