

## Some fragrant fibres and yarns based on chitosan

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### Abstract

Novel fragrant chitosan derivatives, fibres and yarns were prepared. The degree of substitution (d.s.) for Schiff's base was at 0.25–1.00 in the solution state and at 0.19–0.89 in the fibre state. The fragrant chitosan fibres had 4.50–5.16 denier for the titer, 0.40–1.05 gf/denier for the tenacity and 3.9–14.5% for the elongation. A bundle of two silk fibroin filaments was coated with a layer of chitosan, and the chitosan layer was N-modified with the fragrant aldehydes to give rise to fragrant yarns. The yarns had 24.0–33.2 denier for the titer, 2.02–2.75 gf/denier for the tenacity and 9.6–16.9% for the elongation. A portion of the fragrant aldehydes was slowly released from the fragrant chitosan derivatives, fibres and yarns in the open air at room temperature, but little released in a closed dry glass vessel.

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**Keywords:** Chitosan; Fragrant aldehydes; Fragrant chitosan fibres; Fragrant chitosan yarns; Schiff's base; Silk fibroin; Silk-mimic yarns

### 1. Introduction

Some Schiff's base derivatives of chitosan have been reported by several investigators (Dutkiewicz, 1983; Hirano, Yamaguchi, Matsuda, Miura, & Kondo, 1977; Kurita, Isihiguro, & Kitajima, 1988; Moore & Roberts, 1981; Muzzarelli, Tantani, & Emanuelli, 1982; Nud'ga, Plisko, & Danilov, 1973, 1974). The slow release of vanillin fragrance from *N*-(4'-hydroxy-3'-methoxybenzylidene)-chitosan was demonstrated in the open air at room temperature (Hirano et al., 1999). Chitosan fibre is well known as one of biofunctional fibres (Agdoh & Qin, 1996; Hirano, 2001; Hirano et al., 1999), but little is known about fragrant biofibres, bioyarns and biotreads based on chitosan. However, several fragrant fibres based on synthetic polymers have been commercialized (Moto-miya, 1999).

The present work reports (1) the novel nine Schiff's derivatives of chitosan, (2) their fragrant fibres and yarns, and (3) the slow release of fragrances from these fibres and yarns in the open air at room temperature.

### 2. Experimental

#### 2.1. Materials

A chitosan sample A, MW  $5-8 \times 10^{-4}$ , degree of substitution (d.s.)  $<0.01$  for NAc and  $[\alpha]_D^{17} -10^\circ$  (c 0.5, 2% aqueous acetic acid), was chemically modified with each of nine fragrant aldehydes in 2% aqueous acetic acid-methanol (Hirano, Ohe, & Ono, 1976). Chitosan fibre was prepared by the wet-spinning through a viscose rayon spinneret (300 holes and 0.10 mm in hole diameter) of a chitosan sample B, MW  $15-20 \times 10^4$ , d.s. 0.06 for NAc and  $[\alpha]_D^{17} -5^\circ$  (c 0.5, 2% aqueous acetic acid) as reported (Hirano et al., 1999). A bundle of two silk fibroin filaments (ca. 10%) was coated with a layer (ca. 90%) of chitosan to give rise to a silk-mimic N<sub>6</sub>(SII) yarn, which was used in the present study (Nakagawa, Matsukawa, Kimura, Yamane, & Hirano, 2002). Table 1 summarizes the nine fragrant aldehydes used in the present study and their Schiff's base derivatives (D), fibres (F) and yarns (Y).

#### 2.2. Methods

The weight (g) of filaments and yarns in 9000-m length was expressed as denier for the titer, gf/denier for

