as it is between the four-orbital configurations in the monomer.[11] From an alternative viewpoint, the new low-energy $^1Q'(\pi,\pi^*)$ excited state results from the coupled exciton and charge-resonance states of the dimer.[18] The extent of mixing among these states is of central importance in understanding the properties of the bacteriochlorophyll dimer in the photosynthetic reaction center.[1c,d,17b,19]

The spectroscopic results presented here for the Th^{IV} sandwich complexes have identified a new low-energy (π,π^*) state that apparently arises from the significant overlap that should be present whenever porphyrin rings are held within ~3 Å of one another. The weak origin and stronger overtone transitions to this lowest $^1(\pi,\pi^*)$ excited state account for the absorption bands in the 600–700-nm region in strongly interacting porphyrin dimers. The relative intensities of these transitions suggest that vibronic coupling is important in these dimers, as has been proposed for the bacteriochlorophyll special pair of the photosynthetic reaction center.[1d,19b] Our observations on these simple, well-defined sandwich complexes should aid in evaluating the nature of the lowest excited state of the special pair, where exciton and protein effects may also contribute.

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(18) The exciton states are linear combinations of the local-excited configurations and the charge-resonance states are linear combinations of the charge-transfer, or ionic, configurations. Charge-resonance states have been discussed recently for the related Sn^{IV} phthalocyanine sandwich complex.[10b]

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Enzyme-Mediated Asymmetric Decarboxylation of Disubstituted Malonic Acids

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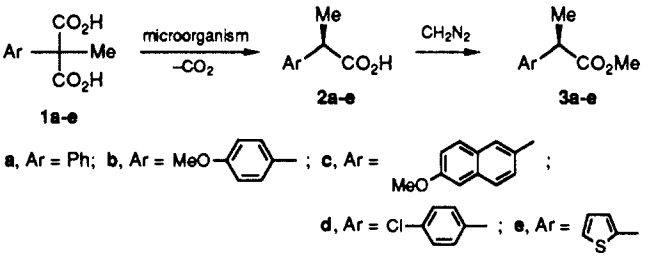
Transformation of a prochiral molecule to a chiral product is one of the most attractive methods of asymmetryic synthesis.[1] Although some efforts have been devoted to enantioselective decarboxylation of disubstituted malonates, only unsatisfactory results have been obtained so far.[2] Thus, we tried enzymatic conversion of the acids, because some biosynthetic routes, such as fatty acid synthesis, involve decarboxylation steps.

First, we screened for a microorganism that is able to grow by utilizing phenylmalonic acid as a sole source of carbon. It was supposed that the first step of the metabolism is decarboxylation giving phenylacetic acid, which would be further oxidized via benzoylformate. If the enzyme responsible for this reaction also acts on disubstituted malonic acids, then chiral acids are expected to be obtained because further metabolism to α-keto acids is impossible. A number of soil samples were examined, and it was found that a few microorganisms grew on phenylmalonic acid. We then selected a bacterium identified as *Alcaligenes bronchisepticus*, which has the ability to realize the asymmetric decarboxylation of α-methyl-α-phenylmalonic acid (**1a**). Fifty milliliters of an inorganic medium[3] containing peptone (50 mg) and phenylmalonic acid (250 mg) was inoculated with *A. bronchisepticus* and shaken for 4 days at 30 °C. To the resulting suspension was added 250 mg of **1a**, and the incubation was continued for an additional 5 days. The broth was extracted, esterified with diazomethane, and purified by preparative TLC, to afford optically active methyl α-phenylpropionate (**3a**). The present enzyme system was applied to some analogous compounds, as summarized in Table I. When the aryl group was phenyl (**1a**), 2-(6-methoxynaphthyl) (**1c**), *p*-chlorophenyl (**1d**), and 2-thienyl (**1e**), the substrates afforded optically active α-arylpropionic acid (**2a,c–e**) in high yields. On the other hand, in the case of *p*-methoxyphenyl-substituted malonate (**1b**), the yield of the desired product (**3b**) was low. The substrate specificity of this reaction is supposed to depend not only on the bulkiness of the aryl group but also on electronic factors.

