Analysis of the Dark-Colored Impurities in Sulfonated Fatty Acid Methyl Ester

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ABSTRACT: A fractionally distilled C_{14}–C_{16} fatty acid methyl ester, derived from palm oil, was sulfonated with gaseous SO_3 in a falling film reactor to form an α-sulfo fatty acid methyl ester (α-SF; unbleached and unneutralized form). The included dark-colored impurities were then separated from α-SF as a diethyl ether-insoluble matter. After purification by thin-layer chromatography, the colored species were analyzed by ion-exchange chromatography, gel-permeation chromatography, and nuclear magnetic resonance spectrometry. These data suggested that the colored species were polysulfonated compounds with conjugated double bonds. Minor components in the raw fatty acid methyl ester, found by gas chromatography/mass spectrometry, were spiked into the purified methyl palmitate and then sulfonated. The unsaturated methyl ester and hydroxy ester showed the worst color results. The methyl oleate and methyl 12-hydroxystearate were then sulfonated and analyzed. Deep black products were obtained, which showed the same properties as the colored species in α-SF. It was concluded that low levels of unsaturated fatty acid methyl esters and hydroxy esters in the fatty acid methyl ester are the main causes of the coloring.

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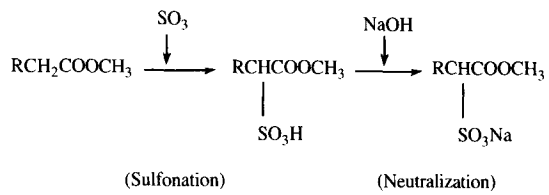
KEY WORDS: Bleach, coloring, methyl ester, palm fatty acid, palm oil, α-SF, α-sulfo fatty acid methyl ester, sulfonation.

The α-sulfonated fatty acid methyl ester (α-SF) sodium salt (α-SF-Na) is an anionic surfactant that has attracted much attention (1) in recent years due to its high detergency (2) and excellent biodegradability (2–4). In general, α-SF-Na is produced by the sulfonation of the fatty acid methyl ester with SO_3, followed by neutralization with sodium hydroxide (Scheme 1):

The study of the sulfonation of the fatty acid methyl ester began in the 1950s (5,6), but the inability to reliably produce large quantities of high-quality material limited industrial production. One of the problems was the undesirable dark color of this surfactant. Some methods for improving the color have been proposed (7,8), and manufacturing of the surfactant has been accomplished by using a hydrogen peroxide bleaching method (7). However, technical improvements for optimization of the bleaching conditions are still needed to simplify the manufacturing process and to improve cost effectiveness. In this work, we studied the properties and structural features of the dark-colored impurities in α-SF.



SCHEME 1

EXPERIMENTAL PROCEDURES

Equipment. A nuclear magnetic resonance (NMR) spectrometer (JNM-GSX400, 400 MHz; JEOL, Ltd., Tokyo, Japan), a high-performance liquid chromatograph (HPLC) (LC-6A; Shimadzu Corp., Tokyo, Japan), and an HPLC multiwavelength detector (MCPD-6000; Otsuka Electronics Co., Ltd., Tokyo, Japan) were used.

Materials. Fractionally distilled C_{14} and C_{16} fatty acid methyl esters, derived from palm oil, were mixed in a weight ratio of C_{14}/C_{16} = 3:7 [purity by gas chromatography (GC), 99.2%; iodine value (IV), 0.5]. Other reagents were purchased from Tokyo Chemical Ind. Co., Ltd. (Tokyo, Japan). For methyl palmitate, the purity was over 99.9%, IV = 0.0. For methyl oleate, purity was over 99.9%. Methyl 12-hydroxy stearate was prepared from 12-hydroxystearic acid through recrystallization and methyl-esterification with diazomethane and had a purity of 97.9%.

Sulfonation. The C_{14}–C_{16} fatty acid methyl ester was sulfonated in a pilot-scale falling-film reactor. The molar ratio (SO_3/methyl ester) was 1.1. The sulfonation mixture was then aged for 90 min at 90°C to let the reaction go to completion. The α-SF thus obtained, in the form of an unbleached and unneutralized mixture, was used for the analyses. The obtained α-SF was deep black, and its Klett color was 5,000.