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Table 1

Nine fragrant aldehydes and their Schiff's bases of chitosan

Fragrant aldehydes	Derivatives (D), fibres (F) and yarns (Y)	Fragrances
Cinnamaldehyde	<i>N</i> -Cinnamylidenechitosan (D1, F1, Y1)	Cinnamon
<i>n</i> -Decylaldehyde	<i>N</i> - <i>n</i> -Decylidenechitosan (D2, F2, Y2)	Rose
Citral	<i>N</i> -Citralidenechitosan (D3, F3, Y3)	Lemon
<i>n</i> -Nonylaldehyde	<i>N</i> - <i>n</i> -Nonanalidenechitosan (D4, F4, Y4)	Rose
10-Undecanal	<i>N</i> -10-Undecanalidenechitosan (D5, F5, Y5)	Rose
<i>n</i> -Heptylaldehyde	<i>N</i> - <i>n</i> -Heptylidenechitosan (D6, F6, Y6)	Almond
Citronellal	<i>N</i> -Citronellalidenechitosan (D7, F7, Y7)	Citronella oil
alpha-Hexylcinnamaldehyde	<i>N</i> -alpha-Hexylcinnamylidenechitosan (D8, F8)	Jasmine
alpha- <i>n</i> -Amylcinnamaldehyde	<i>N</i> -alpha- <i>n</i> -Amylcinnamylidenechitosan (D9, F9)	Jasmine

the tenacity, and % for the elongation. FTIR spectra (KBr disks) were recorded on a Jasco FTIR 5300 spectrometer (Jasco Co., Ltd, Tokyo). Elemental analyses were performed at the Micro-analytical Center of Kyoto University, Kyoto. The d.s. values for Schiff's bases were calculated on the basis of the elemental analysis data. Scanning electron microscopic (SEM) analyses were performed on a scanning electron microscope (S-3000N), Hitachi Ltd, Tokyo.

### 3. Chemical modification

#### 3.1. Fragrant chitosan derivatives

A portion (0.16 g) of the chitosan A was dissolved in 2% aqueous acetic acid (20 ml), and the solution was diluted with methanol (20 ml). To the solution was added the corresponding fragrant aldehyde (3 mol/GlcN) which was dissolved in methanol (10 ml), and the mixture solution was allowed to retain at room temperature overnight (Hirano, Matsuda, Miura, & Iwaki, 1979a; Hirano, Matsuda, & Tanaka, 1979b). (A) In the reaction of chitosan with each of cinnamaldehyde and citronellal, the products appeared as a transparent hydrogel. The hydrogel was homogenized into small pieces in methanol (50 ml) and allowed to retain at room temperature overnight, and (B) in the reaction of chitosan with each of *n*-decylaldehyde (1-decanal), 10-undecanal, *n*-heptylaldehyde (heptanal), alpha-hexylcinnamaldehyde and alpha-*n*-amylcinnamaldehyde, the products appeared as a turbid viscous solution. The turbid solution was adjusted to pH 9–10 by addition of an aqueous NaOH solution to give rise to white precipitates.

The products obtained in the above (A) and (B) was collected by filtration, washed with methanol several times and air-dried to give rise to the corresponding fragrant chitosan derivative (Table 2).

*N*-Cinnamylidenechitosan (D1).  $\nu_{\max}^{\text{KBr}}$  2876 (C–H), 1640 (C=N), and 752 and 690 (mono-substituted benzene)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_9\text{H}_8)_{1.00}\cdot 0.82\text{H}_2\text{O}]_n$ : C, 62.36; H, 6.07; N, 4.85. Found: C, 62.21; H, 6.37; N, 4.74.

*N*-*n*-Decylidenechitosan (D2).  $\nu_{\max}^{\text{KBr}}$  2928 and 2854 (CH), 1670 and 1636 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for

$[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_{12}\text{H}_{24})_{0.96}\cdot 0.70\text{H}_2\text{O}]_n$ : C, 63.16; H, 10.05; N, 4.21. Found: C, 63.10; H, 10.20; N, 4.15.

*N*-Citralidenechitosan (D3).  $\nu_{\max}^{\text{KBr}}$  2925 and 2869 (C–H), 1645 and 1627 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_{10}\text{H}_{16})_{1.00}\cdot 0.98\text{H}_2\text{O}]_n$ : C, 61.41; H, 8.62; N, 4.48. Found: C, 61.32; H, 8.77; N, 4.48.

*N*-*n*-Nonanalidenechitosan (D4).  $\nu_{\max}^{\text{KBr}}$  2926 and 2855 (C–H), 1670 and 1635 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_9\text{H}_{18})_{1.00}\cdot 1.65\text{H}_2\text{O}]_n$ : C, 57.20; H, 9.63; N, 4.45. Found: C, 57.72; H, 9.16; N, 4.50.

