Surface Tension Studies on Novel Allylic Mono- and Dihydroxy Fatty Compounds. A Method to Distinguish *erythro/threo* Diastereomers[1]

G. Knothe*, R.O. Dunn and M.O. Bagby
Oil Chemical Research Unit, NCAUR, USDA, Peoria, Illinois 61604

ABSTRACT: The suitability of the selenium dioxide/*tert.*-butylhydroperoxide system for obtaining allylic mono- and dihydroxy fatty compounds has recently been reported. The surface tension of some selected products was determined in 1 N NaOH and compared to that of some known materials, such as ricinoleic acid. The surface properties of the novel monohydroxy fatty acids are comparable or better than those of the reference materials. The critical micelle concentrations of the novel monohydroxy acids are in the range 10^{-4}–10^{-3} mol/L, depending on their structure. Furthermore, the monohydroxy acids were more effective when the hydroxy group was closer to the functional group at C1. Allylic dihydroxy acids also lowered the surface tension but less so than the monohydroxy compounds. The *erythro* and *threo* diastereomers of the allylic dihydroxy acids can be distinguished by surface tension, with the *threo* diastereomers possessing better surfactant properties. Mixtures of the novel hydroxy fatty acids are also effective, thus obviating the need for complete purification of the products. Side products such as enones, which are formed during the allylic hydroxylations, also lower the surface tension. The products may be suitable for use in microemulsions or as additives in various commercial products.

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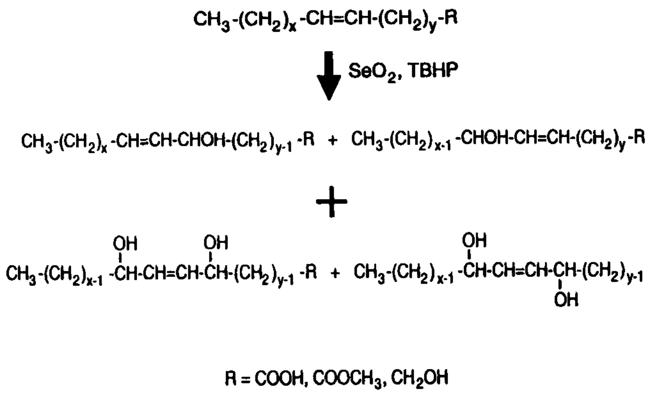
KEY WORDS: Critical micelle concentration, diastereomer characterization, hydroxy fatty acid, selenium dioxide, surface tension, surfactant.

Hydroxy fatty acids and their derivatives are of considerable interest as surfactants. Applications include additives in lubricants, cosmetics and other commercial products (1,2). There are few naturally-occurring hydroxy fatty acids, such as ricinoleic and lesquerolic acids, available. Therefore, much effort has been devoted to obtaining hydroxy fatty acids by other means, such as by microbial conversions (2–7). Chemical syntheses either require lengthy multistep procedures (8,9) or result in vicinal diols when using hydroxylation reagents such as potassium permanganate (10).

Numerous studies provide the surface properties of unsaturated, unsubstituted fatty acids. These compounds and the water/oil/surfactant(/co-surfactant) systems in which they are used have been studied extensively for use in microemulsions (11–17). Other papers (18–20) deal with the influence of the structure of fatty acids (double-bond position and geometry, number of double bonds, chainlength) on the surface properties with occasional investigation of ricinoleic acid. Long-chain fatty alcohols have been investigated for solubilizing methanol in triglycerides (21–22). There are, however, few comparable reports concerned mainly with hydroxy fatty acids (23–25). It was found that hydroxy fatty acids exhibit better surface properties than unsubstituted acids and that the surface properties improved when the hydroxy group was closer to the carboxyl group at C1 (23).

It was recently shown that the long-neglected reagent selenium dioxide, preferably in combination with *tert.*-butylhydroperoxide (TBHP) as coreactant, easily affords fatty acids with enol and enediol functionalities from such common monounsaturated fatty acids as oleic acid (26, 27). The resulting hydroxy fatty acids were a mixture of two allylic monohydroxy fatty acids and *erythro/threo* diastereomers of the allylic dihydroxy fatty acids. Scheme 1 depicts the hydroxy fatty compounds obtained from monounsaturated fatty compounds with the SeO_2/TBHP system. In Scheme 1, for oleic



SCHEME 1

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*To whom correspondence should be addressed at 1815 N. University, Peoria, IL 61604.

acid and oleyl alcohols as starting materials, x = y = 7, and for 11(*Z*)-eicosenoic acid as starting material, x = 9 and y = 7.

