^{13}C NMR ($CDCl_3$) δ 7.3 (q), 7.6 (q), 9.6 (q), 9.8 (q), 10.0 (q), 13.1 (q), 13.4 (q), 14.2 (q), 15.0 (q), 17.5 (q), 35.1 (2 t), 41.1 (d), 45.8 (d), 47.2 (d), 48.6 (d), 51.1 (d), 73.8 (d), 77.6 (d), 119.1 (s), 120.4 (s), 160.3 (s), 160.8 (s), 173.9 (s), 179.4 (s), 210.4 (s), 210.9 (s), 211.8 (s); FABMS m/z 507.2945, $C_{28}H_{43}O_8$ (MH^+) requires 507.2958.

Single-Crystal X-ray Analysis of Baconipyrone. A clear, colorless, and roughly cubic (0.35 × 0.3 × 0.3 mm) crystal of baconipyrone B (**6**) was selected for all crystallographic measurements. Preliminary photographs showed monoclinic symmetry, and accurate lattice constants of a = 12.663 (3) Å, b = 8.958 (2) Å, c = 13.279 (3) Å, and β = 94.38 (2)° were determined from a least-squares analysis of 15 diffractometer measured 2θ-values. Systematic extinctions and density considerations indicated one molecule of composition $C_{28}H_{42}O_8$ formed the asymmetric unit in space group $P2_1$. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a four-circle diffractometer using Cu Kα radiation (1.541 78 Å) and θ:2θ scans of 1.0° plus the Kα separation. Backgrounds were measured at the beginning and end of each scan for 30% of the total scan time. A total of 2188 unique reflections were collected in this manner, and after correction for Lorentz, polarization, and background effects, 2118 (97%) were judged observed. No corrections for absorption or decomposition were judged necessary. A phasing model was found using direct methods and full-matrix least-squares refinements with anisotropic nonhydrogen atoms and fixed isotropic riding hydrogens have converged to a conventional discrepancy index of 0.056 for the observed data. Additional X-ray data are available and are described in the supplementary material paragraph at the end of this manuscript.

Acknowledgment. We thank Dr. Ted Molinski for assistance in collecting the animals. This research was supported by grants from the National Science Foundation (CHE86-03091 to D.J.F.), the National Institutes of Health (CA24487 to J.C.) and the New York State Sea Grant Program.

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Supplementary Material Available: Tables of fractional coordinates, interatomic distances, interatomic angles, and thermal parameters for baconipyrone B (5 pages). Ordering information is given on any current masthead page.

Vallartanones A and B, Polypropionate Metabolites of *Siphonaria maura* from Mexico

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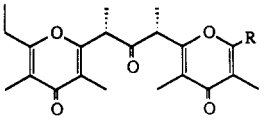
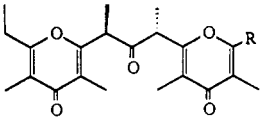
Specimens of *Siphonaria maura* collected near Puerto Vallarta, Mexico, contained two new metabolites of the polypropionate class. Vallartanones A (**6**) and B (**7**) were identified by interpretation of spectral data. Interpretation of the CD spectrum of vallartanone A (**6**) by application of exciton coupling theory provided the absolute configuration. The metabolites of *S. maura* vary according to the collection location.

Pulmonate molluscs of the genus *Siphonaria*, known commonly as false limpets, are intertidal gastropods that are amphibious in that they possess both gills and lungs. The secondary metabolite chemistry of *Siphonaria* species is dominated by compounds of the polypropionate class.[1] An earlier study of the metabolites of *Siphonaria maura* from Costa Rica resulted in the isolation of four closely related pyrones, maurapyrones A–D (**1**–**4**) and the unrelated polypropionate maurenone (**5**).[2] The major problem encountered in the structural elucidation of polypropionates such as maurenone (**5**) has been to define the stereochemistry of noncrystalline compounds, particularly those with noncontiguous chiral centers. In this paper, we report the structural elucidation of two new polypropionate metabolites, vallartanones A (**6**) and B (**7**), by using a combination of spectral and chemical methods.

