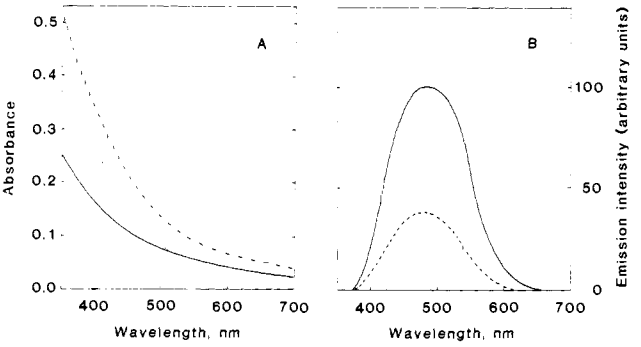

Figure 1. (A) Absorption spectra of 2×10^{-3} M DHP vesicle-entrapped 1×10^{-3} M Cd^{2+} and approximately 3.2×10^{-5} M Rh^{3+}: (—) after removal of external cations, (···) after exposure to H_2S (formation of CdS), (-···) after 60 min of UV irradiation (formation of Rh^0). (B) Fluorescence emission spectra of 2×10^{-3} M DHP vesicle-entrapped 1×10^{-4} M colloidal CdS, under 330-nm excitation: (—) in the absence (before and after UV irradiation under Ar bubbling) (---) and in the presence of approximately 3.2×10^{-5} M Rh^{3+}.

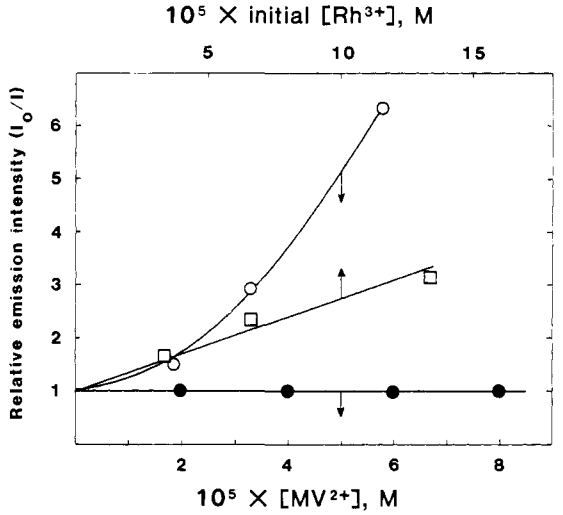

Figure 2. Stern-Volmer plots for the quenching of 2×10^{-3} M DHP vesicle-entrapped 1×10^{-4} M colloidal CdS by coentrapped MV^{2+} (O), coentrapped Rh^{3+} (□), and externally adsorbed MV^{2+} (●).

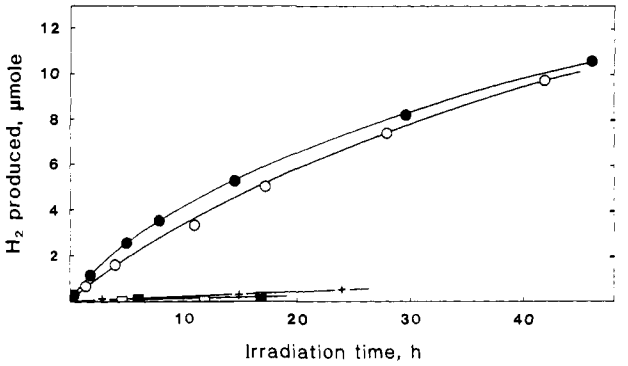

Figure 3. Hydrogen production in deaerated solution as a function of irradiation time using 350-nm cutoff and water filters at 30 °C. Plotted are the amount of hydrogen produced by a 25-mL DHP vesicle solution and measured in the gas phase (16 mL) by GPLC: 2×10^{-3} M DHP, 1×10^{-4} M CdS, rhodium coated as described in the text. In the presence of 10^{-3} M PhSH and at pH approximately 7, adjusted before irradiation (●, O; separate samples, indicating our reproducibility); same sample in the absence of CdS and Rh (+) or in the absence of Rh only (■) or in the absence of PhSH only (□).

by varying the initial concentration of $CdCl_2$ from 0 to 7×10^{-4} M. Irradiation of degassed, vesicle-entrapped, rhodium-coated, colloidal CdS by visible light (450-W xenon lamp, 350-nm cutoff filter) in the presence of 10^{-3} M PhSH resulted in hydrogen formation, which could be sustained for approximately 48 h

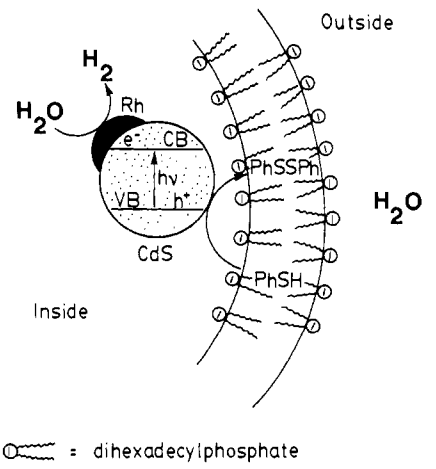

Figure 4. An idealized model for CdS-sensitized water photoreduction by PhSH in aqueous DHP vesicles. The position of the colloid in the vesicles should not be taken for granted, however.