*N*-10-Undecanalidenechitosan (D5).  $\nu_{\max}^{\text{KBr}}$  2926 and 2855 (C–H), 1670 and 1639 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_{11}\text{H}_{20})_{0.90}(\text{H}_2)_{0.10}\cdot 0.77\text{H}_2\text{O}]_n$ : C, 61.58; H, 9.28; N, 4.52. Found: C, 61.36; H, 9.34; N, 4.50.

*N*-*n*-Heptylidenechitosan (D6).  $\nu_{\max}^{\text{KBr}}$  2957 and 2862 (C–H), 1669 and 1636 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_7\text{H}_{14})_{0.76}(\text{H}_2)_{0.21}\cdot 0.73\text{H}_2\text{O}]_n$ : C, 55.35; H, 8.78; N, 5.60. Found: C, 55.23; H, 8.76; N, 5.56.

*N*-Citronellalidenechitosan (D7).  $\nu_{\max}^{\text{KBr}}$  2923 and 2870 (CH), 1645 and 1626 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_{10}\text{H}_{18})_{1.00}\cdot 0.67\text{H}_2\text{O}]_n$ : C, 62.12; H, 9.17; N, 4.53. Found: C, 61.95; H, 9.12; N, 4.47.

*N*-alpha-Hexylcinnamylidenechitosan (D8).  $\nu_{\max}^{\text{KBr}}$  2957 and 2863 (C–H), 1670 and 1645 (C=N), and 750 and 700 (mono-substituted benzene)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_{15}\text{H}_{20})_{0.94}(\text{H}_2)_{0.06}\cdot 1.23\text{H}_2\text{O}]_n$ : C, 65.32; H, 8.23; N, 3.79. Found: C, 65.37; H, 8.21; N, 3.84.

*N*-alpha-*n*-Amylcinnamylidenechitosan (D9).  $\nu_{\max}^{\text{KBr}}$  2957 and 2865 (C–H), 1671 and 1645 (C=N), and 751 and 690 (mono-substituted benzene)  $\text{cm}^{-1}$ . Anal. Calc. for

Table 2  
Some fragrant chitosan derivatives

Derivatives	Yield (g)	d.s. for Schiff's base	Color
D1	0.24	1.00	Brown
D2	0.24	0.96	Yellow
D3	0.21	1.00	Brown
D4	0.24	1.00	White
D5	0.24	0.90	Yellow
D6	n.d.	0.76	White
D7	0.23	1.00	White
D8	0.20	0.94	White
D9	0.18	0.25	White

Table 3  
Some fragrant chitosan fibres

Fibres	Yield (g)	d.s. for Schiff's base	Color	Titer (denier)	Tenacity (g/denier)	Elongation (%)
F1	0.19	0.89	Yellow	4.93	0.97	8.8
F2	0.26	0.87	Brown	4.60	0.40	10.0
F3	0.24	0.82	Brown	5.16	0.59	6.0
F4	0.22	0.80	White	4.96	0.45	11.6
F5	0.24	0.76	Brown	5.01	0.61	5.2
F6	0.21	0.52	White	4.50	0.98	6.9
F7	0.19	0.31	White	5.05	1.05	3.9
F8	0.16	0.19	White	4.66	0.90	14.5
F9	0.16	0.21	White	4.95	0.95	12.0
Chitosan	–	0.00	White	4.69	1.20	13.2

d.s. 0.06 for NAc was excluded.

$[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_{14}\text{H}_{18})_{0.25}(\text{H}_2)_{0.74}\cdot 0.84\text{H}_2\text{O}]_n$ : C, 51.32; H, 7.51; N, 6.30. Found: C, 51.43; H, 7.49; N, 6.34.

### 3.2. Fragrant chitosan fibres

A portion (0.16 g) of chitosan fibres was suspended in methanol (30 ml), and a fragrant aldehyde (3 mol/GlcN) was added. The mixture was allowed to retain at room temperature for 18 h with occasional mechanical stirring. Thus treated fibres were washed with methanol, filtered and air-dried to give rise to the corresponding fragrant chitosan fibres (Table 3).