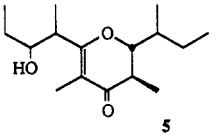
Specimens of *Siphonaria maura* collected at Sayulita, near Puerto Vallarta, Mexico, were stored in acetone. The ethyl acetate soluble material from the acetone extract was purified by flash chromatography on silica followed by LC on Partisil using 45% ethyl acetate in hexane as eluant to obtain vallartanone A (**6**, 29.8 mg, 0.08 mg/animal) and vallartanone B (**7**, 5.6 mg, 0.015 mg/animal).



1 R = n-C_5H_{11}
3 R = i-C_4H_9



2 R = n-C_5H_{11}
4 R = i-C_4H_9



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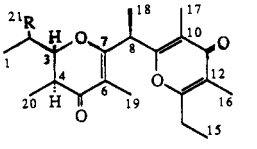
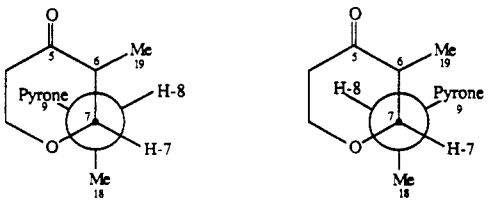


6 R = CH_3 **7** R = H

The molecular formula of vallartanone A (**6**), $C_{21}H_{30}O_4$, was determined from the EIMS molecular ion observed at m/z 346.2145. The presence of the γ-pyrone was indicated by infrared bands at 1645 and 1600 cm^{-1} as well as a UV absorption at 264 nm. The ^1H NMR spectrum contained two methyl singlets at δ 1.96 and 1.94, typical of those on a pyrone ring, and an olefinic methyl singlet at δ 1.75. In addition, four methyl doublets and one methyl triplet were observed. Two methyl doublets at δ 0.84 and 1.08 were coupled to a one proton signal at δ 1.85 which was coupled to a methine signal at δ 3.79 (dd, 1 H, J = 12.9, 2.6 Hz). This signal was further coupled (J = 12.9 Hz) to a signal at δ 2.38, which was also coupled to a methyl

(1) Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 551; **1986**, *3*, 1; **1987**, *4*, 539; **1988**, *5*, 613.
(2) Manker, D. C.; Faulkner, D. J.; Xe, C.-F.; Clardy, J. *J. Org. Chem.* **1986**, *51*, 814.

0022-3263/89/1954-5374$01.50/0



8 (7S*,8R*) $\phi_{7,8}$ = 60° 10 (7S*,8S*) $\phi_{7,8}$ = 180°

Figure 1. Newman projections shown looking down the 7–8 bond for 6,7-dihydrovallartanone A (**8**, 7*S**,8*R**) on left and 6,7-dihydro-8-*epi*-vallartanone A (**10**, 7*S**,8*S**) on right. Size of substituents: C-6 > 0 > H-7, Me-18 > pyrone > H-8.[3] Predicted dihedral angles between H-7 and H-8 ($\phi_{7,8}$) shown for each epimer.

doublet at δ 1.07 (J = 6.8 Hz). A one proton signal at δ 4.17 (q, 1 H, J = 7.1 Hz) was coupled only to the methyl doublet at δ 1.47 and the remaining signals at δ 2.62 (q, 2 H, J = 7.6 Hz) and 1.23 (t, 3 H, J = 7.6 Hz) were assigned to an ethyl group on a pyrone ring. The ^{13}C NMR spectrum, which was assigned by using a 2D $^1H/^{13}C$ HSC experiment, contained signals at δ 179.4 (s), 168.4 (s), 164.4 (s), 119.4 (s), and 118.3 (s) that were typical of a fully substituted pyrone ring, and at 195.2 (s), 160.8 (s) and 108.7 (s) due to the ketone and olefinic carbons in a dihydropyrone ring system. Consideration of both ^1H NMR and ^{13}C NMR data led to the assignment of structure **6** to vallartanone A.