In this paper, we report studies on the surface tension of the allylic mono- and dihydroxy products, as well as side products of the reactions of fatty compounds with SeO_2/TBHP. The surface tension of 1N NaOH solutions (pH 13–14) of these compounds was studied. All experimental parameters were kept constant to attribute observed property differences to differences in the structure of the materials studied.

The allylic mono- and dihydroxy compounds were compared to naturally-occurring ricinoleic acid (12-hydroxy-9(Z)-octadecenoic acid) and microbially-produced 7,10-dihydroxy-8(*E*)-octadecenoic acid (4,5). The keto side products obtained in the allylic hydroxylations with SeO_2/TBHP are also suitable as surfactants.

MATERIALS AND METHODS

The synthesis and characterization of the allylic hydroxy fatty compounds obtained with the SeO_2/TBHP system and used in this study have been described elsewhere (26,27). Several compounds, synthesized with the SeO_2/TBHP reagent system, were investigated and compared with other materials. Purity of the compounds was >98% as determined by gas chromatography–mass spectrometry. Deliberately prepared mixtures of the present compounds checked the effect of other hydroxy products in a sample. Ricinoleic acid (purity >99%) was obtained from Nu-Chek-Prep, Inc. (Elysian, MN). 7,10-Dihydroxy-8(*E*)-octadecenoic acid was obtained by microbial conversion as reported earlier (4).

Surface tension measurements (ring method) were conducted with a Krüss (Charlotte, NC) Digital Tensiometer K10T. The sample vessel was thermostatted at 20°C. Samples were dissolved in 1N NaOH, the original solution was diluted at various concentrations, and the surface tension of these solutions was determined. All data points were determined from quadruplicate measurements. Critical micelle concentrations (CMC) were determined graphically from the plots of surface tension (γ) vs. the logarithm of the concentration (mol L^{-1}) of the compound by extrapolating the two lines formed by the steady surface tension for concentrations above the CMC and the increase in surface tension for concentrations below the CMC. Arrows in Figures 1 and 2 highlight points given by the CMC and γ_{CMC} (surface tension at the CMC) of two compounds.

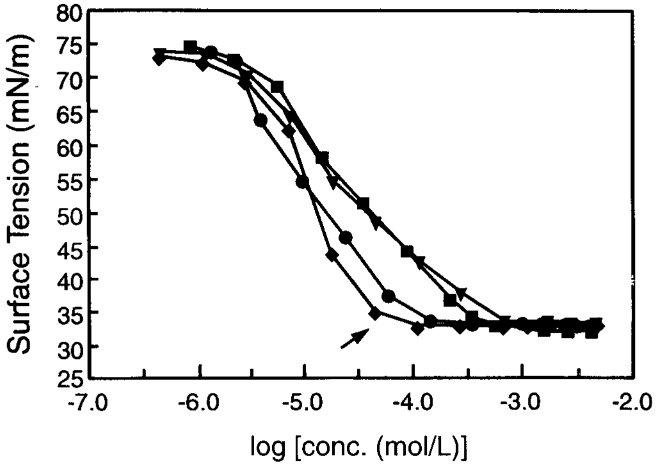

FIG. 1. Plot of the concentration of various allylic monohydroxy fatty acids (in 1N NaOH) vs. surface tension. An arrow highlights the point given by the critical micelle concentration (CMC) and γ_{CMC} of 8-hydroxy-6(*E*)-octadecenoic acid. ▼, Ricinoleic acid; ◆, 8-hydroxy-6(*E*)-octadecenoic acid; ■, 11-hydroxy-9(*E*)-octadecenoic acid; ●, 8-hydroxy-9(*E*)-octadecenoic acid.

