

larger excess (2.5 mol equiv) of titanium tetrachloride was used in order to minimize formation of an as yet unidentified nonpolar byproduct. The conversions of the coupled products **3**, via **4**, into the propargylic alcohols **5** (Scheme II, Table II) were also performed by the previously described procedures.¹ In the case of ketones **4b**, **4d**, and **4e** the base treatment to effect β -elimination resulted in concomitant desilylation giving **5b**, **5d**, and **5e**, respectively.

It is particularly noteworthy that the diastereomeric forms of the coupled products **3** were readily separated by rapid low-pressure column chromatography,^{8b} thus providing a route to propargylic alcohols **5** of 100% optical purity.

The constitution of the propargylic alcohols **5**, which can be presumed to have the *R* configuration on the basis of previous precedents,^{1,3} was confirmed as follows. The optical rotation of alcohol **5b** (Table II, entry 2) is in close agreement with the $[\alpha]_D^{23} +14.8^\circ$ reported for a specimen of (*R*)-(+)-**5b** of approximately 90% optical purity, obtained by classical resolution of racemic material.¹² It is noteworthy that **5b**, which is available optically pure by our method (see above), is an intermediate in the synthesis of methyl (*E*)-2,4,5-tetradecatrienoate, a pheromone of the male dried bean beetle.¹²

The rotation of alcohol **5c** (Table II, entry 3), which has been used for the synthesis of (2*R*,4'*R*,8'*R*)- α -tocopherol,¹³ is in excellent agreement with that calculated¹³ for a sample of 70% ee, namely $[\alpha]_D^{23} +10.15^\circ$ (*c* 4.9, CHCl₃).

The rotations of alcohols **5d** and **5e** (Table II) entries 4 and 5 are in good agreement with those reported¹⁴ for the respective *R* and *S* antipodes, which have been used as intermediates in the synthesis of the ω side chain of prostaglandins (15*R*)- and (15*S*)-PGB₁.¹⁵

The results presented here indicate that the Lewis acid catalyzed reaction of chiral acetals **1a-1e** with silylacetylenes **2a** and **2b** is considerably more diastereoselective than the corresponding reaction with allyltrimethylsilane.¹ Considering that (a) chiral acetals of type **1** are readily available in both enantiomeric forms¹⁶ and (b) removal of the chiral auxiliary in the coupled products **2** is highly efficient, the methodology disclosed here represents an extremely attractive alternative to existing asymmetric syntheses of secondary propargylic alcohols.¹⁷ Numerous examples may be cited that attest to the synthetic versatility of these compounds. In particular alkylation of hydroxyl-protected chiral secondary propargylic alcohols possessing a terminal acetylenic function, i.e., **5** (*R* = alkyl, *R'* = H) has been shown to proceed without noticeable racemization.¹⁸ Equally noteworthy is that compounds of type **5** (*R* = *R'* = alkyl), in which the acetylenic function is nonterminal, are progenitors of the corresponding *E*^{13,19} and *Z*^{13,20}

(8) (a) The crude product was homogeneous with respect to GC and TLC. (b) The product was purified by low-pressure column chromatography using Merck silica gel 60 H for thin-layer chromatography.

(9) (a) The ¹H NMR, IR, and mass spectra were consistent with the assigned structure. (b) A satisfactory combustion analysis was obtained for an appropriately purified specimen of this compound.

(10) The diastereomeric ratio was determined by GC on a 12-m SE-54 capillary column, which showed a base-line separation of the two peaks.

(11) Determined by GC analysis (base-line separation) of (*R*)-(+)-MTPA esters. See: Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543-2549.

(12) Mori, K.; Nukada, T.; Ebata, T. *Tetrahedron* **1981**, *37*, 1343-1347.

(13) Lit. $[\alpha]_D^{25} +13.48^\circ$ (*c* 4.9, CHCl₃), optical purity 93% by MTPA-ester method.¹¹ See: Chan, K. K.; Cohen, N.; De Noble, J. P.; Specian, A. C., Jr.; Saucy, G. *J. Org. Chem.* **1976**, *41*, 3497-3505.