Although the large coupling constant ($J_{3,4}$ = 12.9 Hz) indicated a trans-diaxial relationship between H-3 and H-4, there remained the problem of determining the relative stereochemistry at C-8. Hydrogenation of vallartanone A (**6**) over 5% palladium on carbon gave a mixture of reduced products, the major component of which was the 6,7-dihydro derivative **8**. The ^1H NMR spectrum of 6,7-dihydrovallartanone A (**8**) displayed two additional proton signals at δ 2.23 (dq, 1 H, J = 10, 7 Hz), and 3.34 (dd, 1 H, J = 10, 4 Hz) and an upfield shift of the C-19 methyl signal from δ 1.75 (s, 3 H) to 1.01 (d, 3 H, J = 7.0 Hz). The presence of two olefinic methyl signals at δ 2.00 and 1.97 showed that the γ-pyrone ring remained intact. Extensive homonuclear decoupling allowed complete assignment of all the proton resonances in 6,7-dihydrovallartanone A (**8**). The large coupling constants ($J_{3,4}$ = 10.6 Hz and $J_{6,7}$ = 10 Hz) and the observation of nuclear Overhauser enhancements between H-3 and H-7 defined the stereochemistry about the tetrahydropyrone ring.

The proposed stereochemistry at C-8 is dependent on an analysis of the Newman projections for the preferred conformation of the two possible C-8 epimers of 6,7-dihydrovallartanone A (**8**) that predicts a considerable difference for the $J_{7,8}$ coupling constant (Figure 1). According to Allinger,[3] the 1,3 steric interaction between two methyl groups is greater than the 1,3 steric interaction between a methyl group and phenyl ring. Therefore, in these projections, the most stable conformer is that in which the 18-methyl on C-8 is 180° from the 19-methyl on C-6. The most stable conformer for the 7*S**,8*S** epimer would have a large coupling constant for $J_{7,8}$ because the dihedral angle is approximately 180° while the 7*S**,8*R** epimer has a dihedral angle of about 60° and would be expected to have a small value for $J_{7,8}$, similar to the 4-Hz coupling constant measured for 6,7-dihydrovallartanone A (**8**). In order to validate this assignment, the C-8 epimer of **8** was synthesized. Treatment of vallartanone A with sodium hydroxide in THF gave a mixture of the two epimers at C-8 which were separated by LC. The ^1H NMR spectrum of

(3) Allinger, N. L.; Tribble, M. T. *Tetrahedron Lett.* **1971**, *35*, 3259.

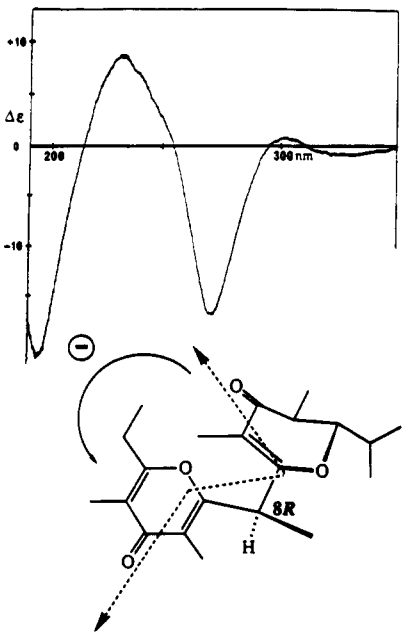
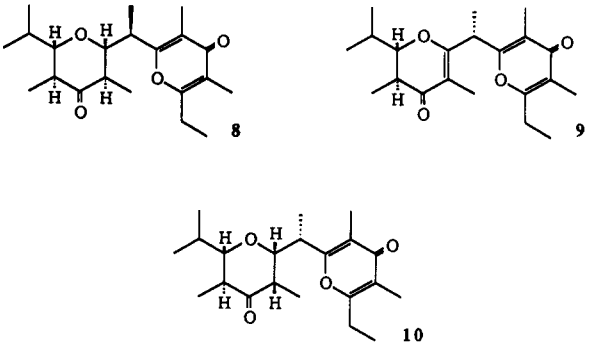


Figure 2. Circular dichroic spectrum of vallartanone A (**6**). The negative split Cotton effect in the CD spectrum indicates that the absolute stereochemistry at C-8 is *R*.