Sulfonation of other samples in this study was carried out on a laboratory scale. Approximately 5 g of the methyl ester was dissolved in 100 mL CCl_4, and the solution was kept at 25°C. Sulfur trioxide was then added dropwise to the sample. The sulfonation mixture was aged for 90 min at 90°C. The solvent was then evaporated, and the sulfonated fatty acid methyl ester was recovered.

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Separation of colored species. Three grams of α-SF were placed in a glass tube for centrifugation. A 35-mL aliquot of diethyl ether was added and stirred. Centrifugal separation was carried out at 3,500 rpm for 5 min, and the yellow supernatant liquid was removed. The extraction with diethyl ether was repeated twice more, and 32.0 mg (1.1%) of the deep-black precipitate was obtained as a diethyl ether-insoluble matter upon drying at the bottom of the glass tube. The precipitate was dissolved in diethyl ether/methanol (90:10), and the sulfonic acid groups ($-SO_3H$), assumed to exist in the molecules of the colored species, were methyl esterified (9) (to $-SO_3CH_3$) by diazomethane. The methyl esterified compound, also a deep-black color, was then developed by thin-layer chromatography (TLC) (Merck Silica gel 60 No. 5745; Merck, Darmstadt, Germany) with hexane/diethyl ether (70:30) as the solvent. Under these TLC conditions, α-SF was developed up to the solvent front. The deep-black compounds remained around the starting position. The silica gel at the starting position was scraped off the plate. The adsorbed compounds were extracted with chloroform/meth-anol and concentrated to dryness (recovery: 2.7 mg, 0.09%).

Ion-exchange chromatography. Two glass columns, packed with 40 mL each of cation- (Dowex 50WX4) and anion- (Dowex 1X2; The Dow Chemical Co., Midland, MI) exchange resin, were connected (upper: cation resin column). A sample was dissolved in ethanol/water (90:10), and the solution was allowed to flow down the columns at 2.0 mL/min. The two columns were then disconnected, and three eluents, 2N HCl, 2N HCl/methanol, and 6N HCl, were consecutively passed through the anion-exchange column.

Gel-permeation chromatography (GPC). The operating conditions were as follows: column, TSK Gel G1000HXL (Tosoh Co., Tokyo, Japan) (4.5 × 300 mm); mobile phase, tetrahydrofuran; flow rate, 1.0 mL/min; detector, refractive index (RI) and visible (VIS) detector, wavelength 430 nm. Because the dark-colored species did not show any specific λ_{max} in the visible region and became yellow-brown when diluted, a wavelength of 430 nm was chosen to detect the colored species.

Measurement of Klett color. The color of the samples, 5% (w/w) α-SF in ethanol, was measured with a Klett–Summerson photoelectric colorimeter. When the color was too deep, solutions were diluted to get measured values under 700, and the values were then converted into 5% solutions.

RESULTS AND DISCUSSION

Characterization of colored species. During the ion-exchange chromatographic analysis of α-SF, the colored species was found to pass through the cation-exchange resin column and to adsorb on the top of the anion-exchange resin column. The colored species were not eluted by the next three eluents (2N HCl, 2N HCl/methanol, and 6N HCl) that were consecutively passed through the column. α-SF itself also was adsorbed on the anion column, but eluted with 2N HCl/methanol. These results indicate a strong anionicity of the colored species. Colored species were then methyl esterified to prevent their irreversible adsorption to the column during GPC analysis (results are shown in Fig. 1). The colored species were eluted earlier than the α-SF itself, and the polyethyleneglycol (PEG) reduced molecular weight was approximately 1,000.

Isolation of colored species and analyses of their partial structure. Separation of the colored species was attempted for a more detailed analysis. They were separated from α-SF as a diethyl ether-insoluble mater and were then methyl esterified and purified by TLC. The colored species isolated in this way were analyzed by GPC (the resulting chromatogram is shown in Fig. 2).

Because the chromatograms, obtained with a VIS and an RI detector, were almost the same, most compounds other than the colored species were assumed to have been removed. Earlier eluted components had higher peak intensities in the chromatogram from a VIS detector, which may suggest that components with higher molecular weights have a higher absorptivity at 430 nm. The PEG-reduced molecular weight of the colored species was distributed from 1,000 to 3,000.

