$\times 10^6$ M^{-1} for **2**, are low compared to that for RuL_3^{2+} by triethylamine ($k_q = 1.4 \times 10^8$ M^{-1} s^{-1}).[35] Although it is difficult to assess precisely the oxidation potential for alkylamines due to their electrochemical irreversibilities, an examination of comparative electron-transfer quenching constants for different metal complexes[35] suggests that the oxidation potentials of **1a** and **2** should be 1.40–1.45 V, very close to that of dibenzylamine.[35]

The results described above show that C–C bond cleavage, as outlined in Scheme I, is indeed an important path for compounds of the general type of **1** and **2**. The occurrence of C–C bond cleavage for radical ions derived from molecules such as **1** and **2** appears to be a reasonable process; the photoinduced σ-bond cleavages in solution observed in the present study are novel and potentially quite useful since relatively long wavelength light can be used to mediate selective scission of a relatively strong covalent bond. Interestingly for compounds such as **1** the electron-transfer photoreaction provides a strong wavelength extension of a reaction (eq 1) ordinarily observed only with UV; for compounds such as **2** the cleavage does not occur in an "unsensitized" process since the compounds have no carbonyl capable of mediating type I cleavage. The photoinduced electron-transfer-mediated σ-bond cleavage should be applicable for a variety of donors with appropriate substituents on the σ-bond terminal carbons. We are presently examining a number of potential substrates to determine both the scope of the reaction as well as their rates and factors controlling them.

Acknowledgment. We are grateful to the L. D. Caulk Dentsply Corporation and the U. S. Department of Energy (Contract DE-AC02-84ER13151) for support of this research.

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The Structure of Methyl Isosartortuoate, a Novel Tetracyclic Tetraterpenoid from the Soft Coral *Sarcophyton tortuosum*

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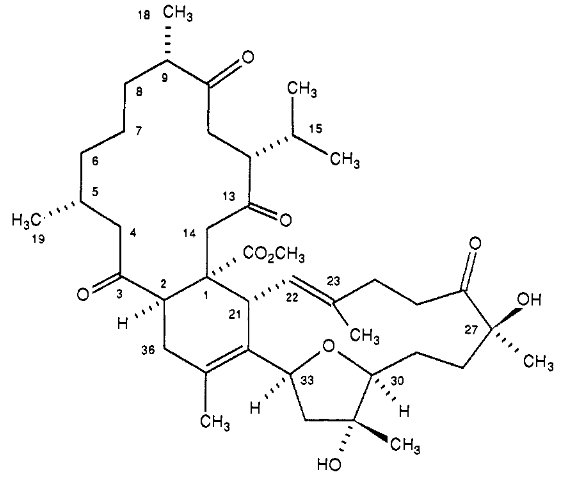
Soft corals have been an unusually productive source of chemically interesting and biologically significant secondary metabolites.[1-3] The vast majority of identified metabolites from soft corals are terpenoid compounds; among the terpenoids, the cembrene family of diterpenoids predominates.[1] In this paper we wish to describe the isolation and structure determination of an unprecedented tetracyclic tetraterpenoid, methyl isosartortuoate (**1**).

Methyl isosartortuoate was isolated from the soft coral *Sarcophyton tortuosum* Tixier-Durivault collected in the South China Sea. The fresh coral was immersed in 95% ethanol, and the alcoholic extract was concentrated and chromatographed on silica gel with acetone/petroleum ether. Compound **1** was obtained as colorless crystals, mp 194–195 °C. A molecular formula of $C_{41}H_{62}O_9$ for **1** was determined by HRMS (M^+, m/z 698.4305, calcd for $C_{41}H_{62}O_9$, 698.4389). The IR spectrum (KBr) indicated the presence of OH groups (3350 and 1105 cm^{-1}), a CO_2R group (1745 and 1215 cm^{-1}), carbonyl groups (1725 and 1712 cm^{-1}), double bonds (1640, 1658, 858, and 700 cm^{-1}), an ether (1080 cm^{-1}), and an isopropyl group (1380 and 1375 cm^{-1}).



