7.0 ± 0.1 (Na_2HPO_4/NaH_2PO_4 (6:4)), containing sufficient NaCl to give a total ionic strength of 100 mM. The concentration of each single-stranded oligonucleotide was estimated from its absorbance at 260 nm (H_2O) and published extinction coefficients[20] for the mononucleotides, without compensation for hypochromicity. A sufficient quantity of each strand was introduced into the buffer to give a ~5 μM solution of that strand. (Thus, the duplex concentration would be ~5 μM whereas the total concentration of both single strands would be ~10 μM.) The strands were annealed by heating at least 10 °C above the T_m, followed by cooling (1 °C/min) at least 14 °C below the T_m. Melting curves were recorded at 260 nm [d(GGT CAC GAG)·d(CTC GTG ACC)] or 273 nm (all others) in a stirred 3-mL cuvette using a spectrophotometer equipped with a temperature-programmable cell holder and a temperature probe. Initial temperatures were selected so that the T_m fell near the midpoint of the 40° temperature gradient used. The temperature was ramped up at a rate of 0.5 °C/min over a period of 80 min. The absorbance was recorded as a function of time, which was converted to temperature, and the transition temperature (T_m) was determined from the midpoint of the resultant sigmoid curve of absorbance vs temperature. In several cases repeated determinations on the same sample verified the reproducibility of the measurements and the reversibility of the thermal transition.

Formation of N^6-Adducts from 1,2,3,4-Tetrahydrophenanthrene-1,2-diol 3,4-Epoxide (2) and 2'-Deoxyadenosine 5'-Monophosphate and Comparison with Adducts Derived from the Coupling of 1 and 3. The adducts were prepared as described[3a,5] from 2'-deoxyadenosine 5'-monophosphate (250 mg in 12.5 mL of H_2O, pH 7.25) and the racemic diol epoxide **2** (5 mg, 20 μmol in 1 mL of acetone). The nucleoside adducts obtained upon enzymatic hydrolysis (*E. coli* alkaline phosphatase, 19 units) were separated by HPLC on a Beckman Ultrasphere ODS column (5 μm, 10 × 250 mm), eluted at 3 mL/min with 11% CH_3CN–30% MeOH–59% H_2O (Figure 1). Absolute configurations were assigned by comparison of the CD spectra of the adducts in MeOH (Figure 2) with those of the previously characterized adducts derived from tetrahydrophenanthrene 3,4-oxide.[5] For these adducts, a strong positive CD band at 225 nm corresponds to (4*S*)-absolute configuration at the N-substituted benzylic carbon atom, and a band at the same wavelength with approximately the same magnitude but opposite sign corresponds to (4*R*)-absolute configuration at this center.

Proton NMR spectra (see Table I) were measured for the pentaacetate derivatives (72 h at rt with pyridine/Ac_2O). These acetates were purified by HPLC on a Du Pont Golden Series SIL column (6.2 × 80 mm) eluted at 2.5 mL/min with 1.5% MeOH–4.9% EtOAc–93.6% CH_2Cl_2: t_R (min) (trans-4*S*-adduct), 3.8; (trans-4*R*-adduct), 3.7; (cis-4*S*-adduct), 3.2; cis-4*R*-adduct), 2.9.

For comparison with the adducts prepared from dAMP, a mixture of **4a** and **4b** was prepared as described from **1** (20 mg) and amino triol **3** (10 mg) in a mixture of DMF (0.7 mL), pyridine (0.03 mL), and HMDS (0.87 mL) at 90 °C for about 18 h. The adducts were directly desilylated with 0.5 mL of n-$Bu_4N^+F^-$ (1 M solution in THF) over 2 h and evaporated to dryness. The entire reaction mixture containing the diastereomeric *early*- and *late*-eluting adducts was subjected to preparative HPLC as described above for the adducts prepared from dAMP. The separated adducts were acetylated with pyridine (100 μL) and Ac_2O (50 μL) in the presence of DMAP (1 mg) at 50 °C overnight. After evaporation of the pyridine, chromatography of the products on a 250-μm silica plate developed with 5% MeOH in CH_2Cl_2 gave 2 mg each of **8** (4*S*) and the corresponding (4*R*)-pentaacetate. The ^1H NMR spectra of both pentaacetates were identical with those of the pentaacetates of the trans adducts derived from the reaction of racemic phenanthrene diol epoxide-2 with dAMP.

Supplementary Material Available: Proton NMR spectra of compounds **4a,b–9** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Partial Synthesis of 9,10-Syn Diterpenes via Tosylhydrazone Reduction: (−)-(9β)-Pimara-7,15-diene and (−)-(9β)-Isopimaradiene[1]

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Received March 9, 1992

(9β)-Pimara-7,15-diene (**3**), a proposed intermediate in the biosynthesis of the momilactone phytoalexins (**1** and **2**) from rice, and its C-13 epimer, (9β)-isopimara-7,15-diene (**4**), were synthesized from methyl pimara- and isopimara-8,15-dien-18-oates (**8b** and **8a**, respectively). Allylic oxidation of **8a** and **8b** as well as the derived diterpene hydrocarbons **15a** and **15b** with chromium trioxide–dipyridine complex afforded 8,15-dien-7-ones **9a**, **9b**, **16a**, and **16b** (35–54%). Lithium–ammonia reduction of **9a**, **16a**, and **16b** gave predominantly *trans,anti,trans*-isopimara- and -pimara-15-en-7-ones **10**, **17a**, and **17b**. In contrast, catecholborane reduction of the tosylhydrazones of **9a** and **9b** provided methyl (9β)-isopimara- and (9β)-pimara-7,15-dien-20-oates (**23a** and **23b**) having the 9,10-syn stereochemistry. The parent diterpenes, **3** and **4**, were obtained by carboxyl-to-methyl conversions. In a collaborative investigation **3** was tentatively identified as one of five diterpene hydrocarbons produced upon incubation of (*E,E,E*)-geranylgeranyl pyrophosphate with a crude enzyme extract from UV-treated rice plants.

The momilactones A (**1**), B (**2**), and C comprise a small group of oxygenated diterpenes isolated from rice husk.[2] Characterized originally as germination inhibitors,[2a] momilactones A and B were subsequently identified[3] as phytoalexins[4] of the rice plant, *Oryza sativa*. The most notable structural feature of these pimara-7,15-diene[5]

(1) Portions of this research were presented at the following meetings of the American Chemical Society: National Convention, Atlanta, GA, April 17, 1991; Great Lakes Regional Meeting, Dekalb, IL, May 31, 1990.

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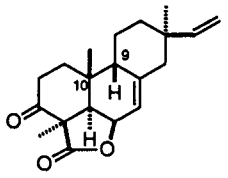
derivatives is the rare 9,10-syn stereochemistry. Other perhydrophenanthrene-based diterpenes having the 9,10-syn relationship are annonalide,[6a,b] icaceine,[6a,b] and the humirianthenolides.[7] The 8,10-syn configuration of isopimara-9(11),15-diene-3β,19-diol,[8] aphidicolin,[9] and stemodine[10] presumably arise from 9,10-syn precursors via 9–8 hydride shift during biosynthesis.[11]



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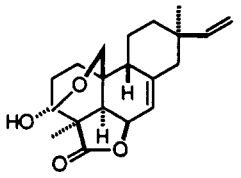

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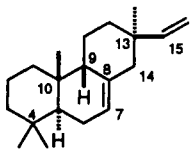

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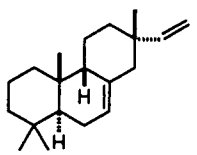


4

It is reasonable to suppose that the momilactones are biosynthesized by oxidative metabolism of (9β)-pimara-7,15-diene (**3**). Although the only known examples of (9α)-pimara-7,15-dienes are evidently the hydroxypalarosanes,[12a] a large number of pimaradiene (**3** with 9αH and $\Delta^{8(14),15}$ diene) and isopimaradiene (**4** with 9αH) derivatives having the normal 9,10-anti stereochemistry occur naturally.[12b]

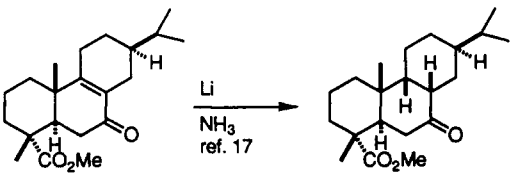
In an investigation concerning the biosynthesis of diterpene phytoalexins in rice, Wickham and West[13] have found that cell-free extracts of UV-treated rice plants have the capacity to catalyze the conversion of [^{3}H]geranylgeranyl pyrophosphate to a mixture of five pimaradiene-like diterpenes, one of which was presumed to be **3**, the hydrocarbon precursor to the momilactones. The objectives of the research described below were the synthesis and characterization of **3** and its C-13 epimer, (9β)-isopimaradiene (**4**), to facilitate the identification of the 9,10-syn diterpenes in the mixture of enzymatic cyclization products.

