While the syntheses of N,N'-bridged porphyrins so far reported are quite limited because of their low yields and poor generality,[11] this work provides a facile synthetic method of novel N,N'-ethenoporphyrins with various substituents on the bridge, the structure of which is also of considerable significance in view of the formation of N,N'-*o*-phenylene bridged protoporphyrin IX when cytochrome P-450 enzymes were inactivated with 1-aminobenzotriazole known as a precursor of benzyne.[12] Our efforts to discover the reaction behaviors of metalloporphyrin π-cation radicals are curently in progress.

Acknowledgment. We are grateful to Prof. David Dolphin for providing us with a sample of N^{21},N^{22}-ethenoOEP hydroperchlorate derived from *N*-(formylmethyl)$OEPCo^{II}$.

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(10) N,N'-Etheno bridged cobalt porphyrins could not be isolated but the hydroperchlorate **9** was obtained even if the 10% $HClO_4$ treatment was omitted in the workup procedure of the reaction of $OEPCo^{II}$, ferric perchlorate, and diphenylacetylene. A similar reductive elimination mechanism can explain the Co-to-N ethyl migration upon one-electron electrochemical oxidation of ethyl(*meso*-tetraphenylporphinato)cobalt(III) giving (*N*-ethyl-*meso*-tetraphenylporphinato)cobalt(II) and cobalt(III) porphyrin π-cation radical has been suggested as an intermediate (Dolphin, D.; Halko, D. J.; Johnson, E. *Inorg. Chem.* **1981**, *20*, 4348).

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Total Synthesis Necessitates Revision of the Structure of Robustadials

Kasturi Lal, Eugene A. Zarate, Wiley J. Youngs, and
Robert G. Salomon*

*Department of Chemistry, Case Western Reserve
University, Cleveland, Ohio 44106*

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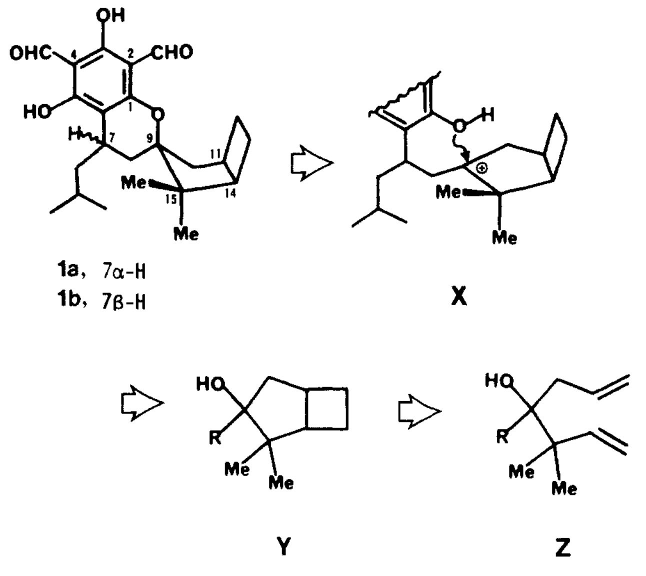
A global resurgence of malaria and the appearance of strains that are resistant to quinine and its analogues provide an urgent need for the identification and total synthesis of new antimalarial natural products. Several active compounds are contained in an antimalarial extract of *Eucalyptus robusta* leaves, a plant used in Chinese herbal medicine.[1] Recently two new compounds isolated from this plant, robustadial A and robustadial B, were assigned bicyclo[3.2.0]heptane structures **1a** and **1b**, respectively, on the basis of NMR, UV, IR, and mass spectral data.[2] We now report the total synthesis of **1a** which we find *not* to be identical with robustadial A, and we postulate a new structure for the natural product.

Presuming that the pyran ring in **1a** could be generated by cyclization of a phenol as in X, our synthetic strategy envisioned a key copper(I)-catalyzed photobicyclization[3] of a diene Z to provide the requisite bicyclo[3.2.0]heptane ring system of Y. Our synthesis of **1a**, outlined in Scheme I[4], built the diene **7** from 1,3,5-trimethoxybenzene (**2**). Friedel–Crafts acylation provided the ketone **3** in which the carbonyl carbon is shielded sterically by two adjacent methoxy groups. Low yields were obtained upon cyanomethylenation of **3** with the anion of (dimethylphosphono)acetonitrile presumably owing to steric congestion. However, lithioacetonitrile,[5] a less bulky nucleophile, added to this carbonyl group to give the benzylic alcohol **4** in excellent yield. After reductive removal of the vestigial hydroxyl group, ketone **6** was elaborated from nitrile **5** by reaction with prenylmagnesium chloride. This appears to be the first example of such a regioselective reaction of this Grignard reagent with a nitrile.[6] The observed preferential electrophilic attack at the more substituted allylic terminus presumably results from pseudointramolecular C–C bond formation as in **14**.