(14) Lit. $[\alpha]_D^{25} +19.8^\circ$, optical purity 100% by MTPA-ester method.¹¹ See: Fried, J.; Lin, C.; Mehra, M.; Kao, W.; Dalven, P. *Ann. N.Y. Acad. Sci.* **1971**, *180*, 38-63.

(15) Pappo, R.; Collins, P.; Jung, C. *Ann. N.Y. Acad. Sci.* **1971**, *180*, 64-75.

(16) Ito, K.; Harada, T.; Tai, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3367-3368.

(17) See inter alia: Mukaiyama, T.; Suzuki, K.; Soai, K.; Sato, T. *Chem. Lett.* **1979**, 447-448. Midland, M. M.; Kazubski, A. *J. Org. Chem.* **1982**, *47*, 2495-2496; 2814-2816.

(18) Johnson, W. S.; Brinkmeyer, R. S.; Kapoor, V. M.; Yarnell, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 8341-8343.

(19) See inter alia: Djerassi, C.; Grant, B. *J. Org. Chem.* **1974**, *39*, 968-970. Johnson, W. S.; Escher, S.; Metcalf, B. W. *J. Am. Chem. Soc.* **1976**, *98*, 1039-1041.

allylic alcohols, as well as of optically active allenes.²¹

Acknowledgment. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research. We also express our appreciation to Professor P. A. Bartlett for helpful discussions and to Dr. A. Tai of the Institute of Protein Research, Osaka University, for the gift of generous samples of (2*R*,4*R*)- and of (2*S*,4*S*)-pentanediol.

(20) See inter alia: Gutmann, H.; Lindlar, H. "Chemistry of Acetylenes", Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; p 360.

(21) For an example see ref 13.

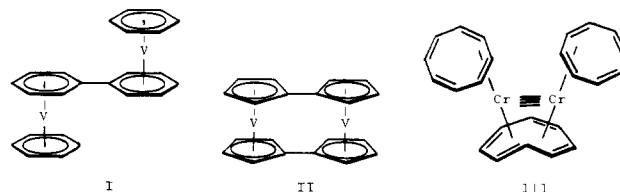
μ -(η^5 : η^5 -Cyclooctatetraene)bis[(η^5 -cyclopentadienyl)-vanadium]: Preparation, Structure, and ESR Characterization of Its Radical Anion

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Electron spin-spin interaction in dinuclear complexes of vanadium, which may be looked at as built from paramagnetic units, ranges from slight— μ (η^6 : η^6 -biphenyl)bis[(η^6 -benzene)vanadium], I, is a diradical with a triplet ground state¹—to extensive—bis-



(fulvalene)divanadium, II, is diamagnetic.² However, very few molecules have been synthesized and characterized structurally, in which genuine vanadium-vanadium bonds pertain.³ This is in stark contrast to the coordination chemistry of chromium, where species with multiple metal-metal bonds are legion.⁴ As an example, the complex μ -(η^5 : η^5 -cyclooctatetraene)bis[(η^4 -cyclooctatetraene)chromium],⁵ III, may be cited. The short metal-metal distance, $d(\text{Cr}-\text{Cr}) = 221.4$ pm, in this species was rationalized in terms of a quadruple Cr-Cr bond, which leads to 18 valence electron shells for the chromium atoms.

An isoelectronic complex with vanadium replacing chromium would demand terminal rings donating five electrons rather than the four electrons furnished by η^4 -cyclooctatetraene. We therefore

(1) Elschenbroich, Ch.; Heck, J. *Angew. Chem.* **1981**, *93*, 278; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 267.

(2) Smart, J. C.; Pinsky, B. L.; Fredrich, M. F.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 4371.

(3) (a) In (η^5 -C₈H₈)₂V₂(CO)₈, $d(\text{V}-\text{V}) = 246$ pm, the bond order is uncertain: Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* **1973**, *95*. (b) An "impossible" V-V double bond is suggested in the case of (μ -PMe₂)₂V₂(CO)₈, $d(\text{V}-\text{V}) = 273$ pm: Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472. (c) "The probable existence of a triple bond between two vanadium atoms" is proposed for V₂(2,6-dimethoxyphenyl)₄, THF, $d(\text{V}-\text{V}) = 220$ pm. Cotton, F. A.; Miller, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886. (d) Preliminary structural data indicate a V-V bond length of ≈ 225 ppm for the complex (C₆H₆)₂V₂(CO)₄. A V-V triple bond is assumed: Atwood, J. D.; Janik, T. S.; Atwood, J. L.; Rogers, R. D. *Synth. React. Inorg. Mei.-Org. Chem.* **1980**, *10*, 397.

