Dynamic Temporal Sensory Transition during Skin Application of Oligosaccharides: Correlation Analysis between Sensation and Physical Properties

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When aqueous solutions of five oligosaccharides and one polyol compound were applied to the skin, tactile intensity and temporal changes, as defined by five Japanese onomatopoeic words, were observed. Moreover, the relationships between the sensations and the physical and chemical properties were investigated.

No difference in the tactile characteristics was observed among the samples during application; however, there was a difference in the characteristics among samples in the sensations of “beta-beta (sticky)”, “gishi-gishi (squeaky)”, and “sara-sara (smooth)” after application. In terms of temporal changes, the sensations of oligosaccharides were first described as “nuru-nuru (slimy)”, which then changed to “gishi-gishi (squeaky)” and later to “beta-beta (sticky)”, “shittori (moist)”, and “sara-sara (smooth)”. Among the samples, a difference was observed in the timing of feeling “beta-beta (sticky)”, “shittori (moist)”, and “sara-sara (smooth)”. The correlation between the “beta-beta (sticky)” feeling, which is a contextually undesirable quality of oligosaccharides, and the physical and chemical properties was determined. A high correlation was observed among adhesiveness, integral value of the application force for the final 20 s of application, and solubility. It was considered that the sticky oligosaccharides have these physical properties that were highly correlated described above.

Key Words: Oligosaccharides / Sensory evaluation / Temporal change / Stickiness / Skin application

1. INTRODUCTION

Saccharide products are typically added to cosmetics for the moisturizing effect and water retention; however, stickiness while drying is an issue in the formulation 1. However, an index to objectively evaluate the tactile sensation caused by saccharides, including “stickiness”, has not been determined. Therefore, in this study, we attempted to differentiate and quantify the tactile characteristics of each saccharide by sensory evaluation, by studying the temporal changes when saccharides were applied to the skin and by examining the relationship between these sensations and the physical properties. The understanding of the mechanism responsible for the tactile sensations will facilitate the development of formulations that suppress the stickiness of saccharides.

The experiments were conducted by using five types of oligosaccharides (sorbitol, glucose, maltose, maltotriose, and trehalose) and 1,3-butandiol, a non-saccharide polyol compound, as a comparative control.

2. EXPERIMENTAL

2.1 Samples

Cosmetic-grade 1,3-butandiol (1,3-BD) was obtained from Daicel Corp. Sorbitol (Sor), glucose (G1) and maltose (G2) were obtained from Fujifilm Wako Pure Chemical Corp. Trehalose (Tre) and maltotriose (G3), which are used in cosmetics and as research reagents, respectively, were prepared by Hayashibara Co., Ltd.

G1 is a monosaccharide represented by the molecular formula C₆H₁₂O₆. G2 and Tre are disaccharides in which two glucose molecules are bonded to α (1 → 4) and α (1 → 1), respectively. G3 is a trisaccharide in which three glucose molecules are bonded to α (1 → 4). Sor is a sugar alcohol obtained by reducing glucose. 1,3-BD is a polyol compound represented by the molecular formula HOCH₂CH₂CH(OH)CH₃.
For experiments, aqueous solutions of 10-70 wt% was used. Purified water was used to prepare the aqueous solutions.

2.2 Physical property measurements

Viscosity\(^2\), adhesiveness\(^3,4\), and application force log using a six-axis force sensor were measured. These properties were considered to be related to the tactile sensation of “stickiness while drying” of saccharides.

2.2.1 Viscosity

Using a rotary rheometer (MCR102; Anton Paar GmbH) and a cone plate (CP-50; 50 mm diameter), the viscosity of each sample (40 wt% solution) was measured at 25 °C and a rotation rate of 100 rpm.

2.2.2 Adhesiveness

A rheometer (CR-500DX-SII; Sun Scientific Co., Ltd.) and a Teflon plate jig (No. 3; 10 mm thickness and 20 mm diameter) were used. An artificial leather piece of 30 mm × 30 mm (Protein leather™ PBZ, Ideatex Japan Co., Ltd.) was fixed to the sample holder, and after dropping 30 µL of the sample (40 wt% solution) onto the center of the artificial leather, the sample holder was raised at a rate of 30 mm/min. After contact with the Teflon plate jig, once the pressure of 2 N was detected, the rise of the sample holder was stopped. The sample holder was lowered at a rate of 30 mm/min after 60 s, and the stress applied to the jig was measured at a sampling rate of 10 ms\(^{-1}\).

