

not be utilized in the analysis of the condensates of the mixtures of NS and  $\beta$ -methylnaphthalenesulfonic acid (MNS) with formaldehyde because of the difficulty of separation of NS and MNS and also their condensates into their components.

This article describes the analysis of low condensed components, monomer and dimer, in the condensates of mixtures of NS and MNS with formaldehyde by high speed liquid chromatography.

### EXPERIMENTAL PROCEDURES

The following three kinds of condensates of the mixtures of NS and MNS with formaldehyde, prepared by mixing both sulfonic acids in certain proportions, were synthesized in our laboratory: condensate A, NS-MNS, 3:1 (mole ratio); condensate B, NS-MNS, 1:1; and condensate C, NS-MNS, 1:3. The condensates of NS or MNS alone with formaldehyde were prepared as standards. The conditions of synthesis of these condensates were as follows: sulfonation of naphthalene or methylnaphthalene with sulfuric acid was carried out for 5 hr at 150-160 C. Then, formaldehyde (0.95-1 mole sulfonic acids) was added to the sulfonic acids during the next 2 hr, maintaining the temperature at 80-90 C. Condensation was continued for 3 hr at 100 C.

The fractionation of monomer and dimer of the condensates was carried out by salting-out chromatography using CM-Sephadex C-50 and 0.005 M magnesium chloride aqueous solution as stationary and mobile phases, respectively, according to the procedure described before (3). Each fractionated effluent containing magnesium chloride was analyzed by a high speed liquid chromatograph (model 830, du Pont de Nemours and Co., Wilmington, Del.) equipped with an UV detector (wave length, 254 nm) for monitoring the column effluent. The column used in this study was 1 m long with an internal diameter of 2.1 mm and was packed with Zipax SAX, a strong anion exchange resin.

### RESULTS

Figure 1 shows the high speed liquid chromatograms for the monomer fractionated from each condensate. The first two small peaks (retention time,  $T_R$ ; 2.9 min, 3.4 min) in front of the main peak in each chromatogram are assumed to be due to both the elution of magnesium salt and other impurities in the fraction. The main peak in Figure 1A is based upon the elution of NS. In Figure 1B, the last peak ( $T_R$ ; 12.8 min) is due to the elution of dimethylnaphthalenesulfonate (DMNS) as an impurity. The main peak of condensate A (NS/MNS, 3/1) was assigned to NS. When

increasing the proportion of MNS in the mixture, other small peaks appeared in the chromatograms, showing the presence of MNS and DMNS. However, not only the main component of condensate A, but also that of the condensate B and C were NS, regardless of the ratios of NS and MNS.

The chromatograms for the dimer are shown in Figure 2. The first peak in each chromatogram is due to the elution of magnesium salt analogous to that in Figure 1. In Figure 2A, two peaks ( $T_R$ ; 4.5 min, 5.4 min) are assumed to be due to the position isomers of the dimeric condensates of NS. As can be seen in Figure 2, it is apparent that each main component of the condensate A, B, and C was the dimeric condensate of NS alone (NS-NS type). Condensates other than the NS-NS dimer (probably NS-MNS or MNS-MNS type) were found in the chromatograms as the proportion of MNS in the mixture increased (Figure 2D and 2E).

### DISCUSSION

On the basis of these data, it seemed reasonable to assume that the main components of monomer and dimer in the condensates of mixtures of NS and MNS with formaldehyde were NS and the dimeric condensate of NS-NS, respectively, regardless of the ratios of NS and MNS. This result suggests that the reaction rate of condensation of MNS is larger than that of NS.

In this study, the mixtures of sulfonic acids were allowed to condense with formaldehyde for 3 hr, but the reaction time for commercially produced condensates for use as dispersing agents is usually much longer. Accordingly, it is thought that MNS or its dimeric condensates scarcely remain in the commercial product.

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## New Quaternary Benzyl Chloride Salts for Inclusion in Hair Cream Rinse Formulations

### ABSTRACT

Quaternary ammonium salts have been prepared from benzyl chloride and amino amides and an amino ester of a long chain fatty acid. These benzyl salts were incorporated in simple hair conditioner formulations containing the quaternary salt, anhydrous lanolin, cetyl alcohol, and water. Preliminary evaluations indicated that the formulations were effective in the

removal of tangles and snarls following washing with ordinary shampoo. The dried hair was easily manageable and had good luster.