(Figure 3). After 48 h, more than 90% of PhSH was consumed. Sustained hydrogen formation is the consequence of electron transfer from PhSH, presumably located in the DHP membranes, to the positive holes in the colloidal CdS. This, in turn, diminishes undesirable electron-hole recombinations and allows electron transfer to the surface of the semiconductor where Rh^0-catalyzed water reduction occurs (Figure 4). In the absence of either CdS, Rh^0, or PhSH, no or very little amount of H_2 is produced. Optimization of surfactant vesicle-entrapped catalyst-coated semiconductors is the objective of our current scrutiny. These systems, along with polymer membrane incorporated semiconductors,[14,15] may well provide means for viable solar energy conversion.

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Registry No. Dihexadecyl phosphate, 2197-63-9; thiophenol, 108-98-5; rhodium, 7440-16-6; cadmium sulfide, 1306-23-6; hydrogen, 1333-74-0.

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Isolation from Pistacia Resins of a Bicyclic Triterpenoid Representing an Apparent Trapped Intermediate of Squalene 2,3-Epoxide Cylization

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Following the establishment of the role of squalene and more specifically (3*S*)-squalene 2,3-epoxide[2,3] in the biosynthesis of polycyclic triterpenoids, we have found that there has been considerable interest and speculation concerning the exact nature of this remarkable biotransformation. The cyclization was originally envisaged as a completely concerted process,[4] a view supported by the failure to trap or otherwise detect any intermediates. However, the most recent work of van Tamelen and his co-workers

(1) Present address: Janssen Pharmaceutica, 2340 Beerse, Belgium.
(2) Willett, J. D.; Sharpless, K. B.; Lord, K. E., van Tamelen, E. E.; Clayton, R. B. *J. Biol. Chem.* **1967**, *242*, 4182.
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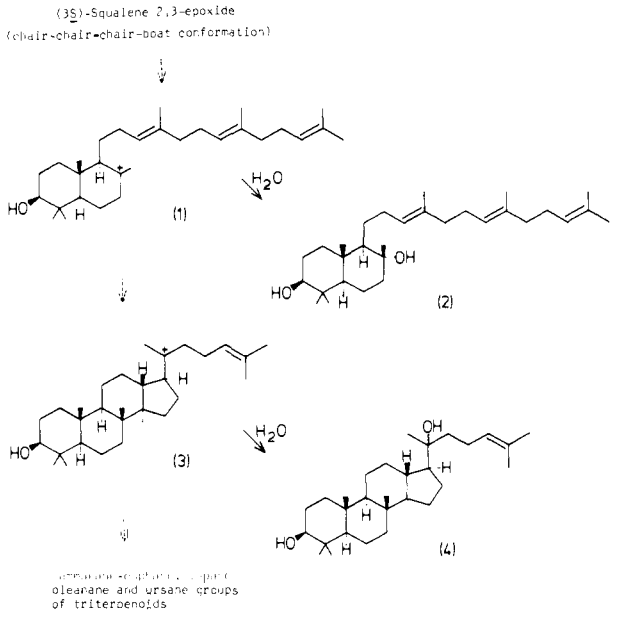
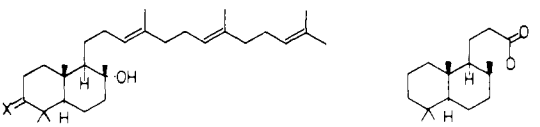
Scheme I



suggests that the cyclization proceeds via a series of discrete, conformationally rigid carbocationic intermediates.[5]

We now report the isolation from gum mastic of a novel bicyclic triterpenoid, **2**,[6] the structure and absolute stereochemistry of which are fully consistent with its formation by interception of the bicyclic carbocation **1** postulated as an intermediate in the cyclization of the chair–chair–boat conformation of (3*S*)-squalene 2,3-epoxide. Significantly, gum mastic also contains a range of *normal* tetracyclic (dammarane, tirucallane) and pentacyclic (lupane, oleanane) triterpenoids. It is interesting to note that the bicyclic diol **2** has the same formal relationship to the C-8 carbocation **1** as the dammarenediols (**4**) have to the C-20 carbocation **3** (Scheme I).

