Table I. Conversion of (9*R*)-[9-^{3}H,4,8-^{14}C]Farnesyl Pyrophosphate (**1a**) and (9*S*)-[9-^{3}H,4,8-^{14}C]Farnesyl Pyrophosphate (**1b**) to Pentalenenes **2a** and **2b** by Pentalenene Synthetase and Distribution of the Label

compd	^{3}H/^{14}C	atom ratio	compd	^{3}H/^{14}C	atom ratio
1a	1.43	(1:2)[a]	**1b**	0.577 ± 0.007	(1:2)
8a	1.45 ± 0.02	1:2[b]	**8b**	0.497 ± 0.009	1:2
(**8a**)	1.28 ± 0.03	0.88:2[c]			
2a	1.48 ± 0.04	1:2	**2b**	0.502 ± 0.006	1:2
9a	1.49 ± 0.06	1:2	**9b**	0.486 ± 0.009	1:2
10a	1.47 ± 0.002	1:2	**10b**	0.478 ± 0.010	1:2
11a	1.46 ± 0.04	1:2			
11a	0.45 ± 0.02	0.31:2[d]			
12a	1.44 ± 0.04	1:2	**12b**	0.014 ± 0.006	0.03:2
			13b	0.525 ± 0.023	1.1:2

[a] Prepared by prenyl transferase reaction; based on the derived farnesyl diphenylurethane. [b] Prepared from farnesyl pyrophosphate (**1a**) reisolated from incubation with pentalenene synthetase. [c] Derived from farnesol reisolated from the pentalenene synthetase incubation and subjected to successive HLADH oxidation-borohydride reduction. [d] Exchanged with 0.2 N NaOD in D_2O-dioxane.[3] Predicted value 0.24:2 (cf. footnote 17).

geranyl pyrophosphate by reverse-phase ion-pairing HPLC.[16] The derived farnesyl diphenylurethane (**8b**) was recrystallized to constant activity (Table I).

For the conversion to pentalenene, (9*R*)-[9-^{3}H,4,8-^{14}C]farnesyl pyrophosphate (**1a**) was incubated with crude pentalenene synthetase,[3] and the resulting pentalenene (**2a**) was diluted with unlabeled pentalenene. Treatment of **2a** with OsO_4 gave diols **9a** and **10a**,[3] each of which was recrystallized to constant activity[17] (Table I). The incubation with (9*S*)-[9-^{3}H,4,8-^{14}C]farnesyl pyrophosphate (**1b**) was carried out by using 130-fold purified pentalenene synthetase which had been shown to be free of phosphatase, prenyl transferase, and isomerase activities.[18] Half of the resulting labeled pentalenene (**2b**) was diluted with inactive pentalenene, and the derived diols **9b** and **10b** were each recrystallized as before (Table I).

The precise location of the tritium in each sample of labeled pentalenene was established by a combination of chemical and microbiological methods[3] (Scheme III). Thus hydroboration-oxidation of **2a** gave the ketone **11a**, which lost greater than 92% of the predicted amount of label from C-8 upon base-catalyzed exchange (Table I). The absence of any tritium at H-1α of **2a** was established by feeding **2a** to intact cultures of *Streptomyces* UC5319 and isolation of the resulting labeled pentalenic acid methyl ester **12a** which had not lost any tritium.[3] By contrast, when the sample of **2b** was fed to cultures of *Streptomyces* UC5319, the derived **12b** had lost all tritium, whereas the co-metabolite *epi*-pentalenolactone F methyl ester (**13b**)[20] showed an unchanged ^{3}H/^{14}C ratio (Table I).

The above results establish that in the cyclization of farnesyl pyrophosphate to pentalenene, H-9re of **1** becomes H-8 of pentalenene, while H-9si undergoes net intramolecular transfer to H-1α of **2**, presumably by a deprotonation-reprotonation mechanism. Since the cyclization has already been shown to involve electrophilic attack on the si face of the 10,11-double bond of **1**,[21] the formal S_E' reaction takes place with net anti stereochemistry. This conclusion is completely consistent with the previously inferred RSR-CT conformation[3,21,22] of the cyclizing substrate, which prevents access by any enzymic base to the H-9re proton.

Acknowledgment. This work was supported by a grant from the National Institutes of Health, GM22172, and by postdoctoral fellowships from the Science and Engineering Research Council (C.A.) and the National Institutes of Health (C.T.K.).

