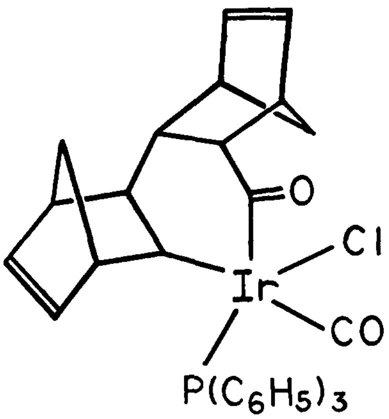

Figure 2.

iridocycle occur at τ 6.69 (1 H) and 7.21 (1 H) in **2** and τ 6.26 (1 H) and 7.62 (1 H) in **3**; the protons α to iridium could not be unambiguously assigned but occur in both **2** and **3** in the region τ 8.4–9.4.

A yellow crystalline compound **4** can be isolated by treating a suspension of **1** in CH_2Cl_2 with CO, followed by the addition of 1 mol of $P(C_6H_5)_3$. Analyses of **4** are consistent with the addition of 2 mol of CO and 1 mol of $P(C_6H_5)_3$ to **1** with the loss of one NBD ligand. [*Anal.* Calcd for $IrC_{34}H_{31}O_2ClP$: C, 56.00; H, 4.25; Cl, 4.87; P, 4.25. Found: C, 56.22; H, 3.46; Cl, 5.06; P, 4.31.]

The nmr spectrum of **4** shows the presence of the uncoordinated vinyl groups of an iridocycle, and sharp absorptions at 2020 and 1695 cm^{-1} in the infrared indicate the presence of both terminal and acyl[18,19] carbonyl groups. Further, the molecular weight (in $CHCl_3$ solution) shows **4** to be monomeric, and thus a structure as in Figure 2 is proposed which has resulted by insertion of CO into one of the Ir–C bonds of the iridocycle to form a cyclic metal acyl derivative.

The mass spectra of these species are of some interest. **1** shows no parent peak corresponding to $Ir(NBD)_3Cl^+$ or any multiple thereof; the highest *m/e* isotopic cluster corresponds to the fragment $[Ir(NBD)Cl]_2^+$ (relative intensity, 4.6). In addition, however, a peak of high relative abundance (42.2) appears at *m/e* 184 corresponding to a NBD dimer liberated from the iridocycle species. Likewise, **2** shows no molecular ion, the only peaks of interest being due to $[Ir(NBD)Cl]_2^+$, $(NBD)_2^+$, and PMe_3^+ (relative intensities 2.8:16.8:66.3). The most intense peak in both **1** and **2** is $C_5H_6^+$. However, the mass spectrum of **3** has the parent peak (*m/e* 568, relative intensity 48.2), but unlike **1** and **2**, no dimer of NBD is observed. Further significant peaks corresponded to products resulting from two stepwise retro-Diels–Alder reactions of the iridocycle moiety, *i.e.*, $Ir(NBD)(acac)(C_9H_{10})^+$, $Ir(NBD)(acac)(C_4H_8)^+$, and $C_5H_6^+$ (relative intensities 55.2:89.6:100)

Evidence that these metallocyclic complexes can be regarded as stabilized intermediates in the metal-promoted dimerization of NBD, rather than artifacts of no mechanistic significance, is provided by the following experiment. When **1** is refluxed in $CHCl_3$ with a fivefold excess of $P(C_6H_5)_3$, ring closure is induced and the NBD dimer is displaced from the iridium atom in *ca.* 35% yield. The dimer is extracted from the reaction mixture with pentane, and its nmr spectrum is identical with that of the exo-trans-exo dimer.[1] No other isomers were detected.

The observation that NBD dimerization proceeds *via* a metal–carbon σ-bonded intermediate adds to the accumulating evidence[13,14,20–22] that concerted mechanisms proposed for transition metal catalyzed symmetry forbidden processes must be carefully evaluated.

Acknowledgments. This work has been supported by the National Research Council of Canada (P. H. B. and A. R. F.), by the National Science Foundation in the form of predoctoral fellowships (S. A. B. and J. R. S) and the Henry and Camille Dreyfus Foundation (J. A. O.).

