

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

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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; $VCl_2 \cdot 2THF$, 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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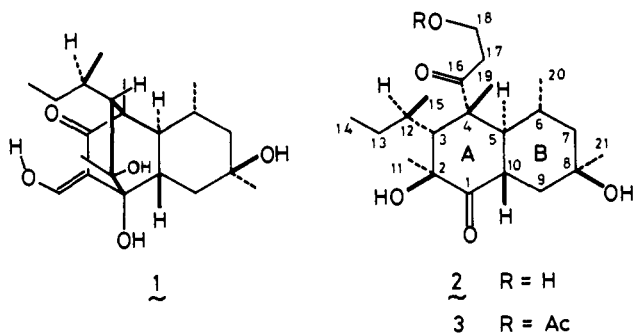
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Betaenones A (1) and B (2) are phytotoxins¹ isolated from



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.

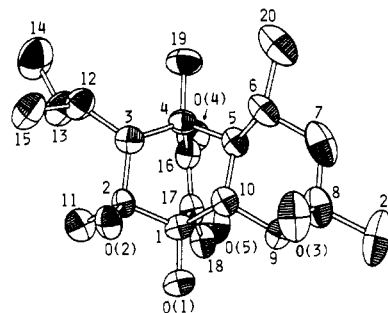


Figure 1. Perspective view of the betaenone A (1) molecule.

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 $C222_1$, $a = 17.745$ (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.

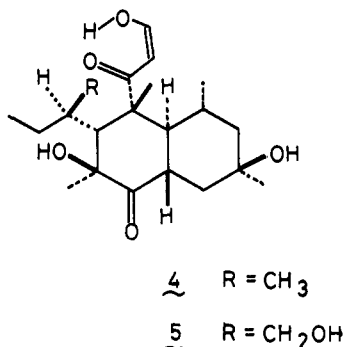
(4) ^{13}C NMR δ 13.8 (q), 16.9 (q), 18.6 (q), 20.5 (q), 22.3 (q), 27.1 (t), 31.4 (q), 32.1 (d), 36.2 (d), 37.6 (d), 40.0 (t), 50.8 (s), 52.6 (t), 52.9 (d), 57.4 (d), 71.5 (s), 74.0 (s), 80.6 (s), 112.5 (s), 158.1 (d), 207.8 (s).

(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).

(3 H, d, $J = 6.8$ Hz), three quaternary CH_3 at δ 1.26, 1.40, 1.57 (each 3 H, s), $\text{O}=\text{CCH}_2\text{CH}_2\text{OH}$ group at δ 2.82 (1 H, dt, $J = 18$ Hz, 4 Hz), 3.11 (1 H, dq, $J = 18$ Hz, 3 Hz), 3.76-3.85 (1 H, m), 3.87-3.97 (1 H, m). Treatment of **2** with Ac_2O in pyridine gave monoacetate **3**, $\text{C}_{23}\text{H}_{38}\text{O}_6$ mp 103.5-108.0 °C, IR ν_{max} (KBr) 3530, 1750, 1710 cm^{-1} . The similarity of the spectral data of betaenone **B** (**2**) with those of betaenone **A** (**1**) suggests that structurally **2** is closely related with **1**. The structure **2** for betaenone **B** was deduced from extensive decoupling measurements in ^1H NMR spectra of the derivatives of **2** and verified by conversion of **2** to **1** as follows. Oxidation of **2** with pyridinium chlorochromate afforded an oily aldehyde, **4** [MS, m/z 366 (M^+);



IR ν_{max} (neat) 1700 cm^{-1} ; ^1H NMR (400 MHz) 5.98 (1 H, d, $J = 4.9$ Hz), 7.74 (1 H, d, $J = 4.9$ Hz), 15.13 (1 H, br, s)], which was treated with $\text{KOH}-\text{MeOH}$ to afford a crystalline compound [mp 150-154 °C; $[\alpha]_{\text{D}} +64.8^\circ$ (c 0.56, CHCl_3)] whose spectral data and behavior on TLC are identical with those of betaenone **A** (**1**). Very recently stemphyloxin (**5**), which is closely related to the aldehyde **4**, was isolated from leaf spot disease fungus (*Stemphylium botryosum*) of tomato.⁸

The absolute configuration of betaenone **B** (**2**) was determined by ORD and CD measurements. Since the B ring of betaenone **B** (**2**) has a chair conformation from the coupling constants⁹ of signals due to C-5, C-9, and C-10 protons in the ^1H NMR spectrum and since under high dilution conditions (0.44×10^{-4} M in CCl_4) the IR spectrum showed an absorption band at 3480 cm^{-1} due to an intramolecular hydrogen bond, twisted cyclohexane conformation was indicated for the A ring of **2**. From a molecular model, it is understandable that steric effects arising from two axially oriented substituents at C-3 ($\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)\text{H}-$) and C-4 (CH_3) would be considerably lessened in such a twisted conformation. Such a conformation of **2** is expected to have a positive octant effect. In fact, ORD and CD measurements exhibited a positive octant effect and a positive curve, respectively, so the absolute configuration of betaenone **B** should be as depicted in **2**, and betaenone **A** is thus **1**. Substitutional patterns of **1** and **2** indicate that biogenetically these compounds are derived via the polyketide pathway. Physiological activities of and biogenetic pathway to betaenones and other metabolites¹⁰ from the same fungus will be investigated.

