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Synthesis and Enzymatic Conversion of Amino Acids Equipped with the Silanetriol Functionality: A Prelude to Silicon Biodiversification

Jade Dussart-Gautheret,^[a] Julie Rivollier,^[b] Cédric Simon,^[a] Alessandro De Simone,^[b] Jérôme Berthet,^[c] Stéphanie Delbaere,^[c] Régina Maruchenko,^[a] Claire Troufflard,^[a] Denis Lesage,^[a] Yves Gimbert,^[d] Gilles Lemière,^[a] Philippe Marlière,^{*,[b]} and Louis Fensterbank^{*,[a]}

Synthetic routes are reported for the three analogues of the simplest L-2-amino-dicarboxylic acids, aspartate, glutamate, and amino adipate, in which the silanetriol group (Si(OH)₃) replaces the distal carboxyl group (CO₂H). Direct access to the silanetriol amino acids relied either on catalytic hydrosilylation of a terminal alkene using triethoxysilane, or on alkylation of a glycine equivalent anion by triallyl(iodomethyl)silane. In both cases, acid hydrolysis afforded the silanetriol amino acids. These

were shown to self-assemble into siloxane Si-O clusters as their concentration in water increased in the pH range of 1–12. Such reversible cross-linking did not prevent silanetriol amino acids from serving as substrates of an aminotransferase enzyme, boding well for their utilization as microbial nutrients to encompass silicon in future stages of metabolism and polypeptide edifices.

Introduction

The chemical constitution common to all known living cells is apparently restricted to the ten elements C, H, N, O, P, S, K, Mg, Zn and Mn.^[1] Certain elements are present in the composition of most species but absent in others, thus *Escherichia coli* is devoid of Na and Cl, *Saccharomyces cerevisiae* of Mo and *Lactobacillus plantarum* of Fe. The templated biosynthesis of informational polymers proceeds by exclusively incorporating the C, H, N, O, P subset in nucleic acids (as catalyzed by RNA and DNA polymerases) and the C, H, N, O, S subset in proteins (as catalyzed by ribosomes).^[2] The only known exception to the

restricted specification of informational bioelements is selenium, the incorporation of which occurs in some proteins of certain species.^[3] Elucidation of the enzymatic machinery that underlies the biosynthesis and coding of selenocysteinyl-tRNA, thereby endowing proteins with the selenol catalytic group, represented a major advance in biochemical and evolutionary understanding.^[4]

Taking selenocysteine as a model, we set out to experimentally add silicon to the list of informational bioelements and more specifically to evolve descendants of common microbial species that would employ the silanetriol group as an additional amino acid side chain in their genetic code. The silanetriol group (pK_a=10) indeed formally corresponds to the substitution of carbon by silicon in the carboxyl group (pK_a=4), which attenuates its acidic character and allows its spontaneous self-condensation into siloxanes, notably silsequioxanes^[5] (Figure 1).

Our objective is twofold. On the one hand, we intend to endow living cells with the self-condensation of silanetriol into siloxane Si-O clusters and explore new types of protein architectures, by introducing non-redox alternatives to disulfide crosslinks and Fe-S clusters.^[6] On the other hand, we intend to ensure the containment of microbial strains requiring a silanetriol amino acid as nutrient. Since no metabolic reaction is known to form Si-C bonds,^[7] silanetriol-dependent cells escaping from a laboratory would be unlikely to acquire a biosynthetic pathway, bypass their nutritional need and disseminate in the wild.^[8]

A few recent experimental advances are relevant for the goal of introducing silanetriol in proteins. The catalytic mechanisms of silicic acid (Si(OH)₄) polymerization by the enzymes silaffin from diatoms and silicatein from sponges have been precisely characterized.^[9] These enzymes are able to connect Si-O bonds without containing silicon in their own structures.