A number of synthetic approaches have been used previously to create the 9,10-syn configuration in bicyclic and tricyclic precursors to various diterpene classes. The syn stereochemistry has been established by Claisen rearrangement,[14] Michael addition,[15,16] lithium–ammonia reduction,[17] Diels–Alder reactions,[15b,c,18,19] and β-keto ester alkylation.[20] Total synthesis of (±)-**3**,[15c] (±)-9β-pimaradiene ($\Delta^{8(14)}$ isomer of **3**),[14b] and (±)-(9β)-sandaracopimaradiene ($\Delta^{8(14)}$ isomer of **4**)[14b] have been reported.

We report a new approach to create the thermodynamically unstable 9,10-syn stereochemistry via catechol borane reduction[21] of pimara-7,15-dien-7-one tosylhydrazones. Partial syntheses of the proposed momilactone precursor (−)-**3** and its C-13 isomer, (−)-**4**, from sandaracopimaric and pimaric acid have been accomplished in this manner. With authentic samples of these 9,10-syn diterpenes, Wickham and West have tentatively identified **3** as one of the diterpenes produced by the UV-elicited cyclases from rice plants.[13]

Results and Discussion

The report by Herz and Schmid[17] that abietic acid-derived enone **5** undergoes lithium–ammonia reduction to give trans,syn,cis keto ester **6** prompted us to investigate conjugate reductions of the structurally related pimara-8-en-7-ones.



5 6

The requisite unsaturated ketones (**9a** and **9b**) were prepared from methyl sandaracopimaradienoate (**7a**)[22] and methyl pimarate (**7b**)[23] by isomerization to their Δ^8 isomers (**8a** and **8b**) with HCl/$CHCl_3$[14b,24] followed by regioselective

(5) The nomenclature used in this paper is based upon the guidelines set forth by J. W. Rowe, Forest Products Laboratory, U.S. Department of Agriculture, Madison, WI. Complete systematic names are given as headings in the Experimental Section. Partial and complete systematic names as well as common names are used elsewhere according to the context. See: Rowe, J. W. *The Common and Systematic Nomenclature of Cyclic Diterpenes*, 3rd ed.; Oct. 1968, Addenda and corrigenda, Feb 1969. See also: *Nomenclature of Organic Chemistry*; Rigaudy, J., Klesney, S. P., Eds.; Pergamon Press: Oxford, 1979; Sections A–F and H, pp 491–511.

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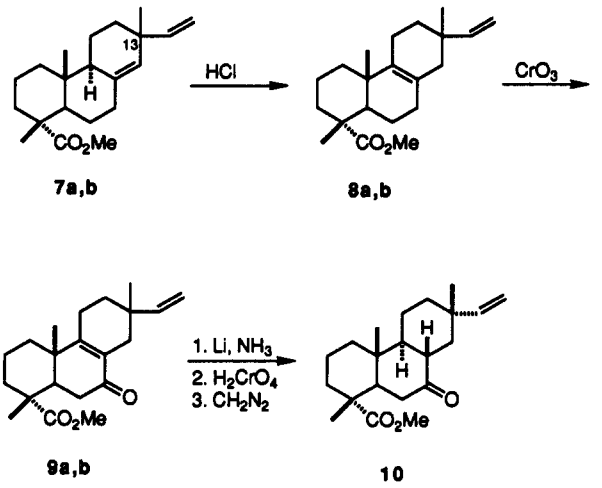
Scheme I



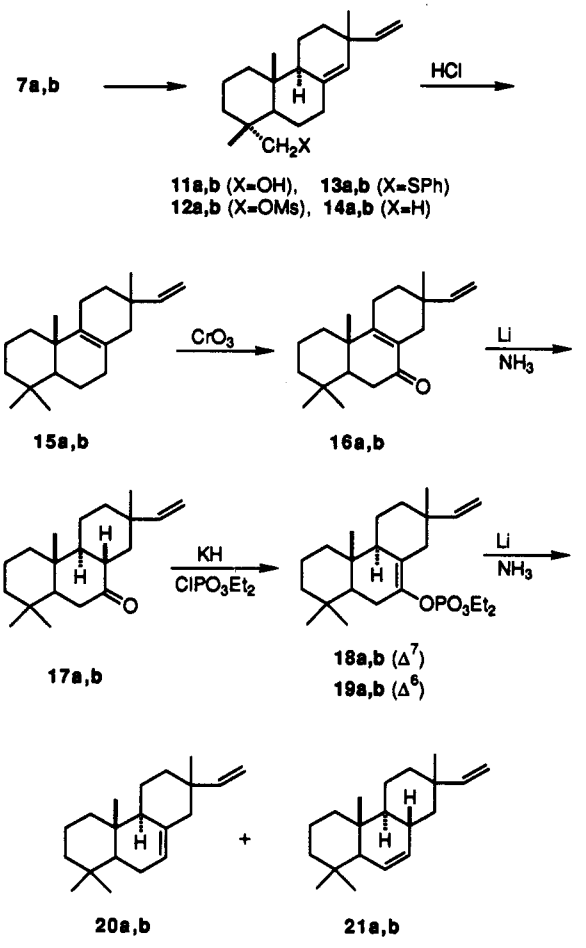
allylic oxidation at C-7[24] with $CrO_3 \cdot (pyr)_2$ in dichloromethane (25 °C, 24 h).[25] The major enone products (**9a** and **9b**) were obtained in 50–54% yield after careful chromatography to separate small amounts of an isomeric keto ester (probably 8-en-11-ones).[24] The agreement of the ^1H NMR spectral data for **9a** with the literature values for this known enone ester[26] confirms that oxidation occurred principally at C-7.

Lithium/ammonia reduction of **9a** according to the literature procedure[17] followed by chromic acid oxidation and esterification afforded the crystalline keto ester **10** in 50% yield. The identity and trans,anti,trans stereochemistry of **10** were firmly established by direct comparisons with an authentic sample.[27]

Similar conjugate reductions of pimar-8-en-7-ones **16a** and **16b** were carried out to determine whether the C-4 ester (or its reduction products) might affect the stereoselectivity of C-9 protonation or, if not, to obtain reference samples of dienes **20a** and **20b**. Esters **7a** and **7b** were converted to sandaracopimaradiene (**14a**) and pimaradiene (**14b**) in four steps:[28] (a) $LiAlH_4$ reduction; (b) mesylation; (c) thiophenoxide displacement; (d) $Li–NH_3$ reduction. Double-bond isomerization and allylic oxidation as above provided the crystalline enones **16a** (45%) and **16b** (35%). Lithium–ammonia reduction of these 8-en-7-ones gave saturated ketones **17a** and **17b** (68% and 56%, respectively). The correspondence of the spectral data and melting point of the product from **16a** with the literature values[29] for the known trans,anti,trans ketone **17a** showed that the 9,10-anti configuration had been re-established.

The 9α stereochemistry of **17a** and **17b** was confirmed by conversion to the Δ^7 enol phosphates **18a** and **18b** and subsequent lithium–ammonia reduction[30] to isopimara-7,15-diene **20a** and pimara-7,15-diene **20b**.[31] The presence

Scheme II



of 10–12% of the isomeic Δ^6 enol phosphates **19a** and **19b** and pimara-6,15-dienes **21a** and **21b** was detected in GC analyses and ^1H NMR spectra. Diene **20a** was separated from **21a** by argentic chromatography and securely identified by direct comparisons with an authentic sample of isopimaradiene prepared from isopimaric acid.[23]

The predominant formation of the 9,10-anti stereochemistry in the lithium–ammonia reductions of **9a**, **16a**, and **16b** is consistent with the usual tendency of this reaction to generate the thermodynamically more stable isomers.[32] It is apparent that the principal difference between these pimar-8-en-ones and **5** is the presence of the 13α substituent (methyl or vinyl) in the former and the larger 13β-isopropyl group. Perhaps the anomalous stereochemical outcome in the reduction of **5** can be attributed to steric interactions of the axial isopropyl group in the 9,10-anti radical anion intermediate. Consequently, reduction occurs via the 9,10-syn conformer which undergoes 9β protonation to generate after hydrolysis the trans,anti,cis isomer. In contrast, the 9,10-syn conformers of the radical anion from the pimar-8-en-7-ones should be destabilized by an additional 1,3-diaxial interaction between the axial 13α CH_3 (or vinyl) and the 11α hydrogen.