14

Copper(I)-catalyzed photobicyclizations are not known for dienes as functionally complex as **7**. The synthetic versatility of this reaction is now demonstrated by the production of **8** in reproducibly good yield upon UV irradiation of **7** in the presence of copper(I) trifluoromethanesulfonate. Monodemethylation of **8** with NaSEt set the stage for generation of the pyran ring. The favorable regioselectivity of this demethylation results from a novel remote neighboring group effect of the tertiary alcohol.[7] Treatment of **9** with $BF_3 \cdot OEt_2$ generated an 8:1:1 mixture of diastereomeric pyrans **10**. The major diastereomer (mp 80–82 °C) was readily isolated by HPLC on a Whatman M-20 μ-porasil column eluting with 35% toluene in hexane. Fortunately this diastereomer has the correct relative configurations for **1a**. This was unambiguously established by X-ray crystal structural analysis (Figure 1) of the derived dibromide **11** (mp 131–133 °C). Lithium–bromine exchange followed by carboxylation, acidification, and O-methylation delivered the diester **12** (mp 135 °C). The dimethyl ether **13** (mp 40–42 °C) of **1a** was obtained from **12** by reduction to a diol which was oxidized to the dialdehyde with pyridinium dichromate. ^1H and ^{13}C NMR analysis clearly show that **13** and robustadial A dimethyl ether are *not* identical. Notably, the ^1H NMR spectrum of the latter only shows resonances for aldehydic, benzylic, and methoxy hydrogens downfield of δ 2.3. In contrast, the ^1H NMR spectrum of **13** shows ab-

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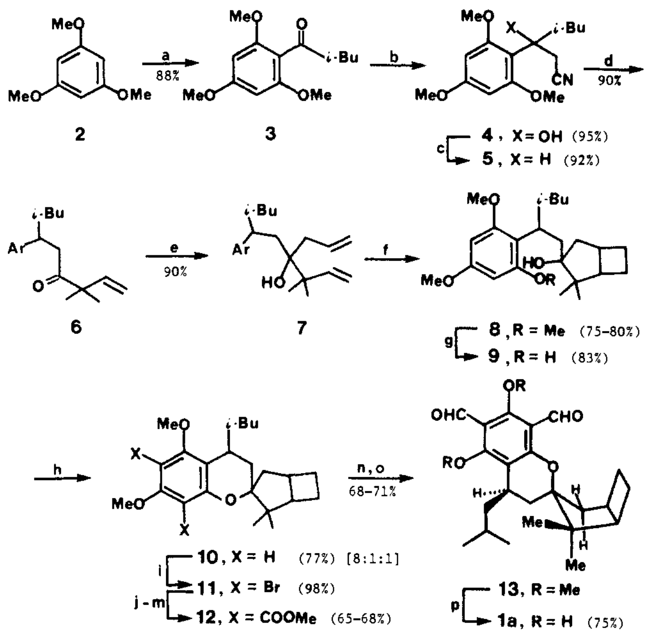
(8) X-ray analysis (Mo Kα radiation): **11** crystallizes from hexane in the triclinic space group $P\bar{1}$, with $a = 9.148$ (2) Å, $b = 10.052$ (2) Å, $c = 13.376$ (4) Å, $\alpha = 93.38$ (2)°, $\beta = 107.13$ (2)°, $\gamma = 104.25$ (2)°, $V = 1158.0$ (5) Å^3, $\rho_{obsd} = 1.48$ g/cm^3, $\rho_{calcd} = 1.48$ g/cm^3, $Z = 2$. Standard direct and difference Fourier methods and least-squares refinement on the basis of 1976 ($I \geq 3\sigma$) reflections led to a final $R = 0.037$.

