The Synthesis and Applied Research of Modified Quaternary Ammonium Salt and Tea Saponin

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Abstract: Tea saponin of functional ingredients extracted from camellia meal, is China's unique natural functional molecules. With silicone oil containing hydrogen and unsaturated polyether silicon hydrogenation reaction, and then esterification with tea saponin, and the tertiary amine hydrochloride reaction of tea saponin was modified organosilicon quaternary ammonium salt and its conversion rate reached 95%, 90% and 90%, respectively. Discussed the tea saponin in tea saponin modified silicone adjusting agent and quaternary ammonium salt content on the properties of shampoo, used in shampoo, optimum dosage of 0.1 to 0.4% (mass fraction). And tea saponin and quaternary ammonium salt content on the properties of shampoo, it turns out that when \( n (\text{tea}) : n (\text{quaternary ammonium salt}) = 2.5 \sim 3.5:1 \), regulate the best performance of shampoo.

Keywords: Tea saponin, Quaternary ammonium salt, Shampoo, Modified.

1. INTRODUCTION

China's tea seed yield the highest in the world, every year there are tens of thousands of tons of oil after the rest of the camellia meal, among them the content of tea saponin can be around 10% \cite{1}. Tea saponin is a good auxiliary agent or soluble powder pesticide, can improve the physical properties of the pesticide, improve liquid in biological or plant surface adhesion, a synergy of pesticides. Tea saponin can automatically degrade, non-toxic, it is in the process of separation, will not affect the performance of chemical pesticide, is advantageous to the pesticide storage. Have been extensively used in herbicide glyphosate, tea saponin on insecticidal double pesticides, especially on glyphosate, give full play to the good performance of glyphosate, to improve the adhesion and moisture absorption in plant, improve the penetration of liquids \cite{2, 3}, and because the good biological activity of tea saponin, also can improve the biological activity of glyphosate. Common tea saponin are shown in Fig. (1).

Tea Saponin belongs to the triterpene saponins, is a kind of high performance natural nonionic surfactant, it has strong foaming, emulsification, dispersion, wetting effect. Currently on the market a lot of tea saponin standard, no tea saponin standard can be purchased at home and abroad, the standard content of the sigma company and only 90% for content reached 99.99%, general laboratory homemade tea saponin concentration is higher. Heikki avoid on the image for biological technology co., LTD gives the production of tea saponin standard \cite{4} shown in Fig. (2).

![Common tea saponin](image)

**Fig. (1).** Common tea saponin.

With the improvement of people's living standard, especially for cosmetic products closely related to people's life of hair products demand is increasing day by day, shampoo is not just a clean hair, as well as nutrition and conditioning the hair, etc. This shampoo is required to use the raw material is update constantly, to improve the performance, as for shampoo conditioner, especially. The commonly used conditioner including quaternary ammonium salt and the gathering of all kinds of oils and fats, fatty alcohols, silicone emulsion, etc. Because of polysiloxane excellent flexibility, film forming, lubricity and inert and mild on the skin, the biology has been increasingly used in personal care products. And cationic organic silicon has electrostatic adsorption to the negatively charged hair, so...
Fig. (2). Tea saponin standard.

easy when shampoo was washed away by water, and give excellent carding to the hair and bright luster and certain hydrophilic antistatic, antimicrobial properties [5, 6]. Although cationic organic silicon has many advantages, but there is also insufficient. Natural tea saponin is made up of all kinds of tea seed, tea, camellia, camellia oil extracted from tea seed cake, after tea seed cake is also called ChaKu, tea seed residue. Our country for the first time in 1979 by industrial methods of tea saponin was isolated from defatted tea seed cake, put into production in 1980. At home and abroad the main methods of extracting tea saponin with water immersion method and organic solvent method and on the basis of this new method popularized.

Personal care product frother for anionic surfactants, cationic exists to a certain extent, inhibit the lasting stability of the bubbles and foam, this limits the use of it. Tea saponin is a kind of green natural surface active agent, has a good emulsification, foaming, dispersion, wetting, and multiple functions such as degreasing, gentle nature, its chemical solution is close to neutral, easily biodegradable. Tea saponin as shampoo, conditioner, strong foaming ability, has the characteristics of good wet comb and light [5], but there is no active group, so it is easy to be washed by water and no adsorption. Author will use strong hydrophilic foamabil is no active group, so it is easy to be washed by water and no

2. THE EXPERIMENT PART

2.1. Experimental Raw Material List in the Following Table

Using surface active role of tea saponin, can be used as a shampoo, detergent, hair dye, lotion, shampoo, wash manage

2.2. The Experimental Device

Laboratory device include temperature control heater, variable speed mixer and three flask of 1000 ml vacuum system; Pilot plant include the match devices, condenser vacuum system and temperature control of electric heating 500L enamel reaction kettle; Test instrument include roche foam, fiber friction coefficient.