8-*epi*-vallartanone A (**9**) was almost identical with that of **8** except for a small upfield shift of H-8 and a divergence of the isopropyl methyl signals. The ^1H NMR data was assigned by using homonuclear decoupling experiments. 8-*epi*-Vallartanone A (**9**) was hydrogenated as before to produce 6,7-dihydro-8-*epi*-vallartanone A (**10**), which is an



epimer of 6,7-dihydrovallartanone A (**8**) at both C-6 and C-8.[4] While $J_{3,4}$ did not change, a small coupling constant observed between H-6 and H-7 ($J_{6,7}$ = 2.0 Hz) indicated their cis relationship. The cis 1,3-diaxial relationship of H-3 and H-7 was determined by observation of a 5% nuclear Overhauser enhancement. The coupling constant ($J_{7,8}$ = 9.8 Hz) observed in 6,7-dihydro-8-*epi*-vallartanone A (**10**) agrees well with the large value predicted from the Newman projections (Figure 1) for the 7*S**,8*S** epimer.

The absolute stereochemistry of vallartanone A (**6**) was assigned from measurements of circular dichroism and consideration of the most stable conformation in solution. Vallartanone A (**6**) can be expected to adopt the conformation shown in Figure 2 in order to minimize the severe strain between the C-6 methyl group and the substituents at C-8. One broad absorption band at 264 nm was observed in the UV spectrum of vallartanone A (**6**) and, by

(4) The hydrogenation of **6** to **8** is assumed to proceed via a cis addition of hydrogen followed by isomerization at C-6 to obtain the more stable tetrahydropyrone in which all alkyl substituents are equatorial: in the hydrogenation of **9** to **10**, we assume that steric interaction between CH_3-19 and the pyrone ring prevents isomerization at C-6.

Table I. ^1H NMR (360 MHz) and ^{13}C NMR (50 MHz) Assignments for Vallartanones A (6) and B (7)

	6		7	
C no.	^1H NMR	^{13}C NMR	^1H NMR	^{13}C NMR
1	1.08 (d, 3 H, J = 6.8)	19.6 (q)	0.97 (t, 3 H, J = 7.3)	10.6 (q)
2	1.85 (m, 1 H)	28.9 (d)	1.65, 1.81 (m, 1 H each)	25.4 (t)
3	3.79 (dd, 1 H, J = 12.9, 2.6)	87.4 (d)	3.86 (m, 1 H)	84.4 (d)
4	2.38 (dq, 1 H, J = 12.9, 6.8)	41.0 (d)	2.29 (dq, 1 H, J = 12.9, 7.0)	42.7 (d)
5		195.2 (s)		195.3 (s)
6		108.7 (s)		108.7 (s)
7		160.8 (s)		160.9 (s)
8	4.17 (q, 1 H, J = 7.1)	38.8 (d)	4.16 (q, 1 H, J = 7.1)	38.6 (d)
9		164.4 (s)†		164.7 (s)††
10		119.4 (s)*		118.9 (s)**
11		179.4 (s)		179.7 (s)
12		118.3 (s)*		118.2 (s)**
13		168.4 (s)†		168.6 (s)††
14	2.62 (q, 2 H, J = 7.6)	24.8 (t)	2.62 (q, 2 H, J = 7.6)	24.8 (t)
15	1.23 (t, 3 H, J = 7.6)	11.2 (q)	1.23 (t, 3 H, J = 7.6)	11.3 (q)
16	1.96 (s, 3 H)	9.4 (q)	1.96 (s, 3 H)	9.3 (q)
17	1.94 (s, 3 H)	9.2 (q)	1.94 (s, 3 H)	9.0 (q)
18	1.47 (d, 3 H), J = 7.1)	14.2 (q)	1.47 (d, 3 H, J = 7.1)	14.3 (q)
19	1.75 (s, 3 H)	8.9 (q)	1.76 (s, 3 H)	8.9 (q)
20	1.07 (d, 3 H, J = 6.8)	10.1 (q)	1.08 (d, 3 H, J = 7.0)	9.5 (q)
21	0.84 (d, 3 H, J = 6.8)	14.6 (q)		

*, **, †, ††Signals may be interchanged.