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[18] *Cf.* acyl carbonyl frequencies of other cyclic metal acyls: 1703,[14] 1700,[4] and 1670 cm^{-1}.[19]

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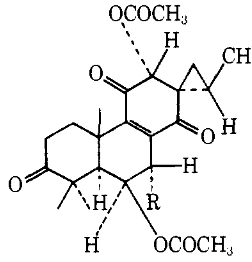
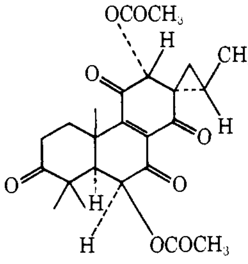
Structure and Absolute Stereochemistry of the Diterpenoid Barbatusin

Sir:

Barbatusin is a novel diterpenoid isolated from the leaves of *Coleus barbathus* (*Labiatae*) and its molecular structure I has been established by X-ray and spectrochemical investigations.



I, R = OH
II, R = $OCOCH_3$
III, R = $OCOC_6H_4Br$



IV

Barbatusin, mp 224–228°, has the molecular formula $C_{24}H_{30}O_8$, assigned on the basis of elemental analysis and mass spectrometry ($M^+ = 446$). The absorption maximum at 235 nm (ε 15,000) indicates a conjugated ketone, and in alkaline ethanolic solution is replaced by two other maxima at 223 (ε 26,800) and 272 nm (sh) (ε 4600), typical of an enolate. The ir spectrum shows the presence of a hydroxyl, an ester, a ketone in a six-membered ring, and an α,β-unsaturated ketone (3500, 1740, 1705, 1670, and 1605 cm^{-1}). The nmr spectrum ($CDCl_3$) was particularly informative in that it revealed three *C*-methyl groups (s at 1.21, 1.24, and

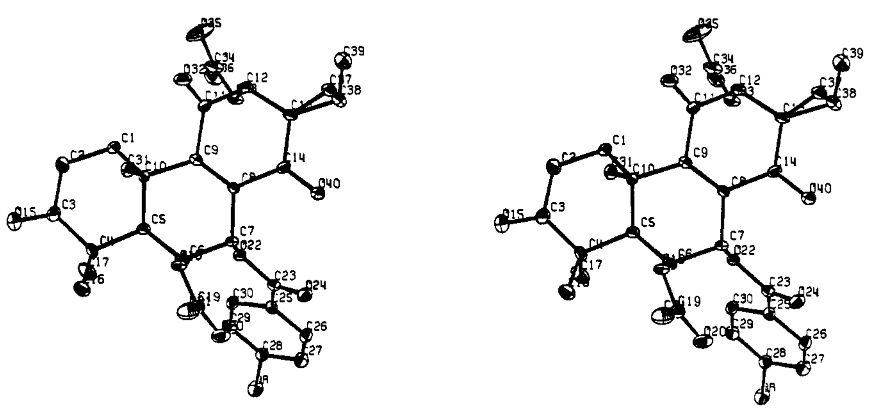


Figure 1. Stereoscopic view of a single molecule of the *p*-bromobenzoyl ester of barbatusin. Hydrogen atoms were omitted for clarity.

1.67 ppm), a secondary *C*-methyl group (d at 1.14 ppm, J = 4 Hz), two acetyl functions (s at 2.02 and 2.10 ppm), two C*H*OAc protons (s at 5.06 and t at 5.28 ppm), one secondary hydroxyl group (br d at 3.45 ppm, J = 5 Hz) which disappears on D_2O shaking, and a proton on the carbon atom bearing the OH group (d of d at 4.68 ppm which collapses to a doublet on D_2O shaking, J = 2.5 Hz). The lack of evidence for a vinyl proton together with the observed ir band at 1605 cm^{-1} indicates that the double bond is tetrasubstituted.

Barbatusin readily formed an acetylated compound II, $C_{26}H_{32}O_9$, mp 184–186°, which has in its nmr spectrum a sharp doublet at 5.75 ppm (J = 2.5 Hz) assignable to the C*H*OAc proton of a third acetyl group (3 H, s at 2.05 ppm), and a *p*-bromobenzoyl ester (III), $C_{31}H_{33}O_9Br$, mp 173–175°.