2.3. Tea Saponin Synthesis Process of Modified Silicone Conditioner

2.3.1. The Preparation of Polyether Modified Silicone[1]

Silicone oil containing hydrogen addition reaction with unsaturated polyether, generate polyether modified silicone with epoxy groups and reaction equations as follows (chemical formula is too long, the branch):

\[
\begin{align*}
\text{CH}_3 + \text{CH}_2 & \rightarrow \text{CHCH}_2\text{OCH}_2\text{H} \quad \text{C} - \text{CH}_2 \\
\text{CH}_3 + \text{CH}_2 & \rightarrow \text{CHCH}_2\text{OCH}_2\text{H} \quad \text{C} - \text{CH}_2 \\
\text{CH}_3 + \text{CH}_2 & \rightarrow \text{CHCH}_2\text{OCH}_2\text{H} \quad \text{C} - \text{CH}_2 \\
\end{align*}
\]

2.3.2. Experimental Raw Material List in the Following Table

Using surface active role of tea saponin, can be used as a shampoo, detergent, hair dye, lotion, shampoo, wash manage
In the type (1), \( p + q = n \), \( m, n, p, q, r, s \) are integer greater than 1, in the type at the same time also must satisfy the following type (2):

\[
R^1 = C_3H_6O(C_2H_4O)_r(C_3H_6O)_s
\]

\[H, R^2 = C_3H_6O \quad HC \quad CH_2\]

Its operating process is: containing hydrogen silicone oil, unsaturated polyether, according to certain proportion to join her in three bottles, add 1 catalyst solution, oil bath heating to 120 ~ 160°C, the reaction of 3 ~ 6 h, when the reaction conversion rate is 95%, stop the reaction, into the next steps.

2.3.2. The Preparation of Tea Saponin Modified Organic Silicon

After purification of tea saponin with reaction, the reaction products under certain conditions, the epoxy groups on the organic silicon ring opening and hydroxyl combination of tea saponin on methylene. According to hydrogen silicone oil, the molecular weight of polyether and structure is different, can generate to meet the requirements of different tea saponin modified organic silicon special surfactant. Its operating process is: the epoxy polyether modified silicone with tea saponin according to certain proportion to join the three reaction in a bottle, water bath heating to 60 ~ 95°C, to join the catalyst, 2, 2 ~ 5 h reaction, determination of the epoxy value, meet the requirements of the epoxy value, stop the reaction.

2.3.3. Tea Saponin Silicone Quaternary Ammonium Reaction

Specific reaction conditions, tea saponin modified organic silicon and tertiary amine hydrochloride aqueous reaction, cationic tea saponin was modified organic silicon special surfactant. Its operating process is: in the second step of reactants to join pre-made good tertiary amine hydrochloride, stir heated to 60 ~ 90°C, constantly adjust their p H, 4 H reaction, determination of the epoxy value, when the reaction reached 95%, stop the reaction, light brown sticky substance.

2.3.4. Main Technical Performance of Products

Product appearance is brown to light brown paste, pH value is 6.0 ~ 8.5, no volatile 60% or higher. It meets the requirements.

2.4. Modified Organosilicon Quaternary Ammonium Salt on the Skin Irritation Test

2.4.1. Test Method

With reference to stimulate the spot test of GB-7919-87 the human body. The tea saponin of modified organosilicon quaternary ammonium salt as quality score 1. 5% aqueous solution; Will be 0. 2 ml solution drops in 2 cm * 2 cm above the size of four layer of gauze, and then apply on the subjects of forearm flexor side skin, covered with cellophane, with no stimulation tape, will apply the paste material removed after 24 h, to observe the skin reactions.

2.4.2. Test Results

By Hunan daily chemical product quality supervision, inspection and authorized test stand, the tea saponin of modified organosilicon quaternary ammonium salt for skin reaction, for the weak of the trigger, the weaker its stimulus to human skin.

3. THE PREPARATION AND EVALUATION OF SHAMPOO

3.1. The Basic Formulation and Preparation Method of Shampoo

There are many different kinds of shampoo on the market, the basic formula of general of shampoo on the market such as shown in Table 2.

The cationic resin in deionized water melon, ears, stir until completely; In turn, adding suitable amount of citric acid; The CAB; AESA, K12 A, heating to 70 ~ 75°C, stir to dissolve; Join the pearl double ester, 6501, 30 min insulation; Cooled to 50°C, join the tea saponin modified silicon conditioner, silicone oil emulsion, antipruritic, essence, stir well after discharge.
3.2. Discuss

3.2.1. Tea Saponin Content on the Influence of the Shampoo

The tea saponin, a conditioner, strong foaming ability, and has the characteristics of good wet hair and bright. Tea saponin of modified organosilicon quaternary ammonium salt in the conditioner in addition to regulate performance, but also adsorption to the hair, the higher the amount of quaternary ammonium salt, the more adsorption in the hair, its flexibility, film-forming property and lubricity, the better. But at the same time there is a cumulative effect, and make the rough hair harden, and foam stability decreased, shampoo shampoo consistency. So, in the design and multiple factors to consider when choosing a molecular structure, choose the content of a reasonable range. Strong hydrophilic foamability of tea saponin with hydrophobic organic silicon soft foam suppression by chemical bonding, by adjusting the molar ratio of the two, make the products have good comb wet performance, and have better performance of the bubble. Tea saponin and quaternary ammonium salt mole ratio on the shampoo performance are shown in Table 3 below.