examination of the UV spectra of model compounds, this was interpreted as two overlapping bands from enone and pyrone $\pi-\pi^*$ transitions. The UV absorbance observed from vallartanone A (6) can be seen as two merged and almost degenerate bands the λ_{max} of which lie at 260 and 276 nm. As a consequence, the γ-pyrone and the α,β-unsaturated ketone constitute two inherently disymmetric chromophores and vallartanone A (6) is observed to be strongly levorotatory ($[\alpha]_D = -176°$). The circular dichroic spectrum of vallartanone A (6) exhibited a distinct negative split Cotton effect, due to exciton coupling with a minimum at 276 nm ($\Delta\epsilon = -16$) and a maximum at 235 nm ($\Delta\epsilon = +8.4$). From exciton coupling theory,[5] the first Cotton effect (that at longer wavelength) is negative and the second is positive when the electronic transition dipole moments of the two chromophores subtend a left-handed helicity, as is exhibited by vallartanone A (6). It follows that vallartanone A (6) has the 8R configuration and the absolute stereochemistry is (3R,4R,8R) as shown in Figure 2.

The minor metabolite, vallartanone B (7) has the molecular formula $C_{20}H_{28}O_4$ and is therefore a lower homologue of vallartanone A (6). The spectral data of vallartanone B (7) are almost identical with those of vallartanone A (6) with the exception of signals in the ^1H NMR spectrum at δ 0.97 (t, 3 H, J = 7.3 Hz), 1.65 (m, 1 H), and 1.81 (m, 1 H) and in the ^{13}C NMR spectrum at 10.6 (q) and 25.4 (t), which are assigned to an ethyl group in 7 that replaces the isopropyl terminus of vallartanone A (6) (Table I). The infrared spectrum was identical with that of vallartanone A, and the optical rotation was of the same sign and magnitude ($[\alpha]_D = -133°$). The similarity of spectral data for vallartanone A (6) and B (7), including identical coupling constants in the ^1H NMR spectrum, suggests that the stereochemistry is the same for both compounds.

The role of the polypropionate metabolite is uncertain. We tested the hypothesis that the polypropionate metabolites might be involved in chemical deterrence by offering specimens of both *Siphonaria maura* and a cooccurring limpet, *Collisella* sp., to their natural tidepool predators that included fish such as blennies and sculpins and decapods such as hermit crabs and brachyurans: both species were consumed with equal enthusiasm. However, a human taste test revealed that *S. maura* has a peppery and bitter taste compared with *Collisella* sp. In laboratory assays, vallartanone A (6) was eaten but vallartanone B (7) was rejected when applied to krill at 100 μg/mg and offered to the fish *Thallasoma lunare*.[6] Vallartanone A (6) is as effective as palmitoleic acid, a natural settling agent,[7] at inducing larval settlement in the tube worm *Phragmatopoma californica*.

The specimens of *Siphonaria maura* from Puerto Vallarta, Mexico, were physically indistinguishable from the specimens collected previously at Jaco Beach, Costa Rica, yet the vallartanones 6 and 7 differ from the maurapyrones 1–4[2] in both molecular size and structure. This is a departure from previous observations that the metabolites of *Siphonaria* species did not vary across the geographical range of the animal: for example, the metabolites of *Siphonaria pectinata* from the Costa del Sol, Spain,[8] were identical with those reported for *S. pectinata* from Florida.[9] Since the polypropionate metabolites are not of dietary origin and, in the case of *S. denticulata*, were shown to be synthesized by the pulmonate mollusc,[10] we must conclude that the populations of *S. maura* in Mexico and Costa Rica have been sufficiently separated to allow them to develop different biosynthetic capabilities.

Experimental Section

Extraction and Chromatography of *Siphonaria maura*. A total of 370 specimens of *S. maura* were collected intertidally from boulder fields at Sayulita near Puerto Vallarta, Mexico. Animals were stored in acetone for 30 days, the solvent was decanted and evaporated, and the remaining aqueous phase was extracted with ethyl acetate (4 × 50 mL) to give 722 mg of a brown oil. The crude organic extract was chromatographed on silica using a grading of solvent of increasing polarity from hexane to ethyl acetate to methanol. The fractions eluted with 70% ethyl acetate in hexane contained UV active components (200 mg). These

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(6) Pawlik, J. R.; Albizati, K. F.; Faulkner, D. J. *Mar. Ecol. Prog. Ser.* **1986**, *30*, 251.