The failure of the preceding enone reductions to generate the 9,10-syn configuration prompted consideration

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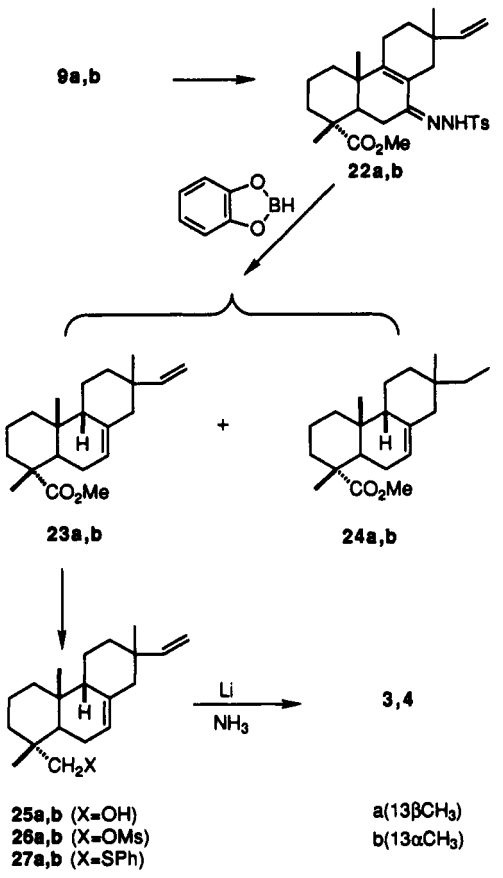
Scheme III



of alternative methods. The catecholborane reduction of enone tosylhydrazones offers a convenient procedure to accomplish conjugate reduction and concommitant deoxygenation, affording allylically rearranged alkenes directly.[21] Although little appears to be known about the stereochemistry of this reaction, the formation of cycloalkene products by hydrogen transfer to the more hindered face of the α,β-ene hydrazones seemed promising.[21a,e]

Reaction of isopimaradienone tosylhydrazone **22a** with 1.1–1.2 equiv of catecholborane in $CHCl_3$ (0 °C, 30 min) followed by addition of sodium acetate and heating at reflux for 50 min afforded a 4:1 mixture of two products which could be separated by chromatography on silver nitrate-impregnated silica gel. The minor product (11%) was identified as a 15,16-dihydroisopimarene (**24a**) on the basis of its empirical formula ($C_{21}H_{34}O_2$ by HRMS analysis) and ^1H NMR spectral characteristics (disappearance of three vinyl protons and appearance of triplet indicating an ethyl substituent).[33]

The major product (56%) from the reduction of **22a** must have the desired 9,10-syn stereochemistry, i.e., the 9β isomer **23a** of methyl isopimarate. The ^1H NMR spectrum shows clearly that the nuclear double bond is in the 7,8-position (doublet at δ 5.23), and the physical properties of the compound (e.g., mp 80–81 °C, $[\alpha]_D$ −142°, t_R = 13.7 min) are distinctly different from those of authentic methyl isopimarate (oil, $[\alpha]_D$ −7.8°, t_R = 17.2 min). A GC analysis of the product mixture before separation

(33) The proportion of this over-reduction product seemed to be diminished when the amount of catecholborane was decreased (1.1 instead of 1.2 equiv). Since 1-octene and cyclopentene undergo slow hydroboration with catecholborane at room temperature, **24a** is presumably formed by subsequent hydroboration of the vinyl group of **23a**. However, **7a** was recovered unchanged after exposure to 1.2 equiv of catecholborane under the conditions of the tosylhydrazone reductions.

Table I. Optical Rotations for 9β Diterpene Esters and Hydrocarbons and the Corresponding 9α Isomers

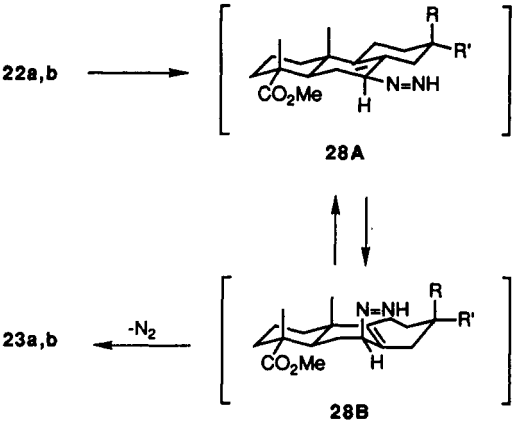
	9βH		9αH	
name	no.	$[\alpha]_D$[a]	no.	$[\alpha]_D$[a]
methyl isopimarate	**23a**	−142	–[b]	−7.8[c], −7.7[d]
methyl pimara-7,15-dien-18-oate	**23b**	−163	–[b]	−28.8[e]
isopimaradiene	**4**	−251	**20a**	−31b,[f] −29,[g] −28[h]
pimara-7,15-diene	**3**	−208	**20b**	*i*

[a] $CHCl_3$ solutions. [b] No structure number assigned. [c] This work. [d] Reference 34a. [e] Reference 34b. [f] Reference 34c. [g] Reference 34d. [h] Reference 14b. [i] Not determined.

of **24a** showed that no more than 2–3% of methyl isopimarate was present, i.e., 9β/9α ratio ≥ 25–30. Catecholborane reduction of **22b** under similar conditions afforded methyl (9β)-pimara-7,15-dien-20-oate (**23b**, 52%) along with the 15,16-dihydro byproduct **24b** (33%).

The parent diterpene hydrocarbons, (9β)-isopimara-7,15-diene (**4**) and the proposed momilactone precursor, (9β)-pimara-7,15-diene (**3**), were prepared from **23a** and **23b** by the same four-step sequence described above. A notable characteristic of the 9β diterpene esters and hydrocarbons is their large negative optical rotations which contrast with the small rotations of the corresponding 9α isomers (see Table I).[34]

The stereochemistry of the tosylhydrazone reductions can be rationalized simply by assuming initial ψ-axial (7α) delivery of hydride from catecholborane to the C=N group,[35] followed by boro sulfinate elimination and β-facial transfer of hydrogen from the diazene intermediate **28** to C-9. Conformational inversion of ring B to a half-boat form (**28A** → **28B**) is presumably necessary for a concerted fragmentation to occur. The complete absence of the thermodynamically more stable Δ^9 isomers **8a** and **8b** is remarkable, considering the energetically unfavorable conformational change required and the expectation of steric interactions between the diazenyl and C-10-methyl groups.



The catecholborane reduction of pimar-8-en-7-one tosylhydrazones affords a simple way to prepare (9β)-isopimaradiene, (9β)-pimara-7,15-diene, and their derivatives. The reaction should be generally effective for regio- and stereoselective synthesis of thermodynamically unstable cycloalkenes from cycloalkenones.

Reference samples of the (9β)-pimaradienes **3** and **4** as well as four 9α-pimaradienes **14a,b** and **20a,b** were sent

(34) References for literature rotations given in Table I: (a) Weissman, G. *Tetrahedron Lett.* **1968**, 2053–2055. (b) Zinkel, D. F.; Magee, T. V. Private communication. (c) Westfelt, L. *Acta Chem. Scand.* **1966**, *20*, 2829–2840. (d) Raldugin, V. A.; Pentegova, V. A. *Chem. Nat. Prod.* **1974**, *10*, 696–697 (transl. of *Khim. Prir. Soedin.* **1974**, 674–675).

(35) ψ-Axial hydride attack predominates in the metal hydride reduction of cyclohexenones: Toromanoff, E. *Top. Stereochem.* **1967**, *2*, 157.

to The University of California, Los Angeles. By means of GC and GC/MS comparisons, Wickham and West identified **3**, *ent*-sandaracopimaradiene (enantiomer of **14a**), and *ent*-kaurene as three of the five diterpenes produced by the UV-elicited cyclases from rice plants.[13] This provides experimental evidence for the existence of (9β)-pimara-7,15-diene (**3**) as an intermediate in the biosynthesis of the momilactones in rice plant.

Experimental Section

General. Melting points were determined on a hot stage microscope and are uncorrected. Analytical GC was performed on a 60-m, DB-5 fused silica capillary column, with a helium flow rate of 0.53 mL/min and a split ratio of 245:1. Flash chromatography was carried out on Woelm 32–64-mm silica gel packed in glass columns. $AgNO_3$-impregnated silica gel was prepared by dissolving $AgNO_3$ in acetonitrile and adding dry silica gel to give the desired ratio (w/w) of silica gel to $AgNO_3$. The acetonitrile was removed under reduced pressure by rotary evaporation, and the treated silica gel was stored in the dark. Analytical TLC was conducted on Merck glass plates precoated with 0.25 mm of silica gel 60F-254 and visualized with either iodine vapor and/or 5% phosphomolybdic acid in 95% ethanol. $AgNO_3$-impregnated TLC plates were freshly prepared by immersion in a solution of 15% $AgNO_3$ in aqueous ethanol and drying at 90 °C for several min.