*N*-Cinnamylidenechitosan fibre (F1).  $\nu_{\text{max}}^{\text{KBr}}$  2876 (C–H), 1636 (C=N), and 752 and 690 (mono-substituted benzene)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_9\text{H}_8)_{0.89}(\text{H}_2)_{0.05}\cdot 0.62\text{H}_2\text{O}]_n$ : C, 61.40; H, 6.41; N, 5.07. Found: C, 61.32; H, 6.42; N, 5.09.

*N*-n-Decylidenechitosan fibre (F2).  $\nu_{\text{max}}^{\text{KBr}}$  2926 and 2855 (C–H), and 1671 and 1636 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_{12}\text{H}_{24})_{0.87}(\text{H}_2)_{0.07}\cdot 0.91\text{H}_2\text{O}]_n$ : C, 61.27; H, 9.89; N, 4.32. Found: C, 61.28; H, 9.76; N, 4.37.

*N*-Citralidenechitosan fibre (F3).  $\nu_{\text{max}}^{\text{KBr}}$  2924 and 2870 (C–H), and 1647 and 1627 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_{10}\text{H}_{16})_{0.82}(\text{H}_2)_{0.06}\cdot 1.20\text{H}_2\text{O}]_n$ : C, 58.25; H, 8.47; N, 4.75. Found: C, 58.25; H, 8.02; N, 4.73.

*N*-n-Nonanalidenechitosan fibre (F4).  $\nu_{\text{max}}^{\text{KBr}}$  2925 and 2855 (C–H), and 1669 and 1636 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_9\text{H}_{18})_{0.80}(\text{H}_2)_{0.14}\cdot 0.89\text{H}_2\text{O}]_n$ : C, 57.34; H, 9.23; N, 5.02. Found: C, 57.34; H, 9.15; N, 5.03.

*N*-10-Undecanalidenechitosan fibre (F5).  $\nu_{\text{max}}^{\text{KBr}}$  2926 and 2855 (C–H), and 1670 and 1640 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_{11}\text{H}_{20})_{0.76}(\text{H}_2)_{0.18}\cdot 0.91\text{H}_2\text{O}]_n$ : C, 59.12; H, 9.03; N, 4.76. Found: C, 59.06; H, 9.25; N, 4.70.

*N*-n-Heptylidenechitosan fibre (F6).  $\nu_{\text{max}}^{\text{KBr}}$  2957 and 2863 (C–H), and 1669 and 1635 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_7\text{H}_{14})_{0.52}(\text{H}_2)_{0.42}\cdot 1.02\text{H}_2\text{O}]_n$ : C, 50.53; H, 8.37; N, 6.04. Found: C, 50.45; H, 8.54; N, 6.05.

*N*-Citronellalidenechitosan fibre (F7).  $\nu_{\text{max}}^{\text{KBr}}$  2920 and 2874 (C–H), and 1667 and 1635 (C=N)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_{10}\text{H}_{18})_{0.31}(\text{H}_2)_{0.63}\cdot 0.91\text{H}_2\text{O}]_n$ : C, 49.82; H, 8.07; N, 6.30. Found: C, 49.70; H, 8.16; N, 6.35.

*N*-alpha-Hexylcinnamylidenechitosan fibre (F8).  $\nu_{\text{max}}^{\text{KBr}}$  2956 and 2862 (C–H), and 1670 and 1645 (C=N), and 750 and 700 (mono-substituted benzene)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_{15}\text{H}_{20})_{0.19}(\text{H}_2)_{0.75}\cdot 1.17\text{H}_2\text{O}]_n$ : C, 48.48; H, 7.59; N, 6.31. Found: C, 48.59; H, 7.51; N, 6.35.

*N*-alpha-n-Amylcinnamylidenechitosan fibre (F9).  $\nu_{\text{max}}^{\text{KBr}}$  2957 and 2865 (C–H), and 1669 and 1846 (C=N), and 751 and 690 (mono-substituted benzene)  $\text{cm}^{-1}$ . Anal. Calc. for  $[\text{C}_6\text{H}_9\text{O}_4\text{N}(\text{C}_2\text{H}_4\text{O})_{0.06}(\text{C}_{14}\text{H}_{18})_{0.21}(\text{H}_2)_{0.73}\cdot 0.75\text{H}_2\text{O}]_n$ : C, 50.41; H, 7.41; N, 6.49. Found: C, 50.78; H, 7.04; N, 6.51.