The ^1H NMR spectrum of the colored species is shown in Figure 3. The broadness of each signal is commonly observed in spectra of high-molecular weight compounds. The overlapped signals around 4 ppm suggest that they are the signals of the methyl groups ($-SO_3CH_3$, $-OCH_3$), and that sulfonate groups are substituted at various positions in the molecule of the colored species. This finding supports the consideration that the colored species are a mixture of polysulfonates. Many signals are also observed in the double-bond region between 5–8 ppm. These signals disappeared when the colored species were treated with a bleaching agent, hydrogen peroxide, which suggests that double bonds take part in the coloring.

According to a previous report (10), as the number of conjugated double bonds in a molecule increases, the color of a

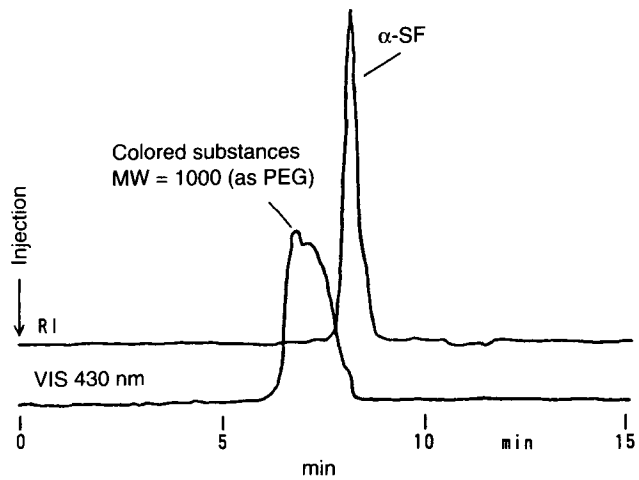

FIG. 1. Gel-permeation chromatogram of an α-sulfo fatty acid methyl ester (α-SF) (methyl esterified). Operating conditions: column: TSK gel G1000HXL (Tosoh Co., Tokyo, Japan) + guard column (7.8 mm × 30 cm); mobile phase, tetrahydrofuran (1.0 mL/min); detector, visible (VIS), 430 nm [0.04 absorbance unit full scale (AUFS), refractive index (RI), 0.32 refractive index unit full scale (RIUFS)]; sample, 3 wt% in tetrahydrofuran, 20 uL. MW, molecular weight.

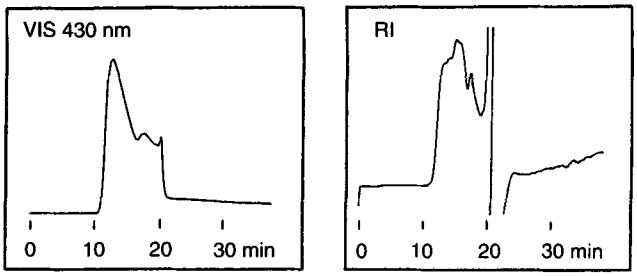

FIG. 2. Gel-permeation chromatogram of colored species from α-SF. Operating conditions [except for column information: TSK gel G1000HXL + G1000HXL + guard column (7.8 mm × 30 cm × 2)], abbreviations, and company source as in Figure 1.

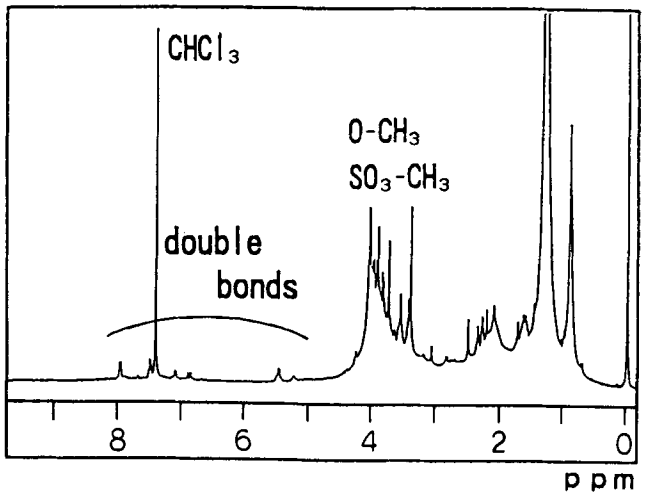

FIG. 3. ^{1}H nuclear magnetic resonance spectrum of colored species isolated from α-SF. Abbreviation as in Figure 1.