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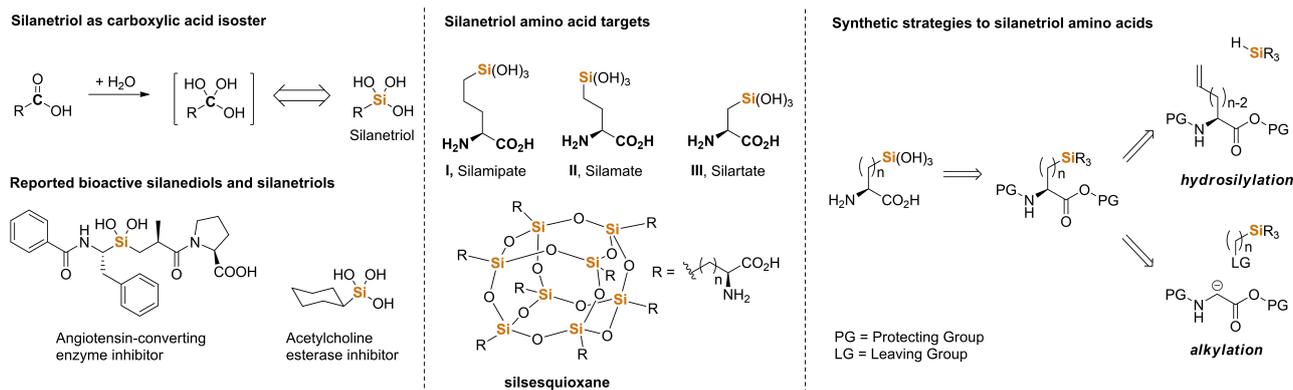


Figure 1. Silanetriol amino acids: background and opportunities.

Very significantly, variants of heme proteins were engineered by the Arnold group to catalyze the formation of Si–C bonds, thereby accomplishing a tour de force for the reason that such bonds do not appear in the structure of any known molecule synthesized by a living organism.^[10] Using orthogonal tRNA/synthetase systems, two silicon-containing amino acids were incorporated into bacterial proteins as NMR probes, namely 4-trimethylsilyl-phenylalanine *ex vivo*^[11] and N6-trimethylsilyl-methoxycarbonyl-lysine *in vivo*.^[12] Silicon is in this case bonded to carbon by its four valences, leaving the biological mobilization of silanetriol *in terra incognita*.

The incorporation of silicon into amino acid and peptide analogues has mainly been studied for medicinal purposes thus far.^[13] Most were derived from commercial alkylsilyl or arylsilyl precursors and handily prepared because of their imperviousness to water. Few examples of amino acids were reported in which silicon is bonded to oxygen atoms, namely alanine^[14] and phenylalanine^[15] dimethylsilanol. Silanediols were pioneered in 1998 by Sieburth as isosteric analogues of the tetrahedral intermediate in peptide bond hydrolysis.^[16] Various proteolytic enzyme inhibitors were discovered following this approach (angiotensin converting enzyme,^[17] HIV protease,^[18] and thermolysin^[19]) as well as a zinc-binding inhibitor of histone deacetylases.^[20] In the same vein, Enghild and Skrydstrup^[21] developed a family of inhibitors of the human neutrophil esterase, a serine protease enzyme. The Sieburth's group also prepared an amino acid bearing a distal silanediol, 6-dihydroxymethylsilyl-L-norleucine, through alkene hydrosilylation and showed that it undergoes acid-dependent siloxane oligomerization.^[22]

Compared to silanols and silanediols, silanetriols form an exotic class of compounds whose synthetic access remains more arduous.^[5] They have mainly been synthesized as precursors of hybrid materials.^[5,23] Their structures based on a geminal tri-hydroxy group mimic the transition state of ester hydrolysis and, indeed, some simple alkyl and aryl silanetriols were found inhibitory to acetylcholine esterase,^[24] validating the potential of these silicon derivatives to interfere with biomolecules.

The ultimate goal of adding a silanetriol-aminoacyl-tRNA to genetic translation first requires interrogating microbial metab-

olism with the precursor amino acid. We found no mention in the literature of assaying silanetriol amino acids as substrates for any enzyme, or as nutrients for any organism, or even describing their synthetic preparation.^[7]