(4) Cotton, F. A. *Chem. Soc. Rev.* **1975**, *4*, 27. Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982.

(5) Synthesis: Breil, H.; Wilke, G. *Angew. Chem.* **1966**, *78*, 942; *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 898. Müller, J.; Holzinger, W.; Köhler, F. H. *Chem. Ber.* **1976**, *109*, 1222. Structure: Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1976**, *15*, 2511.

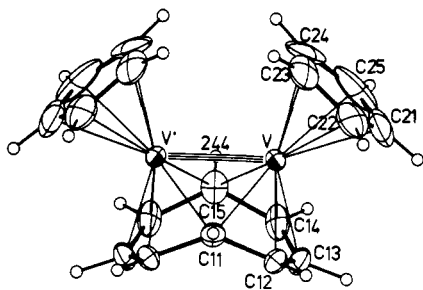


Figure 1. ORTEP drawing of $[(C_5H_5)V]_2C_8H_8$, IV, with thermal ellipsoids for the non-hydrogen atoms at the 30% probability level. The atoms with no labels are related to the labeled ones by the mirror plane perpendicular to the V-V axis. Selected interatomic distances (pm) with estimated standard deviations in parentheses: V-V, 243.9 (1); V-C11, 224.5 (5); V-C12, 212.4 (4); V-C13, 219.9 (6); V-C14, 213.2 (5); V-C15, 224.6 (6); V-C21, 226.4 (6); V-C22, 229.4 (7); V-C23, 226.9 (9); V-C24, 225.5 (7); V-C25, 226.5 (11); C11-C12, 145.6 (6); C12-C13, 137.7 (8); C13-C14, 138.8 (8); C14-C15, 146.4 (6); C11-C15, 304 (1).

attempted the synthesis of the complex $(C_5H_5)_2V_2C_8H_8$.

From THF solutions containing $VCl_2 \cdot 2THF$, NaC_5H_5 , and $K_2C_8H_8$ in the molar ratio 2:2:1 reddish brown, diamagnetic, highly air-sensitive crystals, IV, were obtained⁶ as a minor product,



which according to elemental analysis and mass spectrometry has the composition $C_{18}H_{18}V_2$. According to a single-crystal X-ray diffraction study⁸ (Figure 1), IV contains a bridging cyclooctatetraene ligand connecting two C_5H_5V units. The bridging C_8H_8 ring consists of two virtually planar moieties that are inclined along the axis C11-C15 at a dihedral angle of 124° . The planes of the two C_5H_5 rings are almost parallel to the respective fragments of the bridging C_8H_8 ligand. The slight deviation of 11.9° from a parallel disposition may serve to relieve steric interaction between the two C_5H_5 ligands. IV may be regarded as two "semiopen"⁹ vanadocene sandwich complexes V, which share the

(6) Procedure: To a stirred solution of $VCl_2 \cdot 2THF$ ⁷ in 150 mL of THF, obtained via reduction of VCl_3 (3.12 g, 19.83 mmol) by Zn are added at $-50^\circ C$ in a nitrogen atmosphere first a solution of $K_2C_8H_8$ (1.82 g, 10 mmol) in 100 mL of THF and after 30 min solid NaC_5H_5 (1.85 g, 21 mmol). The suspension is allowed to warm to room temperature and is refluxed for 2 h. After the solvent is stripped off, the residue is sublimed (10^{-4} torr, $140^\circ C$). The sublimate is extracted with 50 mL of low-boiling petroleum ether. After 1 week at $+4^\circ C$ 160 mg (4.8%) of very air-sensitive reddish-brown crystals, IV, are obtained from this solution. IV decomposes at $T > 183^\circ C$ before reaching the melting point. Anal. Calcd for $C_{18}H_{18}V_2$: C, 64.30; H, 5.39; V, 30.30. Found: C, 64.41; H, 5.47; V, 30.18. Mass spectrum (electron impact, 70 eV), m/e 337 (M^+ , 17.5), 336 (M^+ , 100), 334 (16.7), 256 (12.2), 230 (11.2), 221 (11.8), 218 (11.8), 181 (23.7, $M^+ - VC_5H_5$), 153 (27.9), 129 (12.0), 116 (81.8, $VC_5H_5^+$), 105 (23.3), 91 (23.5), 79 (10.2), 73 (19.9), 51 (14.4); 1H NMR (toluene- d_6 , 343 K) δ 5.4 (br, width ≈ 30 Hz) subject to sharpening and upfield shift upon decrease in temperature.