(7) Pawlik, J. R. *Mar. Biol.* **1986**, *91*, 59. Pawlik, J. R.; Faulkner, D. J. *J. Exp. Mar. Biol. Ecol.* **1986**, *102*, 301.

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(9) Biskupiak, J. E.; Ireland, C. M. *Tetrahedron Lett.* **1985**, *26*, 4307.

(10) Manker, D. C.; Garson, M. J.; Faulkner, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1061.

fractions were combined and further purified by flash silica chromatography and HPLC (55% hexane/ethyl acetate, Dynamax silica) to obtain vallartanone A (**6**, 29.8 mg) and vallartanone B (**7**, 5.6 mg).

Vallartanone A (6): white crystals; mp 69 °C; $[\alpha]_D = -176°$ (*c* 0.68, $CHCl_3$); IR ($CHCl_3$) 1645, 1600 cm^{-1}; UV (MeOH) 215 nm (ϵ 12 296), 264 (28 510); ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) see Table I; HRMS *m/z* 346.2145, $C_{21}H_{30}O_4$ requires 346.2144.

Vallartanone B (7): oil; $[\alpha]_D = -133°$ (*c* 0.59, $CHCl_3$); IR ($CHCl_3$) 1645, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) see Table I; HRMS *m/z* 332.1986, $C_{20}H_{28}O_4$ requires 332.1987.

Hydrogenation of Vallartanone A (6). A solution of vallartanone A (**6**, 10.6 mg) in ethyl acetate (3 mL) containing 5% palladium on carbon (10 mg) was stirred vigorously under 1 atm of hydrogen for 18 h. The catalyst was removed by filtration through Celite, the solvent was evaporated, and the residue was purified by HPLC on Partisil (60% hexane–ethyl acetate) to obtain 6,7-dihydrovallartanone A (**8**, 1.2 mg, 11% yield) and recovered vallartanone A (50%).

6,7-Dihydrovallartanone A (8): oil; IR ($CHCl_3$) 1715, 1655, 1595 cm^{-1}; UV (MeOH) 216 nm (ϵ 10 822), 259 nm (ϵ 10 915); ^1H NMR ($CDCl_3$) δ 0.94 (d, 6 H, *J* = 7.0 Hz, H-20, 21), 1.00 (d, 3 H, *J* = 6.6 Hz, H-1), 1.04 (d, 3 H, *J* = 7.0 Hz, H-19), 1.24 (t, 3 H, *J* = 7.0 Hz, H-15), 1.40 (d, 3 H, *J* = 7.0 Hz, H-18), 1.87 (m, 1 H, H-2), 1.97 (s, 3 H, H-16), 2.00 (s, 3 H, H-17), 2.23 (dq, 1 H, *J* = 10.0, 7.0 Hz, H-6), 2.43 (dq, 1 H, *J* = 10.6, 7.0 Hz, H-4), 2.62 (AB q, 2 H, *J* = 15.0, 7.0 Hz, H-14), 3.00 (dd, 1 H, *J* = 10.6, 2.0 Hz, H-3), 3.27 (dq, 1 H, *J* = 7.0, 4.0 Hz, H-8), 3.34 (dd, 1 H, *J* = 10.0, 4.0 Hz, H-7); LRMS *m/z* = 348.3, $C_{21}H_{32}O_4$ requires 348.2.

Epimerization of Vallartanone A (6). Sodium hydroxide (4 M, 1.5 mL) was added to a solution of vallartanone A (**6**, 18.5 mg) in dry THF (3 mL), and the mixture was stirred vigorously under nitrogen for 18 h. The mixture was partitioned between water and ether, and the organic layer was washed with water (1 mL), dried over sodium sulfate, and evaporated to dryness. The residue was purified on ODS-Partisil (75% methanol–water) to obtain a 4:1 mixture of vallartanone A (**6**, 14.2 mg) and 8-*epi*-vallartanone A (**9**, 4.3 mg).