3.2.2. Compared with Domestic Famous Brand of Shampoo

Use tea saponin on modified silicone conditioner is compared with the domestic famous brand of shampoo, such as Table 4.

3.2.3. Shampoo Rational Evaluation

Shampoo of the rational, generally includes hair of dry, wet, skirts, slide may just as well, soft degree and the luster, etc. Hair comb performance refers to the ease of comb with the comb the hair. Here the author adopted the fiber friction

Table 2. Shampoo formula.

<table>
<thead>
<tr>
<th>Component</th>
<th>The Mass Fraction (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AESA</td>
<td>11.0</td>
</tr>
<tr>
<td>Group of tea saponin silicon conditioner</td>
<td>0.1-0.4</td>
</tr>
<tr>
<td>K_{12 A}</td>
<td>10.0</td>
</tr>
<tr>
<td>Silicone oil emulsion</td>
<td>1-1.5</td>
</tr>
<tr>
<td>6501</td>
<td>2.0</td>
</tr>
<tr>
<td>Antipruritic</td>
<td>0.5</td>
</tr>
<tr>
<td>CAB-30</td>
<td>5.0</td>
</tr>
<tr>
<td>Pearl double ester</td>
<td>1.5</td>
</tr>
<tr>
<td>Cationic melon ear glue</td>
<td>0.25—0.3</td>
</tr>
<tr>
<td>Essence</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>Citric acid</td>
<td>Moderate amount</td>
</tr>
<tr>
<td>Deionized water</td>
<td>Add to 100</td>
</tr>
</tbody>
</table>

Table 3. Tea saponin and quaternary ammonium salt mole ratio on the influence of the shampoo.

<table>
<thead>
<tr>
<th>T</th>
<th>Since the Match Makings</th>
<th>Shampoo a</th>
<th>Shampoo b</th>
<th>Shampoo c</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (tea saponin): n (quaternary ammonium salt)</td>
<td>0</td>
<td>1.5:1</td>
<td>2.5:1</td>
<td>3.5:1</td>
</tr>
<tr>
<td>Dry friction coefficient</td>
<td>0.21</td>
<td>0.14</td>
<td>0.13</td>
<td>0.14</td>
</tr>
<tr>
<td>Wet friction coefficient</td>
<td>0.22</td>
<td>0.17</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>Luster</td>
<td>general</td>
<td>good</td>
<td>very good</td>
<td>very good</td>
</tr>
<tr>
<td>5 min amount of bubbles (mm)</td>
<td>142</td>
<td>140</td>
<td>145</td>
<td>146</td>
</tr>
</tbody>
</table>

Note: Tea saponin content of modified organosilicon quaternary ammonium salt in shampoo for 0.25%.
Table 4. Shampoo performance comparison.

<table>
<thead>
<tr>
<th>Project</th>
<th>Homemade Shampoo 1</th>
<th>Homemade Shampoo 2</th>
<th>1 # Domestic Famous Brand of Shampoo</th>
<th>2 # Domestic Famous Brand of Shampoo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry friction coefficient</td>
<td>0.13</td>
<td>0.14</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>Wet friction coefficient</td>
<td>0.16</td>
<td>0.18</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td>Luster</td>
<td>Very good</td>
<td>good</td>
<td>good</td>
<td>good</td>
</tr>
<tr>
<td>Bubbles (mm)</td>
<td>142</td>
<td>110</td>
<td>145</td>
<td>140</td>
</tr>
</tbody>
</table>

Note: Homemade shampoo joined the 0.1 to 3% of tea saponin modified silicone shampoo; the 2# mixed shampoo joined the 0.3% of organosilicon quaternary ammonium salt of shampoo.

CONCLUSION

This is the first tea saponin and organic silicon through chemical bond, the preparation of a new type of cationic surface active agent, used in shampoo, it turns out that when n (tea saponin): n (quaternary ammonium salt) = 2.5 ~ 3.5:1, regulate the best performance of shampoo, can significantly enhance the hair dry, wet comb performance [11-19]; Have certain antibacterial itching; Relatively general of organosilicon quaternary ammonium salt, the bubble is exquisite and rich and has good moisturizing performance, with shampoo 1 its good performance in organic silicon quaternary ammonium salt [9], with the domestic famous brand of shampoo [10].

REFERENCES


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