and purified, seemed quite stable. Attempts to convert the amino lactone **5** to the lactam **6** were unsuccessful in boiling dioxane or xylene or EtOH–$CHCl_3$, but **6** was obtained in about 50% yield from a solution of **5** in TFA–CH_2Cl_2 after 18 h. In subsequent trials, partial conversion of **5** to **6** was achieved in about the same yield with anhydrous magnesium sulfate in refluxing toluene for 24 h. The lactam **6** was reduced by BH_3–THF complex, and the hydrolyzed reaction mixture, in CH_2Cl_2 solution, was divided into two portions. Efforts to isolate the expected tertiary base **7** from one portion afforded only the dihydrodibenzopyrrocoline **8**, apparently formed by air-oxidation of **7** as reported by Robinson and Sugasawa.[1] The second portion of the reaction mixture was treated with methyl iodide to give crystalline *O*-methylcryptaustoline iodide (**1**).

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. Infrared spectra were recorded as paraffin oil mulls on a P.E. Model 727 spectrophotometer; NMR spectra were obtained in $CDCl_3$ solutions on a P.E. R-600 spectrometer; melting points (Mel-Temp apparatus) were taken in open capillaries and are uncorrected.

3,4-Dimethoxy-6-[(3,4-dimethoxy-6-nitrophenyl)acetyl]-phenylacetic Acid (3). To a paste of keto acid **2** (5 g) in HOAc (15 mL) was added dropwise a cold solution of HNO_3 (5 mL) in HOAc (10 mL) with stirring and cooling in an ice bath. After 20 min, the dark brown solution was poured into cold water (300 mL), and the tan precipitate was collected by suction filtration and washed with water to give the nitro keto acid **3** (4.8 g, 85.7%). The product was recrystallized from dioxane–HOAc as pale yellow crystals: mp 213–214 °C; IR 3355, 1730 (C=O), 1520 and 1330 (NO_2) cm^{-1}; ^1H NMR δ 7.81–6.77 (m, 4 H), 4.64 (s, 2 H), 3.97 (s, $4OCH_3$), 3.78 (s, 2 H). Anal. Calcd for $C_{20}H_{21}NO_9$: C, 57.28; H, 5.05; N, 3.34. Found: C, 57.47; H, 5.13; N, 3.69.

1-(3,4-Dimethoxy-6-nitrobenzyl)-6,7-dimethoxy-3-isochromanone (4). A suspension of nitro keto acid **3** (1.8 g) in EtOH (20 mL) was treated wiith $NaBH_4$ (0.3 g) in small portions. After 3 h additional $NaBH_4$ (0.3 g) was added; after standing for 30 min, the reaction mixture was diluted carefully with water (120 mL), and the solution was acidified with 20% HCl to pH 3. On gentle warming, the nitro lactone (**4**) precipitated as a light yellow solid and was recrystallized from toluene–EtOAc as nearly colorless plates (1.2 g): mp 217–218 °C; IR 1735 (C=O), 1530 (asym NO_2), 1335 (sym NO_2) cm^{-1}; ^1H NMR δ 7.65 (s, 1 H), 6.73 (s, 1 H), 6.63 (s, 1 H), 5.54 (m, 1 H), 3.93 (s, $2OCH_3$), 3.62 (s, 2 H), 3.25 (m, 2 H). Anal. Calcd for $C_{20}H_{21}NO_8$: C, 59.55; H, 5.25; N, 3.47. Found: C, 59.21; H, 5.18; N, 3.40.

1-(3,4-Dimethoxy-6-aminobenzyl)-6,7-dimethoxy-3-isochromanone (5). Fe dust (15 g) was added with good mixing to a suspension of nitro lactone **4** (5.2 g) in HOAc (100 mL) at 60 °C over a 1.5-h period. The heating and stirring were continued for 2 h more, and the reaction mixture was added to cold H_2O (700 mL). The solids were collected and extracted with boiling $CHCl_3$ (3 × 30 mL). The $CHCl_3$ extracts were evaporated, and the residue was diluted with hot MeOH, filtered, and cooled to give a tan solid (3.5 g) in several crops. The original aqueous filtrate was extracted with CH_2Cl_2 (3 × 30 mL), and the organic layer was evaporated to give an additional 0.8 g of amino lactone **5**. The crude product was recrystallized from EtOH–toluene as colorless crystals: mp 223–224 °C; IR NH_2 doublet at 3500 and 3420, ν_{CO} at 1740 cm^{-1}; ^1H NMR δ 6.61–6.00 (m, 4 H), 5.68 (m, 1 H), 3.84 and 3.80 ($4OCH_3$), 3.52 (s, 2 H), 3.15 (m, 2 H), 2.15 (s, NH_2); mass spectrum, *m/e* (relative intensity) 373 (M^+, 14), 372 (4), 340 (50), 339 (68), 330 (22) 329 (100). Anal. Calcd for $C_{20}H_{23}NO_6$: C, 64.33; H, 6.21; N, 3.75. Found: C, 64.41; H, 6.19; N, 3.51.