compound gradually changes from yellow to red. From that, it is predicted that conjugated double bonds act as a chromophore in the colored species, and that bleaching by hydrogen peroxide is performed through the addition of hydroxyl groups to the conjugated double bonds. Accordingly, considering the properties and molecular weight, we concluded that the colored species are polysulfonated compounds with conjugated double bonds.

Effect of minor components on coloring. It has been reported (8) that the color of sulfonic acids and neutralized compounds becomes worse when saturated fatty acid methyl esters are sulfonated in the presence of compounds with unsaturated bonds or alcoholic OH groups. We also have found by GC/mass spectrometric analysis that a palm oil fatty acid methyl ester contains unsaturated methyl esters, keto esters, diesters, hydroxy esters, fatty acids, and lactones as minor components. The effect of these minor components on the coloring was examined. Sulfonation of minor, component-spiked methyl palmitate was carried out with CCl_4 as a reaction medium (the results are listed in Table 1). Compounds with an unsaturated bond or alcoholic OH group showed the worst effect on coloring. Also, a secondary alcohol affected the coloring more severely than a primary alcohol, and a ketone remarkably decreased the conversion. Under these sulfonation conditions,

TABLE 1
The Effect of Minor Compounds on Coloring

	Conversion (%)	5% Klett color
Methyl Palmitate	96.8	760
+ Lauric acid	98.3	1500
+ 1-Dodecanol	90.3	6000
+ 4-Dodecanol	85.0	9000
+ 1-Dodecanal	97.9	2000
+ 2-Decanone	63.2	7000
+ Methyl 12-Hydroxystearate	98.9	24000
+ Methyl Oleate	98.9	26000

the Klett color of the sulfonated C_{14}–C_{16} fatty acid methyl ester was 2,000. The Klett color of the sulfonation product of this methyl ester obtained in the falling-film reactor was 5,000. The mildness of the reaction conditions, that is, the use of a reaction medium, might cause this difference in color.

Analysis of sulfonated products of methyl oleate. Methyl oleate, which caused the worst effect on coloring, was itself

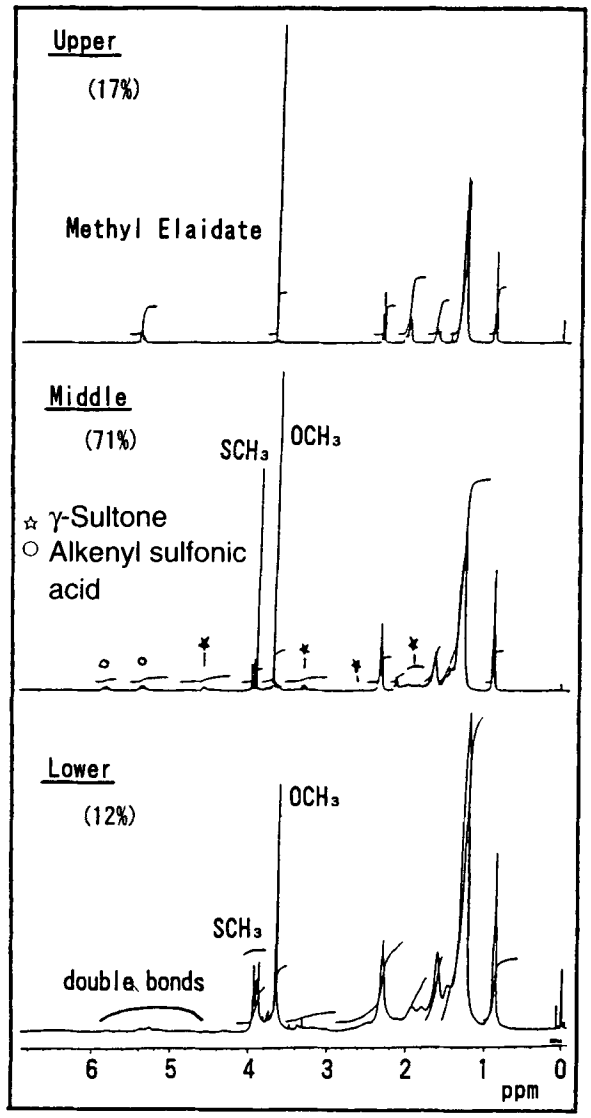

FIG. 4. ^{1}H nuclear magnetic resonance spectra of thin-layer chromatographic fractions of sulfonated products of methyl oleate.