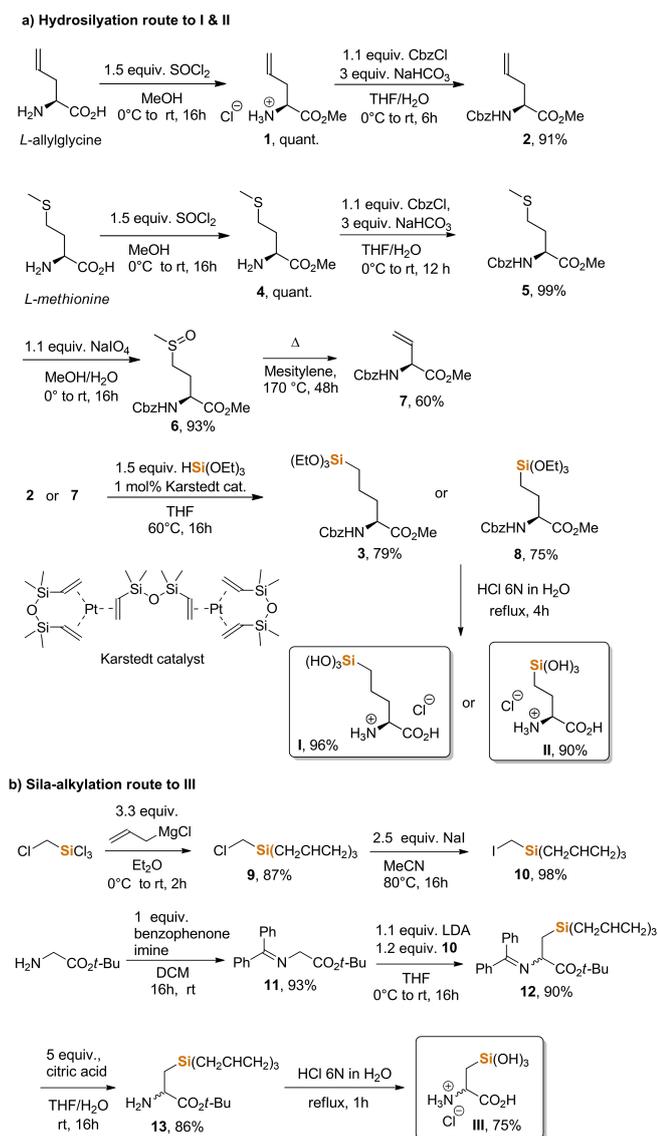
Herein we report the chemical syntheses of three amino acids equipped with a side chain ending with the silanetriol group (I–III, see Figure 1) as analogues of the simplest L-2-amino diacids, respectively amino adipate, glutamate and aspartate (the two latter belonging to the canonical set of protein monomers and the former serving as intermediate in the lysine biosynthetic pathway of certain species). Following thorough structural and biochemical protocols, the three novel silanetriol amino acids were demonstrated to undergo enzymatic transamination and to generate the corresponding silanetriol oxo acids.

Results and discussion

We contemplated two reaction classes to forge the key carbon-silicon bonds of silanetriol amino acids I–III. The first consisted of the transition metal-catalyzed hydrosilylation, the second of the alkylation of a glycol anion by a silyl electrophile (sila-alkylation). An inherent difficulty in such synthetic routes is to introduce the required functional groups in the appropriate order, relying on masked silanetriol groups to be eventually deprotected.

Given the ready availability of allylglycine, the synthesis of Silamipate I by hydrosilylation was first attempted (Scheme 1a). L-allylglycine was quantitatively esterified using thionyl chloride in methanol to give **1**, followed by amino group protection as benzyl carbamate (**2**, 91%). Several catalytic systems for the key hydrosilylation step were comparatively tried, the platinum-based Karstedt catalyst giving the best yield of the triethoxysilyl compound **3** (up to 70%). One-pot triple deprotection (triethoxysilane, N-carbamate, methyl ester) was performed with excellent yield by acid hydrolysis with 6N HCl. After freeze-drying, the target molecule I was obtained with an excellent yield of 85%.

A similar route was followed to synthesize Silamate II (Scheme 1a). Vinylglycine intermediate **7** was prepared in four



Scheme 1. Synthetic access to silanetriol amino acids I–III.

steps from L-methionine according to the literature.^[25] After protection of the amino and carboxyl groups (5), oxidation of sulfur using sodium periodate yielded the corresponding sulfoxide 6. Thermal elimination of sulfenic acid in mesitylene gave the desired precursor 7 in 60% yield, which needed thorough purification prior to the hydrosilylation step. The latter proceeded smoothly to give 8 with a yield of 73%, accompanied in some reactions by the hydrogenation product (maximum 5%). In that case, careful separation of the two compounds by column chromatography was carried out, to avoid contamination of II by the amino acid norvaline. Finally, a triple deprotection as above gave the expected Silamate II with an excellent yield of 90%. The same reaction sequence was applied to the commercially available ¹⁵N-labeled L-methionine and afforded the corresponding ¹⁵N-Silamate with comparable yield (see SI).

The hydrosilylation reaction was also considered to prepare Silartate III. Thus, easily accessible protected dehydroalanine was engaged in the previous conditions but no silylated adduct was formed. Alkylation of Schiff base derivatives of glycine by the O'Donnell method seemed worth exploring.^[26] Triallyl(iodo-methyl)silane 10, obtained by the Finkelstein reaction on the corresponding chloride 9,^[27] was assayed as an electrophile bearing a masked silanetriol function. Indeed, triallylsilanes are known to convert into silanetriols through acid treatment.^[28] To our delight, the alkylation of the Schiff base 11 with 10 went smoothly. Hydrolysis with citric acid provided the free amine 13, and then with 6N HCl, in just one hour, the expected Silartate III in racemic form in 75% yield (Scheme 1b).