The relationship between the movement distance of the sample holder (x) and the test force (y) at the time of lowering was plotted, and the area (integral value) of the test force portion showing a negative value was considered as the adhesiveness value.

2.2.3 Application force log analysis

An acrylic plate was fixed to the upper surface of a six-axis force sensor (SFS055F100M0R5U6; Leptorino Inc.)\(^5\), and 2.5 cm × 5.0 cm artificial leather (Protein leather™ PBZ) was fixed to its upper surface. A total of 10 µL of the sample (20 wt% solution) was dropped onto the artificial leather; the sample was applied until dry by moving the finger left and right at a constant speed (two reciprocations per second). At a sampling rate of 10 ms\(^{-1}\) and impulse response of 100 Hz, the changes in application force in the lateral direction Fx and application force in the vertical direction Fz were measured.

The integral of the absolute values of Fx and Fz for 20 s after the start of application and 20 s before the end of application of each sample (hereinafter abbreviated as \(\int Fx\)-start, \(\int Fx\)-end, \(\int Fz\)-start, and \(\int Fz\)-end) were obtained (Fig. 1).

2.3 Sensory test

The procedure for the sensory test was based on the method used by Akiyama et al.\(^6\)–\(^8\).

2.3.1 Selection of sensory panel

Panel selection was conducted by single-blind study. A total of 10 µL aliquot of Sor aqueous solution or G3 aqueous solution (10, 20, 30, 40, 50, 60 or 70 wt%) was dropped onto the artificial leather (Protein leather™ PBZ), and a questionnaire was submitted regarding the tactile sensation when smeared with the finger. From 33 Hayashibara employee volunteers, eight participants (two men and six women) who were highly sensitive to “slimy” and “sticky” were selected as the sensory test panel.

2.3.2 Selection and definition of onomatopoeic terms\(^9\)

The selection of onomatopoeic terms that express the tactile sensations was conducted by double-blind study. The selected sensory test panel (section 2.3.1) was asked to apply a 20 wt% sample solution (1,3-BD, Sor, G1, G2, G3, or Tre) to their forearms and openly discuss the terms related to the tactile sensations. As a result, five Japanese onomatopoeic terms were selected and their definitions were made known to the sensory test panel (Table I).

2.3.3 Temporal sensory evaluation

After washing the forearm with soap, the panel was acclimatized to an environment of 22 ± 1 °C, 50 ± 10 % RH for more than 15 min. A total of 20 µL each of the sample and purified water were dropped from a position 7 cm and 10 cm from the wrist, respectively. The sample and purified water were simultaneously applied to an area of 3-7 cm\(^2\) by using with a metronome (80 beats/min).
When the sample began to feel different from that of purified water, the panel was asked to report it verbally in the above-mentioned terms, and time when the sensation started was recorded. The water application end time and sample application end time were also recorded.

Immediately after the end of sample application, the strength of each tactile sensation during application was evaluated on a 5-point scale by the semantic differential method. Three minutes after the end of sample application, the strength of each tactile sensation after application was evaluated in the same manner. If there was a sensation that was not reported during the application but became apparent after the application, the time was recorded.

The sensory evaluation was a double-blind study and the evaluation of two samples was carried out on the medial side of the left and right forearms for every test. In order to evaluate six samples, the tests were performed three times per person at intervals of 4 days or more.

### 2.3.4 Tactile strength analysis

The strength of tactile sensations during application and the strength of tactile sensations after application for each sample were aggregated to obtain the average values. The Kruskal-Wallis test and the Steel-Dwass’s multiple comparison test were carried out to detect significant differences among the samples.

#### 2.3.5 Temporal change analysis of tactile sensations

Because the application time differed among individual participants, the relative appearance time of each tactile sensation was calculated by considering the end of water application as 1.0. The relationship between the relative time \(x\) and the cumulative number of participants who perceived the tactile sensation \(y\) was plotted in a graph at intervals of 0.25 relative time.