8-*epi*-Vallartanone A (9): oil; ^1H NMR ($CDCl_3$) δ 0.95 (d, 3 H, *J* = 6.9 Hz), 0.96 (d, 3 H, *J* = 6.9 Hz), 1.07 (d, 3 H, *J* = 6.9 Hz, H-20), 1.23 (t, 3 H, *J* = 7.7 Hz, H-15), 1.49 (d, 3 H, *J* = 7.0 Hz, H-18), 1.73 (s, 3 H, H-19), 1.94 (s, 3 H), 1.95 (s, 3 H), 2.00 (m, 1 H, H-2), 2.45 (dq, 1 H, *J* = 12.8, 6.9 Hz), 2.61 (q, 3 H, *J* = 7.7 Hz, H-14), 2.62 (q, 3 H, *J* = 7.7 Hz, H-14), 3.71 (dd, 1 H, *J* = 12.8, 2.8 Hz, H-3), 4.14 (q, 1 H, *J* = 7.0 Hz, H-8).

Hydrogenation of 8-*epi*-Vallartanone A (9). A solution of 8-*epi*-vallartanone A (**9**, 4.3 mg) in ethyl acetate (3 mL) containing 5% palladium on carbon (5 mg) was stirred vigorously under 1 atm of hydrogen for 18 h. The catalyst was removed by filtration through Celite, the solvent was evaporated, and the residue was purified by HPLC on Partisil (60% hexane–ethyl acetate) to obtain 6,7-dihydro-8-*epi*-vallartanone A (**10**, 0.25 mg, 5.5% yield), the starting material (**9**, 1.0 mg, 24% yield), and several other unidentified products.

6,7-Dihydro-8-*epi*-vallartanone A (10): oil; UV (MeOH) 215 nm (ϵ 9222), 259 nm (ϵ 12 350); ^1H NMR ($CDCl_3$) δ 0.95 (d, 3 H, *J* = 6.5 Hz, H-20), 1.01 (d, 3 H, *J* = 6.9 Hz, H-21), 1.04 (d, 3 H, *J* = 7.2 Hz, H-19), 1.12 (d, 3 H, *J* = 6.9 Hz, H-1), 1.19 (t, 3 H, *J* = 7.6 Hz, H-15), 1.35 (d, 3 H, *J* = 6.9 Hz, H-18), 1.90 (m, 1 H, H-2), 1.94 (s, 3 H, H-17), 2.00 (s, 3 H, H-16), 2.21 (dq, 1 H, *J* = 7.2, 2.0 Hz, H-6), 2.58 (q, 2 H, *J* = 7.6 Hz, H-14), 2.65 (dq, 1 H, *J* = 10.8, 6.5 Hz, H-4), 3.12 (dd, 1 H, *J* = 10.8, 2.2 Hz, H-3), 3.18 (dq, 1 H, *J* = 9.8, 6.9 Hz, H-8), 3.73 (dd, 1 H, *J* = 9.8, 2.0 Hz, H-7); EIMS *m/z* 348.3.

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Notes

Electrochemistry in Micellar Media. Dimerization of Electroreducible Amphiphilic Aromatic Ketones in Aqueous Media: A Stereochemical Approach

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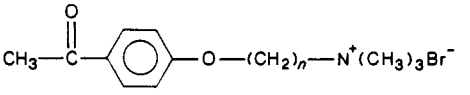
During the past decade, numerous studies have reported the influence of surfactants on electrochemical mechanisms.[1] Previous papers from our laboratory have described the electrochemical behavior of amphiphilic molecules such as [(4-acetylphenoxy)alkyl]trimethylammonium salts[2-4] **1–5**. The ability of some of them to give micelles or mixed micelles when a second surfactant is added (i.e., cetyltrimethylammonium bromide, CTAB) affects the electrochemical processes.[4] As we reported in the latter work, compounds **1–5** follow two different electrochemical reduction models depending on the hydrocarbon chain length: The first concerns the ketones **1–3**, bearing a short hydrocarbon chain. They are not included within micelles of CTAB, and the reduction occurs, under such conditions, through a surfactant (CTAB) adsorbed layer at the mercury electrode.



1, *n* = 3
2, *n* = 4
3, *n* = 6
4, *n* = 8
5, *n* = 10

The second is observed with compounds **4** and **5**, possessing the two longest hydrocarbon chains. They are able to form micelles themselves, and in the presence of CTAB

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