(7) Köhler, F. H.; Prössdorf, W. Z. *Naturforsch. B* 1977, 32B, 1026.

(8) A large thin flat needle of IV was measured on a four-circle diffractometer (CAD4, Enraf-Nonius); space group $Pnma$, $Z = 4$; $a = 1186.0$ (4), $b = 1595.1$ (4), and $c = 782.0$ (7) pm; 1164 independent reflections with $F^2 > 2\sigma$ were collected in the range $2^\circ < \theta < 30^\circ$ with graphite-monochromated $Mo K\alpha$ radiation using ω scans over $(1 + 0.357\theta)^\circ$ plus 25% of this width before and after the reflection for background determination. Because of the very anisotropic shape of the crystal a numeric absorption correction was applied ($\mu = 11.8$ cm^{-1}). The structure has been solved by direct methods (MULTAN 80) and standard difference Fourier techniques. The hydrogen positions of the C_8H_8 ring could be refined with individual isotropic temperature factors. Due to strong thermal vibrations of the C_5H_5 atoms, these H atoms were treated as "riding" on the C atoms at a distance of 100 pm. The refinement by a weighted full-matrix least-squares method (weight $w = 3/\sigma^2(F_o)$) included anisotropic thermal parameters for all non-hydrogen atoms. The final R factors was $R_F = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.0405$ and $R_w = \sum \sqrt{w} ||F_o| - |F_c|| / \sum \sqrt{w} F_o = 0.0409$.

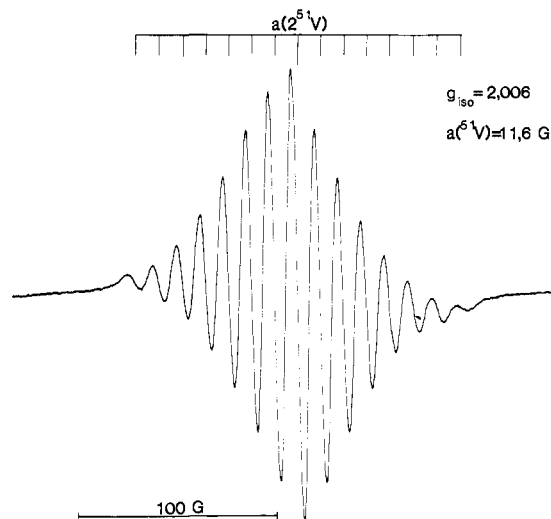


Figure 2. ESR spectrum of the radical anion $[(C_5H_5)V]_2C_8H_8^-$ in methyltetrahydrofuran at $-35^\circ C$; counterion, potassium.

two terminal carbon atoms of their open pentadienyl ligands.