### INTRODUCTION

Although many new surface-active compounds have been reported in the past few years, many closely related compounds that could have desirable properties for specialty applications have not been prepared. Specifically, the

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quaternized long chain fatty acid substituted diamines are examples; their essential structural features are the quaternary nitrogen and amide nitrogen. The amide group can be replaced by an ester group by substituting an alkanolamine for the diamine. In general, this class of long chain cationic compounds has good surface activity and the potential for fungicidal and bactericidal properties. Thus, specific members of the class may be uniquely suitable for incorporation into a wide variety of cosmetic formulations (1,2). In hair cream rinse formulations, for example, this cationic action results in some absorption onto the hair of a film of the compound. This film gives a soft smooth feel and makes the hair easier to comb with greater manageability. The potential fungicidal and bactericidal effects, which are probably independent of the surface activity, may be helpful as dandruff inhibitors.

### EXPERIMENTAL PROCEDURES

Quaternized salts were prepared from compounds having amide and ester intermediate groups. Dimethylaminoethylpalmitamide was prepared by acylating dimethylethylenediamine with palmitoyl chloride; triethylamine was used as the HCl scavenger. The HCl salt formed was filtered off and the product eluted through an alumina column with chloroform as the solvent. N-Methyl-N'-palmitoylpiperazine was prepared as above by reacting methyl piperazine and palmitoyl chloride. 1,3-Bis-(dimethylamino)-2-propanol was reacted with palmitoyl chloride, with triethylamine again as the HCl scavenger, to give the 1,3-bis-(dimethylamino)-2-propyl palmitate. The quaternary salts were obtained by combining equimolecular amounts of benzyl chloride with the amino amides and 2 moles of benzyl chloride with the amino ester and allowing the salts to form at room temperature. Initial warming of the mixture to solubilize the compounds increased the rate of salt formation only slightly. The salts were recovered by washing out excess unreacted amide or ester and benzyl chloride with petroleum ether and filtering the salt free. The amide salts crystallized easily from a mixture of ethanol and ethyl ether. The amino ester salt was more difficult to handle, since it became thick and glassy with the addition of hydrocarbon solvents. This washed material did produce a white solid when all of the solvent was allowed to evaporate off under slow warming. Molecular structure was confirmed by IR and NMR spectral analyses of both the intermediate amino amides and the amino esters and their quaternary salts. Characteristic  $\text{C}=\text{N}^+$  stretching observed at 5.98 micrometers confirmed the structure of the amino amide intermediates. The appear-

ance of the 3.20 micrometer stretching band associated with monosubstituted benzene confirms the formation of the benzyl chloride salts. Typical strong ester carbonyl stretching at 5.73 micrometers was observed in the spectrum of 1,3-bis-(dimethylamino)-2-propyl palmitate with the appearance of the characteristic stretching band of monosubstituted benzene at 2.96 micrometer with the formation of the benzyl chloride salt. Integrated NMR spectra for each of the compounds gave proton counts indicative of each compound. No bands were observed to indicate impurities as a result of side reactions. Elemental analyses were in good agreement with theoretical values.

Each of the quaternary salts was incorporated in a cream rinse utilizing a simple formulation containing 10% quaternary salt, 3% cetyl alcohol, 2% lanolin, and 85% water. Both the cetyl alcohol and lanolin function as emollients, which induce hydration of dry skin and assist in protecting the hair. The preparation was slightly acidic (pH 6), a condition beneficial to both hair and scalp (3). The cream rinse was applied to wet hair immediately following shampooing. Actual dilution of the rinse in the hair was ca. 15 to 1. A preliminary evaluation of the formulations indicated the following: tangles and snarls usually associated with combing wet hair were eliminated completely; there was no loss of color of dyed hair or staining of bleached hair; there was no adverse effect upon the type or quantity of wave set or other intermediates added to the hair; and bleached dry hair was less affected than nonbleached hair, which, when dry, had good luster, easy manageability, and a natural appearance.

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