Oxidation of barbatusin in acidic conditions (Jones reagent) affords a product, barbatusinone (IV), $C_{24}H_{28}O_8$, mp 205–208°. The absorption maxima at 218 (ϵ 15,000), 235 (ϵ 17,700), and 253 nm (sh) (ϵ 14,000) are, in alkaline ethanolic solution, immediately replaced by two intense maxima at 224 (ϵ 25,900) and 275 nm (ϵ 14,000), a fact which strongly suggests the presence of a β-diketone functionality. This indication is supported in the ir by a band at 1640 cm^{-1} which falls in the range of absorption frequencies for β-diketones[1] and by treatment of a solution of IV with titanium trichloride which gives an orange color reaction, characteristic of enolized β-diketones.[2] These spectra defined the functions of the eight oxygen atoms in the molecule of barbatusin. The complete molecular structure and absolute configuration of barbatusin were determined by the single-crystal X-ray analysis of the *p*-bromobenzoyl ester (III) of barbatusin. The parallelepiped-shaped yellow crystals of III contain one molecule of benzene of solvation in the crystal asymmetric unit. Crystal data are: $C_{31}H_{33}O_9Br \cdot C_6H_6$, mol wt 707.7, monoclinic, a = 10.135 (3), b = 24.184 (6), and c = 7.707 (2) Å, β = 109° 46 (2)′, V = 1777 Å^3, Z = 2, d_c = 1.32 g cm^{-3}; space group $P2_1$. A total of 2028 nonzero reflections out to 2θ = 130° were measured on a Picker FACS-1 diffractometer using Cu Kα radiation. The structure was solved by the heavy atom method and was refined by full-matrix least-squares methods incorporating and varying anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all except four hydrogen atoms, whose isotropic thermal parameters were held constant at B_θ = 6.5 Å^2. The hydrogen atoms on the solvated benzene molecule could not be located. The final R factor for the enantiomer with the absolute configuration shown in III and in Figure 1 was 0.064. The absolute configuration was determined by using the anomalous scattering of the bromine atom and was established by Hamilton's test for a one-dimensional hypothesis with rejection of the alternative configuration at the 99.5% confidence level (R_w^+/R_w^- = 0.066/0.068). This assignment was further confirmed by measuring the Bijvoet pairs of eight reflections which showed large differences in F_c in the structure factor calculation. The absolute configuration about C-10 of barbatusin is the same as that of royleanone.[3]

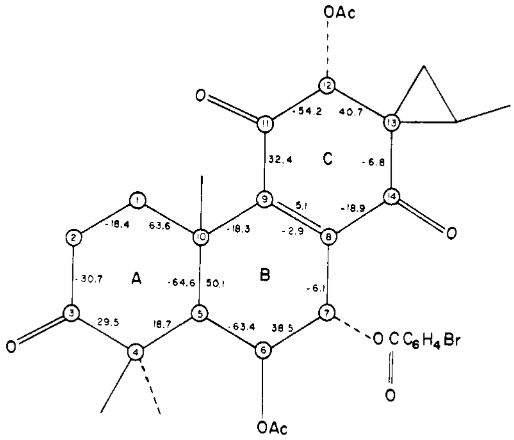


Figure 2. Torsion angles around the nucleus of the barbatusin molecule. The angle ABCD is considered positive if, when looking along the B–C bond, A has to be rotated clockwise to eclipse D.

The torsion angles around the carbon skeleton are shown in Figure 2. Ring A exists in distorted boat conformation with the carbonyl group pointing toward the β side of the molecule. Ring B is a distorted half-chair with C-5 and C-6 0.54 and 0.21 Å below and above the best plane through the other four atoms. There is evidence for considerable steric interaction between C-31 and O-18, C-31 and O-32, and C-16 and O-18; the respective distances are 2.979 (14), 3.009 (15), and 2.938 (17) Å. Ring C could be de-

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scribed as a half-chair conformation with C-11 and C-12 being 0.24 and 0.47 Å on opposite sides of the best plane (average deviation 0.06 Å) through the other four atoms. The C-11═O-32 carbonyl group points to the β side of the molecule. There are considerable distortions from planarity about the conjugated 1,4-diketone portion of the molecule with torsion angles as great as 32.4°. The dispositions of the C-3═O-15 and C-14═O-40 carbonyl groups are such that they do not bisect the bonds to the geminal disubstituents on the adjacent carbon atoms.

Barbatusin seems to be related biosynthetically to the ferruginol class of diterpenes[4] as well as to a number of quinonoid diterpenes isolated from various sources,[3,5] in particular from *Labiatae* species,[6] with the rare feature of containing a methylcyclopropyl ring at the C-13 atom.[7] In view of the reactivity of the cyclopropane molecule, barbatusin may represent an interesting and unusual intermediate in the biosynthesis of some naturally occurring quinonoid diterpenes.[8,9]

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(9) The final values for the atomic coordinates, thermal parameters, and observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of this journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-598.