THF, diethyl ether, and 1,2-dimethoxyethane were freshly distilled from sodium benzophenone ketyl. Pyridine and DMF were distilled from CaH_2 and stored over 4A molecular sieves.

Methyl Isopimara-8(14),15-dien-18-oate (Methyl Sandaracopimarate, 7a). A 40:43:17 mixture (10 g) of sandaracopimaric, dehydroabietic, and isopimaric acids isolated by Drengler[22a] from sandarac gum tears (Wunderlich-Dietz Corp.) was esterified with 1.1 M CH_2N_2 in ether. Methyl sandaracopimarate (**7a**) was separated from a 5-g portion of the resulting ester mixture (10.3 g) by column chromatography of silica gel impregnated with 10% $AgNO_3$.[22a] Elution with 5% ether in hexane afforded 2.12 g of methyl dehydroabietate and 2.52 g of **7a**, mp 66–68 °C (lit.[36] mp 68–69 °C), contaminated by about 15% methyl isopimarate (GC analysis at 250 °C).

Methyl Pimara-8(14),15-dien-18-oate (7b). Pimaric acid (92% purity, 7% sandaracopimaric acid)[23] was esterified with CH_2N_2 as described above. The yield of **7b** was 2.07 g (99%), and the purity (92% purity according to GC analysis at 250 °C) was sufficient for use in the next reaction: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.77, 0.99, 1.20 (3 s, 9 H, $3CH_3$), 3.66 (s, 3 H, OCH_3), 4.85–4.99 (m, 2 H, CH=CH_2), 5.13 (br s 1 H, H at C-14), 5.72 (dd 1 H, J = 10.6, 16.7 Hz, CH=CH_2). The spectral data agree with the literature.[37]

Methyl Isopimara-8,15-dien-18-oate (8a). The following procedure is similar to one reported by Herz.[24a] A solution of 520 mg (1.65 mmol) of ester **7a** in 20 mL of $CHCl_3$ was stirred and cooled in an ice–salt bath as dry HCl was bubbled through it for 50 min. After an additional 1 h, the solution was washed with ice–water, 10% Na_2CO_3, and water. The organic layer was dried ($MgSO_4$) and evaporated to afford 510 mg (98%) of a colorless liquid. The product was sufficiently pure (98% pure by GC analysis) for use in the next reaction: ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.97, 0.98, 1.19 (3 s, 9 H, 3 CH_3), 3.66 (s, 3 H, OCH_3), 4.84–4.93 (m, 2 H, CH=CH_2), 5.76 (dd 1 H, J = 10.9, 17.5 Hz, CH=CH_2).

Methyl Pimara-8,15-dien-18-oate (8b): yield 514 mg (99%); colorless liquid; IR (film) 3081 (vinyl), 1727 (C=O), 1636, 909 (CH=CH_2) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95, 0.98, 1.19 (3 s, 9 H, 3 CH_3), 3.67 (s, 3 H, OCH_3), 4.87 (dd, 1 H, J = 1.0, 10.9 Hz, *trans*-CH=CH_2), 4.91 (dd, 1 H, J = 1.0, 17.7 Hz, *cis*-CH=CH_2), 5.80 (dd, 1 H, J = 10.7, 17.7 Hz, CH=CH_2).

Methyl 7-Oxoisopimara-8,15-dien-18-oate (9a). The following procedure was based upon one in the literature.[25] A solution of 2.56 g (25.6 mmol) of CrO_3 (dried over P_2O_5 under reduced pressure for 48 h) in 150 mL of dry CH_2Cl_2 was rapidly stirred as 4.04 g (51.2 mmol) of dry pyridine was added slowly at 0 °C. The ice bath was removed, and the dark red solution was allowed to stir at 25 °C for 10 min. To the resulting solution was added a solution of 0.54 g (1.71 mmol) of ester **8a** in 15 mL of dry CH_2Cl_2 over 2 min at 25 °C. The heterogeneous mixture was stirred for 24 h and diluted with 80 mL of ether. The dark supernatant solution and the black precipitate were placed on a column containing 20 g of Florisil on top of 10 g of silica gel, and the column was washed twice with 50-mL portions of ether. The combined eluates were dried ($MgSO_4$) and evaporated under reduced pressure. Purification of the yellow residue by column chromatography on 50 g of silica gel (1:7 ether–hexane as the eluant) gave 0.32 g (54%) of the known[26] keto ester **9a** as an oil: IR (film) 3081 (vinyl H), 1727 (C=O, ester), 1661 (C=O, enone), 1617, 914 (CH=CH_2) cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.01, 1.11, 1.26 (3 s, 9 H, 3 CH_3), 3.66 (s, 3 H, OCH_3), 4.86 (dd, 1 H, J = 1.5, 17.6 Hz, *cis*-CH=CH_2), 4.93 (dd, 1 H, J = 1.5, 10.8 Hz, *trans*-CH=CH_2), 5.69 (dd, 1 H, J = 10.8, 17.6 Hz, CH=CH_2); MS m/e (relative intensity) 330 (M^+, 26), 315 (16), 289 (53), 255 (50), 229 (58), 91 (33), 41 (27). The spectral data agree with the literature values.[26]

Methyl 7-oxopimara-8,15-dien-18-oate (9b) was prepared by the preceding procedure. Purification by column chromatography afforded 0.69 g (50%) of enone ester **9b** as an oil: IR (film) 3083 (vinyl H), 1725 (C=O, ester), 1661 (C=O, enone), 1617, 914 (CH=CH_2) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97, 1.09, 1.27 (3 s, 9 H, 3 CH_3), 3.67 (s, 3 H, OCH_3), 4.82–4.97 (m, 2 H, CH=CH_2), 5.74 (dd, 1 H, J = 10.0, 17.6 Hz, CH=CH_2); HRMS calcd for $C_{21}H_{32}O_2$ m/e 316.2402, found m/e 316.2410.

Methyl 7-Oxoisopimar-15-en-18-oate (10). The following reactions were carried out according to literature procedures.[17] A solution of 29 mg (4.2 mmol) of lithium (1% sodium) in 20 mL of liquid NH_3 was stirred and cooled at −78 °C under N_2 as 138 mg (0.42 mmol) of enone ester **9a** in 4 mL of dry THF was added dropwise. The cooling bath was removed, and the solution was allowed to warm to −33 °C and stir for 1 h. The bulk of the liquid NH_3 was evaporated, the residue was suspended in 15 mL of water, and the suspension was extracted with ether (3 × 12 mL). The combined ether extracts were washed with 10% NaOH (10 mL) and water (10 mL), dried ($MgSO_4$), and evaporated. A solution of the residue in 5 mL of acetone and was added dropwise to a solution of chromic acid reagent[38] (0.9 mmol) in 20 mL of acetone at 0 °C. A dark precipitate separated immediately. The mixture was stirred for 2 h, diluted with 15 mL of water, and extracted with ether (3 × 15 mL). The ether extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was dissolved in 20 mL of dry ether and esterified with 1.1 M CH_2N_2 in ether. After 1 h at rt the solvent was evaporated and the oily liquid was purified by column chromatography on 80 g of silica gel with 1:5 ether–hexane as eluant. Recrystallization from methanol–water afforded 68 mg (50%) of white solid: mp 75–76 °C (lit.[27] mp 76 °C). A mixture of this material with an authentic sample (mp 74–75 °C)[27] melted at 73–75 °C. GC analysis by coinjection of ester **10** and the authentic sample gave one peak (t_R = 4.56, 250 °C). The spectral properties of the authentic sample are identical to the following data for enone ester **10**: IR (KBr) 3082 (vinyl H), 1715 (C=O), 1638, 912 (CH=CH_2) cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95, 1.12, 1.23 (3 s, 9 H, 3 CH_3), 3.65 (s, 3 H, OCH_3), 4.82–5.02 (d of three-line m, AB part in ABX system, 2 H, CH=CH_2), 5.81 (dd, 1 H, J = 10.4, 17.5 Hz, CH=CH_2).

Isopimara-8(14),15-diene (sandaracopimaradiene, 14a) and pimara-8(14),15-diene (14b) were prepared from the corresponding diterpenes esters **7a** and **7b** as described for the 9β esters below (**23a,b** → **4** and **3**). Yields and physical properties (mp, IR, and ^{1}H NMR data; ^{13}C NMR data for **14b**; MS data for **14a** and **14b**) for **11a,b**–**14a,b** are provided in the supplementary material. **14a**: mp 39–40 °C; $[\alpha]^{23}_D$ −13° (*c* 1.2, $CHCl_3$) [lit.[39] mp 39–40 °C; $[\alpha]^{23}_D$ −12° (*c* 0.2, $CHCl_3$); lit.[40] mp 41–42 °C, $[\alpha]^{23}_D$ −12° (*c* 0.22, $CHCl_3$)]. **14b**: $[\alpha]^{23}_D$ +99° (*c* 1.2, $CHCl_3$) [lit.[34c] $[\alpha]^{23}_D$

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+100° (c 2.4, $CHCl_3$); lit.[40b] $[\alpha]^{25}_D$ +99° (c 0.5, $CHCl_3$)].