The bonding relation of C11 and C15 to the two vanadium atoms of the binuclear complex is most simply described by drawing two resonance structures for IV. In this way, the fact that the longest metal-carbon bonds are V-C11 and V-C15 and the largest C-C bond distances are C11-C12 and C14-C15 can be accounted for. Furthermore, in each of the resonance forms one of the vanadium atoms gains an 18 valence electron configuration if a V-V triple bond is assumed. It should be mentioned, that the diamagnetism of IV does not require the inference of a V-V triple bond since the pentadienyl ligand was shown to be more effective than the cyclopentadienyl ligand in causing a low-spin configuration: whereas vanadocene possesses a $^4A_{1g}$ ground state,¹⁰ only one unpaired electron is present in bis(pentadienyl)vanadium ($^2A_{1g}$).^{9d} Therefore, a single V-V bond would suffice to explain the diamagnetic nature of IV albeit leaving the vanadium atoms with 16 valence electron shells. The bond length $d(V-V) = 244$ pm in IV does not by itself permit an unequivocal assignment of bond order. Whereas the singlet ground state of IV only implies that the V-V bond order must be odd, comparison with existing structural data³ suggests that in IV either a rather long V-V triple bond or a very short single bond is encountered. A similar dilemma exists in the description of the V-V bond order in $(C_5H_5)_2V_2(CO)_5$.^{3a}

IV readily forms the radical anion IV^- upon treatment with potassium in methyltetrahydrofuran. The ESR spectrum of IV^- in fluid solution is shown in Figure 2. The multiplicity (15 equidistant lines) and the value of the isotropic hyperfine coupling constant [$a(^{51}V) = 11.6$ G], which is about half the value¹¹ observed for vanadocene in fluid solution [$a(^{51}V) = 27.4$ G], imply that the unpaired electron is delocalized over both moieties of IV^- . The small g anisotropy¹² and the fact that ESR is observed at room

(9) "Open metallocenes" contain the pentadienyl ligand, $C_5H_7^-$, instead of cyclopentadienyl, $C_5H_5^-$. The preparation of bis(pentadienyl) complexes of Fe, Mn, Cr, V, and Ti has recently been reported: (a) Wilson, D. R.; DiLullo, A. D.; Ernst, R. D. *J. Am. Chem. Soc.* 1980, 102, 5928. (b) Wilson, D. R.; Liu, J.; Ernst, R. D. *Ibid.* 1982, 104, 1120. (c) Böhm, M. C.; Eckert-Maksic, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *Ibid.* 1982, 104, 2699. (d) Liu, J.; Ernst, R. D. *Ibid.* 1982, 104, 3737.

(10) (a) Prins, R.; Van Voorst, J. D. W. *J. Chem. Phys.* 1968, 49, 4665. (b) Warren, K. D. *Struct. Bonding (Berlin)* 1976, 27, 45.

(11) (a) McConnell, H. M.; Porterfield, W. W.; Robertson, R. E. *J. Chem. Phys.* 1959, 30, 442. (b) Robertson, R. E.; McConnell, H. M. *J. Phys. Chem.* 1960, 64, 70. A complete numerical agreement is not to be expected since the different ligand properties of open $C_5H_7^-$ (pentadienyl) and closed $C_5H_5^-$ (cyclopentadienyl) effect a low-spin state $^2A_{1g}$ for $(\eta^5-C_5H_7)_2V$ as opposed to $^4A_{1g}$ for $(\eta^5-C_5H_5)_2V$.⁹ Furthermore, the shorter metal-ring distances in open metallocenes should cause more extensive metal \rightarrow ligand spin delocalization and may be responsible for the fact that $a(^{51}V; IV^-) < 1/2 a(^{51}V; Cp_2V)$. The ideal reference compound $(\eta^5-C_5H_5)V(\eta^5-C_5H_7)$ has not yet been prepared.

temperature point to an orbitally nondegenerate ground state for IV^- . These facts can be accommodated under the assumption that in IV two units of $C_5H_5VC_5H_7$ with the individual electron configuration of vanadocene¹⁰ $[(e_{2g}; x^2 - y^2, xy)^2(a_{1g}; z^2)^1]$ interact. Whereas at the metal-metal distance $d(V-V) = 244$ pm the overlap of the two pairs of e_{2g} orbitals should be extensive, $V(3d_{z^2})-V(3d_{z^2})$ interaction is expected to be weak. Therefore, the frontier MO sequence $(e_{2g})(a_{1g})(a_{1g}^*)(e_{2g}^*)$ leading to the configuration $(e_{2g})^4(a_{1g})^2$ for binuclear IV is a reasonable one. The small splitting between a_{1g} and a_{1g}^* and the concomitant weakly antibonding character of a_{1g}^* would then explain the ease of formation of the radical anion IV^- in an orbitally nondegenerate ground state as well as the population of a triplet state with increasing temperature as suggested by the 1H NMR results.⁶

Acknowledgment. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie.

