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Use of Phenolic Compounds as Stabilizing Agents for Silicon-Based Molecules

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Abstract

In order to circumvent the problem of silanols polymerization in food supplement or cosmetics, the stabilizing power of phenolic molecules such as vanillin and frambinone was evaluated using two different siliceous molecules: orthosilicic acid and monomethylsilanetriol. NMR analyses confirmed the absence of polymeric species in formulations, conferring it a good bioavailability. The Silicon-phenol complexes demonstrated interesting biological properties on skin, collagen and cellular ageing proving that this complex reveals all the power of Silicon.

Keywords: Silicon; Orthosilicic acid; Monomethylsilanetriol; Bioavailability

Abbreviations:

OSA: Orthosilicic Acid; MMST: Monomethylsilanetriol; OSA-VC: Orthosilicic Acid Vanillin Complex; MMST-FB: Monomethylsilanetriol-Frambinone Complex; HMDS: Hexamethyldisiloxane.

Introduction

Silicon is one of the most common elements in nature. In its natural aqueous environment, Silicon is initially found in the form of Orth silicic acid. Unfortunately, it quickly undergoes polycondensation and is converted into inorganic natural forms, such as the well-known silica and silicates [1,2]. Those Silicon compounds are barely insoluble in aqueous medium, leading to a weak effect on living organisms [3,4]. However, Silicon, even as a trace element, plays a major biological role and must be considered as a key element for life. It affects different processes, having both structural and metabolic roles. It is indeed an architect of the structure of connective tissues but also favors de novo synthesis of its elements. Silicon is thus an essential element for the human body and for lots of other species [5-8]. Various studies conducted on human have highlighted that ageing is correlated with a significant decrease of Silicon levels in organs such as skin or arteries [9]. The slowdown in intestinal Silicon absorption is, among others, to be blamed for this decrease. It is therefore of first importance that, all life long, Silicon could be provided in appropriate quantity [10]. To be sure that this adequate amount can be achieved, it is necessary to overcome the problem of Silicon absorption. Indeed, even if Silicon is very abundant in its natural state, water insoluble mineral forms, such as silica and silicates, or amorphous forms, such as clays or opals, does not constitute bioavailable Silicon sources [11]. In our diet, Silicon is mainly found as aluminosilicates or silica and has therefore a very low bioavailability [12,13].

Complexes of bioavailable silicon molecules

In order to overcome this problem, in the present research, we focused on the elaboration of Silicon complexes with well-defined properties such as bioavailability, stability, safety and without the presence of halogenated siliceous molecules as in the case of the traditional use of HMDS (Hexamethyldisiloxane). To ensure the best efficiency of the molecules, we also studied if the complexes, once formulated, could still ensure the commonly accepted positive biological effect of Silicon on skin, hair, nails, collagen, elastin, connective tissues, bones, cartilage and on cellular ageing. Thanks to their physico-chemical properties, the obtained complexes will have to reach the heart of the cells to maximize their biological effect.

Currently, different sources of bioavailable Silicon can be found on the market. Among these, we can cite organosiliceous compounds and orthosilicic acid (OSA) [14-16]. Organosiliceous are less likely to polymerize than OSA (due to the organic moieties which can act sterically but also which replace a potentially reactive hydroxide group) but not all organosiloxanes could be used in all applications because of their synthesis pathway using halosilane, alkoxysilane, aminosilane, arylsilane or alkylsilane, making them not suitable for food or biological preparations [17]. OSA is suitable for all kind of preparations and exhibits a maximum of OH functions, giving the molecule a very good bioavailability but also a higher risk of condensation, making a stabilization system completely necessary. It has indeed been shown that the number of free hydroxyl group on the Silicon atom (silanols functions) is a major key factor for both the solubility and the biological activity of the chemicals [18]. This is why our research was oriented to two types of siliceous molecules, organosiliceous complexes (more accurately MMST complexes) and OSA complexes with the aim to obtain the best-balanced combination of bioavailability and stability. MMST and OSA are represented in Figure 1.

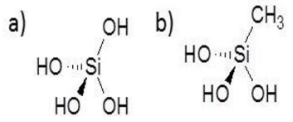

Figure 1: Structure of (a) OSA and (b) MMST.