2,3,9,10-Tetramethoxy-6-oxo-5,6,12,12a-tetrahydrodibenzo[*b*,*g*]pyrrocoline (6). (A) In CH_2Cl_2–TFA. Amino lactone **5** (3 g) was dissolved in a solution of CH_2Cl_2 (15 mL)–trifluoroacetic acid (15 mL), and after 18 h, the solution was poured into water (120 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was reextracted with water and evaporated. The residual solids were recrystallized from aqueous MeOH to give a rose-colored product (1.5 g), which was purified by passage through a short column of alumina and recrystallized from MeOH–H_2O as colorless lactam **6** mp 199–200 °C; IR 1655 (C=O) cm^{-1}; mass spectrum *m/e* (relative intensity) 355 (M^+, 100), 340 (93); ^1H NMR δ 7.98 (s, 1 H), 6.85–6.77 (m, 3 H), 5.30 (m, 1 H), 3.95 ($4OCH_3$), 3.69 (s, 2 H), 3.58 (m, 2 H). Anal Calcd for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.31; H, 6.04; N, 3.87.

Additional crops of solid (0.3 g) from the methanol solution proved to be starting amino lactone (**5**).

(B) In Toluene–$MgSO_4$. A suspension of **5** (1.0 g) in toluene (50 mL) and anhydrous $MgSO_4$ was allowed to reflux for 24 h. The hot mixture was filtered and was diluted with petroleum ether to 75 mL and cooled. An ivory-colored solid (0.6 g), mp 188–190 °C, was isolated. This product was identical in melting point and IR spectrum with the lactam from part A.

The insoluble solids were extracted with CH_2Cl_2, and starting amino lactone (0.2 g) was recovered on exaporation and recrystallization from EtOH.

***O*-Methylcryptaustoline Iodide (1) and 2,3,9,10-Tetramethoxy-5,6-dihydrodibenzo[*b*,*g*]pyrrocoline (8).** Lactam **6** (1 g) was added to a solution of BH_3–THF complex (35 mL). The solid dissolved only after gentle heating, and the turbid solution was allowed to stand for 20 h. The reaction mixture was hydrolyzed with 10% NaOH and largely evaporated; the residual oil was diluted with water (120 mL) and extracted with CH_2Cl_2 (40 mL). The CH_2Cl_2 solution was divided into two equal parts. One portion was diluted with MeOH (5 mL) and treated with excess MeI. A colorless solid (0.5 g), mp 220–223 °C, separated. The *O*-methylcryptaustoline iodide (**1**) was recrystallized twice from aqueous EtOH as colorless needles: mp 241–243 °C (lit.[11] mp 243–245 °C; lit.[1] mp 242–243 °C); mass spectrum, *m/e* (relative intensity) 341 (M^+ – 142). Anal. Calcd. for $C_{21}H_{26}NO_4 \cdot 0.5\ H_2O$: C, 51.22; H, 5.52; N, 2.85. Found: C, 51.23; H, 5.53; N, 2.88.

The second portion of the CH_2Cl_2 extract was evaporated, and the oily residue was redissolved in MeOH and diluted carefully with water. A light-gray crystalline solid (0.25 g), mp 195–197 °C, separated on standing. The crude solid was chromatographed on silca gel and recrystallized from toluene–hexane solution to give the dihydrodibenzopyrrocoline **8**: mp 204–205 °C (lit.[11] mp 202–204 °C; lit.[1] mp 201–203 °C); mass spectrum, *m/e* (relative intensity) 339 (M^+, 100) 324 (89); ^1H NMR 7.22 (s, 1 H), 7.10 (s, 1 H), 6.80 (s, 1 H), 6.79 (s, 2 H), 3.98 ($4OCH_3$), 4.18 (t, 2 H, J = 6 Hz).