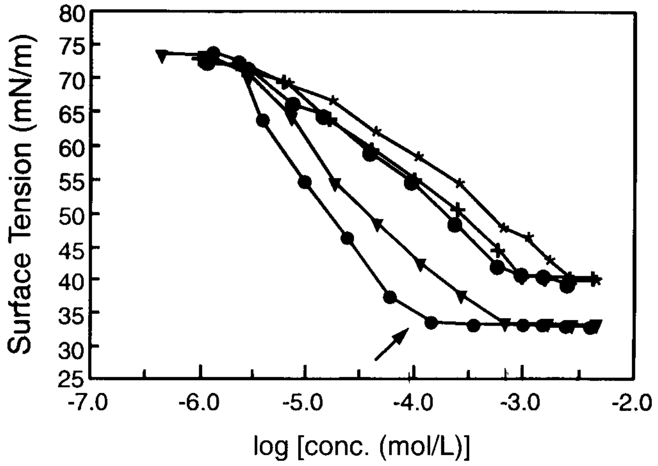

FIG. 2. Plot of the concentration of various dihydroxy acids (in 1N NaOH) vs. surface tension. The plots of ricinoleic acid and 8-hydroxy-9(*E*)-octadecenoic acid are included for comparison purposes. An arrow highlights the point given by the CMC and γ_{CMC} of 8-hydroxy-9(*E*)-octadecenoic acid. Abbreviations as in Figure 1. ▼, Ricinoleic acid; •, 8-hydroxy-9(*E*)-octadecenoic acid; ●, 7,10-dihydroxy-8(*E*)-octadecenoic acid; ✳, erythro-8,11-dihydroxy-9(*E*)-octadecenoic acid; ✚, threo-8,11-dihydroxy-9(*E*)-octadecenoic acid.

RESULTS AND DISCUSSION

The allylic mono- and dihydroxy compounds and enones listed in Table 1 were selected for surface tension studies, and the results were compared with those of the natural products. The methyl esters of 8-hydroxy-9(*E*)-octadecenoic acid, and 11-hydroxy-9-(*E*)-octadecenoic acid were also investigated. Two mixtures of some compounds were prepared to demonstrate the suitability of the unresolved reaction product mixtures for reducing surface tension. All synthetic, oxygenated materials were obtained by the reaction of fatty compounds with the SeO_2/TBHP system according to Scheme 1.

Figure 1 compares the surface tension of solutions of four monohydroxy acids [ricinoleic acid, 8-hydroxy-6-(*E*)-octadecenoic acid, 11-hydroxy-9-(*E*)-octadecenoic acid and 8-hydroxy-9(*E*)-octadecenoic acid]. Figure 2 shows the results for *erythro*- and *threo*-8,11-dihydroxy-9(*E*)-octadecenoic acid and for 7,10-dihydroxy-8(*E*)-octadecenoic acid. For comparison purposes, ricinoleic acid and 8-hydroxy-9(*E*)-octadecenoic acid are included again. Figure 3 depicts again 8-hy-

TABLE 1
Critical Micelle Concentrations (CMC) and Corresponding Surface Tensions in 1N NaOH of Fatty Compounds Derived from the Reaction of Monounsaturated Fatty Acids and Esters with SeO_2/*tert.*-Butylhydroperoxide

Compound	CMC (mol/L)	γ_{CMC} (mN/m)[a]
Synthetic compounds		
8-Hydroxy-6(*E*)-octadecenoic acid	5×10^{-5}	32.9
8-Hydroxy-9(*E*)-octadecenoic acid	8×10^{-5}	33.1
11-Hydroxy-9(*E*)-octadecenoic acid	4×10^{-4}	32.5
10-Hydroxy-11(*E*)-eicosenoic acid	3×10^{-4}	31.9
13-Hydroxy-11(*E*)-eicosenoic acid	1×10^{-3}	31.6
9(*E*)-Octadecene-1,8-diol	2×10^{-3}	40.8
9(*E*)-Octadecene-1,11-diol	4×10^{-3}	36.3
8-Oxo-9(*E*)-octadecenoic acid	4×10^{-4}	32.2
11-Oxo-9(*E*)-octadecenoic acid	4×10^{-4}	31.5
e-8,11-Dihydroxy-9(*E*)-octadecenoic acid[b]	3×10^{-3}	39.8
t-8,11-Dihydroxy-9(*E*)-octadecenoic acid[b]	1×10^{-3}	40.7
e-10,13-Dihydroxy-11(*E*)-eicosenoic acid[b]	4×10^{-4}	41.5
t-10,13-Dihydroxy-11(*E*)-eicosenoic acid[b]	4×10^{-4}	37.9
Natural comparison materials		
Ricinoleic acid	5×10^{-4}	33.5
7,10-Dihydroxy-8(*E*)-octadecenoic acid[c]	7×10^{-3}	40.6

[a] Blank value for 1N NaOH on the tensiometer used in the present work: 75.5 mN/m. Blank value for water: 71 mN/m.
[b] *e* = *erythro*, *t* = *threo*.
[c] Absolute configuration *R,R* (*threo* diastereomer).