Gum mastic is an abundantly available resin obtained from the Mediterranean shrub *Pistacia lentiscus* L;[7] it has been extensively used as a varnish for paintings.[8] After extensive chromatography of the neutral fraction[9] from gum mastic, we have now isolated, as the third most abundant component (ca. 1.3% of the total resin), compound **2** as a gum. The 400-MHz ^{1}H NMR spectrum of **2** showed the presence of four methyl singlets (δ 0.77, 0.80, 1.00, and 1.14), four vinylic methyl groups (δ 1.60, 1.60, 1.61, and 1.68), a proton geminal to a hydroxy group (δ 3.32, dd, J = 6 and 9 Hz), and three vinylic protons (δ 5.10, 5.12, and 5.17). Treatment with acetic anhydride in pyridine at room temperature readily afforded a monoacetate, $C_{32}H_{54}O_3$ (MS and CI-MS). Comparison of the ^{13}C NMR spectra of the bicyclic diol **2** and its derivatives with spectra of authentic samples of ambrein, sclareol, and *all-trans*-squalene conclusively established the structure, **2**, of the diol. The absolute configuration was established as follows: oxidation of the bicyclic diol **2** (pyridinium chlorochromate–CH_2Cl_2) gave the ketol **5** (99%), which upon Wolff–Kischner reduction afforded the 3-desoxy derivative **6** (63%). Finally, two-phase oxidation



(5) X=O
(6) X=H_2

(7)

of (6) ($KMnO_4$–H_2O/PhH–*n*-$Bu_4N^+Br^-$; room temperature) gave (+)-ambreinolide (7), mp 143–144 °C, $[\alpha]_D$ +33° (*c* 0.45 in $CHCl_3$), identical in every respect with an authentic sample.[10]

While other partially cyclized triterpenoids have been described, these normally appear to be products of aberrant modes of cyclization[11] (or laboratory synthesis[12]). One example is the aforementioned ambrein, in which partial cyclization has occurred at both ends of the squalene chain. In contrast, the diol **2** is the first[6] example of a bicyclic triterpenoid that retains all of the regio- and stereochemical features necessary for continued cyclization and occurs in a system that clearly has the enzyme(s) needed for more complete cyclization.

Acknowledgment. We thank Drs. J. S. Mills and R. White of the National Gallery, London, for provision of generous quantities of gum mastic and for their interest and advice, Drs. G. Ohloff, B. J. Willis, and A. J. Connock for generous gifts of authentic samples, the University of London Intercollegiate Research Service for some of the spectra, and the National Gallery, London, and the S.E.R.C. for financial support.

Registry No. 2, 89362-84-5; (3*S*)-squalene 2,3-epoxide, 54910-48-4.

Supplementary Material Available: Structures and ^{13}C NMR data of **6**, ambrein, and *all-trans*-squalene and mass measurements on the monoacetate of **2** (2 pages). Ordering information is given on any current masthead page.

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(6) Since this communication was submitted, a report has appeared (Shiojima, K.; Arai, Y.; Masuda, K.; Kamada, T.; Ageta, H. *Tetrahedron Lett.* **1983**, *24*, 5733) that describes the characterization of two further bicyclic triterpenes with the same carbon skeleton as that of compound **2**. It is especially interesting that, while these were again found alongside tetra- and pentacyclic triterpenes, all the compounds isolated were *hydrocarbons*; the source was a species of fern in which the cyclization of squalene does not involve prior oxygenation but is believed instead to be initiated by direct proton transfer to the hydrocarbon. Therefore both in the proton-transfer mechanism and in the route via squalene oxide, which is utilized by higher plants, the cyclization sequence may be interrupted at the bicyclic stage.
(7) The bicyclic diol **2** also occurs in the resin from at least one other Pistacia species, *P. terebinthus*.
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(11) See, for example: Barton, D. H. R.; Overton, K. H. *J. Chem. Soc.* **1955**, 2639. Chawla, A.; Dev, S., *Tetrahedron Lett.* **1967**, 4837. Shmueli, U.; Carmely, S.; Groweiss, A.; Kashman, Y. *Ibid.* **1981**, 709. Ravi, B. N.; Wells, R. J. *Aust. J. Chem.* **1982**, *35*, 39. McCabe, T.; Clardy, J.; Minale, L.; Pizza, C.; Zollo, F.; Riccio, R. *Tetrahedron Lett.* **1982**, *23*, 3307.
(12) van Tamelen and co-workers have synthesized a stereoisomer of 2: van Tamelen, E. E.; Lees, R. G.; Grieder, A. *J. Am. Chem. Soc.* **1974**, *96*, 2253, 2255.

Self-Sensitized Photooxidation of Protoporphyrin IX and Related Free-Base Porphyrins in Natural and Model Membrane Systems. Evidence for Novel Photooxidation Pathways Involving Amino Acids[1]

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Free-base porphyrins and metalloporphyrins have been well established as sensitizers of singlet oxygen in photooxidation processes.[2-4] They are also implicated as photosensitizers in a number of photobiological processes such as the genetic disorder

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