Note Added in Proof. Recently, we have also prepared the analogous chromium complex $[(C_5H_5)Cr]_2C_8H_8$.¹³

Registry No. IV, 85249-98-5; IV^- , 85234-88-4; $VC1_2 \cdot 2THF$, 21729-44-2; NaC_5H_5 , 4984-82-1; $K_2C_8H_8$, 59391-85-4.

Supplementary Material Available: Tables of atomic positional and anisotropic thermal parameters, observed and calculated structure factors, additional interatomic distances and angles, and distances to "best planes" (11 pages). Ordering information is given on any current masthead page.

(12) $\Delta g_{\parallel, \perp}(IV^-, MTHF, 115 K) < 0.1$. A detailed analysis and interpretation of the spectra of IV^- in rigid solution as well as a magnetic susceptibility study will be communicated in a future publication.

(13) Elschenbroich, Ch.; Heck, F.; Massa, W.; Schmidt, R. *Angew. Chem., Int. Ed. Engl.*, in press.

Structures of Betaenones A and B, Novel Phytotoxins from *Phoma betae* Fr.

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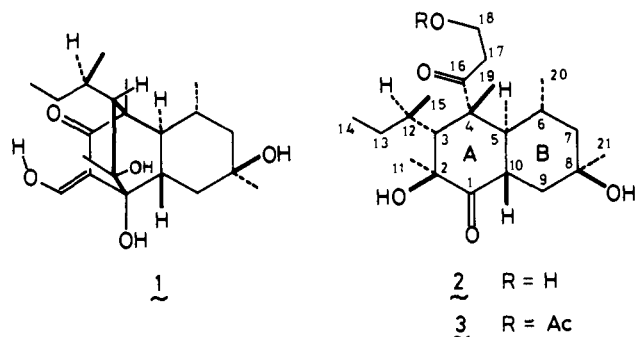
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Betaenones A (1) and B (2) are phytotoxins¹ isolated from



culture filtrates of *Phoma betae* Fr., the causal fungus of leaf spot disease of sugar beet, and induce chlorosis on the leaves of the host plant at 1×10^{-4} and 1×10^{-3} M, respectively.² We report

(1) For a general outline on phytotoxins from plant pathogenic microorganisms, see: Durbin, R. D., Ed. "Toxins in Plant Disease"; Academic Press: New York, 1981.

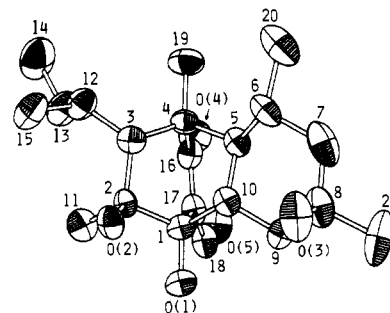


Figure 1. Perspective view of the betaenone A (1) molecule.

here the structure determination of these novel phytotoxins using X-ray analysis and chemical correlation.