These syntheses could be scaled up to gram quantities. This made it possible to conduct structural as well as biochemical studies. Focusing on Silamate II, we investigated the effect of pH (< 2 and > 11) duration (0, 8 and 17 days) and concentration (0.01 to 0.22 M) on condensation processes by the silanetriol group (see SI). Multinuclear NMR studies were carried out. ¹³C and ²⁹Si NMR spectra were found highly informative to this end, demonstrating the formation of siloxane crosslinks upon increasing concentration but without significant influence of pH and time. In accordance with the literature,^[29] ²⁹Si NMR shifts allowed to distinguish free silane triols, mono-crosslinked (M), di-crosslinked (D) and tri-crosslinked (T) structures (Figure 2). In parallel, ¹H NMR spectra and DOSY experiments at c=0.01 M revealed the evolving spectral resolution from poorly-resolved signals for just-prepared samples to well-resolved resonances after some hours or days. This is highly suggestive of depolymerisation of siloxane networks liberating monomer II as already observed by Sieburth.^[22]

We then investigated the interaction of our new-to-nature amino acids with a biocatalyst. The three compounds I–III were

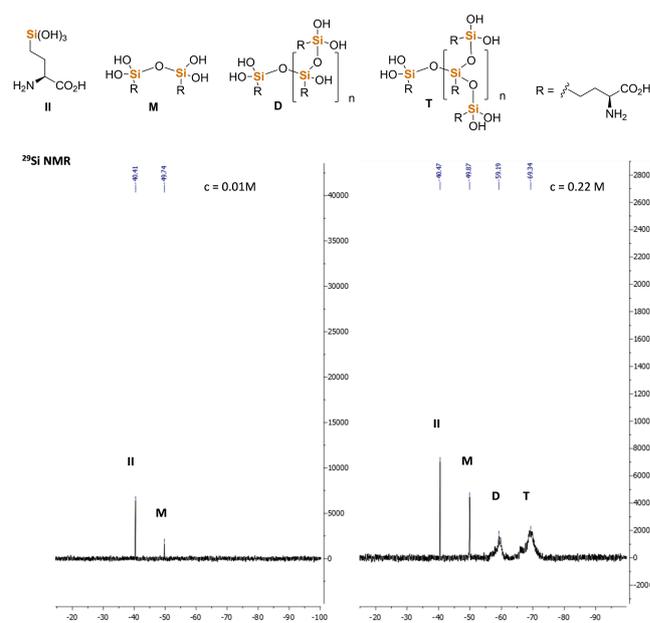
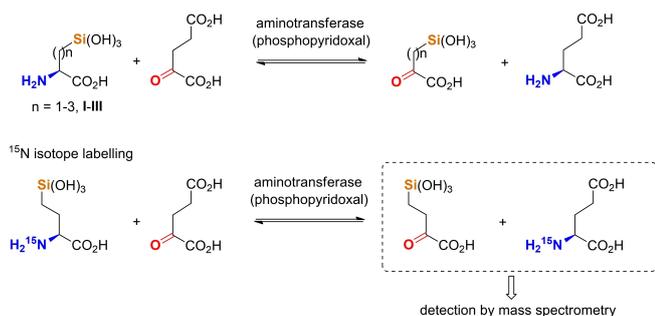


Figure 2. ²⁹Si NMR evidence for siloxane crosslinking by Silamate II upon increasing concentration. Other parameters such as temperature, pH and time are identical (pH < 2, 20 °C, 0 day).



Scheme 2. Enzymatic transamination of silanetriol amino acids I–III and ^{15}N .

engaged in transamination reactions using 2-oxoglutarate as a co-substrate and a commercial aminotransferase as a catalyst and pyridoxal 5'-phosphate (PLP) as co-catalyst (Scheme 2, see also SI). The enzyme (according to the vendor Sigma Aldrich) is of bacterial origin and shows an elevated activity in converting oxoglutarate to L-glutamate using a wide spectrum of L-amino acids.

Application of the enzymatic assay to the three silanetriol amino acids I–III resulted in the formation of a product chromatographically indistinguishable from glutamate (as detected by ninhydrin after TLC). MS analysis corroborated these observations by showing the formation of an entity with the mass of glutamate and also, except in the reaction of III, of entities whose masses corresponded to silanetriol oxo acids in the proportions expected for the natural isotopes of silicon (^{28}Si , ^{29}Si , and ^{30}Si). Subjected to the same enzymatic assay, ^{15}N -L-silamate led to the appearance of an entity with the mass expected for ^{15}N -L-glutamate.