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(17) As a control, a portion of the recovered farnesol resulting from the endogenous phosphatase activity in the pentalenene synthetase preparation was converted to the corresponding diphenylurethane (^{3}H/^{14}C 1.45), while the remainder was oxidized to farnesal by incubation with HLADH and NAD^+. Sodium borohydride reduction of farnesal and recrystallization of the derived diphenylurethane (^{3}H/^{14}C 1.28) established the presence of 12% of the tritium label at H-1re of the recovered farnesol, indicating that a portion of the DMAPP in the preparation of **1a** had been converted to (1*R*,5*R*,9*R*)-[1,5,9-^{3}H]farnesyl pyrophosphate by the combined action of endogenous DMAPP-IPP isomerase and prenyl transferase subsequently shown to be present in the crude pentalenene synthetase preparation. The proportion of tritium label at H-9re of the farnesyl pyrophosphate sample was therefore calculated to be 76%.
(18) Pentalenene synthetase, isolated as previously described,[19] was purified to a specific enzyme activity of 545 nmol/h/mg protein. For the preparative scale incubation, **1b** (0.40 nmol) was incubated for 1 h at 30 °C with 25 μg of pentalenene synthetase in 200 mM Tris, pH 8.4, containing 20 mM $MgCl_2$ and 5 mM β-mercaptoethanol.
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Selective Binding of One Enantioface of Monosubstituted Alkenes to the Chiral Transition Metal Lewis Acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$

Gerardo S. Bodner, Jesús M. Fernández, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112
Received February 3, 1988

In recent years, dramatic advances have been made in methodology for the asymmetric hydrogenation and epoxidation of alkenes.[1,2] However, the best optical yields are obtained with functionalized alkenes that are capable of two-site binding to the reagent or catalyst. In the case of Rh(I)-catalyzed asymmetric hydrogenation, only alkenes that are substituted with polar groups, such as α-amino acrylic acid derivatives, are reduced in significant optical yields.[1] Similarly, Ti(IV)-catalyzed asymmetric epoxidation is most effective for allylic alcohols.[2] To our knowledge, no homogeneous binding agent exists that efficiently and predictably discriminates between the enantiofaces of simple monosubstituted alkenes $H_2C{=}CHR$.[3-5]

(1) This literature is extensive. For recent lead articles, see: (a) Landis, C. R.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 1746. (b) Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.-I.; Kasahara, I.; Noyori, R. *Ibid.* **1987**, *109*, 1596. (c) Alcock, N. W.; Brown, J. M.; Maddox, P. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1532. (d) Zwick, B. D.; Arif, A. M.; Patton, A. T.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 910. (e) Hayashi, T.; Kawamura, N.; Ito, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7876.
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(3) Consiglio has obtained quite high enantioface selectivities in the binding of monosubstituted alkenes to the ruthenium fragment $[(\eta^5\text{-}C_5H_5)Ru(L)(L')]^+$ (L, L' = chiral diphosphine), but propene and 3-methyl-1-butene appear to bind *opposite* faces, and structural characterization has not yet been possible: (a) Consiglio, G.; Pregosin, P.; Morandini, F. *J. Organomet. Chem.* **1986**, *308*, 345. (b) Consiglio, C.; Morandini, F. *Ibid.* **1986**, *310*, C66.

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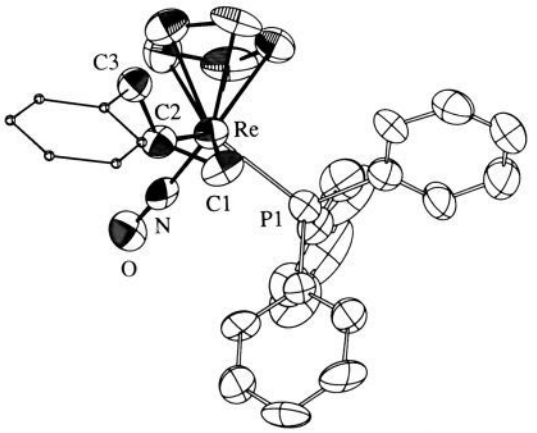


Figure 1. Structure of the cation of (*RR,SS*)-[(η^5-C_5H_5)Re(NO)(PPh_3)($C_6H_5CH_2CH{=}CH_2$)]$^+PF_6^-$ (**2a**PF_6^-). For clarity, one phenyl ring is shown with reduced thermal ellipsoids. Key bond lengths (Å) and angles (deg): Re–C1, 2.24 (2); Re–C2, 2.25 (2); Re–P1, 2.42 (1); Re–N, 1.73 (2); N–O, 1.19 (2); C1–C2, 1.40 (3); C2–C3, 1.47 (3); N–Re–P1, 89.4 (5); N–Re–C1, 104.1 (8); N–Re–C2, 92.8 (7); P1–Re–C1, 80.3 (6); P1–Re–C2, 114.8 (6); C1–Re–C2, 36.3 (7); Re–N–O, 173.7 (14); C1–C2–C3, 123.0 (17).