Isopimara-8,15-diene (15a) and pimara-8,15-diene (15b) were prepared from **14a** and **14b** by the same procedure used for **8a**. Recrystallization from aqueous ethanol gave 453 mg (99%) of diene **15a**: mp 51–52 °C (lit.[14b] mp 52–53 °C); IR (film) 3081 (vinyl H), 1639, 999, 909 ($CH=CH_2$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.84, 0.89, 0.96, 0.97 (4 s, 12 H, 4 CH_3), 4.78–4.94 (m, 2 H, $CH=CH_2$), 5.72 (dd, 1 H, J = 10.8, 17.4 Hz, $CH=CH_2$). The yield of diene **15b** was 452 mg (98%): IR (film) 3081 (vinyl H), 1638, 997, 911 ($CH=CH_2$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.84, 0.89, 0.93, 0.95 (4 s, 12 H, 4CH_3), 4.81–5.00 (4-line m, 2 H, $CH=CH_2$), 5.81 (dd, 1 H, J = 10.6, 17.8 Hz, $CH=CH_2$).

Isopimara-8,15-dien-7-one (16a) and pimara-8,15-dien-7-one (16b) were prepared by oxidation of **15a** and **15b** by the same procedure described for **9a**. Purification by flash chromatography of silica gel with 1:5 ether–hexane as eluent followed by recrystallization from aqueous methanol gave 214 mg (45%) of dienone **16a**: mp 135–136 °C; IR (KBr) 3087 (vinyl H), 1659, 1617 (enone), 910 ($CH=CH_2$) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.88, 0.92, 1.01, 1.09 (4 s, 12 H, 4 CH_3), 4.84 (dd, 1 H, J = 1.2, 17.5 Hz, *cis*-$CH=CH_2$), 4.92 (dd, 1 H, J = 1.2, 10.7 Hz, *trans*-$CH=CH_2$), 5.68 (dd, 1 H, J = 10.6, 17.5 Hz, $CH=CH_2$).

Purification by chromatography in the same manner afforded 167 mg (35%) of dienone **16b**. Recrystallization from aqueous methanol gave the analytical sample: mp 86–87 °C; IR (KBr) 3080 (vinyl H), 1659, 1616 (enone), 910 ($CH=CH_2$) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.89, 0.93, 0.95, 1.07 (4 s, 12 H, 4 CH_3), 4.87, 4.92 (2 m, 2 H, $CH=CH_2$), 5.75 (dd, 1 H, J = 10.5, 17.8 Hz, $CH=CH_2$). The ^1H NMR spectral data for **16a** and **16b** were taken from spectra (see supplementary material) of impure samples from earlier runs which contained substantial proportions of a byproduct.

Isopimar-15-en-7-one (17a). A solution of 84 mg (12.2 mmol) of lithium (1% sodium) in 25 mL of freshly distilled liquid NH_3 was stirred and cooled at −78 °C as 350 mg (1.22 mmol) of dienone **16a** in 3 mL of dry THF was added dropwise. After removal of acetone–dry ice bath, the resulting solution was allowed to stir at −33 °C for 1 h and the excess lithium was destroyed by adding solid NH_4Cl until the blue color disappeared. The NH_3 was evaporated, the residue was suspended in water, and the suspension was extracted with ether (3 × 10 mL). The combined organic extracts were washed twice with 10% NaOH (2 × 10 mL) and water (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Purification by flash chromatography on 80 g of silica gel with 10% ether in hexane as eluant followed by recrystallization from acetone gave 242 mg (68%) of enone **17a**: mp 127–128 °C (lit.[29] 126–127 °C); $[\alpha]^{23}_D$ −16.6° (c 3.9, $CHCl_3$); IR (KBr) 3082 (vinyl H), 1697 (C=O), 1639, 999, 911 ($CH=CH_2$) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.85, 0.88, 0.95, 1.09 (4 s, 12 H, 4 CH_3), 2.31, 2.40 (2 m, 3 H, CH_2COCH), 4.87 (d, 1 H, J = 7.2 Hz, *trans*-$CH=CH_2$), 4.95 (d, 1 H, J = 12.6 Hz, *cis*-$CH=CH_2$), 5.81 (dd, 1 H, J = 7.9, 12.6 Hz, $CH=CH_2$). These spectral data are similar to the literature values (60-MHz ^1H NMR in CCl_4).[29]

Pimar-15-en-7-one (17b). Reduction of dienone **16b** was carried out by the preceding procedure. Recrystallization of the product from water–acetone gave 175 mg (56%) of product: mp 91–92 °C; IR (KBr) 3082 (vinyl H), 1700 (C=O), 1636, 911 ($CH=CH_2$) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.84, 0.87, 0.98, 1.02 (4 s, 12 H, 4 CH_3), 4.93 (dd, 1 H, J = 1.2, 17.7 Hz, *cis*-$CH=CH_2$), 5.03 (dd, 1 H, J = 1.2, 10.9 Hz, *trans*-$CH=CH_2$), 5.66 (dd, 1 H, J = 10.8, 17.7 Hz, $CH=CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 18.6, 21.2, 27.7, 31.5, 32.9, 33.6, 36.2, 36.4, 36.8, 37.3, 38.6, 39.3, 41.8, 45.8, 54.7, 56.1, 112.6, 145.9, 214.2.

Isopimara-7,15-diene (20a). A. From Ketone 17a. The following procedure is similar to one reported by Senter.[41] A 34-mg (0.28 mmol) portion of 35% KH dispersion in mineral oil was washed three times with pentane under N_2. A suspension of the oil-free KH in 1.5 mL of dry THF containing 47 mg (0.25 mmol) of 18-crown-6 (Aldrich Chemical Co.) was rapidly stirred at 25 °C as 72 mg (0.25 mmol) of ketone **17a** in 0.5 mL of THF was added in one portion. After 10 min, 215 mg (1.2 mmol) of diethyl chlorophosphate was added, and the resulting solution was stirred at rt for 1.5 h. Saturated $NaHCO_3$ was added, and the product was isolated by extraction with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with saturated NaCl, dried ($MgSO_4$), and evaporated. Purification of the residue by flash chromatography on 10 g of silica gel with 1:7 ether–hexane as eluent provided 55 mg (52%) of a 7:1 mixture of enol phosphates **18a** and **19a** as a colorless oil. This mixture was used in the next reaction without further purification. The following NMR data for **18a** and **19a** were obtained from a spectrum of the mixture. Enol phosphate **18a**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (s, 9 H, 3 CH_3), 0.94 (s, 3 H, CH_3), 1.35 (t, 6 H, J = 7.2 Hz, OCH_2CH_3), 2.68 (br d, 1 H, J = 15 Hz, H at C-9), 4.05–4.20 (five-line m, 4 H, OCH_2CH_3), 4.84–4.98 (six-line m, 2 H, $CH=CH_2$), 5.83 (dd, 1 H, J = 10.2, 17.4 Hz, $CH=CH_2$). The presence of **19a** was inferred from weak absorptions in the vinyl region of the ^1H NMR (200 MHz, $CDCl_3$) spectrum: δ 4.82–4.95 (m, 2 H, $CH=CH_2$), 5.48 (br s, 1 H, H at C-6), 5.71–5.88 (m, 1 H, $CH=CH_2$).

Lithium–ammonia reduction of the enol phosphate mixture was carried out as described before for enone **16a**. The 1:8 ratio of **21a** and **20a** (t_R = 10.39 and 10.93 min) was determined by GC analysis (250 °C). The two products were separated by column chromatography on silica gel impregnated with 10% $AgNO_3$ (5 g). Elution with hexane provided 4 mg (10%) of the less polar isomer **21a** (TLC R_f 0.85 on $AgNO_3$-silica gel using 1:4 ether–hexane): ^1H NMR (200 MHz, $CDCl_3$) δ 0.84, 0.84, 0.90, 1.02 (4 s, 10 H, 4 CH_3), 4.88 (m, 2 H, $CHCH_2$), 0.54 (four-line m, 2 H, C-6,C-7 olefinic H), 5.81 (dd, 1 H, J = 10.5, 17.5 Hz, $CH=CH_2$). Further elution gave 20 mg (57%) of diene **20a** (TLC R_f 0.65 on $AgNO_3$ silica gel using 1:4 ether–hexane). The GC retention time (by coinjection) and ^1H NMR spectrum of the major diene are identical to those of authentic isopimaradiene (see below).