Altogether, our enzymatic results established that the three silanetriol amino acids which we synthesized undergo enzymatic transamination and that spontaneous condensation reactions into siloxanes (including silanetriol oxo acid products) do not thwart biocatalysis.

Conclusions

The results reported herein bode well for the future biodiversification of silicon and the incorporation of silanetriol as an additional functionality of proteins *in vivo*. They suggest that silanetriol amino acids will serve as nitrogen sources for bacteria expressing appropriate aminotransferases. The transamination products, silanetriol oxo acids, will likely give rise to aldehydes and acyl-CoA thioesters through the action of thiamine enzymes^[30] and in turn generate an unprecedented cascade of secondary metabolites.^[31] A swell of metabolic innovation is to be expected from the synthetic availability of silanetriol amino acids and their propensity to undergo the enzymatic conversions of canonical amino acids.

Experimental section

General procedure for hydrosilylation

To a solution of alkene **2** or **7** (1 equiv.) in tetrahydrofuran (0.1 M) at room temperature were added triethoxysilane (1.5 equiv.) and 0.01 equiv. Karstedt catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetra-methylsiloxane complex, 2% of Pt in xylenes). The reaction was stirred at 60 °C for 16 h. The reaction was evaporated to dryness and the black residue was purified by flash chromatography on silica to afford the desired products after drying under pressure (slightly yellow oils, 1.33 g of **3**, 79% yield or 1.18 g of **8**, 75% yield).

General procedure for hydrolysis

To an aqueous hydrochloric solution (6N, 17 mL) at gentle reflux (heating 115 °C) was added a solution of **3** or **8** in methanol and the reaction mixture was stirred at reflux for 4 h in the open air. The clear solution was cooled down to room temperature, degassed by bubbling of argon and lyophilised to give a pure white solid (182 mg of **I**, 96% yield or 142 mg of **II**, 90% yield).

General procedure for transamination

Triethanolamine buffer solution preparation

To a 30 mL beaker equipped with a magnetic stirrer, HPLC grade water (10.0 mL), triethanolamine (0.250 g), s(4 mg) were added. Under gentle stirring at rt, concentrated HCl was added dropwise. After pH reached 7.5 (indicated by a pH meter), the total volume was then adjusted to 15.0 mL by adding HPLC grade water. The buffer solution was used directly for transamination.

To a 5 mL vial equipped with a magnetic stir bar was added the Silanetriol amino acid (0.01 mmol) and the oxoglutarate (1.46 mg, 0.01 mmol). The triethanolamine buffer at pH = 7.5 (1.0 mL) and the transaminase (1.0 mg) were then added sequentially. The reaction vial was capped by a screw cap and stirred vigorously (1000 rpm) at 37 °C for 24 h. After 24 h, the reaction was filtered through a PTFE membrane 0.2 μm and directly analyzed by ultrahigh-resolution mass spectrometry.

Supporting Information

The authors have cited additional references within the Supporting Information.^[32–34]

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.



Data Availability Statement

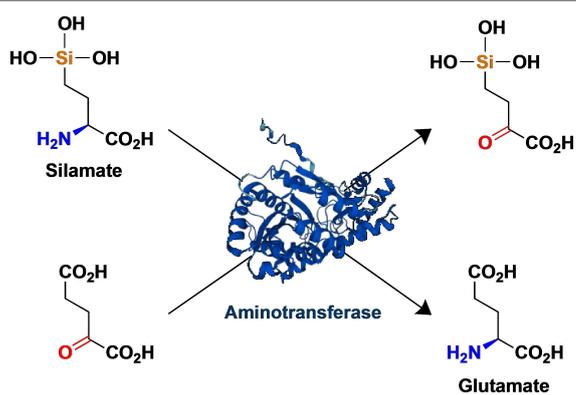
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: aminotransferases · cluster compounds · hydrosilylation · silanetriols · xenobiology

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RESEARCH ARTICLE



A silanetriol moiety can be appended to amino acid precursors in a straightforward manner, affording unexplored sila-analogues of aspartate, aminoadi-

pate, and glutamate. They were engaged in an enzymatic process, which opens up broad perspectives for the biologization of silicon.

Dr. J. Dussart-Gautheret, Dr. J. Rivollier, Dr. C. Simon, Dr. A. De Simone, Dr. J. Berthet, Prof. S. Delbaere, R. Maruchenko, C. Troufflard, Dr. D. Lesage, Dr. Y. Gimbert, Dr. G. Lemièrre, Dr. P. Marlière, Prof. L. Fensterbank**

1 – 6

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