### 3. RESULTS

#### 3.1 Physical and chemical properties

As physical properties that are likely to be related to stickiness while drying, viscosity, adhesiveness, and application force log integral values (refer 2.2.3, \(\int F_x-\text{start}, \int F_x-\text{end}, \int F_z-\text{start}, \int F_z-\text{end}\)) of six samples were measured (Table II).

The viscosity and adhesiveness were measured at 40 wt% because no difference was observed among the samples at 20 wt% concentration (data not shown). The application force log integral values were measured at 20 wt%. Molecular weight, solubility, and number of intramolecular OH groups were also annexed to facilitate the association with the molecular structure.

| Sample | Water/\(\int F_x-\text{BD}\) | Sor | G1 | G2 | G3 | Tsc |
|---|---|---|---|---|---|---|
| Viscosity (mPa·s), 40 wt% soln. \(n=3\) | mean 86 | 410 | 430 | 450 | 480 | 610 | 450 |
| SEM | 0.20 | 0.010 | 0.010 | 0.33 | 0.33 | 0.33 | 0.010 |
| Adhesiveness (mN·mm), 40 wt% soln. \(n=3\) | mean 58 | 85 | 120 | 100 | 110 | 120 | 100 |
| SEM | 28 | 29 | 50 | 10 | 41 | 69 | 61 |

#### Integral value of the application force \((N\cdot\text{sec})\), 20 wt% soln. \(n=3\)

| \(\int F_x-\text{start}\) | mean 11 | 8.5 | 12 | 14 | 16 | 12 | 14 |
| SEM | 1.0 | 0.54 | 0.69 | 0.80 | 1.1 | 0.45 | 0.31 |
| \(\int F_x-\text{end}\) | mean 28 | 26 | 61 | 68 | 78 | 61 | 37 |
| SEM | 0.94 | 0.16 | 7.1 | 9.3 | 10 | 6.1 | 1.0 |
| \(\int F_z-\text{start}\) | mean 6.1 | 6.2 | 5.6 | 8.7 | 11 | 7.9 | 6.9 |
| SEM | 0.56 | 0.27 | 0.31 | 0.34 | 3.3 | 0.32 | 0.20 |
| \(\int F_z-\text{end}\) | mean 14 | 20 | 26 | 30 | 26 | 24 | 23 |
| SEM | 0.19 | 1.7 | 5.9 | 4.3 | 2.1 | 0.84 | 0.68 |

#### Chemical Properties

| Molecular weight | 18 | 90 | 182 | 180 | 360 | 504 | 378 |
| No. of OH group | 1 | 2 | 6 | 5 | 8 | 11 | 8 |
| Solubility (wt%) | * | * | 70 | 47 | 51 | 70 | 40 |
3.2 Comparison of tactile sensation strength

Figure 2 shows the sensory scores for the sensations of each sample during and after 3 min of application. No significant difference was observed among the samples during application for any tactile sensation. In contrast, after application for 3 min, significant differences and trends were observed in the four categories “gishi-gishi (squeaky)”, “beta-beta (sticky)”, “shittori (moist)”, and “sara-sara (smooth)”. From these results, it was concluded that there is no significant degree of difference among the samples with respect to the tactile sensations during application, but there is a clear difference after application.

3.3 Temporal change analysis

In order to correct for differences in test dates and between individuals, the temporal changes of the tactile sensations were analyzed, considering the end of water application as 1.0. As shown in Table III, the application end times of the samples were 1.11 – 1.25 relative time, and the evaluations 3 min after application were 2.83 – 3.02 relative time. Table III also summarizes the mean relative time at which each tactile sensation appeared, as a guide for comparing the sensory changes between the samples.

The cumulative numbers of participants who reported each tactile sensation every 0.25 relative time are plotted in Fig. 3 (Refer to Fig. 3A for the application evaluation scheme).