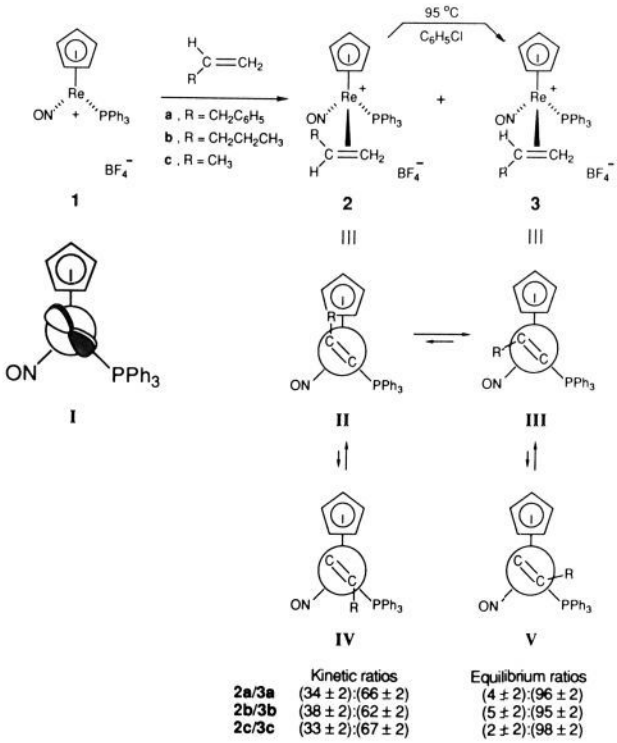
We recently described the facile generation of a reagent that acts as the functional equivalent of the chiral, optically active rhenium Lewis acid [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+BF_4^-$ (**1**)[6,7] and its reaction with ethylene to give alkene complex [(η^5-C_5H_5)Re(NO)(PPh_3)($H_2C{=}CH_2$)]$^+BF_4^-$.[6] In this communication, we report that **1** binds one enantioface of monosubstituted alkenes with thermodynamic selectivities of ≥95:5.

Methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) and HBF_4·Et_2O were reacted (CH_2Cl_2, −78 °C) to give **1** as previously reported.[6] Addition of allylbenzene (10 equiv, −78 to −20 °C) gave a (34 ± 2):(66 ± 2) mixture of alkene complex diastereomers (*RR,SS*)- and (*RS,SR*)-[(η^5-C_5H_5)Re(NO)(PPh_3)($H_2C{=}CHCH_2C_6H_5$)]$^+BF_4^-$ (**2a**BF_4^-, **3a**BF_4^-; 90%), as assayed by ^1H and ^{31}P NMR spectra of the crude reaction mixture.[8] Complexes **2a**BF_4^- and **3a**BF_4^- differ in the alkene enantioface bound to **1**, as illustrated (for one set of enantiomers) in Scheme I. Product assignments were verified by independent syntheses[8,9] and a crystal structure, as described below.

Similar experiments were conducted with 1-pentene (10 equiv) and propene (excess, 130 psi). These gave a (38 ± 2):(62 ± 2) mixture of 1-pentene complexes (*RR,SS*)- and (*RS,SR*)-[(η^5-C_5H_5)Re(NO)(PPh_3)($H_2C{=}CHCH_2CH_2CH_3$)]$^+BF_4^-$ (**2b**BF_4^-, **3b**BF_4^-; 91%) and a (33 ± 2):(67 ± 2) mixture of propene complexes (*RR,SS*)- and (*RS,SR*)-[(η^5-C_5H_5)Re(NO)(PPh_3)($H_2C{=}CHCH_3$)]$^+BF_4^-$ (**2c**BF_4^-, **3c**BF_4^-; 91%).[8]