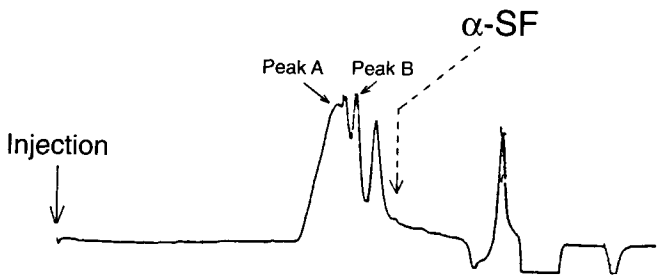

FIG. 5. Gel-permeation chromatogram of the colored species in the sulfonation products of methyl oleate. Operating conditions: column: TSK gel G3000HXL + G200HXL + G1000HXL + guard column (7.8 mm × 30 cm × 2); mobile phase; tetrahydrofuran (1.0 mL/min); detector, RI, 0.32 RIUFS; sample, 3 wt% in tetrahydrofuran, 20 μL. Abbreviations as in Figure 1.

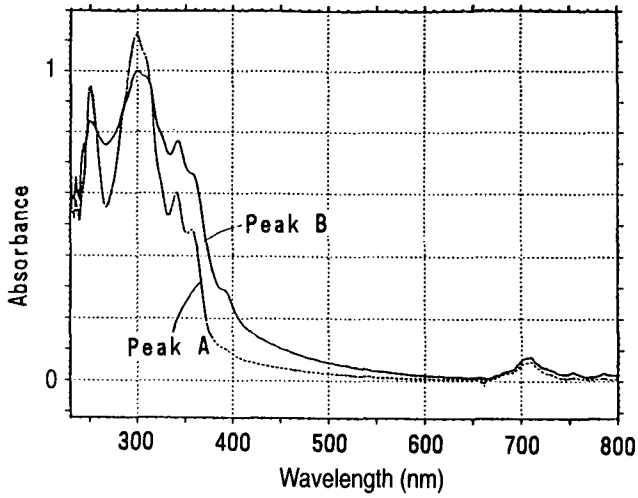

FIG. 6. Ultraviolet spectrum of the peaks shown in Figure 5.

sulfonated, and deep-black products were obtained. Ion-exchange chromatography of these products proved that the colored species were strongly anionic, which is similar to the colored species in α-SF.

The sulfonation products of methyl oleate were then methyl esterified and submitted for a TLC separation. They were divided into three groups—the upper, middle, and lower parts—and then extracted. The ^{1}H NMR spectra of the TLC fractions are illustrated in Figure 4. The upper fraction contained unreacted methyl ester. All unreacted ester was converted into the *trans* isomer (methyl elaidate). The middle fraction contained γ-sultone and alkenyl sulfonic acid. The deep-black products were in the lower fraction.

The lower fraction was analyzed by GPC, as shown in Figure 5. The PEG-reduced molecular weight of the colored species was 1,000–3,000, and the chromatogram pattern showed the polymerization distribution. The ultraviolet spectrum of the lower fraction, measured with a multiwavelength detector, is shown in Figure 6. The colored species gave almost the same VIS spectrum, independent of their molecular weight, and they showed maximum absorption bands around 200, 300, 340, 360, 390, and 710 nm. This means that the structures of their chromophore are almost the same.