Scheme I^a



^{a}(a) $Me_2CHCH_2COCl/AlCl_3$; (b) $LiCH_2CN$; (c) Et_3SiH/CF_3COOH; (d) $Me_2C{=}CHCH_2MgCl$; (e) $CH_2{=}CHCH_2MgBr$; (f) $CuOTf/h\nu$; (g) EtSNa/DMF; (h) $BF_3{\cdot}OEt_2/CH_2Cl_2$; (i) Br_2/CH_2Cl_2; (j) n-BuLi/THF; (k) CO_2; (l) HCl; (m) CH_2N_2; (n) DIBAlH/PhMe; (o) PDC; (p) BCl_3.

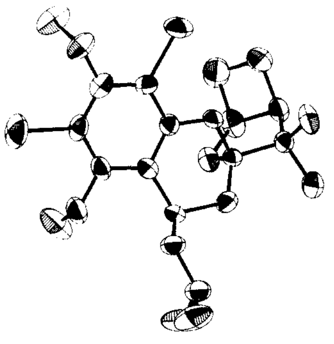
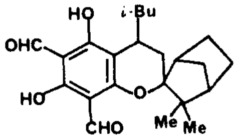


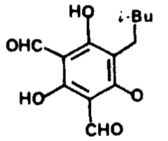
Figure 1. X-ray structure of **11**.[8]

sorptions between δ 2.37 and 2.74 which we assign to the methine hydrogens at positions 11 and 14. Demethylation of **13** with BCl_3 completed our total synthesis of **1a** (mp 129–130 °C).

Evidently, the structures of robustadial A, and presumably robustadial B, are isomeric with those proposed previously.[2] Several facts lead us to postulate a bicyclo[2.2.1]heptane structure **15** for the robustadials. Thus, the aromatic acetogenin isopentyl



15



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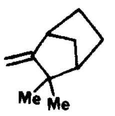

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portion **16** of robustadials is identical with that found in the euglobals, a family of acetogenin terpenoids isolated from buds and leaves of *Eucalyptus globulus*.[9] Generally, the remaining terpenoid portion of the euglobals corresponds to known terpenes or sesquiterpenes. The remaining terpenoid portion of **15** corresponds to a known terpene, camphene (**17**). Furthermore, ^1H NMR resonances above δ 2.3 are reasonable for the bridgehead methine hydrogens of a bicyclo[2.2.1]heptyl moiety. Finally, the presumption of a cyclobutyl moiety in robustadials was supported by the appearance of a peak in the high-resolution mass spectrum at m/e 28 (C_2H_4).[2] Our postulated structure **15** for the robustdials is only tenable if the mass spectrum of camphene exhibits major fragments corresponding to those observed for the terpene portion of robustadials. Indeed, the mass spectrum of camphene not only shows a peak at m/e 28.046 (21%, C_2H_4) but also peaks at m/e 91 (30%), 107 (39%), and 136 (23%) corresponding to prominant peaks in the mass spectrum of robustadials.[2]

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Supplementary Material Available: Tables of data collection details, fractional atomic coordinates, and anisotropic thermal parameters for non-hydrogen atoms of **11**, as well as analytical and spectral data for all new compounds (9 pages). Ordering information is given on any current masthead page.

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Photofragment Infrared Fluorescence in the Photodissociation of Gas-Phase $Mn_2(CO)_{10}$

R. G. Bray,* P. F. Seidler, J. S. Gethner, and R. L. Woodin

Exxon Research and Engineering Co.
Corporate Research Science Laboratories
Annandale, New Jersey 08801

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We report here the first application of frequency- and time-resolved infrared fluorescence[1] to investigate the structure and dynamics of organometallic intermediates. Photolysis at 351 nm of gas-phase $Mn_2(CO)_{10}$[2] produces vibrationally excited species which have been identified by characteristic emission near 2000 cm^{-1}. Bimolecular collisional energy transfer rates of one of these species have been measured for seven collider gases.

Samples of $Mn_2(CO)_{10}$ (7–60 mtorr) contained in a glass cell at 79–80 °C were irradiated with a XeF excimer laser (351 nm, 15-ns pulse width, 2-Hz repetition rate) using low laser fluences (<100 μJ cm^{-2} per pulse) to minimize multiphoton absorption processes.[3] An InSb detector monitored the transient infrared fluorescence over the 3950–1800-cm^{-1} region at right angles to the photolysis beam. The amplified detector output was then averaged over 100 pulses with a transient digitizer.

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