7), 367 (51), 223 (26), 157 (87), 156 (53), 143 (30), 75 (31), 73 ($(CH_3)_3Si^+$, 100).

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Supplementary Material Available: GC graphs of hydrolysis products, ^{13}C and ^1H NMR data of compounds **2-4**, **6-9**, and **11-13**, and ^{13}C and ^1H NMR spectra of compounds **1**, **5**, **10**, and **14-17** (18 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.

Cyclization Reactions of the *o*-Naphthoquinone Diterpene Aethiopinone. A Revision of the Structure of Prionitin[1]

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The 4,5-seco-20(10→5)-*abeo*-abietane derivative aethiopinone (1), a natural *o*-naphthoquinone isolated from some *Salvia* species, was subjected to a series of acid-catalyzed reactions which yielded phenalene derivatives (**2**, **6**, **9**, and **11**) and other cyclization products (**3** and **10**). The 11-nor derivative **3** is formed by an intramolecular [4 + 2] cycloaddition reaction, and a mechanistic pathway for the formation of the phenalene derivatives **6** and **11** is also proposed. These transformations of aethiopinone (1) allowed the partial syntheses of the naturally occurring diterpenes salvipisone (**8**), salvilenone (**9**), and the racemic form of prionitin (**11**), a rearranged abietane diterpenoid previously isolated from the root of *Salvia prionitis*, to which structure **12** had been attributed only on the basis of NMR spectroscopic studies. In the light of the results reported herein, including an X-ray analysis of compound **11**, the structure **12** assigned to prionitin must be changed to **11**.

The roots of various species of sage, *Salvia* spp. (Labiatae), are used throughout the world in folk medicine to treat a wide variety of ailments.[4] The chemical composition of these plant materials has been studied extensively over the last 50 years, and their organic extracts are particularly rich in abietanoids and diterpene quinone pigments. These substances have attracted considerable attention because many of them exhibit significant cytotoxic,[5] antibacterial,[6] antioxidant,[7] antiinflammatory,[8] antineoplastic,[9] and antiplatelet aggregation[10] activities.

Aethiopinone[5a,11] (1, Chart I, 4,5-seco-20(10→5)-*abeo*-abieta-4(18),5(10),6,8,13-pentaene-11,12-dione[12]) is a rearranged diterpenoid easily available from the root of *Salvia aethiopis*.[13] We have focused our attention on the utility of this substance (1) as an expedient starting material for obtaining several biologically active rearranged abietane derivatives previously isolated from the roots of some *Salvia* species. In this paper, we report some acid-catalyzed cyclizations of aethiopinone (1) which allowed the formation of compounds **2**, **3**, and **6-11**. Two of these substances have previously been isolated from the roots of *S. aethiopis*[11b] (compound **8**, salvipisone), *Salvia moorcraftiana*[14a] and *Salvia miltiorrhiza*[14b] (compound **9**,

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(12) The nomenclature and numbering system for all these compounds are based on those in abietane diterpenes. This decision was taken since the substances described herein can be biogenetically generated from an abietane derivative.

(13) Aethiopinone (1) was isolated as the extract.[11b]) constituent of the acetone extract of the root of *Salvia aethiopis* (0.58% on dry plant material, 24.8% of the extract).[11b] This sage is profusely widespread in Southern and South-Eastern Europe and North Africa.