Betaenone A [1: $C_{21}H_{34}O_5$, mp 153–155 °C; $[\alpha]_D^{20} +61.2^\circ$ (c 1.1, $CHCl_3$); EI MS, m/z 366 (M^+); UV λ_{max}^{EtOH} 278 nm (ϵ 6300)] shows IR (KBr) bands at 1655 and 1578 cm^{-1} assignable to the α,β -unsaturated ketone and a band at 3400 cm^{-1} due to OH groups that resisted acetylation. The 1H NMR spectrum (400 MHz) of 1 showed the presence of one CH_2CH_3 at δ 0.88 (3 H, t, $J = 7.1$ Hz), two $CHCH_3$ at δ 0.98 (3 H, d, $J = 6.4$ Hz), and 1.14 (3 H, d, $J = 6.8$ Hz), three quaternary CH_3 at δ 1.16, 1.17, 1.25 (each 3 H, s), and one vinylic proton at δ 7.16 (1 H, s). The ^{13}C NMR spectrum (OFR)⁴ exhibited the presence of the six CH_3 , three CH_2 , six CH , and six quaternary carbons including one carbonyl carbon. Single crystals of betaenone A (1) were submitted to X-ray analysis. The crystal data were as follows: $C_{21}H_{34}O_5 \cdot CH_3OH$, orthorhombic, space group $C22_1$, $a = 17.745$ (7) Å, $b = 19.474$ (6) Å, $c = 12.937$ (8) Å, $Z = 8$, $D_c = 1.184$ $g\ cm^{-3}$. The intensity data of 1999 reflections with $2\theta < 130^\circ$ were collected on an automatic, four-circle diffractometer with graphite-monochromated $Cu\ K\alpha$ radiation by means of a θ - 2θ continuous-scan technique. The structure was solved by the Monte Carlo direct method,⁵ using the 30 strongest reflections as the starting set. The 153rd random phase set led to the correct solution; an E map based on 497 phases afforded all 28 non-hydrogen atoms. After several refinement cycles by the least-squares method using carbon atomic scattering factors for all non-hydrogen atoms had been carried out, the oxygen atoms were assigned by taking account of the resulting isotopic temperature factors and interatomic distances. The structure thus obtained was refined by the block-diagonal-matrix least-squares method with anisotropic temperature factors. A difference Fourier map revealed the locations of all hydrogen atoms except those of the methanol methyl group. Further least-squares refinements were repeated including the hydrogen atoms, giving a final R value of 0.076. The molecular framework obtained is shown in Figure 1. Structurally betaenone A (1) has unique highly substituted tricyclo[6.2.2.0²⁷]dodecane skeleton.⁶

Betaenone B (2) exhibits the following physical constants: powder; $C_{21}H_{36}O_5$ deduced from elemental analysis of monoacetate 3; mp 103.5–108.0 °C; m/z 368 (M^+); $[\alpha]_D^{20} 0^\circ$ (c 1.0, $EtOH$), UV λ_{max}^{EtOH} 259 (ϵ 133); IR ν_{max} (KBr) 3400, 1710 cm^{-1} ; ^{13}C NMR (OFR, INEPT) showed 21 carbons.⁷ 1H NMR (400 MHz) showed the presence of one CH_2CH_3 at δ 0.86 (3 H, t, $J = 7$ Hz), two $CHCH_3$ at δ 0.67 (3 H, d, $J = 6.4$ Hz) and 1.15

(2) Details of biological activities will be reported elsewhere by Dr. R. Sakai, Obihiro University.

(3) Satisfactory elemental analyses were obtained for 1 and 3, and all compounds numbered here were chromatographically homogeneous and gave MS, IR, and NMR (^{13}C and 1H) spectra consistent with their structures.

(4) ^{13}C NMR δ 13.8 (q), 16.9 (q), 18.6 (q), 20.5 (q), 22.3 (q), 27.1 (t), 31.4 (q), 32.1 (d), 36.2 (d), 37.6 (d), 40.0 (t), 50.8 (s), 52.6 (t), 52.9 (d), 57.4 (d), 71.5 (s), 74.0 (s), 80.6 (s), 112.5 (s), 158.1 (d), 207.8 (s).

(5) Furusaki, A. *Acta Crystallogr., Sect. A*, 1979, A35, 220.

(6) Other examples of tricyclo[6.2.2.0²⁷]dodecane derivatives from natural sources are tricyclosolidagolactone (Yamaura, S.; Ito, M.; Hasegawa, I.; Ohba, S.; Saito, Y. *Tetrahedron Lett.* 1981, 22, 739) and asatone (Yamamura, S.; Terada, Y.; Chen, Y.; Hong, M.; Hsu, H.; Sasaki, K.; Hirata, Y. *Bull. Chem. Soc. Jpn.* 1976, 49, 1940).

(7) Six CH_3 (δ 13.6, 20.4, 21.5, 23.4, 23.9, 31.1), five CH_2 (δ 25.1, 41.5, 43.9, 47.7, 58.4), five CH (δ 29.1, 35.8, 40.3, 46.6, 57.3), and five quaternary carbons (δ 52.9, 68.7, 77.3, 216.9, 217.6).