Table III

| Sample          | 1,3-BD | Sor | G1 | G2 | G3 | Tre |
|-----------------|--------|-----|----|----|----|-----|
| nuru-nuru (slimy) | mean   | 0.15 | 0.32 | 0.29 | 0.40 | 0.27 | 0.31 |
|                 | SEM    | 0.046 | 0.11 | 0.084 | 0.15 | 0.070 | 0.12 |
|                 | n      | 8     | 8   | 7   | 8   | 8    |     |
| gishi-gishi (squeaky) | mean | * 0.65 | 0.57 | 0.52 | 0.59 | *     |
|                 | SEM    | *     | 0.57 | 0.52 | 0.59 | *     |
|                 | n      | 2     | 6   | 8   | 8   | 8    |     |
| beta-beta (sticky) | mean   | 1.9   | 0.74 | 1.6 | 1.6 | 1.2 | 1.7 |
|                 | SEM    | 0.44  | 0.16 | 0.53 | 0.42 | 0.32 | 0.44 |
|                 | n      | 6     | 7   | 7   | 8   | 6    | 7    |
| shittori (moist) | mean   | 1.4   | 1.3  | 1.3 | 1.6 | 1.7 | 1.1 |
|                 | SEM    | 0.40  | 0.26 | 0.33 | 0.47 | 0.44 | 0.21 |
|                 | n      | 8     | 7   | 6   | 5   | 7    |     |
| sara-sara (smooth) | mean | * 0.061 | 0.031 | 0.069 | 0.063 | 0.025 | 0.049 |
|                 | SEM    | *     | 0.031 | 0.069 | 0.063 | 0.025 | 0.049 |
|                 | n      | 1     | 2   | 1   | 2   | 2    | 7    |

3 min after application

4. DISCUSSION

4.1 Relationships between strength of each tactile sensation and temporal change

Immediately after the application of any sample, “nuru-nuru (slimy)” (Fig. 3A) was reported first. Additionally, this sensation was reported during the application of every sample, but was not reported after application. “Nuru-nuru (slimy)” was thought to indicate that the participants felt a slightly higher viscosity and slipperiness than water. Even for the strength of sensation, no difference was observed among the samples from the start of application and after application.

Only two participants reported “gishi-gishi (squeaky)” (Fig. 3B) in 1,3-BD; however, this sensation was reported after “nuru-nuru (slimy)” and before “beta-beta (sticky)” by four to eight participants for other samples. There were also participants who newly reported it in the evaluation 3 min after application for Sor, G1, G2, and G3. Before the test, it was assumed that the sensation would change to “beta-beta (sticky)” after feeling “nuru-nuru (slimy)”; however, for the oligosaccharides, the panel reported the sensation as “gishi-gishi (squeaky)”. This tactile sensation is considered to be the representation of vibration caused by the stick-slip phenomenon and a feeling of resistance when rubbing skin. Negligible differences in the strength and temporal change of this sensation during application were observed among the saccharides. Among the saccharides, for “gishi-gishi (squeaky)”, the difference in the sensation strength and the increase in the number of participants who reported it after the application.

Fig. 2 Tactile sensation strength score. The mean sensory scores ± SEM (n = 8) for the sensations of each sample during (A) and after 3 min (B) of application are shown. *p < 0.05, **p < 0.1 (Kruskal-Wallis test). *p < 0.05, **p < 0.1 (Steel-Dwass’s multiple comparison test)
The frequency of reports for “beta-beta (sticky)” (Fig. 3C) was concentrated after “nuru-nuru (slimy)” and “gishi-gishi (squeaky)” and when dry. In contrast to “nuru-nuru (slimy)” and “gishi-gishi (squeaky)”, each sample has its own characteristics. G2 and G3 showed a sharp rise in the number of participants reporting this sensation when dry, while 1,3-BD, Sor, G1, and Tre rose moderately. It is thought that the differences in physical properties among the samples became noticeable as they became concentrated on the skin surface by application.

For the “shittori (moist)” sensation (Fig. 3D), there is a difference among the samples in how quickly it was reported. Focusing on the time at which the reported participants reached 50%, 1,3-BD was the fastest and G3 was the slowest. The earlier it was reported, the higher the sensory score after application, thereby showing a correlation between the two.

Reporting of the “sara-sara (smooth)” sensation (Fig. 3E) was observed in the evaluation after the end of application of Tre, and the appearance rate for the other samples was low. Only Tre had a higher sensory score than the other samples.