### 3.3. Fragrant chitosan yarns

A portion (0.16 g) of N<sub>o</sub>(SII) was suspended in methanol (30 ml), and a fragrant aldehyde (3 mol/GlcN) was added. The mixture was treated as described in the fragrant fibres to give rise to the corresponding fragrant yarn in 0.18–0.27 g (Table 4).

### 3.4. The release of fragrances

The release of fragrances from the fragrant fibres and yarns was examined in the open air and in a closed glass vessel at room temperature. The qualitative release was detected by smelling, and the quantitative release was analyzed by decrease in the d.s. for Schiff's base on the elemental analyses.

Table 4  
Some fragrant chitosan yarns

Threads	Color	Titer (denier)	Tenacity (g/denier)	Elongation (%)
Y1	Light yellow	33.2	2.17	16.3
Y2	Light brown	29.3	2.47	16.9
Y3	Light brown	32.4	2.17	14.9
Y4	White	31.0	2.10	9.6
Y5	Light brown	24.0	2.21	11.8
Y6	White	28.2	2.75	10.5
Y7	White	32.7	2.02	10.0
Cinnamylidene-N <sub>o</sub> (SII)	White	33.2	2.45	15.6
N <sub>o</sub> (SII)	White	24.4	2.60	18.8

Table 5

The release of fragrant aldehydes from the fragrant chitosan fibres as examined by decrease in d.s. for Schiff's base

Filaments	Period (days) <sup>a</sup>			
	0	154	195	265
<i>In the open air</i>				
F1	0.89	0.86	0.85	0.44
F3	0.82	0.76	n.d.	0.53
F5	0.76	0.67	n.d.	n.d.
<i>In a closed glass vessel</i>				
F1	0.89	0.90	0.88	0.87
F2	0.87	n.d.	0.87	n.d.
F3	0.82	n.d.	0.80	0.78
F4	0.80	n.d.	0.81	n.d.

d.s. Value was calculated on the basis of the elemental analysis.

<sup>a</sup> Started on June 17, 2001.

## 4. Results and discussion

### 4.1. Chemical modification

By chemical modification, D1–D9 (d.s. 0.25–1.00) were isolated in 0.18–0.27 g, and F1–F9 (d.s. 0.31–0.87) were isolated in 0.16–0.26 g. The low d.s. value (0.19–0.21) in

F8 and F9 is considered due to a steric hindrance for chemical modification. In the FTIR spectra, absorptions at 1669–1635 and 1639–1617  $\text{cm}^{-1}$  for C=N bonds were detected in D1–D9 and F1–F9, and absorptions at 2970–2928  $\text{cm}^{-1}$  for C–H bonds and  $\sim 1659 \text{ cm}^{-1}$  for C–N bonds were detected in Y1–Y7. However, the Schiff's base absorptions did not detect in Y8 and Y9.

### 4.2. Some physical properties

The fragrant chitosan filaments (F1–F9) had 4.50–5.16 denier for the titer, 0.40–1.05 gf/denier for the tenacity and 3.9–14.5% for the elongation. The titer value was similar to that (4.69 denier) of the original chitosan filament, but their tenacity and elongation were lower than those (1.20 gf/denier and 13.2%) of the original chitosan filament. The fragrant chitosan yarns (Y1–Y7) had 24.0–33.2 denier for the titer, 2.02–2.75 gf/denier for the tenacity and 9.6–16.9% for the elongation. These values were essentially similar to those (24.7 denier, 2.60 gf/denier and 18.8%) of the original filament N<sub>o</sub>(SII) yarn.