Equilibration experiments showed the thermodynamic alkene enantioface binding ratios to be considerably higher than those obtained above. When the (34 ± 2):(66 ± 2) **2a**BF_4^-/**3a**BF_4^- mixture was heated in C_6H_5Cl at 95 °C (16 h, homogeneous conditions), a (4 ± 2):(96 ± 2) **2a**BF_4^-/**3a**BF_4^- mixture formed. Complex **3a**BF_4^- was subsequently isolated in 89% yield (80% from methyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3)). Under similar conditions, the above **2b**BF_4^-/**3b**BF_4^- and **2c**BF_4^-/**3c**BF_4^- mixtures equilibrated to (5 ± 2):(95 ± 2) and (2 ± 2):(98 ± 2) mixtures. Workup gave **3b**BF_4^- and **3c**BF_4^- in 90% and 97% yields (82% and 88% from (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3)), respectively.[8]

Scheme I. Selective Binding of One Enantioface of Monosubstituted Alkenes by the Chiral Lewis Acid [(η^5-C_5H_5)Re(NO)(PPh_3)]$^+BF_4^-$



	Kinetic ratios	Equilibrium ratios
2a/3a	(34 ± 2):(66 ± 2)	(4 ± 2):(96 ± 2)
2b/3b	(38 ± 2):(62 ± 2)	(5 ± 2):(95 ± 2)
2c/3c	(33 ± 2):(67 ± 2)	(2 ± 2):(98 ± 2)

We have previously shown that β-hydride abstraction from secondary alkyl complexes (η^5-C_5H_5)Re(NO)(PPh_3)(CHRR′) affords independent entry into diastereomerically pure alkene complexes.[9] Accordingly, reaction of (*SS,RR*)-(η^5-C_5H_5)Re(NO)(PPh_3)($CH(CH_3)CH_2C_6H_5$)[9] with $Ph_3C^+PF_6^-$ gave an authentic sample of the less stable allylbenzene complex diastereomer, (*RR,SS*)-(η^5-C_5H_5)Re(NO)(PPh_3)($H_2C{=}CHCH_2C_6H_5$)]$^+PF_6^-$ (**2a**PF_6^-). Workup gave **2a**PF_6^- as a yellow powder (83%) or, following acetone/ether crystallization, yellow prisms. The structure was confirmed crystallographically (Figure 1), and the angle of the Re—C=C plane with the Re–P vector was found to be 20°.

This impressive alkene enantioface recognition can be rationalized from stereoelectronic principles. Lewis acid **1** has the d orbital HOMO shown in I (Scheme I).[10] Alkene ligands should adopt conformations that maximize overlap of their π^* orbitals with this HOMO, as in II–V (Scheme I). Rotamers II and III, which have their larger RCH= terminus anti to the bulky PPh_3 ligand, should be sterically preferred. The alkyl substituent in III is directed at the small NO ligand, whereas the alkyl substituent in II is directed at the larger η^5-C_5H_5 ligand (see Figure 1). Hence, alkene complex diastereomers that can adopt rotamer III (**3**BF_4^-) are expected to be more stable. Apparently, the difference in enantioface binding energies is on the order of 2.1–2.3 kcal/mol (95 °C).

(4) Brookhart and Brown have prepared racemic propene complex [(η^5-C_5H_5)Fe(CO)(PPh_3)($H_2C{=}CHCH_3$)]$^+X^-$ from alkylidene and allyl complex precursors. One diastereomer is significantly more stable ($K_{eq} > 4$): (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Aris, K. R.; Brown, J. M.; Taylor, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 2222.

(5) See, also: (a) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (b) Tomioka, K.; Nakajima, M.; Koga, K. *Ibid.* **1987**, *109*, 6213. (c) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *Ibid.* **1988**, *110*, 1968.

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(8) Complexes **3a**–**c**BF_4^- and **2a**PF_6^- were characterized by microanalysis, NMR (^1H, ^{13}C, ^{31}P), and IR spectroscopy (Supplementary Material); **2a**–**c**BF_4^- were similarly characterized as mixtures with **3a**–**c**BF_4^-; NMR assignments were confirmed by comparisons to authentic samples of **2a**PF_6^-, **2c**PF_6^-, and **3c**PF_6^-.[9]

(9) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958.

