stereochemistry is the same as in secologanin, and hence the new alkaloid can be formulated as 5-oxostrictosidine (**1**).

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Zusammenfassung. Für ein neues glukosidisches Indolalkaloid aus *Adina rubescens* wird anhand instrumentalanalytischer Untersuchungen die Struktur von 5-Oxostrictosidin vorgeschlagen.

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Synthesis of Litorin

A nonapeptide of the formula H-Pyr-Gln-Trp-Ala-Val-Gly-His-Phe-Met-NH_2[1], corresponding to the proposed sequence of litorin[2], was synthesized by conventional methods. Relevant information pertaining to its synthesis is summarized in the Figure and in the Table.

The free nonapeptide, after the removal of the dinitrophenyl group with a large excess of 2-mercaptoethanol[3] in solution of HMPT-DMF-H_2O (4:1:1) maintained at pH 8 with Na_2CO_3, was finally secured as hydrochloride by treatment with HCl-AcOH and desalting through a column of amberlite XAD-2 (eluent:H_2O and then MeOH-H_2O 50%). It was found to be homogeneous and showed the same electrophoretic and chromatographic

[1] The amino acids used, with the exception of glycine, have the L-configuration. Symbols and abbrevations are in accordance with the recomandations of the IUPAC-IUB Commission on Biochemical Nomenclature, J. Biol. Chem. *247*, 977 (1971). Pyr = pyroglutamic acid.
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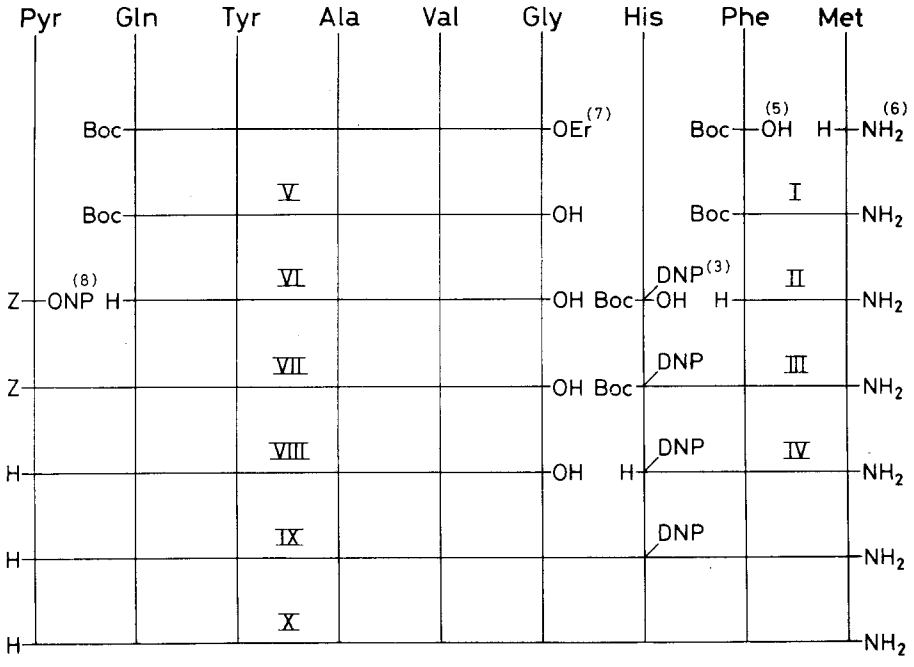
Data on litorin and the intermediates obtained during the synthesis*

Number	Compound	Formula	Method[a]	Reaction[b] solvent	Yield (%)	Crystallization solvent[c]	Melting[d] point	Optical[e] rotation	$E_{1.2}$[f] (Glu)	$E_{5.8}$[g] (Glu)
I	Boc-Phe-Met-NH_2	$C_{19}H_{29}N_3O_4S$	M.A.	THF	70	MeOH-EtOAc	193–195°	—	—	—
II	H-Phe-Met-NH_2·HCl	$C_{14}H_{21}N_3O_2S$·HCl	HCl	AcOH	98	MeOH-Et_2O	210–212°	+14°	0.85	—
III	Boc-His(DNP)-Phe--Met-NH_2	$C_{31}H_{38}N_8O_9S$	DCCI + HOSu	THF-DMF	65	MeOH-Et_2O	135–140°d	— 8°	—	—
IV	H-His(DNP)-Phe-Met--NH_2·HCl	$C_{26}H_{30}N_8O_7S$·HCl	HCl	AcOH	90	MeOH-Et_2O	155–160°d	+30°	0.98	—
V	Boc-Gln-Trp-Ala--Val-Gly-OH	$C_{31}H_{45}N_7O_{10}$	NaOH	MeOH-H_2O	84	MeOH-Et_2O	156–157°	−47°	—	0.32
VI	H-Gln-Trp-Ala-Val-Gly-OH·TFA	$C_{26}H_{37}N_7O_8$·$C_2F_3HO_2$	TFA	—	90	MeOH-Et_2O	170–172°	+29°	0.51	—
VII	Z-Pyr-Gln-Trp-Ala--Val-Gly-OH	$C_{39}H_{48}N_8O_{12}$	ONP	DMF	80	AcOH-Et_2O	230–232°d	−52°	—	0.24
VIII	H-Pyr-Gln-Trp-Ala--Val-Gly-OH	$C_{31}H_{42}N_8O_{10}$	H_2	DMF	95	DMF-Et_2O	239–240°d	−43°	—	0.25
IX	H-Pyr-Gln-Trp-Ala-Val-Gly-His(DNP)--Phe-Met-NH_2	$C_{57}H_{70}N_{16}O_{16}S$	DCCI + HOSu	DMF-HMPT	66	DMF-MeOH	180–182°d	−25°	—	—
X	H-Pyr-Gln-Trp-Ala--Val-Gly-His-Phe-Met--NH_2·HCl (litorin hydrochloride)	$C_{51}H_{69}N_{14}O_{11}S$·HCl	M.E. pH 8	HMPT-DMF-H_2O(4:1:1)	60	MeOH-EtOAc	237°d	−22°	0.40	—