B. From Isopimaric Acid. Esterification of isopimaric acid (isopimara-7,15-dien-18-oic acid)[23] with CH_2N_2 afforded methyl isopimarate: $[\alpha]^{23}_D$ −7.8° (c 5.1, $CHCl_3$) [lit.[34a] $[\alpha]^{23}_D$ −7.7° (c 4.3, $CHCl_3$)]; IR (film) 3080 (vinyl H), 1637, 914 ($CH=CH_2$) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.86, 0.90, 1.27 (3 s, 9 H, 3 CH_3), 3.64 (s, 3 H, OCH_3), 4.87 (dd, 1 H, J = 1.3, 10.6 Hz, *trans*-$CH=CH_2$), 4.93 (dd, 1 H, J = 1.3, 17.5 Hz, *cis*-$CH=CH_2$), 5.31 (br d, 1 H, J = 4.3 Hz, H at C-7), 5.80 (dd, 1 H, J = 10.8, 17.6 Hz, $CH=CH_2$); ^{13}C NMR (90 MHz, $CDCl_3$) δ 15.2, 17.3, 17.9, 19.9, 21.4, 25.1, 35.0, 36.0, 36.7, 36.9, 38.7, 45.1, 45.9, 46.4, 51.8, 51.9, 109.2, 121.0, 135.4, 150.1, 179.0; MS m/z (relative intensity) 316 (M^+, 29), 301 (19), 287 (15), 257 (49), 256 (47), 241 (100), 187 (35), 133 (32), 121 (42), 119 (41), 105 (49), 91 (34), 79 (33), 55 (31), 41 (28).

The ester was converted to the diterpene hydrocarbon as described below for the 9β isomers. The data for isopimara-7,15-diene (**20a**) are as follows: $[\alpha]^{23}_D$ −31.0° (c 2.1, $CHCl_3$) [lit.[34c] $[\alpha]^{23}_D$ −31.3° (c 1.8, $CHCl_3$), lit.[14b] $[\alpha]^{25}_D$ −28° (c 0.2, $CHCl_3$), lit.[34d] $[\alpha]^{20}_D$ −28° ($CHCl_3$)]; IR (film) 3081 (vinyl H), 1638, 909 ($CH=CH_2$) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.87, 0.87, 0.88, 0.92 (4 s, 12 H, 4 CH_3), 4.87 (dd, 1 H, J = 1.3, 10.7 Hz, *trans*-$CH=CH_2$), 4.93 (dd, 1 H, J = 1.3, 17.5 Hz, *cis*-$CH=CH_2$), 5.37 (br s, 1 H, H at C-7), 5.81 (dd, 1 H, J = 10.7, 17.5 Hz, $CH=CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.0, 18.8, 20.2, 21.5, 22.4, 23.4, 32.8, 33.6, 35.4, 36.2, 36.9, 39.9, 42.2, 46.2, 50.4, 52.0, 109.1, 121.7, 135.5, 150.5; MS m/z (relative intensity) 272 (M^+, 52), 257 (70), 243 (23), 187 (36), 148 (46), 133 (48), 119 (57), 109 (100), 91 (63), 81 (58), 55 (55), 41 (73).

Pimara-7,15-diene (20b) was prepared from enone **17b** by the procedures described in method A above. A 1:7 mixture (62 mg, 77%) of enol phosphates **18b** and **19b** was determined by GC analysis (250 °C) (t_R = 16 and 17 min). This mixture (62 mg, 77%) was used for the next reaction without further purification. The following NMR data for **18b** and **19b** were obtained from a spectrum of the mixture. **18b**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.80, 0.90, 0.93, 0.99 (4 s, 12 H, 4 CH_3), 1.36 (t, 6 H, J = 7.1 Hz, OCH_2CH_3), 2.95 (dd, 1 H, J = 1.8, 17.9 Hz, H at C-9), 4.06–4.27 (five-line m, 4 H, OCH_2CH_3), 4.90–5.07 (six-line m, 2 H, $CH=CH_2$), 5.67 (dd, 1 H, J = 10.1, 17.9 Hz, $CH=CH_2$). **19b**: ^1H NMR δ 0.88, 0.93, 0.96, 0.98 (4 s, 12 H, 4 CH_3), 4.24–4.38 (m, 4 H, OCH_2CH_3), 4.82–5.05 (m, 2 H, $CH=CH_2$), 5.25 (br s, 1 H, H at C-6), 5.82 (m, 1 H, $CH=CH_2$).

Reduction of enol phosphates **18b** and **19b** as described above provided 20 mg (70%) of a mixture of dienes **20b** and **21b**. A 1:7 isomer ratio (t_R = 10.01 and 10.58 min) was determined by GC analysis (250 °C). No further purification was carried out. The

(41) Senter, P. D. Ph.D. Thesis, University of Illinois, Urbana, IL, 1981; pp 90–92.

following NMR data for the dienes were obtained from a spectrum of the mixture. Spectral data for **20b**: IR (film) 3080 (vinyl H), 1635, 910 (CH=CH_2) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.79, 0.87, 0.91, 0.96 (4 s, 12 H, 4 CH_3), 4.81–5.13 (five-line m, 2 H, CH=CH_2), 5.37 (br s, 1 H, H at C-7), 5.69 (dd, 1 H, J = 10.2, 17.1 Hz, CH=CH_2); MS m/z (relative intensity) 272 (M^+, 48), 257 (100), 230 (27), 187 (20), 161 (19), 148 (80), 133 (44), 119 (44), 109 (75), 105 (52), 91 (43), 81 (36), 79 (32), 55 (29), 41 (37). The spectral data agree with the data in the literature.[31] Spectral data for **21b**: ^1H NMR (200 MHz, $CDCl_3$) δ 0.78, 0.81, 0.90, 0.95 (4 s, 12 H, 4 CH_3), 4.88 (m, 2 H, CH=CH_2), 5.65 (m, 2 H, C-6, C-7 olefinic H), 5.76 (m, 1 H, CH=CH_2); MS m/z (relative intensity) 272 (M^+, 40), 257 (68), 187 (52), 119 (40), 105 (78), 91 (68), 81 (72), 79 (53), 69 (38), 67 (50), 41 (100).

Methyl 7-Oxoisopimara-8,15-dien-18-oate *p*-Toluenesulfonylhydrazone (22a). The following procedure was based upon one in the literature.[42] A solution of 182 mg (0.55 mmol) of enone ester **9a** in 10 mL of absolute ethanol was heated in an oil bath at 70 °C as 154 mg (0.83 mmol) of *p*-tosylhydrazide was added. The solution was heated at reflux for 60 min, and the cooled solution was evaporated under reduced pressure. Purification of the residue by chromatography on 40 g of silica gel (1:4 ether–pentane as the eluant) gave 235 mg (86%) of **22a** as a white solid. Recrystallization from pentane–$CHCl_3$ gave the analytical sample: mp 213–214 °C; IR (KBr) 3210 (NH), 1717 (C=O), 1620, 914 (CH=CH_2), 1597 (C=N) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.90, 1.01, 1.23 (3 s, 9 H, 3 CH_3), 2.43 (s, 3 H, PhCH_3), 3.66 (s, 3 H, OCH_3), 4.84 (dd, 1 H, J = 1.2, 17.5 Hz, *cis*-CH=CH_2), 4.91 (dd, 1 H, J = 1.2, 10.8 Hz, *trans*-CH=CH_2), 5.71 (dd, 1 H, J = 10.8, 17.5 Hz, CH=CH_2), 7.20 (br 1 H, NH), 7.31 (d, 2 H, J = 7.9 Hz, ArH at C3′), 7.88 (d, 2 H, J = 7.9 Hz, ArH at C2′).

Anal. Calcd for $C_{28}H_{38}N_2SO_4$: C, 67.47; H, 7.63; N, 5.62. Found: C, 67.25; H, 7.87; N, 5.57.

Methyl 7-Oxopimara-8,15-dien-18-oate *p*-Toluenesulfonylhydrazone (22b). Reaction of **9b** with tosylhydrazide by the preceding procedure afforded 186 mg (70%) of tosylhydrazone **22b** as a white solid. Recrystallization from pentane–$CHCl_3$ gave the analytical sample: mp 193–195 °C; IR (KBr) 3211 (NH), 1713 (C=O), 1630, 910 (CH=CH_2), 1596 (C=N) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87, 0.90, 1.23 (3 s, 9 H, 3 CH_3), 2.43 (s, 3 H, PhCH_3), 3.66 (s, 3 H, OCH_3), 4.79–4.93 (m, 2 H, CH=CH_2), 5.76 (dd, 1 H, J = 10.6, 17.6 Hz, CH=CH_2), 7.16 (br, 1 H, NH), 7.38 (d, 2 H, J = 8.1 Hz, ArH at C3′), 7.86 (d, 2 H, J = 8.1 Hz, ArH at C2′).