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The following fragments were suggested by the ^1H and ^{13}C NMR: a methyl ester (δ_C 174.4 (s), 51.2 (q); δ_H 3.55 (3 H, s)), four carbonyl groups (δ_C 215.1 (s), 213.6 (s), 213.2 (s), and 208.7 (s)), and a tri- and tetra-substituted double bond (δ_C 136.4 (s), 135.1 (s), 127.9 (d), 126.1 (s); δ_H 4.90 (1 H, d)). Since these functionalities accounted for seven degrees of unsaturation, methyl isosartortuoate had to be tetracyclic. Four carbons, not counting the methyl ester, were attached to oxygen, most plausibly as one ether (δ_C 87.1 (d), 75.16 (d); δ_H 5.06 (1 H, dd, J = 12.0, 5.0 Hz), 3.47 (1 H, dd, J = 12.5, 1.5 Hz)) and two tertiary hydroxyls. Nine methyl groups were identified, one of which was the methyl ester. The others were two olefinic (δ_C 22.21 (q), 21.23 (q); δ_H 1.85 (3 H, s), 1.64 (3 H, s)), one isopropyl group (δ_C 17.72 (q), 17.46 (q); δ_H 1.00 (3 H, d), 0.71 (3 H, d, J = 6.8 Hz), two methyls attached to quaternary oxygen bearing carbons (δ_C 25.9 (q), 23.9 (q); δ_H 1.35 (3 H, s), 1.27 (3 H, s)), and two secondary methyls (δ_C 19.7 (q), 19.0 (q); δ_H 1.13 (3 H, d, J = 7.0 Hz), 0.86 (3 H, d, J = 7.0 Hz)). The number of methyl groups combined with the parent molecular formula suggested that **1** was terpenoid in origin. The ^{13}C NMR spectrum also showed six methine groups and 12 methylene groups. Since no examples of tetracyclic tetraterpenoids were known, and the ^1H NMR and ^{13}C NMR spectra did not unambiguously suggest a structure for **1**, the structure was defined by X-ray diffraction.

Crystals of **1** formed in the tetragonal space group $P4_12_12$ with $a = b = 9.547$ (2) Å and $c = 92.722$ (7) Å. Block diagonal least-squares refinements have converged to a conventional crystallographic residual of 0.096 for the observed reflections. Additional crystallographic parameters are available and are described in the supplementary material. A computer-generated perspective drawing of the final X-ray model of **1** is given in Figure 1. Hydrogens are not shown and the absolute stereochemistry portrayed is arbitrary. There are regions of the structure where the thermal motions were large, and a poorly resolved structure resulted. This was most marked in the C5–C8 region and the methyl groups where the average isotropic thermal parameter 11.3 $Å^2$ vers. 7.5 $Å^2$ for the rest of **1**. Bond shortening, the usual consequence of large thermal motions, was quite noticeable in the C5–C8 region. However, when riding corrections[4] were introduced, the geometry was consistent with structure shown as **1**. The NMR data for methyl isosartortuoate (**1**) also supported this formulation and clearly indicated that there was no 1,2-disub-

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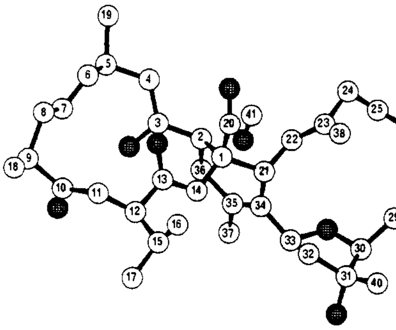

Figure 1. Computer-generated perspective drawing of the X-ray model of methyl isosartortuoate (**1**). Oxygen atoms are crosshatched, hydrogens are omitted for clarity, and no absolute configuration is implied.

stituted double bond. A summary of the significant ^{1}H NMR data and decoupling experiments is given in the supplementary material.

Methyl isosartortuoate (**1**) is the first tetraterpenoid of this structural type, and its biosynthesis is not known. Since diterpenes of the cembrene[2] class are commonly found in soft corals, a plausible biogenesis would involve generation of the cyclohexene ring by a Diels–Alder coupling of two cembrenes. This would generate the carbon skeleton of isosartortuoate in an efficient manner. The most obvious precursors suggested by this scheme have not yet been identified as natural products, but examples of the various functionalities can be found in known marine cembrenes.[1] If the proposed Diels–Alder reaction had an endo transition state, the stereochemistries at C1, C2, and C21 would be those observed in **1**.

