FOAMING COMPONENTS IN RAW CANE SUGARS

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ABSTRACT

Sugar solutions foam remarkably in purification process of the refinery when some raw cane sugars are melted, resulting in difficulty in operation. Some Formosan, Australian and domestic raw sugars had a high foamability, regardless of their polarization levels.

An attempt has been made to identify the components mainly responsible for the foaming observed in some raws. The main component was found to be one of steroid saponins. Its sapogenin had an unsaturated sterol ring and sugars consisting of glucose, xylose, rhamnose, arabinose and unidentified sugar.

INTRODUCTION

In recent years, cane sugar refiners have experienced the remarkable foaming of sugar solutions in melting, carbonatation and crop boiling stations when some raw cane sugars are being processed resulting in sugar loss and difficulty in instrumental operation.

Much work on foam in the sugar industry has been directed towards identifying the foaming substances present in beet sugars and sugar beet. They have been found to be saponin (Sigel) and peptides (Oldfield and Dutton). However, no one has dealt with the components of raw cane sugar capable of causing foam.

This paper describes the test procedure for foaming power, the comparison of foamability of raw cane sugars from different origins, the separation procedure for foaming substances, and the identification of foaming substances.

MATERIALS AND METHODS

Procedure of Foaming Test

Raw cane sugar solution was poured into a column in the apparatus shown in Fig. 1. After bubbling with nitrogen gas for one minute, the height of foam was measured at one minute interval. The height of foam at the moment the nitrogen
gas current is stopped was taken as 100 and reduction ratio in foam height was calculated.

**Removal of Foaming Substances**

1) Centrifuging: Suspended matter in 60° Bx sugar solution was removed by centrifuging at 18,000 rpm for 30 minutes at room temperatures.

2) Dry lead: One percent of dry lead on sugar was added to 60°Bx sugar solution. The precipitate formed was removed by centrifuging.

3) Powdered active carbon: Powdered active carbon ZnCl₂ activated, Shirasagi, Takeda Chemicals K.K.) was added to 60°Bx sugar solution and then heated at 60°C for one hour. The resulting solution was centrifuged and adjusted to 60°Bx.

4) Ethanol: Ethanol was added to 60% sugar solution to give a 70% ethanol concentration. The solution was allowed to stand overnight in a refrigerator and centrifuged. The supernatant was concentrated under vacuum to remove ethanol and adjusted to 60°Bx.

**Separation and identification of foaming substances**

1) Determination of nitrogen compounds in the ethanol precipitate: Ethanol was added to a 60°Bx solution of raw sugars to give a 70% ethanol concentration. After cooling in a refrigerator overnight, the treated solution was centrifuged. The precipitate was dissolved in a small volume of water, and poured into digestion flask with K₂SO₄ catalyst and sulfuric acid. After heating, nitrogen compounds in the precipitate was determined by the Micro-Kjeldahl method.

2) Absorption and separation of foaming substances with active carbon: Six kilograms of raw sugar (Japanese raw sugar No. 2) was dissolved in 4 liters of water. Three hundred grams of active carbon was added to the sugar solution, and stirred for 4 hrs. at room temperature. After stirring, 100g of kieselguhr was added and filtered. The active carbon was extracted with 93% ethanol as shown in Fig. 8.

3) Hydrolysis of ethanol extract: Eleven milliliters of 2N-HCl-50%-ethanol solution was added to 113 mg of the above ethanol extract and hydrolyzed in boiling water for 2 hrs. After adding water, the hydrolyzed solution was allowed to stand overnight. The precipitate was collected by filtration, and extracted with hot chloroform-methanol (1:1). The extract was concentrated under vacuum to dryness. Yield: 24.7 mg - (3) - a. The filtrate was neutralized with Dowex-2 (OH-ion type) ion exchange resin and concentrated under vacuum to dryness. Yield: 14.4 mg. - (3) - b.

4) Florisil column chromatography of (3)-a which was extracted with ben-
zene. The residue was dissolved in ethanol. The benzene solution was poured on Florisil column (1 x 10cm) and eluted with 200 ml of benzene. After eluting with benzene, the above ethanol solution was poured on the Florisil column. The Florisil column was eluted successively with 200 ml each of 5%, 10%, 20% chloroform-benzene, 20% ethanol-benzene and ethanol. Each fraction was concentrated and dried under vacuum.