Although many studies have conducted the sensory evaluation for evaluating “tactile strength”\(^{10-12}\), evaluation of the temporal change has not been widely reported. In 2019, Nakano \textit{et al.} presented a method for temporal change evaluation by using an eye tracker\(^{13}\). Through the use of oral data sampling, we were able to track the temporal changes of five types of tactile sensations. By tracking temporal changes, it was found that a transient “gishi-gishi (squeaky)” tactile sensation appears during the application of oligosaccharides.

### 4.2 Correlation analysis between sensory evaluation and physical and chemical properties

To elucidate the stickiness mechanism of oligosaccharides, correlation analysis was performed between the strength score of “beta-beta (sticky)”, the mean relative time at which it was reported, and the various physical and chemical properties discussed in section 3.1. The results are presented in Table IV. If the absolute value of the correlation coefficient is 0.7 or more, it is judged to be correlated.

| Viscosity | Adhesiveness | Integral value of the application force | Chemical Properties |
|-----------|--------------|----------------------------------------|---------------------|
| 0.65      | 0.94         | 0.85                                   | 0.73                |
| 0.27      | 0.57         | 0.97                                   | 0.30                |
| -0.26     | -0.77        | -0.46                                  | -0.38               |
| 0.94      | -0.77        | 0.85                                   | -0.38               |
| 0.57      | 0.73         | 0.30                                   | -0.38               |
| -0.26     | -0.77        | -0.46                                  | -0.38               |
| 0.65      | 0.57         | 0.97                                   | 0.73                |
| 0.27      | 0.30         | 0.30                                   | -0.38               |
| -0.26     | -0.77        | -0.46                                  | -0.38               |

Fig. 3 Temporal change of each tactile sensation. (cumulative number of participants per 0.25 relative time is shown). *Relative time: relative time of appearance of each tactile sensation when the end time of water application was taken as 1.0.
A positive correlation was found between the “beta-beta (sticky)” sensory score during application and adhesiveness, $\int F_{x\text{-end}}$, number of intramolecular OH groups, and solubility. In addition, a positive correlation was found between the “beta-beta (sticky)” sensory score 3 min after application and $\int F_{x\text{-end}}$, $\int F_{z\text{-start}}$, and $\int F_{z\text{-end}}$. In contrast, a negative correlation was found between the mean relative time at which “beta-beta (sticky)” was reported in the temporal change analysis and the adhesiveness and solubility.

No physical property values were found to have high correlation with the three sensory evaluations of sensation strength during and after application and the appearance time for tactile sensation. However, adhesiveness, $\int F_{x\text{-end}}$, and solubility were found to be highly correlated with two of the sensory evaluations.

From this correlation analysis, it was observed that the samples that exhibited strong stickiness early during application tend to have high adhesion and high solubility, and those which exhibited strong stickiness during and after application tend to have high $\int F_{x\text{-end}}$. In addition, it was considered that a substance that requires a higher force to move the finger before the end of application is more likely to feel sticky.

In this study, we mainly considered the stickiness and physical characteristics of oligosaccharides. However, for example, the different texture between G2 and Tre, both of which are composed of two glucose molecules, could not be elucidated. We would like to analyze the correlation between physical properties and texture other than stickiness.

5. CONCLUSIONS

In order to analyze the stickiness of saccharides, temporal sensory evaluations were performed for five types of oligosaccharides (Sor, G1, G2, G3 and Tre) and polyol 1,3-BD when applied to the skin. And the relationships between the sensations and the physical and chemical properties were investigated. It was found that the oligosaccharides first typically felt “nuru-nuru (slimy)”, then “gishi-gishi (squeaky)”, and later “beta-beta (sticky)”, “shittori (moist)”, and “sara-sara (smooth)”. There was a small difference in the timing of feeling “nuru-nuru (slimy)” and “gishi-gishi (squeaky)” among the samples; however, for “beta-beta(sticky)”, “shittori (moist)”, and “sara-sara (smooth)”, the characteristics of each sample were differentiated in terms of the strength and timing of the sensation. In addition, it was found that the physical properties associated with stickiness included adhesiveness, $\int F_{x\text{-end}}$, and solubility.

From these results, it was considered that the stickiness of saccharides can be partially predicted by measuring their physical and chemical properties, before the sensory evaluation. It was also considered that this method could be applied to develop the formulation that suppress the stickiness of saccharides.

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