These fragrant chitosan derivatives, fibres and yarns were stable in water and aqueous alkaline solutions, but the chitosan layer on N<sub>o</sub>(SII) was solubilized in 2% aqueous acetic acid. The fragrant fibres and yarns of

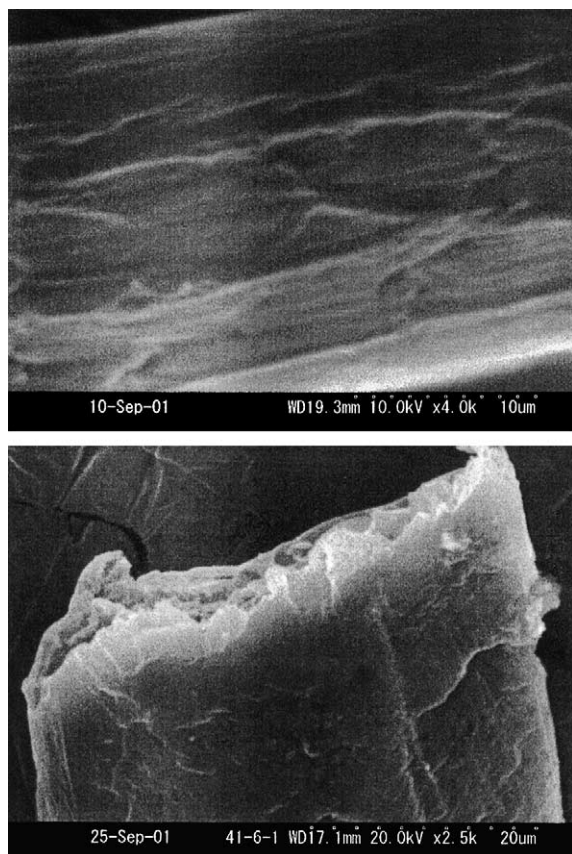


Fig. 1. SEM photographs of the surface (up) and vertical section (down) of N-cinnamylidenechitosan filament F1 (ca. 28  $\mu\text{m}$  in diameter).

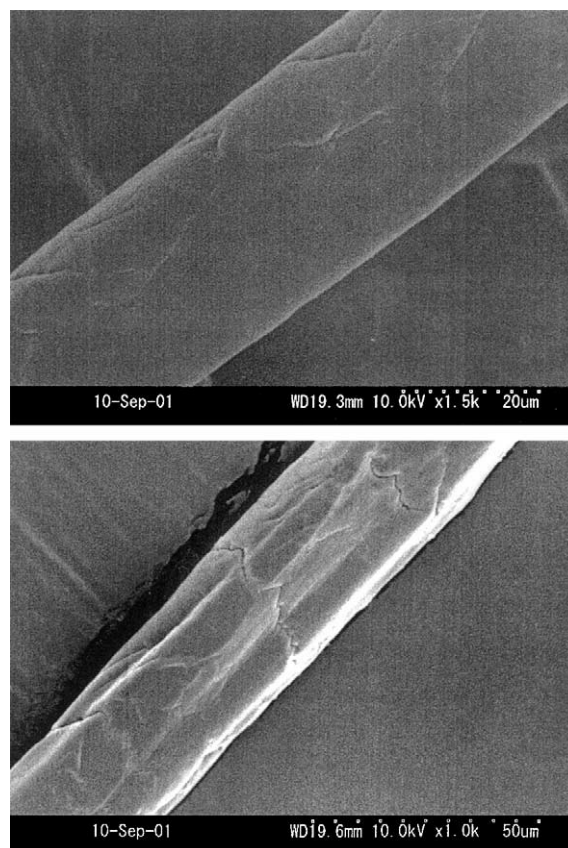


Fig. 2. SEM photographs of the surface (up) of F3 (ca. 30  $\mu\text{m}$  in diameter) and that (down) of F6 (ca. 32  $\mu\text{m}$  in diameter).



cinnamylidene-, decylidene-, citralidene- and undecalidene-chitosans were in brown to light brown color.

#### 4.3. The release of fragrances

Fragrances were qualitatively detected by smelling in those chitosan derivatives, fibres and yarns in the open air at room temperature. When F1 was allowed to retain in the open air at room temperature for 265 days, the d.s. for cinnamylidene group decreased from 0.89 to 0.44, and the original yellow color faded to a light yellow or white color. Similarly, the d.s. for citralidene group in F3 decreased from 0.82 to 0.53 on standing in the open air at room temperature for 265 days. These data indicate that Schiff's base in the fragrant fibres is slowly hydrolyzed by atmospheric moisture, and the corresponding fragrant aldehyde is released. However, a little was released in a dry closed glass vessel (Table 5).