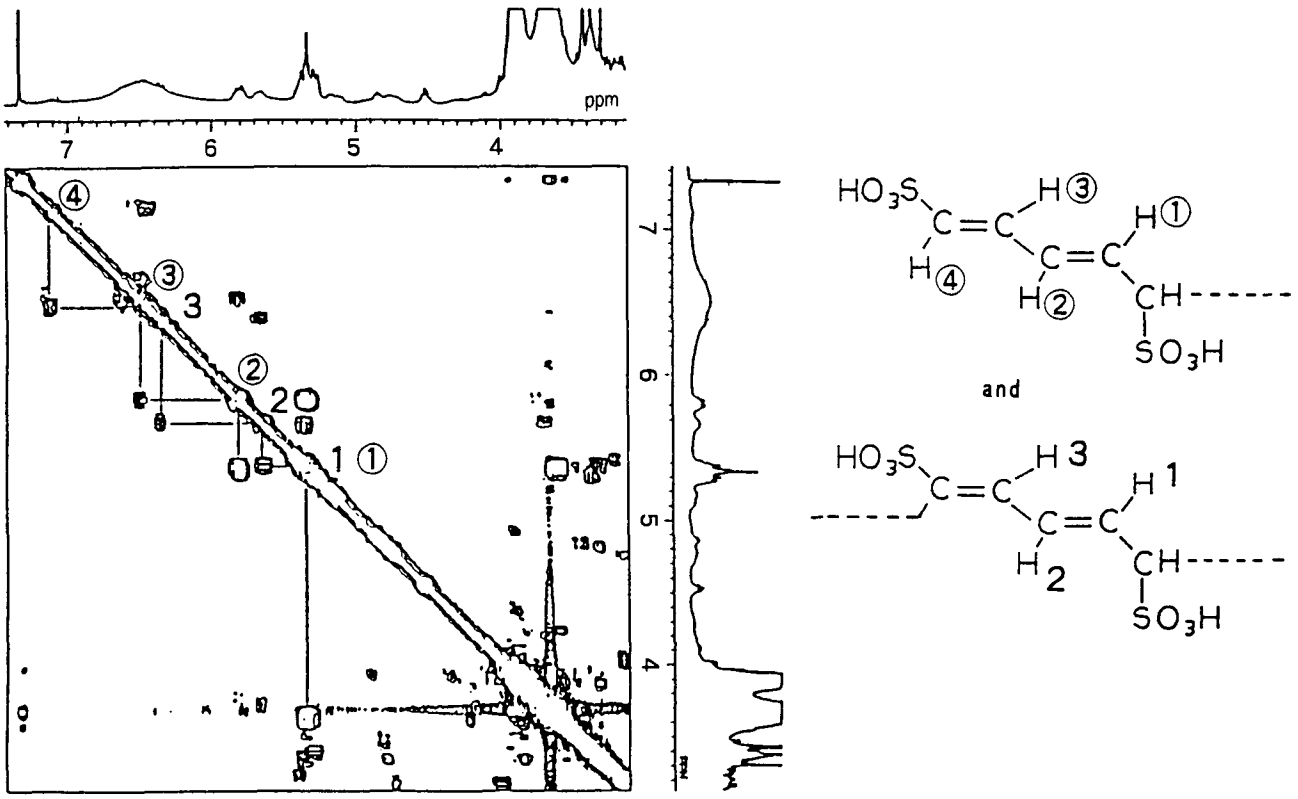

FIG. 7. ^{1}H–^{1}H correlation spectrum of colored species in the sulfonated products of methyl oleate.