Acknowledgment. We are grateful to Dr. S. Naito, Hokkaido National Agricultural Experimental Station, Sapporo, for a generous gift of the strain *Phoma betae* Fr. PS-13.

Registry No. **1**, 85269-22-3; **2**, 85269-23-4; **3**, 85269-24-5; **4**, 85269-25-6.

Supplementary Material Available: Listings of atomic coordinates and bond distances of betaenone **A** (1 page). Ordering information is given on any current masthead page.

(8) Strobel, G. A. 7th World Congress on Animal, Plant and Microbial Toxins, Brisbane, July 1982. Barash, I.; Pupkin, G.; Netzer, D.; Kashman, Y. *Plant Physiol.* **1982**, *69*, 23.

(9) ^1H NMR (400 MHz) δ 2.31 (1 H, dt, $J = 14$ Hz, 3 Hz, eq 9-H), 2.49 (1 H, dd, $J = 14$ Hz, 11 Hz, 5-H), 2.66 (1 H, ddd, $J = 14$ Hz, 11 Hz, 3 Hz, 10-H).

(10) Several phytotoxins related to aphidicolins were recently isolated: Ichihara, A.; Oikawa, H.; Hayashi, K.; Hashimoto, M.; Sakamura, S., to be submitted for publication.

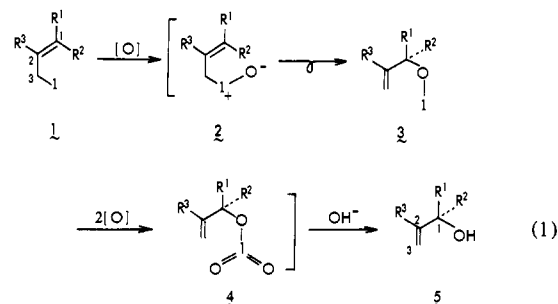
Oxidatively Assisted Hydrolysis of Allylic Iodides to Rearranged Allylic Alcohols. A New Example of [2,3] Sigmatropic Rearrangement

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[2,3] sigmatropic rearrangement of allylic amine oxides,¹ sulfoxides,² and selenoxides³ has long received widespread interest because of its theoretical and synthetic importance, but no such rearrangement has been known for allylic halogen oxides. This communication proposes a hitherto unknown rearrangement of allylic iodoso compound **2** to allylic hypiodite **3**, which occurs when allylic iodides **1** are oxidized with peracid to give rearranged allylic alcohols **5** (eq 1). To our knowledge, this reaction rep-



resents the first example of a sigmatropic rearrangement involving allylic halogen oxides. It was developed to furnish a new regioselective method for preparing **5** from **1** (eq 1).

Recently, interest has been directed to a facile conversion of a simple alkyl iodide into the corresponding alcohol by oxidation with *m*-chloroperbenzoic acid (*m*-CPBA) followed by hydrolysis.⁴ This reaction was applied to convert allylic iodide **6** into allylic alcohol **7** in our previously developed synthetic route to the 1-oxacephem skeleton^{5,6} (Scheme I). Contrary to our expectation, allylic alcohol **7** was formed in only moderate yield and accompanied by a large amount of aldehyde **8**.⁷ However, substantial improvement was effected by performing the reaction in a two-phase system using excess amounts of a peracid and an inorganic base (Table I).

In addition to such a significant change in the reaction conditions, we observed the following distinct differences in reaction mode between the previously reported procedures^{4a,b} and the present one. First, whereas $1/3$ equiv of iodine was liberated in the oxidation of saturated alkyl iodides, no iodine but 1 equiv of sodium iodate was formed in the oxidation of allylic iodides. Second, while only 1.33 equiv (2.0 equiv in practice)^{4a,b} of peracid

(1) Thyagarajan, B. S.; Hillard, J. B.; Reddy, K. V. *Tetrahedron Lett.* **1974**, 1999-2002.

(2) (a) Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *J. Am. Chem. Soc.* **1968**, *90*, 4869-4876. (b) Tang, R.; Mislow, K. *Ibid.* **1970**, *92*, 2100-2104. (c) Evans, D. A.; Andrews, G. C.; Sims, C. L. *Ibid.* **1971**, *93*, 4956-4957. (d) For a general review, see: Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147-155.

(3) (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1972**, *94*, 7154-7155. (b) For a general review, see: Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 22-30.

(4) (a) Reich, H. J.; Peake, S. L. *J. Am. Chem. Soc.* **1978**, *100*, 4888-4889. (b) Macdonald, T. L.; Narasimhan, N.; Burka, L. T. *Ibid.* **1980**, *102*, 7760-7765. (c) Cambie, R. C.; Chambers, D.; Lindsay, B. G.; Rutledge, P. S.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans I* **1980**, 822-827. (d) Davidson, R. I.; Kropp, P. J. *J. Org. Chem.* **1982**, *47*, 1904-1909.

(5) Nagata, W. *Philos. Trans. R. Soc. London, Ser. B* **1980**, *B289*, 225-230.

(6) Yoshioka, M.; Tsuji, T.; Uyeo, S.; Yamamoto, S.; Aoki, T.; Nishitani, Y.; Mori, S.; Satoh, H.; Hamada, Y.; Ishitobi, H.; Nagata, W. *Tetrahedron Lett.* **1980**, *21*, 351-354.

(7) See supplementary material for this information.