droxy-9(*E*)-octadecenoic acid and 11-hydroxy-9(*E*)-octadecenoic acid, as well as two mixtures of hydroxy fatty acids: (**1**) 8-hydroxy-9(*E*)-octadecenoic acid (51.6 wt%) and 11-hydroxy-9(*E*)-octadecenoic acid (48.4 wt%) and (**2**) 8-hydroxy-9(*E*)-octadecenoic acid (32.2 wt%), 11-hydroxy-9(*E*)-octadecenoic acid (30.6 wt%), *erythro*-8,11-dihydroxy-9(*E*)-octadecenoic acid (18.2 wt%), and *threo*-8,11-dihydroxy-9(*E*)-octadecenoic acid (19 wt%). These mixtures were prepared to simulate the composition of hydroxy products obtained from the reactions.

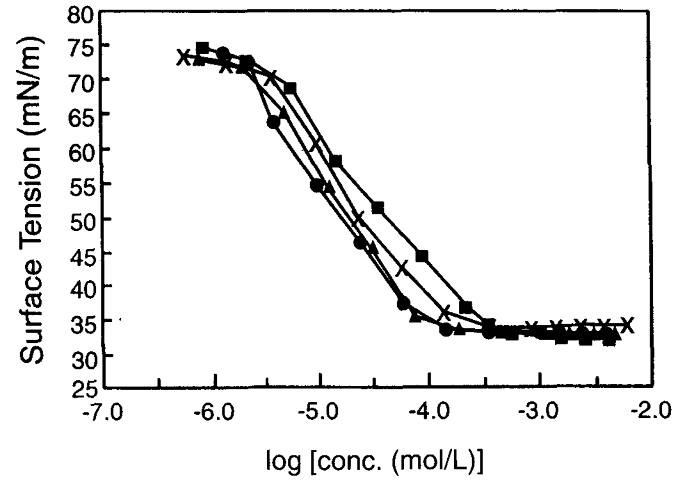

FIG. 3. Plot of the concentration (in 1N NaOH) of arbitrarily prepared mixtures of the hydroxy fatty acids derived from oleic acid with SeO_2/*tert.*-butylhydroperoxide vs. surface tension. The plots of individual 8-hydroxy-9(*E*)-octadecenoic acid and 11-hydroxy-9(*E*)-octadecenoic acid are included for comparison purposes. Key as in Figure 1, plus ▲, mixture of 8-hydroxy- and 11-hydroxy-9(*E*)-octadecenoic acid (132:124); ✖, mixture of ▲ plus *erythro*- and *threo*-8,11-dihydroxy-9(*E*)-octadecenoic acid (127:121:72:75).

Table 1 lists the CMCs and the surface tensions at the CMC (γ_{CMC}) for the compounds investigated here. It is divided into subsections for the synthetic compounds and the natural comparison materials.

The allylic monohydroxy acids are the best surfactant materials of the studied compounds. The "overoxidized" side products with oxo instead hydroxy groups also lower the surface tension. However, their yields in these reactions are low (26,27). The oxo products may nevertheless constitute part of a mixture of products suitable for application and need not necessarily be removed from the crude product mix.

There are differences in the surface properties of the individual compounds. As mentioned previously, the monohydroxy acids are better surfactants than the dihydroxy acids. This contradicts the conclusion of Parra *et al.* (5), who stated that surface properties improve with the number of hydroxy groups. These authors had compared 7,10-dihydroxy-8(*E*)-octadecenoic acid to saturated monohydroxy acids.

Among the monohydroxy acids, 8-hydroxy-6(*E*)-octadecenoic acid is the most effective material, followed by 8-hydroxy-9(*E*)-octadecenoic acid. 11-Hydroxy-9(*E*)-octadecenoic acid and ricinoleic acid exhibit the more similar surface activity. The latter two compounds are also structurally more similar. Also, 10-hydroxy-11(*E*)-eicosenoic acid has a lower CMC than 13-hydroxy-11(*E*)-eicosenoic acid. The conclusion is that proximity of the hydroxy group to the functional group at C1 enhances the surface activity. Apparently, it is also advantageous to position the double bond between the hydroxy group and the functional group at C1, instead of on the side of the terminal methyl group, as shown by 8-hydroxy-6(*E*)-octadecenoic acid and 8-hydroxy-9(*E*)-octadecenoic acid (Fig. 2). For the two alcohols studied here, these observations hold for the CMC, but not for the γ_{CMC}.