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Registry No. (±)-**1**, 17138-48-6; **2**, 26954-85-8; **3**, 83573-15-3; (±)-**4**, 83573-16-4; (±)-**5**, 83573-17-5; (±)-**6**, 83573-18-6; **8**, 20975-17-1.

Conformation of Long-Chain *erythro*- and *threo*-Tartrates in the Micellar State

F. M. Menger* and P. C. Vasquez

Department of Chemistry, Emory University, Atlanta, Georgia 30322

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Despite intense current interest in micelles, only two previous reports specifically compare conformations of head-group units inside assemblages with those in the

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Table I. Coupling Constants of the Methine Protons of Tartaric Acid Derivatives in D_2O at pD 10.0[a]

compd	aggregation state	J_{AB}, Hz
ethyl *erythro*-tartarate	monomeric	4.2
ethyl *threo*-tartarate	monomeric	2.1
dodecyl *erythro*-tartarate	micellar	4.2
dodecyl *threo*-tartarate	micellar	2.1

[a] All NMR spectra were run at a concentration of 0.02 M.

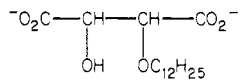
monomeric state. Takahashi et al.[1] found that the percentage of *trans*-*N*-octanoylsarcosinate (eq 1) increases

cis trans (1)

from 46% to 76% when the critical micelle concentration is exceeded. Menger and Jerkunica[2] showed in an NMR study of *o*-alkyl-DL-tyrosines that the population of conformer a changes from 52% to 66% and conformer b from

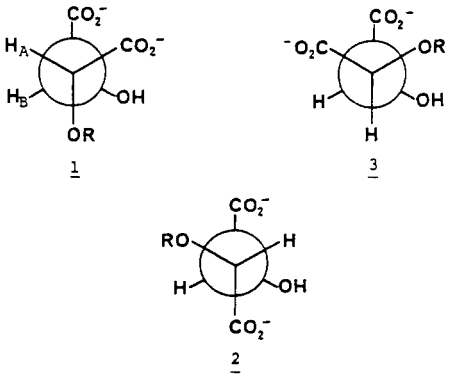
a b

24% to 8% upon micellization. We were interested in exploring further the subtleties of micellar conformation using long-chain tartrate derivatives:



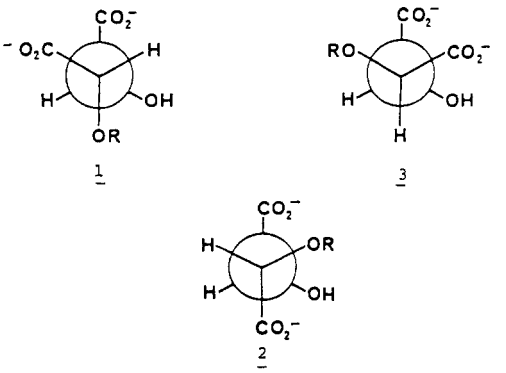
Several features of this system seemed attractive at the onset of the project. (1) The conformation about the central C–C bond can be assessed by ^1H NMR by using coupling constants from isolated AB quartets. (2) Interesting comparisons between erythro and threo diastereomers are possible. (3) Monomer and micelle systems can be readily obtained by varying the chain-length of the alkyl substituent (i.e., ethyl vs. dodecyl); chain-length should not otherwise affect conformational properties.

Table I lists coupling constants for the methine protons for the ethyl and dodecyl derivatives of tartaric acid (D_2O, pD 10.0). Coupling constants differ for erythro and threo analogues but not for the monomeric and micellar states. There is no question that the dodecyl compounds do in fact form micelles because surface tension vs. concentration plots display the usual sharp break corresponding to a cmc of 0.013 M. Unfortunately, solubility problems prevented the use of high surfactant concentrations, so that NMR spectra were run at 0.02 M. Since only about 35% of the surfactant exists in the micellar state at this low concentration,[3] the observed coupling constants for the dodecyl derivatives represent weighted averages of both monomeric and micellar parameters. This creates no complications because of the following. (1) Micellization (partial as it is) has absolutely no effect of the coupling constant; thus the relative proportion of monomeric to micellar surfactant need not be taken into account. (2) NMR spectra at a 0.03 M concentration (where 57% of the material is now micellar) give the same coupling constants as those at 0.02 M. We conclude inescapably that both *erythro*- and *threo*-tartrate derivatives retain their monomeric conformations within the Stern layer of micelles.