(10) (a) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865. (b) Georgiou, S.; Gladysz, J. A. *Tetrahedron* **1986**, *42*, 1109. (c) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

In order for the above chemistry to have practical application, the alkene complex diastereomers must equilibrate without significant epimerization at rhenium. Thus, optically active **1** was prepared from (+)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(CH_3).[11] Addition of allylbenzene and propene gave mixtures of (*RR*)-**2a**BF_4^-/(*RS*)-**3a**BF_4^- and (*RR*)-**2c**BF_4^-/(*RS*)-**3c**BF_4^- with $[\alpha]_{589}^{23}$ of 86° and 115°. These were assumed to be optically pure,[6] and $[\alpha]_{589}^{23}$ for (*RR*)-**2a**BF_4^- (128°) and (*RS*)-**3a**BF_4^- (65°) were estimated from a series of extraction-enriched samples.[12] Equilibration (95 °C, 10–13 h, C_6H_5Cl) gave (9 ± 2):(91 ± 2) (*RR*)-**2a**BF_4^-/(*RS*)-**3a**BF_4^- and (6 ± 2):(94 ± 2) (*RR*)-**2c**BF_4^-/(*RS*)-**3c**BF_4^- mixtures with $[\alpha]_{589}^{23}$ 58° and 84°. Hence, alkene complexes (*RS*)-**3**BF_4^- can be prepared in both high diastereomeric *and* enantiomeric purity.

Metal alkene complexes have a rich chemistry and can be elaborated to organic compounds in numerous ways, such as by stereospecific nucleophilic attack on the alkene face anti to the metal.[13] Hence, the methodology developed herein for the selective binding of one enantioface of monosubstituted alkenes should lead to useful applications in asymmetric organic synthesis.

Acknowledgment. We thank the NIH for support of this research.

Supplementary Material Available: Tables of data for new compounds,[8] crystallographic data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **2a**PF_6^- (12 pages); table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

(11) Merrifield, J. H.; Strouse, C. E.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1204.

(12) Complex (*RS*)-**3a**BF_4^- could not be crystallized from the (34 ± 2):(66 ± 2) (*RR*)-**2a**BF_4^-/(*RS*)-**3a**BF_4^- mixture. However, a $[\alpha]_{589}^{23}$ versus mol % plot gives $[\alpha]_{589}^{23}$ for each component; $[\alpha]_{589}^{23}$ = 86°, 80°, and 77° for (34 ± 2):(66 ± 2), (25 ± 2):(75 ± 2), and (20 ± 2):(80 ± 2) mixtures, respectively.

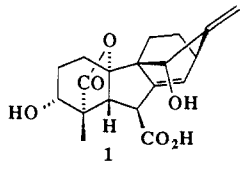
(13) (a) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 409–415 and 826–847.

Synthesis and Confirmation of Structure of the Antheridium-Inducing Factor from the Fern *Anemia mexicana*

Mark Furber and Lewis N. Mander*

Research School of Chemistry
Australian National University
G.P.O. Box 4, Canberra, A.C.T. 2601, Australia
Received March 3, 1988

The structure of the antheridium-inducing factor from the fern *Anemia phyllitidus* has been established as **1** on the basis of structural studies undertaken by Nakanishi et al.[1] and a total synthesis of the racemate accomplished by Corey and Myers.[2] More recently, we have prepared **1** from gibberellin A_7.[3] A



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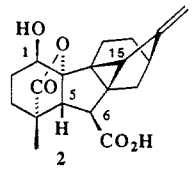
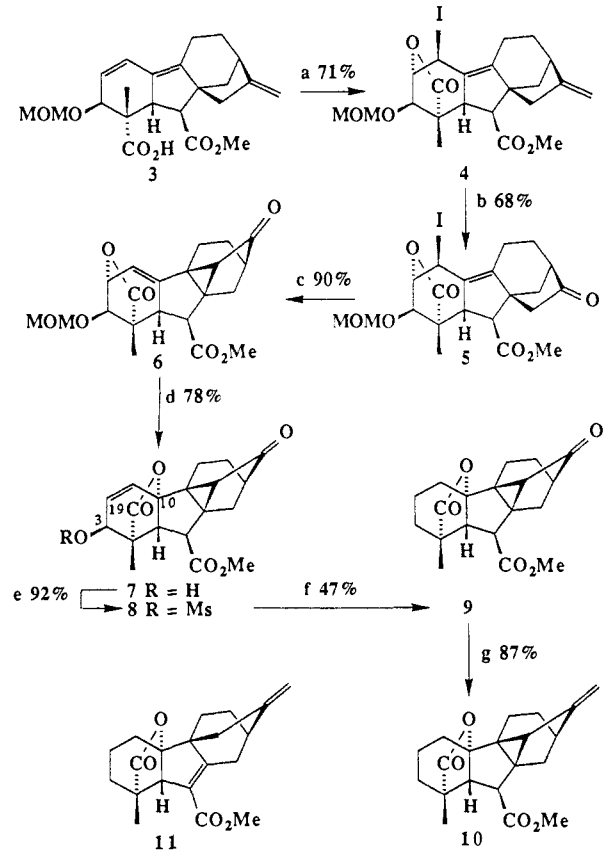