#### 4.4. Scanning electron microscopic analyses

The scaly surface of the original chitosan filament (Hirano et al., 1999) faded on an increase in d.s. for Schiff's base. A scaly surface still existed on the surface of F6 (d.s. 0.52 for Schiff's base), and a relatively smooth surface

Table 6

Apparent densities of some fragrant chitosan filaments and yarns

	Diameter analyzed by SEM ( $\mu\text{m}$ )	Titer (denier)	Density (denier/ $\mu\text{m}$ in diameter)
<i>Fibres</i>			
Chitosan	31	5.44	0.18
F1	28	4.93	0.18
F3	30	5.14	0.17
F6	32	4.50	0.14
<i>Yarns</i>			
N <sub>o</sub> (SII)	53	24.4	0.46
Cinnamylidene-N <sub>o</sub> (SII)	58	33.2	0.59

appeared on both the surfaces of F1 (d.s. 0.89 for Schiff's base) and F3 (d.s. 0.82 for Schiff's base) (Figs. 1 and 2). Essentially no definite fibril organization was found in the vertical section of F1. However, wide lengthwise strips exist on the surface of Y1 and N<sub>o</sub>(SII) (Fig. 3).

#### 4.5. The fibril organization

The yarn titer increased slightly on the Schiff's base modification as observed with N<sub>o</sub>(SII) and Y1, which had 24.4 and 33.2 denier, respectively. The yarn titers of N<sub>o</sub>(SII) and Y1 were five to six times higher than F1 (4.93 denier) and chitosan filament (5.44 denier). The calculated apparent densities (denier/ $\mu\text{m}$  in diameter) of these fragrant yarns were about three times higher than those of chitosan filament and F1 (Table 6), and the fibril organization in these fragrant yarns was more dense than those in the fragrant fibres.

## 5. Conclusion

Novel fragrant chitosan derivatives, fibres and yarns were prepared by treatment with nine fragrant aldehydes. d.s. for Schiff's base was significantly affected by the organization of fibres and yarns and by the chemical structure of fragrant aldehydes. A portion of the fragrances was slowly released in the open air at room temperature. The present fragrant derivatives, fibres and yarns will be usable as a novel fragrant biomaterial in the wide fields including air-filters, cosmetics and textiles.

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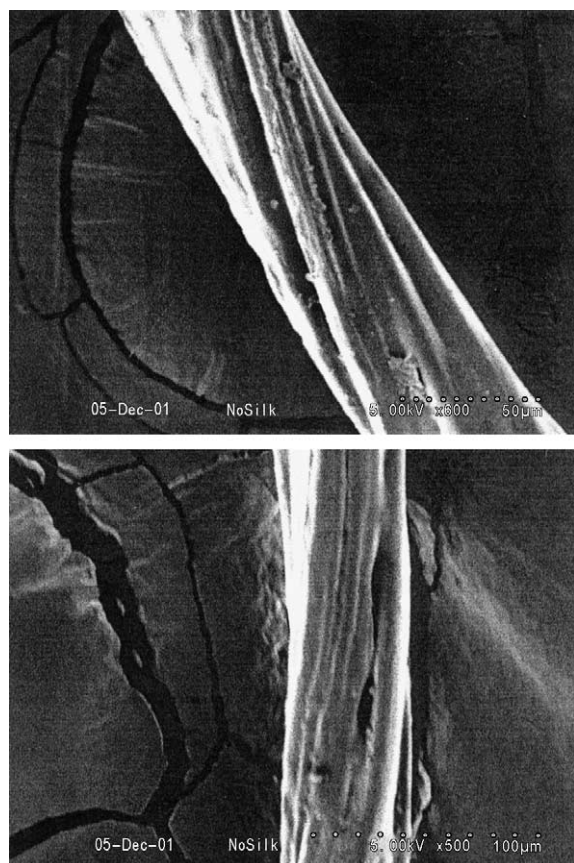


Fig. 3. SEM photographs of the surface (up) of *N*-cinnamylidenechitosan (SII) yarn and that (down) of N<sub>6</sub>(SII) yarn.

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