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Supplementary Material Available: Details of the X-ray structure determination of **1** including tables of fractional coordinates, thermal parameters, interatomic distances, interatomic angles, and ^{1}H NMR data (6 pages). Ordering information is given on any current masthead page.

Flowing Afterglow Negative Ion Photoelectron Spectroscopy of Dirhenium: Evidence for Multiple Bonding in Re_2 and Re_2^-

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Although there is now an extensive spectroscopic literature concerning homonuclear diatomics of first-row transition metals, relatively little is known about dimers of the second and third transition series.[1] Theoretical calculations for third-row systems predict more comparable ($n + 1$)s and nd orbital sizes and energies than for their lighter congeners, due primarily to relativistic effects.[2] This trend is expected to yield enhanced d–d bonding in third-row dimers, a prediction consistent with reported[3] mass spectrometric dissociation energies. Spectroscopic confirmation of these predictions has not yet been possible, due to the nearly[4] total lack of data for dimers of open d-shell third-row metal atoms.

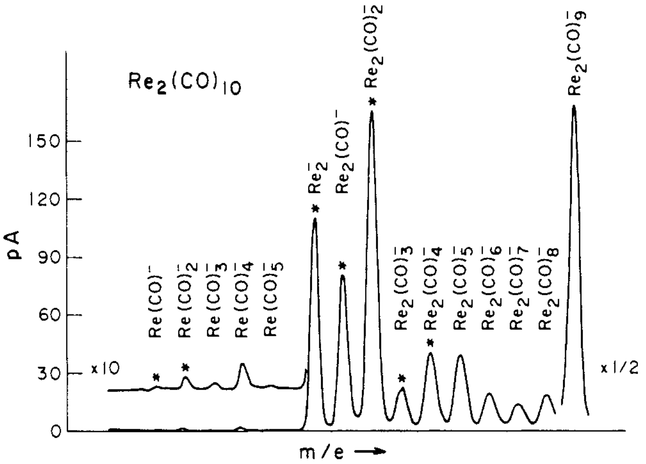

Figure 1. Negative ion mass spectrum following dissociation/ionization of $Re_2(CO)_{10}$ in a flowing afterglow apparatus incorporating a microwave discharge ion source. Anions marked by asterisks photodetached at 488 nm.

In this paper, we report the first spectroscopic observation of Re_2 and Re_2^-, obtained by negative ion photoelectron spectroscopy. This system provides an excellent test of the predicted enhancement of multiple bonding in heavier members of an isoelectronic metal dimer series. Although strong d–d bonding is suggested by the pervasiveness of multiple Re–Re bonding in stable coordination compounds,[5] a weak bond in the bare Re_2 molecule might be expected in view of the van der Waals bonding[6] in its first-row congener, Mn_2. The data reported here provide gas-phase vibrational frequencies for Re_2 and Re_2^-. Their high vibrational force constants indicate that multiple Re–Re bonding does indeed occur in both the neutral and anionic dimers.

These results also illustrate a new synthetic route to metal–metal bonded, coordinatively unsaturated metal carbonyl anions. There has recently been much interest in the synthesis and chemical characterization of mononuclear transition-metal carbonyl anions.[7] The production of $Re_2(CO)_n^-$, $n = 0$–9, reported here suggests that the gas-phase chemistries of these dinuclear reactive intermediates are also potentially characterizable by flowing afterglow techniques.

Anions were prepared in our flowing afterglow source[8] by seeding $Re_2(CO)_{10}$ vapor in a 150 STP cm^3 s^{-1} He flow ~10 cm downstream of a 2.45-GHz microwave cavity discharge. The anions were then gently extracted and mass-selected by a Wien filter, yielding the mass spectrum displayed in Figure 1. All possible fragment $Re_n(CO)_m^-$ metal carbonyl anions were detected. The species marked by asterisks, and only these, were observed to photodetach at 488.0 nm, implying electron affinities below ~2.2 eV. The spectra of the ligated anions will be reported in a future publication.

To obtain the photoelectron spectrum reported here, the mass-selected Re_2^- ion beam crossed by the intracavity radiation of a cw argon ion laser. A small fraction of the photodetached

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