1 3 2

Figure 1. Conformations of the *erythro*-tartrate derivative.



1 3 2

Figure 2. Conformations of the *threo*-tartrate derivative.

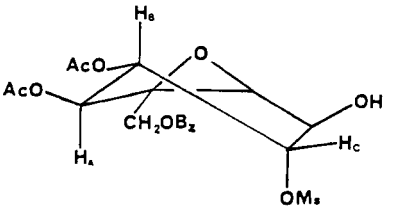


Figure 3. Compound for which J_{AB} = 5.5 Hz and J_{BC} = 2 Hz.

In order to analyze the variation in coupling constants from erythro to threo, but lack of change from monomer to micelle, we assume that three conformations suffice to describe the system (Figure 1 for erythro and Figure 2 for threo). This assumption is, of course, not strictly correct; its impact is lessened, however, by our focusing on *changes* in conformational populations rather than on absolute numbers. We also assume, in concert with previous observations,[2] that *erythro*-1 and *threo*-1 in Figures 1 and 2 should be favored in the micellar state. Both carboxylates are directed away from the hydrocarbon tail in these conformations. On the other hand, *erythro*-2 and *threo*-2 should be the most stable members of their trios from an electrostatic point of view (both carboxylates being anti). If micellization plays a role in the rotamer population, then aggregation should *decrease* J_{AB} for the erythro compound; *erythro*-1 with its gauche protons would assume greater importance relative to *erythro*-2 with its anti protons. In contrast, micellization favors *threo*-1 over *threo*-2 and should therefore *increase* J_{AB}. Since neither effect is observed, electrostatic repulsion between the two carboxylates must determine the conformation in both the monomeric and micellar states.

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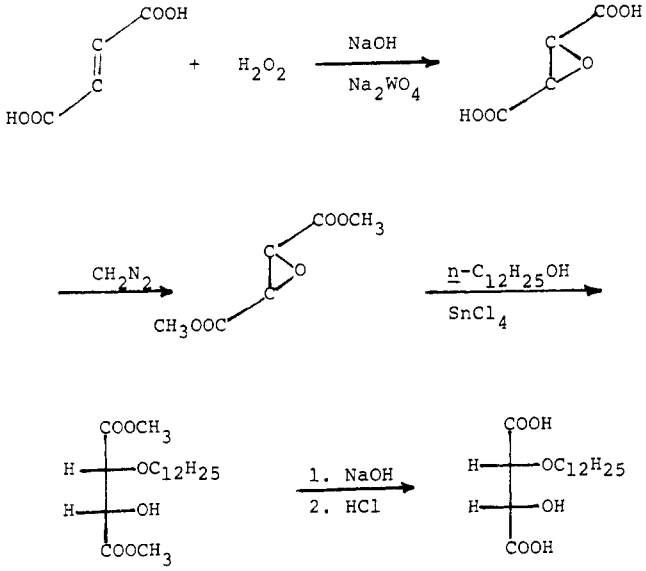
(3) Percent = 100([surfactant] − cmc)/[surfactant].

Scheme I. Synthesis of *O*-*n*-Dodecyl-*erythro*-Tartaric Acid[a]



[a] The threo diastereomer was prepared in a similar fashion by starting with maleic acid.

The above analysis implies that conformations *erythro*-**2** and *threo*-**2** predominate for the two diastereomers and that, consequently, the erythro form should possess a larger J_{AB} than the threo form. This is exactly what is observed (4.2 vs. 2.1 Hz). The generally low values for the vicinal coupling constants are undoubtedly related to the well-known effect of electronegative substituents.[4] We see an example of this effect in the compound shown in Figure 3[5] for which J_{AB} = 5.5 Hz and J_{BC} = 2 Hz. Our data and interpretation are reasonable with respect to these numbers.