Anal. Calcd for $C_{28}H_{38}N_2SO_4$: C, 67.47; H, 7.63; N, 5.62. Found: C, 67.61; H, 7.64; N, 5.55.

Methyl (9β)-Isopimara-8,15-dien-18-oate (23a) and Methyl (9β)-Isopimar-7-en-18-oate (24a). The following procedure is a modified version of a literature method.[21a] A solution of 130 mg (0.26 mmol) of tosylhydrazone **22a** in 10 mL of $CHCl_3$ was degassed by evacuating and filling with N_2 three times. The solution was stirred and cooled at 0 °C as 38 mg (0.04 mL, 0.31 mmol) of catecholborane (Aldrich Chemical Co.) was quickly added. After 30 min, the solution was allowed to warm to rt, and 82 mg (0.6 mmol) of sodium acetate trihydrate and then 5 mL of $CHCl_3$ were added. The resulting suspension was refluxed for 50 min. The cooled $CHCl_3$ solution was washed twice with 10% Na_2CO_3 (15 mL each) and once with saturated NaCl (15 mL). Drying ($MgSO_4$) and evaporation of solvent gave 60 mg of oily liquid which was a 4:1 mixture of **23a** and **24a** (t_R = 13.7 and 14.1 min) according to GC analysis (250 °C). Coinjection with authentic methyl isopimarate showed that no more than 2–3% of the 9α diene was present. The two products were separated by column chromatography on silica gel impregnated with 15% $AgNO_3$ (5 g) using 1:20 ether–pentane as eluant. The minor product, **24a**, was eluted first (TLC R_f 0.86 on $AgNO_3$-silica gel using 1:4 ether–pentane as developing solvent). The yield of **24a** was 9 mg (11%): $[\alpha]^{23}_D$ −119° (*c* 5.7, $CHCl_3$); IR (film) 1728 (C=O), 1246, 1190, 1146 (CO, methyl ester) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.73 (t, 3 H, J = 7.6 Hz, CH_2CH_3), 0.81, 0.96, 1.24 (3 s, 9 H, 3 CH_3), 3.66 (s, 3 H, OCH_3), 5.20 (d, 1 H, J = 0.8 Hz, H at C-7); MS m/z (relative intensity) 318 (M^+, 17), 303 (24), 259 (28), 258 (39), 150 (56), 121 (100); HRMS calcd for $C_{21}H_{34}O_2$ m/e 318.2559, found m/e 318.2568.

Further elution gave 46 mg (56%) of **23a** (TLC R_f 0.29 on $AgNO_3$-silica gel using 1:4 ether–pentane as developing solvent). Recrystallization from aqueous methanol gave the analytical sample: mp 80–81 °C; $[\alpha]^{23}_D$ −142° (*c* 4.6, $CHCl_3$); IR (film) 3079 (vinyl H), 1727 (C=O), 1638, 911 (CH=CH_2) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.97, 1.00, 1.24 (3 s, 9 H, 3 CH_3), 3.65 (s, 3 H, OCH_3), 4.88–5.01 (m, 2 H, CH=CH_2), 5.23 (d, 1 H, J = 5.5 Hz, H at C-7), 5.88–5.96 (six-line m, 1 H, CH=CH_2); ^{13}C NMR (90 MHz, $CDCl_3$) δ 17.7, 18.0, 22.5, 25.2, 29.4, 34.7, 35.7, 37.7, 38.8, 39.0, 39.5, 46.3, 49.6, 51.8, 53.3, 111.2, 118.8, 136.9, 145.6, 179.2; MS m/z (relative intensity) 316 (M^+, 37), 301 (35), 256 (93), 241 (100), 187 (26), 175 (50), 148 (76), 133 (68), 121 (98), 105 (82), 93 (53), 81 (51); HRMS calcd for $C_{21}H_{32}O_2$ m/e 316.2402, found m/e 316.2411.

Methyl (9β)-pimara-7,15-dien-18-oate (23b) and methyl (9β)-pimar-7-en-18-oate (24b) were prepared by the preceding procedure. A 2:1 ratio of **23b** and **24b** was determined by GC analysis (same conditions as above) on the crude product (t_R = 14.43 and 14.75 min). Purification as described above gave 32 mg (29%) of the less polar ene ester **24b** (TLC R_f 0.85 on $AgNO_3$-silica gel using 1:4 ether pentane as developing solvent). Recrystallization from aqueous methanol provided an analytical sample: mp 66–68 °C; $[\alpha]^{23}_D$ −138° (*c* 10.5, $CHCl_3$); IR (film) 1727 (C=O), 1246, 1188, 1144 (CO, methyl ester) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.73, 0.96, 1.24 (3 s, 9 H, 3 CH_3), 0.82 (t, 3 H, J = 7.3 Hz, CH_2CH_3), 3.66 (s, 3 H, OCH_3), 5.20 (d, 1 H, J = 0.5 Hz, H at C-7); MS m/z (relative intensity) 318 (M^+, 13), 303 (16), 259 (21), 258 (234), 150 (57), 121 (100), 109 (34), 107 (35), 105 (28), 93 (86), 81 (27), 79 (26), 69 (24), 55 (55), 41 (35); HRMS calcd for $C_{21}H_{34}O_2$ m/e 318.2559, found m/e 318.2564.

Further elution gave 57 mg (52%) of diene ester **23b** (TLC R_f 0.30 on $AgNO_3$-silica gel). Recrystallization from aqueous methanol gave the analytical sample: mp 63–65 °C; $[\alpha]^{23}_D$ −163° (*c* 4.9, $CHCl_3$); IR (film) 3081 (vinyl H), 1727 (C=O), 1638, 909 (CH=CH_2) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90, 0.97, 1.25 (3 s, 9 H, 3 CH_3), 3.66 (s, 3 H, OCH_3), 4.86 (dd, 1 H, J = 1.5, 9.5 Hz, *trans*-CH=CH_2), 4.94 (dd, 1 H, J = 1.5, 16.9 Hz, *cis*-CH=CH_2), 5.25 (d, 1 H, J = 5.4 Hz, H at C-7), 5.82 (dd, 1 H, J = 10.5, 17.7 Hz, CH=CH_2); ^{13}C NMR (90 MHz, $CDCl_3$) δ 17.7, 18.0, 21.8, 22.5, 25.0, 25.3, 34.8, 35.7, 37.9, 38.8, 39.1, 46.4, 47.9, 51.9, 53.4, 109.2, 119.1, 136.9, 150.3, 179.3; MS m/z (relative intensity) 316 (M^+, 48) 301 (27), 257 (55), 241 (100), 187 (35), 175 (26); HRMS calcd for $C_{21}H_{32}O_2$ m/e 316.2402, found m/e 316.2398.

(9β)-Isopimara-7,15-dien-18-ol (25a). A suspension of 12 mg (0.32 mmol) of $LiAlH_4$ in 15 mL of dry ether was rapidly stirred and cooled at 0 °C as 60 mg (0.19 mmol) of ester **23a** in 5 mL of dry ether was added dropwise. The mixture was allowed to warm to rt and stirred for 2 h. The excess hydride and aluminum salts were hydrolyzed by adding 10% NaOH until a white solid precipitated.[43] The solid was filtered and washed well with ether (2 × 5 mL). The combined filtrates were washed with saturated NaCl solution, dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the oily residue by flash chromatography on a 3-g column of silica gel with 1:4 ether–hexane as eluant and by recrystallization from aqueous ethanol provided 50 mg (90%) of dienol **25a**: mp 120–121 °C; IR (film) 3350 (OH), 3080 (vinyl H), 1635, 918 (CH=CH_2) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.88, 0.98, 1.00 (3 s, 9 H, 3 CH_3), 3.16, 3.35 (AB dd, 2 H, J = 11.1 Hz, CH_2OH), 4.88–4.98 (m, 2 H, CH=CH_2), 5.26 (br s, 1 H, H at C-7), 5.90 (five-line m, 1 H, CH=CH_2).

(9β)-Pimara-7,15-dien-18-ol (25b). Recrystallization from aqueous ethanol gave 51 mg (94%) of **25b**: mp 100–103 °C; IR (film) 3340 (OH), 3084 (vinyl H), 1638, 909 (CH=CH_2) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89, 0.89, 0.98 (3 s, 9 H, 3 CH_3), 3.17, 3.37 (AB dd, 2 H, J = 10.8 Hz, CH_2OH), 4.85 (dd, 1 H, J = 1.5, 8.9 Hz, *trans*-CH=CH_2), 4.93 (dd, 1 H, J = 1.5, 16.2 Hz, *cis*-CH=CH_2), 5.29 (br s, 1 H, H at C-7), 5.83 (dd, 1 H, J = 10.8, 17.8 Hz, CH=CH_2).