Table I. Enzyme-Mediated Asymmetric Decarboxylation



entry	substrate	substrate concn, %	yield of 3, %	ee, % (confign)	$[\alpha]_D$, deg
1	**1a**	0.3	87	91 (*R*)	
2	**1a**	0.4	93	96 (*R*)	
3	**1a**	0.5	90	98 (*R*)	−96 (*c* 1.1, EtOH)[a]
4	**1b**	0.1	48	99 (*R*)	−71 (*c* 1.1, $CHCl_3$)[b]
5	**1b**	0.2	35	97 (*R*)	
6	**1c**	0.3	95	>95 (*R*)	
7	**1c**	0.5	96	>95 (*R*)	−76 (*c* 1.0, $CHCl_3$)[c]
8	**1d**	0.3	95	98 (*R*)	−67 (*c* 1.1, $CHCl_3$)
9	**1d**	0.5	85	97 (*R*)	
10	**1e**	0.3	98	95 (*S*)	−40 (*c* 1.1, $CHCl_3$)
11	**1e**	0.5	97	91 (*S*)	

[a] Literature,[4] *S* form, $[\alpha]^{28}_D$ +93.3° (*c* 0.96, EtOH). [b] Literature,[4] *S* form, $[\alpha]^{21}_D$ +75.3° (*c* 1.02, $CHCl_3$). [c] Literature,[4] *S* form, $[\alpha]^{21}_D$ +78.4° (*c* 1.05, $CHCl_3$).

The absolute configurations of **3a–c** were revealed to be *R* by comparison of the specific rotation with reported values.[4] Chloro derivative **3d** was reduced with $PdCl_2$–$NaBH_4$ (90%), to give **3a**,[5] which exhibited $[\alpha]_D$ −96° (*c* 0.82, ethanol), indicating the absolute configuration to be *R*. Desulfurization (Raney Ni)[6] of **3e** followed by hydrolysis and hydrogenation afforded (*R*)-(−)-α-methylcaproic acid (total 44%), $[\alpha]_D$ −16° (*c* 3.8, ether). Thus the absolute configuration of **3e** is determined to be *S*.[7] Optical purities of the products (**3**) were determined by HPLC analysis (CHIRALCEL OJ) or 400-MHz ^1H NMR measurements in the presence of a chiral shift reagent [Eu(hfc)$_3$] (for **3c**).

In order to clarify the mechanism and examine the substrate specificities, the racemic monoethyl ester of **1a** was subjected to

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the enzymatic reaction, and both enantiomers were recovered almost quantitatively. Accordingly, the substrates must be the free acids, and additional studies are now under way.

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Synthesis of (±)-11,*O*(3)-Dihydropseudopterolide

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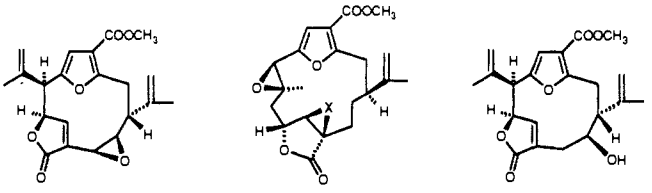
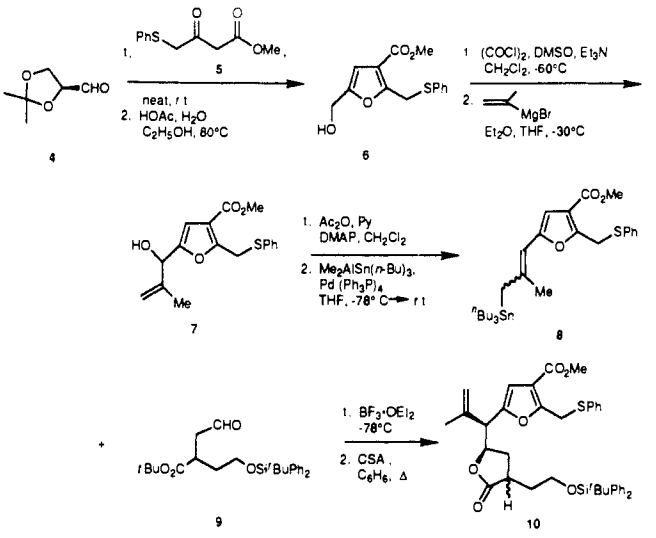
Pseudopterolide (**1**), a potent cytotoxic furanocembranolide that inhibits cell cleavage but not nuclear division much like cytochalasin D, was isolated and characterized in 1982.[2] Its 12-carbon macrocyclic ring is shared by the lesser oxygenated analogues kallolide A and B.[3] Pukalide (**2a**),[4] epoxypukalide (**2b**),[5] and lophotoxin,[6] on the other hand, are characterized by a somewhat larger (14C) central core.[7] Despite the biomedical importance of many of these marine products,[8] synthetic accomplishments in the area have been few and mostly preliminary in nature.[9] Herein we describe the first successful approach to a pseudopterane, viz., **3**, and detail a concise scheme for effecting the interlinking of sensitive, highly oxygenated functional groups in close transannular proximity.