5) Thin-layer chromatography: The eluates of Florisil column chromatography were analyzed by thin-layer chromatography, under the following condi-
tions: Developer; CH\textsubscript{3}-EtOH(95:5), Detecting agent: SbC\textsubscript{13} reagent, TLC plate; Spotfilm-silica gel (Tokyo Kasei Kogyo K.K.) 20 x 20 cm. (3)-b was dissolved in a small volume of water, and subjected to thin layer chromatography for sugar, under the following conditions. Developer; n-BtOH-Pyridine-Water (6 : 4 : 3), Detecting agent: AgNO\textsubscript{3}-NaOH reagent, TLC plate; Spotfilm-cellulose (Tokyo Kasei Kogyo K.K.) 20 x 20 cm. TLC plate of (3)-b was developed three times.

6) Gas-liquid chromatography: (3)-b was dried by azeotropic distillation with alcohol, and freeze-dried. Its gas liquid chromatogram was taken according to the method of Miki et al\textsuperscript{3}.

7) Infrared spectra: The IR spectra were taken in a KBr tablet by a Hitachi Model EPI-2S infrared spectrophotometer.

RESULTS AND DISCUSSIONS

Condition of Foaming Test

The principle of foaming test adopted is to generate foams and measure their stability. The data obtained are expressed in terms of the breaking rate of foams. First run was made only for wetting the inner wall of a column, and an average of five values were obtained from second to sixth runs.

Fig. 2 shows relationship between the temperature of sample solution and breaking rate of foams. With increased temperature, the breaking rate of foam decreased to an adequate level. Since the sample solution, however, was concentrated in a test column at 70\degree C, 60\degree C was adopted in the following experiment.

![Figure 2. Relation between stability of foam and temperature of sugar solution](image_url)
FIGURE 3. Relation between stability of foam and sugar concentration

FIGURE 4. Foamability of raw sugars
With decrease in the concentration of sample solution, the breaking rate of foams increased as shown in Fig. 3. In this study, 60°Bx was adopted as a standard concentration.

**Foamability of Raw Cane Sugars**

Twelve raw cane sugars from Thailand, Philippines, Australia, Formosa made in 1978 and domestic made in 1976 and 1978 were tested and compared with granulated sugar. Of the 12 raws, 8 raws had a considerably high foamability as experienced in sugar refinery. Thailand and Philippine raws which contained a large amount of impurities, had no foamability, while the raws having good quality had a high foaming power as shown in Fig. 4.

![Graph showing foamability comparison](image)

**FIGURE 4.** Removal of foaming substances

**Removal of Foaming Substances Present in Raw Cane Sugars**

In relation to the separation of foaming substances, the authors tried to confirm whether foaming substances in raw sugar solution could be removed by a simple physical or chemical treatment. The results obtained were as follows:

1) After centrifuging suspended matter in sugar solution, the resulting solution had still high foaming power as shown in Fig. 5.
2) No foaming substances could be removed by the dry lead treatment as shown in Fig. 5.

3) The alcohol treatment was found to be effective, that is, with increasing the concentration of alcohol, the foaming power became lower as shown in Fig. 6.

4) Fig. 5 also shows that the foaming substances could be removed completely by the treatment with active carbon. The optimum dosage of active carbon was 0.83% on sugar as shown in Fig. 7.

From the above results, the foaming substances were considered to be water soluble compounds having a relatively high molecular weight.
Nitrogen Compounds in Alcohol Precipitates from Raw Sugar

Since some peptides have been well known to be one of natural foaming substances and the alcohol treatment was found to be effective for decreasing the foaming power of raw sugars as shown in Fig. 6, the nitrogen compounds in the alcohol precipitates from raw sugars were determined quantitatively. Table 1 shows that there was no relationship between the above quantity and the foamability of raw sugars, that is, Thailand and Philippine raws which contained a large amount of nitrogen compounds in their alcohol precipitates had no foamability.

<table>
<thead>
<tr>
<th>Raw Sugar</th>
<th>Nitrogen compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan No.</td>
<td></td>
</tr>
<tr>
<td>1 ('76)</td>
<td>26.6 ppm</td>
</tr>
<tr>
<td>2 ('78)</td>
<td>26.6</td>
</tr>
<tr>
<td>3 (&quot;&quot;&quot;)</td>
<td>30.2</td>
</tr>
<tr>
<td>4 (&quot;&quot;&quot;)</td>
<td>16.0</td>
</tr>
<tr>
<td>5 (&quot;&quot;&quot;)</td>
<td>28.0</td>
</tr>
<tr>
<td>6 (&quot;&quot;&quot;)</td>
<td>22.4</td>
</tr>
<tr>
<td>7 (&quot;&quot;&quot;)</td>
<td>42.8</td>
</tr>
<tr>
<td>8 (&quot;&quot;&quot;)</td>
<td>66.6</td>
</tr>
<tr>
<td>Formosa</td>
<td>56.0</td>
</tr>
<tr>
<td>Australia</td>
<td>36.4</td>
</tr>
<tr>
<td>Philippines</td>
<td>60.2</td>
</tr>
<tr>
<td>Thailand</td>
<td>42.0</td>
</tr>
</tbody>
</table>