(9β)-Isopimara-7,15-dien-18-yl methanesulfonate (26a) was prepared according to a literature method.[22a,44] A solution of 54

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(43) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; J. Wiley: New York, 1967; Vol. 1, p 581.

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mg (0.19 mmol) of alcohol **6a** and 38 mg (0.04 mL, 0.38 mmol) of triethylamine in 15 mL of CH_2Cl_2 was stirred and cooled at 0 °C as 39 mg (0.03 mL, 0.34 mmol) of methanesulfonyl chloride was added slowly. The solution was stirred for 30 min at 0 °C and poured into 20 mL of ice-cold water. The organic layer was washed successively with cold 10% HCl, 10% $NaHCO_3$, and saturated NaCl (15 mL of each). Drying ($MgSO_4$) and solvent removal under reduced pressure afforded a sticky solid. Recrystallization from aqueous ethanol provided 63 mg (90%) of **26a** as white needles: mp 120–122 °C; IR (film) 3082 (vinyl H), 1636, 959 (CH=CH_2), 1175 (CO) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.98, 0.98, 1.00 (3 s, 9 H, 3 CH_3), 2.98 (s, 3 H, OSO_2CH_3), 3.82, 3.93 (AB dd, 2 H, J = 9.4 Hz, CH_2O), 4.88–5.00 (m, 2 H, CH=CH_2), 5.62 (br d, 1 H, J = 4.2 Hz, H at C-7), 5.82 (six-line m, 1 H, CH=CH_2).

(9β)-Pimara-7,15-dien-18-yl Methanesulfonate (26b). Recrystallization from aqueous ethanol gave 64 mg (91%) of **26b**: mp 112–115 °C; IR (film) 3081 (vinyl H), 1638 (CH=CH_2), 1173 (CO) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88, 0.98, 0.99 (3 s, 9 H, 3 CH_3), 3.00 (s, 3 H, OSO_2CH_3), 3.82, 3.95 (AB dd, 2 H, J = 9.5 Hz, CH_2OH), 4.86 (dd, 1 H, J = 1.6, 8.9 Hz, *trans*-CH=CH_2), 4.94 (dd, 1 H, J = 1.6, 15.1 Hz, *cis*-CH=CH_2), 5.29 (br s 1 H, H at C-7), 5.82 (dd, 1 H, J = 10.9, 17.3 Hz, CH=CH_2).

(9β)-18-(Phenylthio)isopimara-7,15-diene (27a). An 84-mg portion of 50% NaH oil dispersion was washed with three 5-mL portions of dry pentane to remove the mineral oil. A suspension of the remaining 42 mg (0.86 mmol) of oil-free NaH in 15 mL of dry DMF (freshly distilled from CaH_2) was stirred under N_2 as 0.09 mL (0.86 mmol) of thiophenol was added to form sodium thiophenoxide. After 5 min, a solution of 63 mg (0.17 mmol) of mesylate **26a** in 5 mL of dry DMF was added. The resulting solution was heated at 120–130 °C (oil bath temperature) for 4 h, cooled to rt, and poured into 20 mL of cold 10% HCl. The solution was extracted with three 10-mL portions of ether. The combined ether extracts were washed with 10% NaOH (2 × 10 mL) and saturated NaCl (2 × 10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the residue by flash chromatography on 80 g of silica gel with hexane as eluant gave 57 mg (85%) of **27a** as a colorless liquid: IR (film) 3077 (vinyl H), 1638, 909 (CH=CH_2), 737 (aromatic), 688 (R–S–R) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.97, 1.01, 1.04 (3 s, 9 H, 3 CH_3), 2.90 (s, 2 H, CH_2S), 4.91–5.00 (m, 2 H, CH=CH_2), 5.20 (br s, 1 H, H at C-7), 5.92 (six-line m, 1 H, CH=CH_2), 7.12–7.38 (m, 5 H, aromatic H).

(9β)-18-(Phenylthio)pimara-7,15-diene (27b): yield 55 mg (82%); IR (film) 3077 (vinyl H), 1638, 909 (CH=CH_2), 737 (aromatic), 690 (R–S–R) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90, 0.97, 1.05 (3 s, 9 H, 3 CH_3), 2.92 (AB dd, 2 H, J = 12.1 Hz, CH_2S), 4.84–4.98 (d of three-line m, 2 H, CH=CH_2), 5.23 (br s, 1 H, H at C-7), 5.82 (dd, 1 H, J = 10.9, 17.3 Hz, CH=CH_2), 7.12–7.40 (m, 5 H, aromatic H).

(9β)-Isopimara-7,15-diene (4). A solution of 11 mg (1.5 mmol) of Li (1% sodium) in 15 mL of freshly distilled liquid NH_3 was stirred and cooled at −78 °C under N_2 as 57 mg (0.15 mmol) of thioether **27a** in 2 mL of dry THF was added dropwise. The cooling bath was removed, and the solution was allowed to warm to −33 °C over a few min. After 1 h at −33 °C the excess Li was destroyed by adding ethanol until the blue color disappeared. The NH_3 was evaporated, the residue was suspended in water, and the suspension was extracted with ether (3 × 10 mL). The combined ether extracts were washed twice with 10% NaOH (2 × 10 mL) and water (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Purification of the residue by column chromatography on 60 g of silica gel with hexane as eluant gave 30 mg (74%) of diene **4** as a white solid. Recrystallization from aqueous ethanol gave the analytical sample: mp 77–79 °C; $[\alpha]^{23}_D$ −251° (c 2.9, $CHCl_3$); IR (film) 3082 (vinyl H), 1636, 912 (CH=CH_2) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.87, 0.90, 0.93, 1.00 (4 s, 12 H, 4 CH_3), 4.92–4.97 (5-line, m, 2 H, CH=CH_2), 5.29 (br d, 1 H, J = 5.4 Hz, H at C-7), 5.91 (6-line m, 1 H, CH=CH_2); ^{13}C NMR (90 MHz, $CDCl_3$) δ 18.8, 22.2, 22.7, 23.7, 25.3, 29.6, 32.8, 33.5, 35.1, 36.8, 38.8, 39.6, 43.0, 43.4, 49.6, 53.1, 111.1, 119.5, 136.8, 145.9; MS m/z (relative intensity) 272 (M^+, 41), 257 (68), 229 (30), 187 (24), 148 (76), 133 (48), 124 (43), 119 (49), 109 (100), 81 (44), 41 (35); HRMS calcd for $C_{20}H_{32}$ m/z 272.2504, found m/z 272.2501.

(9β)-Pimara-7,15-diene (3) was prepared from **23b** and purified by the preceding procedures. The yield was 39 mg (96%): $[\alpha]^{23}_D$ −208° (c 3.0, $CHCl_3$); IR (film) 3081 (vinyl H), 1638, 908 (CH=CH_2) cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 0.88, 0.89, 0.91, 0.94 (4 s, 12 H, 4 CH_3), 4.86 (dd, 1 H, J = 1.1, 10.4 Hz, *trans*-CH=CH_2), 4.93 (dd, 1 H, J = 1.1, 17.6 Hz, *cis*-CH=CH_2), 5.31 (br d, 1 H, J = 4.5 Hz, H at C-7), 5.82 (dd, 1 H, J = 10.8, 17.6 Hz, CH=CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz) 18.8, 21.8, 22.1, 22.7, 23.8, 25.0, 32.9, 33.5, 35.1, 36.8, 37.8, 38.8, 43.0, 43.6, 48.0, 53.2, 109.1, 119.9, 136.7, 150.5; MS m/z (relative intensity) 272 (M^+, 68), 257 (80) 243 (27), 229 (20), 187 (43), 148 (55), 133 (56), 119 (68), 109 (100), 81 (55), 41 (51); HRMS calcd for $C_{20}H_{32}$ m/e 272.2504, found m/e 272.2500. The ^1H NMR, ^{13}C NMR ($\Delta\delta \leq$ 0.1 ppm), and MS data agree very well with those reported for (±)-3[15c] with the exception of one ^{13}C NMR signal (δ_c 53.1 vs 55.3).

Acknowledgment. We are grateful to Prof. C. A. West and K. A. Wickham for discussions and provision of unpublished results during this collaboration. We thank Dr. Duane F. Zinkel[23] for providing pimaric and isopimaric acid and Dr. Bernard Delmond[27] for a reference sample of **10**. Financial support was provided by a grant from the National Institutes of Health (GM 13956).

Supplementary Material Available: Yields, recrystallization solvents, and physical properties (mp, IR, and ^1H NMR data; ^{13}C NMR data for **14b**; MS data for **14a** and **14b**) for **11a,b–14a,b** and ^1H NMR spectra for **3**, **4**, **9b**, **15b**, **16a,b**, **23a,b**, **25a,b**, **26a,b**, and **27a,b** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.