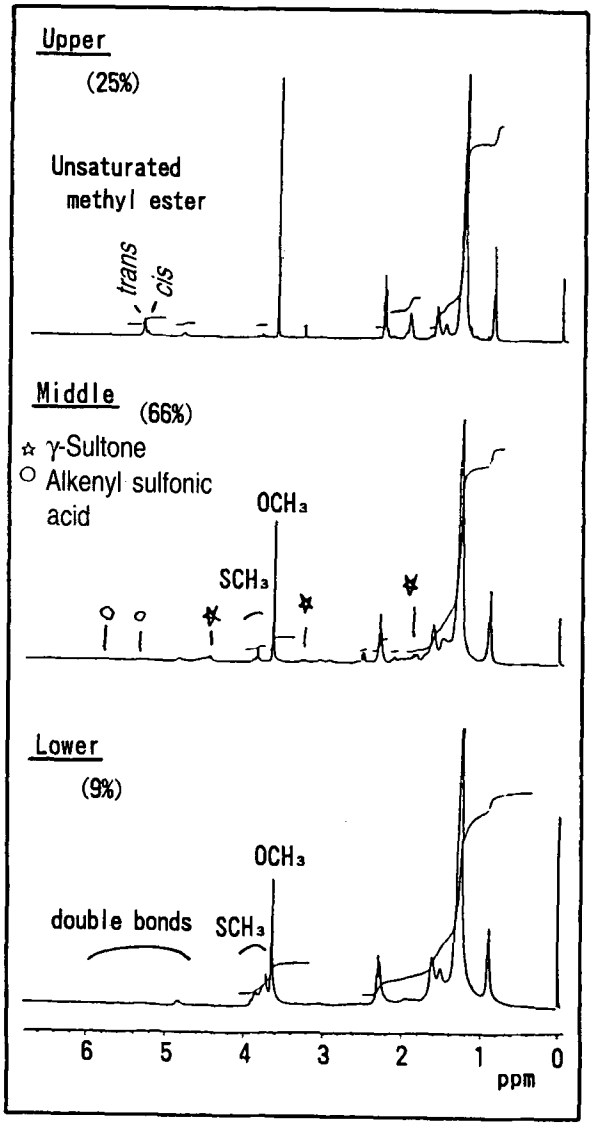

FIG. 8. ^{1}H nuclear magnetic resonance spectra of thin-layer chromatographic fractions of sulfonated products of 12-hydroxystearate.

Amiya *et al.* (11) studied the structure of some colored compounds and proved with two-dimensional NMR that the conjugated double bonds in the molecule were the chromophore. We applied this procedure for the analysis of the lower fraction and found a similar partial structure. The ^{1}H–^{1}H correlated spectroscopy (COSY) spectrum of the lower fraction is illustrated in Figure 7. The methine proton connected to the sulfonate group is commonly observed at around 3.7 ppm. Starting from this signal, spin couplings between protons were checked, and it appeared that at least two kinds of conjugated double bonds existed (illustrated in Fig. 7). Because the integration of each signal is not consistent with the structure shown in Figure 7, the whole structure is still not clarified. However, we interpreted this result to mean that the conjugated double bonds found by the COSY spectrum are the chromophore of the colored species.

Analysis of sulfonated products of methyl 12-hydroxystearate. The reaction product of methyl 12-hydroxystearate with SO_3 was also deep black. The color species was strongly anionic. The products were methyl esterified and fractionated into three parts by TLC in the same manner as the methyl oleate. The ^{1}H NMR spectra of the TLC fractions are illustrated in Figure 8. The upper fraction contained unsaturated methyl esters (mixture of *cis* and *trans* forms) instead of methyl 12-hydroxystearate. The middle fraction contained γ-sultone and alkenyl sulfonic acid. The colored species were in the lower fraction. The PEG-reduced molecular weight of the colored species obtained by GPC was approximately 1,500.

The composition of the sulfonation products of 12-hydroxystearate seems similar to those of the methyl oleate. From these facts, the following reaction mechanism can be deduced: At first, methyl 12-hydroxystearate is converted into the unsaturated methyl ester during the dehydration reaction by SO_3. The resulting unsaturated methyl ester is sulfonated with SO_3 in the same manner as methyl oleate. The ^{1}H NMR spectrum of the TLC lower fraction confirms the presence of double bonds. Also, many $-SO_3CH_3$ signals appeared around 3.8 ppm. From these findings, it is estimated that the colored species found in the sulfonation products of 12-hydroxystearate are polysulfonated compounds with conjugated double bonds.

In conclusion, the coloring species contained in α-SF were more strongly anionic than α-SF itself, and their molecular weight was high. Chromatographic and spectrometric studies lead to the conclusion that the colored species were polysulfonated compounds with conjugated double bonds. Minor components contained in the raw material were sulfonated, and the reaction products were analyzed. Unsaturated fatty acid methyl esters and hydroxy esters were found to be the main causes of the coloring. A reaction mechanism for the conversion of impurities to the colored species has not yet been clarified. We are now studying this aspect.

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