Because sterical hindrance plays a key role in chemical reactions, especially in polymerization, we choose to use phenolic or polyphenolic compounds containing at least one aromatic ring and one or more hydroxyl group to complex the silanols functions. Hydrogen bonds will (weakly) link the hydroxyls groups of silanols (from OSA or MMST) with hydroxyl or carbonyl groups of phenolic compounds without any reaction process. Esterification between the two parts of the complex is therefore excluded. In our case, two phenols are of major interest: 1-(4 hydroxyphenyl)-3-butanone (frambinone) and 4-Hydroxy-3-methoxybenzaldehyde (vanillin), represented in Figure 2.

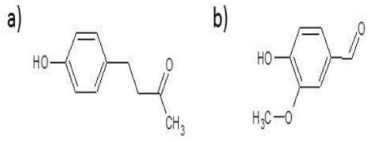

Figure 2: Structure of (a) Frambinone and (b) Vanillin.

Synthetic route of stable complexes

The synthesis of the different complexes follows the same procedure, detailed here for the MMST-FB complex and schematically illustrated in Figure 3. In the present inquisition, 410 gm of 1-(4 hydroxyphenyl)-3-butanone is dissolved at 40°C in 467 gm of ethanol 40%. 290 ml of water is added, and the pH is first adjusted to 4.8 with 85% phosphoric acid. 2890 gm of potassium methylsiliconate is added. The synthesis process allows the complete hydrolysis of the precursor and liberation of free hydroxyls groups. Hydrolysis is immediately followed by the formation of the stable, bioavailable Silicon complexes. The final pH of the solution is controlled and adjusted a second time to a value of 4.8. Silicon content is 0.3 wt/v 0/0 and the ratio between Si and stabilizing agent percentage (wt/v%) is 0.37. The dissolution step occurs so that the ratio between the final volume of solution and the precursor volume is 225.

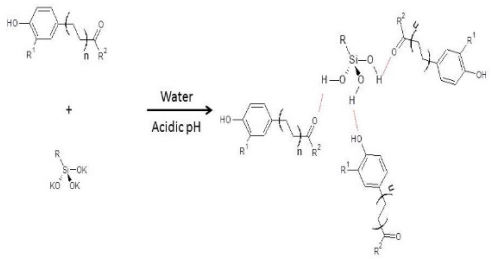

Figure 3: Schematic representation of stable complexes of Silicon synthesis, where n=0, 2; R=-OH or –CH3; R1=-H or –OCH3 and R2=-H or –CH3. Hydrogen bonds are represented in red.

Analysis concerning bioavailability and stability were carried out with complexes with 1-(4 hydroxyphenyl)-3-butanone as stabilizing agents (MMST-FB). MMST-FB shown a good bioavailability as 58% of the ingested dose was excreted in urine of healthy volunteers 4 hours after ingestion (dosage by ICP-MS). We have previously reported the bioavailability of another complex containing OSA and vanillin and the excreted dose was 21% [19]. The difference between the two complexes can be due to the donor inductive effect of the methyl group of MMST, stabilizing the hydrogen bonds. For OSA-VC (orthosilicic vanillin complex), intestinal transport was shown to occur via passive diffusion via the paracellular pathway through the intercellular tight junctions and accumulate intracellularly, probably by an uptake mechanism of facilitated diffusion [20]. The transport mechanism of MMST-FB must to be confirmed. MMST-FB exhibited a very good long-time stability. NMR analyses indeed highlighted the presence of the monomeric form of Silicon only, maintaining its very good bioavailability for months. Such kind of complexes was also shown to interact with lipid bilayers, because the phenolic moiety has greater affinity for specific lipid, leading to insertion into the bilayer and spatial segregation of lipids.

The very stable form MMST-FB can be used for cosmetic formulation. A creamy emulsion was formulated and this one, once applied in the human body, shown positive effects on skin, collagen, cellular ageing proving that this complex reveals all the power of Silicon.

In conclusion, we postulated that phenolic compounds can be used as stabilizing agent in order to develop stable and bioavailable forms of Silicon, either for organosiliceous compounds or for orthosilicic acid. The complexation process occurs via hydrogen bonding and avoids the polymerization of the Silicon molecule into less absorbable forms, giving all its potential to the element.

Conclusion

In this work, we postulated that phenolic compounds can be used as stabilizing agent in order to develop stable and bioavailable forms of

Silicon, either for organosiliceous compounds or for orthosilicic acid. We evidenced (by NMR analyses) that the complexation, via hydrogen bonding, between those compounds (OSA, MMST) and phenolic compounds (Frambinone, Vanillin) stabilizes the siliceous molecules, avoiding polymerization into less absorbable forms. Bioavailability of the complexes is also achieved, as well as their use in cosmetic formulations.

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