2

further antheridiogen has been obtained from the related species, *Anemia mexicana*,[4] for which structure **2** has been proposed on the basis of biogenetic considerations and minimal spectroscopic evidence.[5] Given the very considerable difficulties involved in the isolation of even microgram quantities of this new substance, there appeared to be little prospect of gathering further evidence for this formulation, and we accordingly embarked upon a synthesis of **2**. In this communication we describe the successful completion of this undertaking which has confirmed the tentative structural assignment and furnished adequate supplies of this new antheridiogen for the first time.

Before attempting the synthesis of **2**, we elected to prepare **10**[6] so that it might be possible to establish a set of reference spectra for the basic cyclogibberellane structure and verify the plausibility of formula **2**, especially the location of the hydroxy group in the 1β position.[7] The preparation of **10** is outlined in Scheme I, with the sequence as far as lactone **6** following closely the route taken earlier in our synthesis of **1**, except that this had commenced with the 3α-epimer of **3**.[3] Thus, diene acid **3** was converted into

Scheme I



[a] Reagents and conditions: (a) KI_3, K_2CO_3, THF–Et_2O–H_2O, 24 °C, 15 min; (b) O_3, Py, CH_2Cl_2, −78 °C; 5 s then Me_2S; (c) KH, THF, 0 → 24 °C over 45 min; (d) Ph_2BBr, CH_2Cl_2, −30 → −15 °C; (e) $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0 °C, 6 h; (f) H_2, 5% Pd–$BaCO_3$, EtOAc, Py, 1 atm, 24 °C, 14 h; (g) CH_2Br_2, $TiCl_4$, Zn, CH_2Cl_2, 24 °C, 5 min.

(1) Nakanishi, K.; Endo, M.; Näf, U.; Johnson, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 5579–5581. This factor has also been isolated from *A. hirsuta* (Zanno, P. R.; Endo, M.; Nakanishi, L.; Näf, U.; Stein, C. *Naturwissenschaften* **1972**, 512), *A. rotundifolia*, and *A. flexuosa* (Yamane, H.; Nohara, K.; Takahashi, N.; Schraudolf, H. *Plant Cell Physiol.* **1987**, *28*, 1203–1207).

(2) Corey, E. J.; Myers, A. G. *J. Am. Chem. Soc.* **1985**, *107*, 5574–5576. Corey, E. J.; Myers, A. G.; Takahashi, N.; Yamane, H.; Schraudolf, H. *Tetrahedron Lett.* **1986**, *27*, 5083–5084.

(3) Furber, M.; Mander, L. N. *J. Am. Chem. Soc.* **1987**, *109*, 6389–6396.

(4) Nester, J. E.; Veysey, S.; Coolbaugh, R. C. *Planta* **1987**, *170*, 26–33.

(5) Furber, M.; Mander, L. N.; Nester, J. E.; Takahashi, N.; Yamane, H., submitted for publication.

(6) This compound was also considered as a candidate for the structure of the less abundant but more potent antheridiogen from *Lygodium japonicum*. Cf. Yamane, H.; Takahashi, N.; Takeno, K.; Furuya, M. *Planta* **1979**, *147*, 251–256. Yamane, H.; Satoh, Y.; Nohara, K.; Nakayama, M.; Murofushi, N.; Takahashi, N.; Takeno, K.; Furuya, M.; Furber, M.; Mander, L. N., submitted for publication.

(7) Nomenclature and numbering based on the *ent*-gibberellane skeleton: *The Common and Systematic Nomenclature of Cyclic Diterpenes*, 3rd revision; Rowe, J. R., Ed., Forest Product Laboratory, U.S. Department of Agriculture: WI, 1968. The location of this group was based on the presence of a peak at *m/z* 116 in the mass spectrum of the derived trimethyl silyl ether methyl ester (Cf. Kirkwood, P. S.; MacMillan, J. *J. Chem. Soc., Perkin Trans. 1*, **1982**, 689–697) and on the assumption of anisotropic deshielding of H(5) and H(15) in the putative structure.

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