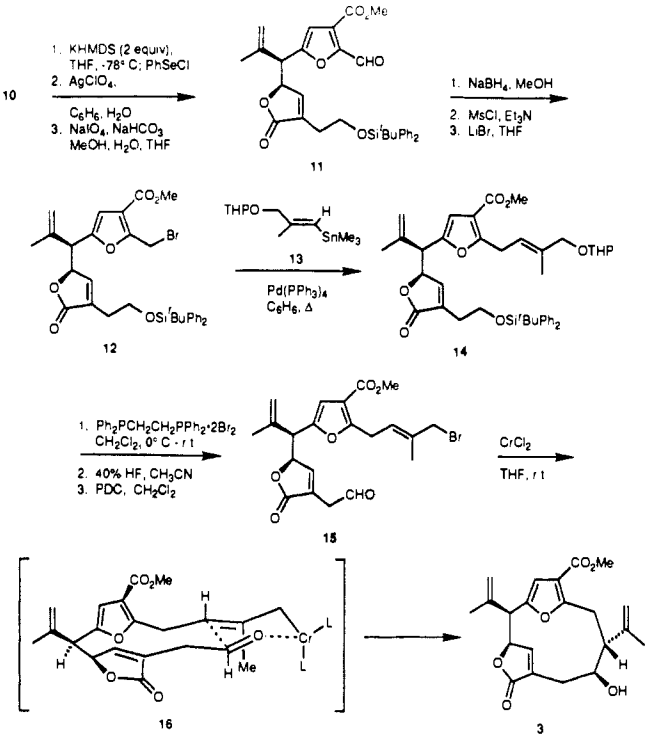
1 2a, X=unsaturation b, X=O 3

In light of the dismal prospects for arrival at a suitably functionalized furan by direct acylation methods,[10] 2,3-*O*-isopropylidene-D-glyceraldehyde (**4**)[11] was condensed with **5**[12] in an adaptation of the procedure developed by Aparicio for glucose[13] and then heated in aqueous acetic acid to give **6** (60%, Scheme I). Swern oxidation of **6** was most effective (98%) in making

Scheme I



Scheme II



available the aldehyde, reaction of which with 2-propenylmagnesium bromide produced **7** efficiently. Direct acetylation of this allylic alcohol was followed by conversion to **8** (64%) according to the method of Trost.[14] The 82:18 *E*/*Z* distribution of isomeric allylstannanes was not expected to be of stereochemical consequence in the ensuing condensation reaction.[15]

With maximum convergency as our goal, aldehyde **9** was next prepared. This objective was conveniently realized by silylation of 2-bromoethanol with *tert*-butyldimethylsilyl chloride and conversion to the iodide for the purpose of enhancing electrophilicity. Sequential alkylation of this halide with *tert*-butyl lithioacetate and allyl bromide in a THF-HMPA solvent system proceeded well (71% overall) to provide an ester, ozonolysis of which delivered **9** (90%). In this instance, it was imperative that the ozonide be degraded with triphenylphosphine.

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