The conclusion that proximity of the hydroxy group to C1 enhances the surface properties had been reached by other authors (23) for the saturated 2-hydroxy- and 3-hydroxyoctadecanoic acids and is extended in the present work to allylic monohydroxy acids. These authors (23) had also found that 2-hydroxyhexadecanoic acid was an effective surfactant, but that 16-hydroxyhexadecanoic acid was unsuitable. These observations were interpreted in terms of a more favorable hydrophilic–lipophilic balance (HLB) for compounds with the hydroxy group close to C1. The HLB also explains the poorer surfactant properties of the allylic dihydroxy compounds. Due to the high number of hydroxy groups, there is less of the lipophilic part of the molecule available for micelle formation, and the HLB is thus shifted toward the hydrophilic part of the molecule.

Among the dihydroxy compounds, the *threo* diastereomers possess better surface properties than the *erythro* congeners.

This is shown for the *erythro*/*threo* pairs of 8,11-dihydroxy-9(*E*)-octadecenoic acid and 10,13-dihydroxy-11(*E*)-octadecenoic acid (Table 1 and Fig. 2). Microbially-produced 7,10-dihydroxy-8(*E*)-octadecenoic acid behaves similar to the *threo* compounds, and other methods (26–28) have shown that it is a *threo* diastereomer (absolute configuration *R,R*). Besides known differences in other physical properties, such as melting point and solubility, it is possible to distinguish *erythro*/*threo* diastereomers by their surface properties. To the best of our knowledge, distinguishing *erythro*/*threo* isomers by surface tension has not been previously reported.

Chainlength also affects the surface properties of allylic hydroxy fatty compounds. The two monohydroxyeicosenoic acids studied here exhibit slightly lower γ_{CMC} than the monohydroxyoctadecenoic acids, but the CMCs themselves are higher (which is also a result of the distance of the hydroxy group from C1). The dihydroxyeicosenoic acids show higher CMCs than the corresponding octadecenoic acids. We also attempted to study the mono- and dihydroxy acids derived from erucic acid [13(*Z*)-docosenoic acid], but these compounds were insufficiently soluble in 1N NaOH. The influence of double bond configuration could not be studied because all products were obtained with *trans* configuration (*trans* is the configuration usually obtained in other synthetic sequences and microbial conversions). For methyl ricinoleate (*cis* double bond), lower critical micellization temperature was found than for methyl ricinelaidate (*trans* double bond) (19). This coincided with the results on other unsubstituted, unsaturated fatty acids.

The two mixtures exhibited satisfactory surface properties (Fig. 3). The surface tension of the mixture composed only of the monohydroxy acids is nearly identical to that of 8-hydroxy-9(*E*)-octadecenoic acid. This is so because the surface properties are oriented toward the behavior of the better surfactant (29). However, the plot for the mixture containing two mono- and two dihydroxy compounds is situated between those of the mono- and dihydroxy acid. Here, the concentration of the best surfactant in the mixture [8-hydroxy-9(*E*)-octadecenoic acid] is too low to compensate for the reduced surfactant properties of the other compounds.

Although the esters [methyl 8-hydroxy-9(*E*)-octadecenoate and methyl 11-hydroxy-9(*E*)-octadecenoate] decreased the surface tension to the range of the monohydroxy acids, they did so at considerably higher concentrations ($>10^{-2}$ mol/L), and CMCs were not determined. The esters are therefore not included in Table 1. The diols [9(*E*)-octadecene-1,8-diol and 9(*E*)-octadecene-1,11-diol], derived from unsaturated fatty alcohols, also displayed poorer surface properties. It has already been reported that fatty alcohols with one OH group at C1 have only limited applicability as surfactants (23). Therefore, the effectiveness of these compounds as surfactants significantly depends on the nature of the functional group at C1, as has been discussed above for the CMC and γ_{CMC} of compounds with an OH group at C1.

In conclusion, most monohydroxy acids are effective surfactants and are competitive with naturally-occurring materials, such as ricinoleic acid. Allylic dihydroxy acids and products derived from fatty alcohols are less effective as surfactants. Surface tension is another physical property for effectively distinguishing *erythro*/*threo* diastereomers of dihydroxy fatty acids. The allylic hydroxy compounds may be suitable for use in microemulsions or co-solvency or as additives in commercial products.

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