Separation and identification of Adsorbates by Active Carbon

Raw sugar solutions was treated with active carbon and the absorbed substances were extracted with hot 93% ethanol. This extract was responsible for foaming, while the extract with sodium hydroxide solution according to the procedure shown in Fig. 8 was slightly soluble in water and had no foaming power.
60B x raw sugar solution

Active carbon

Filtration
Add active carbon
Washing with water
Extraction with 93% EtOH

Active carbon
Extraction with 1% NaOH
NaOH solution
Neutralization with HCl
Precipitate

EtOH solution on
Add water
Saturation with NaCl
Extraction with n-BtOH
Dehydration with Na₂SO₄
Concentration
Add acetone
Precipitate

FIGURE 8. Separation of foaming compound

Infrared Spectrum of Ethanol Extract

The IR spectrum of acetone precipitates obtained from the ethanol extract according to the procedure shown in Fig. 8 was similar to that of an authentic specimen of saponin as shown in Fig. 8.

FIGURE 9. IR spectra of ethanol extract and authentic saponin.
Chloroform-Methanol Extract from Acid Hydrolysate of Ethanol Extract

The acid hydrolysate (3)-a of ethanol extract was extracted with a mixture of chloroform-methanol. The resulting extract was fractionated by chromatography on a column of Florisil and each fraction was subjected to analysis by TLC.

Two spots with Rf values 0.68 (purple) and 0.88 (yellowish orange, yellow under flourescence) from benzene fraction, two spots with Rf values 0.02 (yellow) and 0.21 (yellow) from 20% ethanol-benzene fraction and the spot with Rf value 0.0 from ethanol fraction were detected respectively, as show in Fig. 10. No spot

![Diagram](image)

1: 2: 5% CHCl₃ - Bz eluate, Bz eluate
3: 10% CHCl₃ - Bz eluate,
4: 20% CHCl₃ -Bz eluate,
5: 20% EtOH - Bz eluate, 6: EtOH eluate

Developing : CHCl₃ - EtOH (95 : 5)
Detection : 15% SbCl₃ - CHCl₃, Silica-gel G-60

FIGURE 10. Thin-layer chromatogram of eluates from Florisil column
was detected from chloroform-benzene fraction. The places corresponding to Rf values 0.68 and 0.88 on the plate, were cut off and eluted with benzene. Their IR spectra are shown in Fig. 11 and 12. These substances indicated a positive reaction to SbCl₃ and Liebermann-Bruchard reagent.

The data obtained suggested that the above substances had an unsaturated sterol ring.

![Figure 11. IR spectrum of benzene eluate (Rf 0.88 on thin-layer chromatogram)](image1)

![Figure 12. IR spectrum of benzene eluate (Rf 0.68 on thin-layer chromatogram)](image2)

**Sugars in Acid Hydrolysate of Ethanol Extract**

Fig. 13 represents chromatograms for the TLC separation of sugars in the acid hydrolysate (3)-b) of ethanol extract. Xylose, arabinose or mannose, glucose and galactose existed in (3)-b. Since the separation of arabinose and mannose, was
however, incomplete inspite of three successive developments, (3)-b was subjected to analysis by GLC. By the GLC separation, glucose, xylose, rhamnose, arabinose glucose and the corresponding sugar to Rg 0.59 were contained in (3)-b.

**Figure 13.** Thin-layer chromatogram of sugars in hydrolysate of ethanol extract S: Sample, M: Marker, Rha: Rhamnose

**Figure 14.** Gas-liquid chromatogram of sugars in hydrolysate of ethanol extract
The foaming substances were considered to be steroid saponins which are known to have a strong foaming power and play an important role in the foaming of raw cane sugars.

REFERENCES


COMPUESTOS QUE PRODUCEN ESPUMACION EN LOS AZUCARES CRUDOS

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RESUMEN

Las soluciones de azucar cruda tienen mucha espuma durante el proceso de clarification en la refineria produciendo así problemas de operacion. Se encontró que algunos azúcares de Taiwan, Australia y nacionales producían mucha espuma sea cual fuere su polarizacion.

Se ha hecho un intento para identificar los principales compuestos responsables de la espinmacion observada en algunos crudos. Los compuestos mas importante resultó ser del grupo de esteroidas saponificados. Su sapogenico tenía un anillo de esterol no saturado y los azucares consistian de glucosa, xilosa, ramosa, arabinosa y un azucar no identificada.