Amino acid ratios in acid hydrolysate[h] of compound X (litorin hydrochloride): $Glu_{1.94}$, $Gly_{1.00}$, $Ala_{1.00}$, $Val_{0.95}$, $Met_{1.00}$, $Phe_{0.95}$, $His_{0.99}$. *All compounds (except II, IV and VI, which were not analyzed) gave correct combustion values for C, H and N. [a] M.A., mixed anhydride with N-methylmorfoline and ethyl chloroformate (activation time: 2 min at −15°); DCCI + HOSu, activated ester prepared in situ from N,N'-dicyclohexylcarbodi-imide and N-hydroxysuccinimide (2 h at 0° and 2 h at 24°); HCl, dry HCl (~1,3 *N*); NaOH, 1 *N* sodium hydroxide; TFA, trifluoroacetic acid at 0°; ONP, *p*-nitrophenyl ester; H_2, hydrogenation in the presence of 10% palladium-charcoal; M.E., 2-mercaptoethanol; pH 8, maintained at pH 8 with solid Na_2CO_3. [b] THF, tetrahydrofuran; AcOH, glacial acetic acid; DMF, N,N'-dimethylformami de; MeOH, methanol; H_2O, water; HMPT, hexamethyl phosphoric triamide. [c] EtOAc, ethyl acetate; Et_2O, diethyl ether. [d] d, with decomposition. [e] Optical rotations were measured at 24°, c = 1. The solvents used are MeOH for II, III, IV, V and VI; AcOH for VII, VIII and IX; 95% AcOH for X. [f] Electrophoretic mobility in HCOOH/CH_3COOH/H_2O (615:500:3885) with glutamic acid as standard. [g] Electrophoretic mobility in CH_3COOH/pyridine/H_2O (50:450:4500) with glutamic acid as standard. [h] Trp is decomposed during acid hydrolysis (105° for 16 h).



Synthesis of Litorin.

mobilities, the same degradative pattern and the same biological properties[4] of natural litorin[5–8].

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Riassunto. Viene riportata la sintesi della piroglutamil-glutaminil-triptofil-alanil-valil-glicil-istidil-fenilalanil-metioninamide, un peptide identico per proprietà fisiche, chimiche e biologiche alla litorina.

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H_2S as Sulfur Source in *Lemna minor* L.: II. Direct Incorporation into Cysteine and Inhibition of Sulfate Assimilation

Sulfate is the normal sulfur source of plants[1], but they are able to use other compounds to provide at least part of their sulfur requirements[2–4]. For Lemnaceae H_2S is of special interest, because they often grow on ponds where sulfide can be detected[5]. In these habitats, where H_2S is available to the plants together with SO_4^{2-}, an interesting question is how much the uptake and the assimilation of the oxidized compound is inhibited by the reduced one.

In a previous report we showed that H_2S inhibits the uptake of sulfate[6]. Here we shall present evidence for a direct incorporation of H_2S into cysteine. A simultaneous inhibition of the sulfate assimilation appears to be very probable.

Table I shows the result of an isotope-competition experiment: *Lemna minor* L. (strain-number 6580 of the collection of LANDOLT[7] were cultivated with radioactive $^{35}SO_4^{2-}$ in the nutrient solution and atmospheric air containing 0 or 6 ppm H_2S. After 10 and 15 days of cultivation, the specific activities of sulfate in the nutrient solution and in the plant material and of cysteine were determined. Cysteine was taken, because, from the quantitative standpoint, the most important pathway in the assimilation of sulfate is via cysteine[1].

The specific activity of sulfate and cysteine in the organisms cultivated with air is identical to the specific activity of sulfate in the nutrient solution.

In plants cultivated with air containing H_2S, the specific activity of sulfate in the plant material is only 1.25% that of the sulfate of the nutrient solution; H_2S provides the rest. The specific activity of cysteine is 50 times lower than that of sulfate present in the plant material, suggesting that 6 ppm H_2S almost completely blocks the assimilation of sulfate. This effect could be based on the inhibition of the enzymes of sulfate assimila-

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