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Dramatic Rate Enhancement of the Aquation of the Tris(oxalato)chromate(III) Anion by Surfactant Solubilized Water in Benzene

Sir:

Racemization, aquation, and ligand-exchange reactions of tris(oxalato)chromate(III) anion, $Cr(C_2O_4)_3{}^{3-}$, have been discussed in terms of a "one-ended dissociation"[1-3] (Scheme I). The subsequent fate of the octahedral site on the metal ion vacated by such a dissociation, however, has not been unequivocally established. One school favors a rate determining step which involves the synchronous Cr–O bond breaking and nucleophilic attack by water (path A)[2,3] while there are arguments in support of an alternative mechanism in which the octahedral site remains vacant during the Cr–O bond breaking (path B).[1,4] Kinetic investigations of the dependence of the aquation rate on water concentration would provide sufficient evidence to allow a distinction between these alternative pathways. Since the uncatalyzed rate of aquation for the $Cr(C_2O_4)_3{}^{3-}$ is extremely slow (there is only 9.4% conversion to *cis*-$Cr(C_2O_4)_3(H_2O)_2{}^-$ in 522 hr at 47°[1c]), such an investigation is not feasible. To overcome this problem we have localized $Cr(C_2O_4)_3{}^{3-}$ and water in the hydrophilic cavity of surfactant aggregates dissolved in benzene. In this system we not only find rate enhancements of the "neutral" rate by factors up to 5×10^6 with respect to that in water but can precisely control the concentrations of both water and $Cr(C_2O_4)_3{}^{3-}$.

Aquation of $Cr(C_2O_4)_3{}^{3-}$ has been investigated in water solubilized by surfactant aggregates of octylammonium tetradecanoate (OAT), dodecylammonium propionate (DAP), and hexadecyltrimethylammonium butyrate (CTABu) in benzene.[6] Typical rate profiles of pseudo-first-order rate constants, k_ψ, against surfactant concentration are shown in Figure 1.[9] The rate constant for aquation of $Cr(C_2O_4)_3{}^{3-}$ to *cis*-$Cr(C_2O_4)_2$-

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(3) K. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).

(4) Indirect support for path B came from the inertness[5] of the coordinated water of the *cis*-diaquobisoxalatochromate(III) anion, $Cr(C_2O_4)_2(H_2O)_2{}^-$. The one-ended dissociation of $Cr(C_2O_4)_3{}^{3-}$ must be reversible in order to allow the other end to dissociate. If the vacant octahedral site were aquated, this water would necessarily be labile, contrary to the behavior of $Cr(C_2O_4)_2(H_2O)_2{}^-$.

(5) J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc. A*, 1413 (1968).

(6) Formation of OAT, DAP, and CTABu aggregates, containing three to seven monomers, has been demonstrated in benzene by ^1H nmr investigations. Changes in the appropriate proton magnetic resonance frequencies as functions of surfactant concentration established that the polar carboxyl and ammonium groups are located at the interior of the aggregates while the hydrophobic hydrocarbon chains are in contact with the nonpolar benzene. In keeping with current terminology[7] we have called these aggregates "reversed" or "inverted" micelles. The concentration at which aggregation occurs, *i.e.*, the critical micelle concentration or cmc, for OAT, DAP, and CTABu in benzene has been determined to be $(1.9\text{–}2.2) \times 10^{-2}$, $(3\text{–}7) \times 10^{-3}$, and 1.4×10^{-3} *M*, respectively.[8]

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(9) Rate measurements were carried out by following the decrease in absorbance at 416 nm spectrophotometrically. Reactions were initiated by injecting known volumes (5–20 μl) of aqueous solutions of $K_3[Cr(C_2O_4)_3] \cdot 3H_2O$ to thermostated surfactant solutions (5 ml) in carefully dried benzene. Good first-order plots were obtained in all cases up to 90% reaction. The product of the reaction was identified as $Cr(C_2O_4)_2(H_2O)_2{}^-$ from its known spectrum.[2] k_ψ was independent of substrate concentration in the range $(1\text{–}20) \times 10^{-4}$ *M*.