The conformational stability of the tartrates upon micellization differs from the cases mentioned above [1,2] where perturbations are clearly observed. Even with these, however, the changes are small from an energy standpoint. We conclude that the head-group units within the Stern layer of micelles must be loosely packed and well separated by water. This is completely consistent with our "porous cluster" model[6-8] in which the micelle is viewed as a disorganized assemblage with rough surfaces, water-filled pockets, and no intimate contact among head groups.

Experimental Section

Coupling constants were obtained by averaging ten tracings from a Varian EM-390 spectrometer set at a sweep width of 2 ppm. Surface tension data were secured with the aid of a Fisher Tensiomat.

***O*-*n*-Dodecyl-*erythro*-tartaric Acid and *O*-*n*-Dodecyl-*threo*-tartaric Acid.** Since direct *O*-alkylations of tartaric acid failed (NaH or BuLi, RBr or ROTs, DMF), we utilized the pathway shown in Scheme I. Epoxidation of furmaric acid (to give ultimately erythro compound) and maleic acid (to give ultimately threo compound) was carried out by using the procedure of Payne and Williams.[9] The diacids suspended in ether were then esterified with diazomethane at 0 °C to give dimethyl *trans*-epoxysuccinate [mp 70–72 °C (lit.[10] mp 73 °C)] and dimethyl *cis*-epoxysuccinate [bp 110 °C (0.75 mm)]. Ring opening of the epoxides to form the dodecyl ethers failed in our hands using: (1) dodecanol plus H_2SO_4 catalyst;[11] (2) dodecanol plus boron trifluoride etherate catalyst;[12] (3) sodium dodecoxide in DMF or THF. However, the desired products were obtained as colorless oils (which were not further purified) with $SnCl_4$ as the catalyst (0.04 mol of dimethyl epoxysuccinate, 0.08 mol of *n*-dodecanol, and 0.64 g of $SnCl_4$ heated with stirring at 85 °C for 1 h and at 115 °C for 3 h). Hydrolysis of the methyl esters was accomplished with 3.5 M NaOH in refluxing methanol for 2.5 h. The erythro diacid melted at 147–148 °C (white crystals from water), gave a neutralization equivalent of 158.5 (calcd 159.2), and had an elemental analysis as follows: C, 59.86; H, 9.58 (calcd for $C_{16}H_{30}O_6$: C, 60.35; H, 9.50). The threo product melted at 125–127 °C (white crystals from water), gave a neutralization equivalent of 159.1, and had an elemental analysis as follows: C, 60.00; H, 9.32. NMR spectra confirmed the structure of the products.[13,14]

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Registry No. *O*-Ethyl *erythro*-tartrate dianion, 83693-40-7; *O*-ethyl *threo*-tartrate dianion, 83693-41-8; *O*-dodecyl *erythro*-tartrate dianion, 83693-42-9; *O*-dodecyl *threo*-tartrate dianion, 83693-43-0; dimethyl *cis*-epoxysuccinate, 56958-97-5.

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(13) For full details see the Ph.D. thesis of P.C.V. entitled "Part I. Studies on the Trajectory of Proton Transfer Reactions. Part II. Conformation Studies of Surfactant Molecules", Emory University, 1982.
(14) Attempts to place a dodecanoyl group on the OH of the dodecyltartrates failed. These double-chained compounds would have permitted a conformational study of molecules in vesicle bilayers.

m-Chloroperoxybenzoic Acid–Potassium Fluoride System: Study of Its Stability and Reaction with α-Methylstyrene

F. Camps,* J. Coll, A. Messeguer, and F. Pujol

Instituto de Quimica Bio-Orgânica, CSIC, c/o J. Girona Salgado, s/n Barcelona-34, Spain

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The strong interaction between fluoride ions and compounds with acidic hydrogens is well documented in the literature.[1] In this context, we have recently reported a preliminary account of the extension of this interaction to peroxy carboxylic acids, by the use of the MCPBA–KF system in the Baeyer–Villiger oxidation of aromatic aldehydes and in the epoxidation of olefins.[2] As we had stated, one of the practical advantageous effects of adding KF to solutions containing *m*-chloroperbenzoic acid (MCPBA) and *m*-chlorobenzoic acid (MCBA) was the complete removal of these acids by precipitation. However, we anticipated that this addition could result in the concomitant labilization of the hydroperoxide bond, which is considered to be critical for the stability of the organic peroxy acid.[3] Accordingly, we deemed that an evaluation of the stability of the above system was required to es-

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