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Table I. ^{1}H NMR Spectroscopic Data of Compounds 2–6 and 11[a]

H	2	3	4	5	6	11
1α	3.17 ddd	2.76 ddd	~2.6[b]	b	3.15 ddd	3.16 ddd
1β	2.81 dddd	b	~2.6[b]	b	2.76 br ddd	2.79 dddd
2α	1.69 qd	b	b	b	1.64 qd	1.65 qd
2β	2.19 dddd	b	b	b	2.16 dddd	2.17 dddd
3β	3.40 br dd	b	b	b	3.32 dd	3.34 dd
6	7.05 br d	7.16 br d	6.95 br d	6.94 br d	7.14 br d	7.07 br d
7	7.50 br dd	7.06 br d	6.90 br d	6.94 br s	7.85 br d	7.68 br dd
12			4.36 dd	4.44 dd		
14	7.36 br t	7.03 d	6.31 br s	6.24 br s		
15	3.14 sept d	3.22 sept d	2.80 sept d	2.76 sept d	3.74 sept	3.52 sept
16 (3 H)[c]	1.33 d	1.16 d	1.24 d	1.20 d	1.41 d	1.40 d
17 (3 H)[c]	1.29 d	1.16 d	1.18 d	1.15 d	1.32 d	1.31 d
18 (3 H)	1.73 s				1.71 s	1.71 s
18α		2.55 d	2.09 dd	2.03 dd		
18β		2.89 dd	2.29 ddd	2.06 br dd		
19 (3 H)	1.18 s	1.21 d	1.35 d	1.26 br s	1.16 s	1.17 s
20 (3 H)	2.37 br s	2.25 br s	2.20 br s	2.18 br s	2.37 br s	2.37 br s
OMe						3.88 s
J						
1α,1β	16.5	15.0	b	b	16.5	16.5
1α,2α	4.2	4.9	b	b	4.1	4.2
1α,2β	2.5	4.2	b	b	2.5	2.6
1β,2α	12.3	b	b	b	12.3	12.3
1β,2β	4.6	b	b	b	4.6	4.5
2α,2β	12.3	b	b	b	12.3	12.3
2α,3β	12.3	b	b	b	12.3	12.3
2β,3β	4.5	b	b	b	4.7	4.6
6,7	8.4	7.7	7.7	0	8.7	8.4
6,14	<0.2	<0.2	<0.2	<0.2		
7,1β	0.8	0	0	0	<0.4	0.9
7,20	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
12α,18α			6.9			
12α,18β			5.3			
12β,18α				8.0		
12β,18β				8.4		
14,3β	0.7	0	0	0		
14,15	0.7	0.7	0.7	0.7		
15,16(17)	6.9	6.9	6.8	6.9	7.0	7.0
18α,18β		15.0	14.3	14.1		
18β,19		0.6	0.5	<0.2		

[a] Chemical shifts are reported in ppm downfield from internal TMS; *J* values in hertz. All spectra were recorded at 300 MHz, in $CDCl_3$ solution. All these assignments were confirmed by double resonance experiments and homonuclear COSY spectra. [b] Overlapped signal. [c] Interchangeable assignments.

salvilenone[14b]). Salvilenone has also been prepared synthetically.[14c,d] Moreover, the derivative 11 [(3-*rac*)-4,12-epoxy-14-methoxy-3,11-cyclo-4,5-seco-20(10→5)-*abeo*-abieta-5(10),6,8,11,13-pentaene[12]] showed physical and spectroscopic data identical (apart from the specific rotation) to those previously reported for prionitin, a natural diterpenoid isolated from the root of *S. prionitis*, to which structure 12 has been attributed on the basis of NMR spectroscopic studies.[15]

Results and Discussion

Treatment of aethiopinone (1) with 80% sulfuric acid at 0 °C for 5 min gave compounds 2 and 3 (39% and 14% yields, respectively), besides starting material (1, 25%). The same derivatives 2 and 3, but in a different ratio (5.8% and 58% yields, respectively), together with decomposition products, were also obtained when a solution of compound 1 in benzene was treated with boron trifluoride etherate at room temperature for 3 h.

The structure of the phenalene derivative 2 was in agreement with its ^{1}H and ^{13}C NMR spectra (see Tables I and II, respectively), NOE experiments (see Table III), and other spectroscopic and analytical data (see Experimental Section), and further confirmed by single-crystal X-ray diffraction analysis. Figure 1 shows the molecular structure of one of the enantiomers of the racemic form

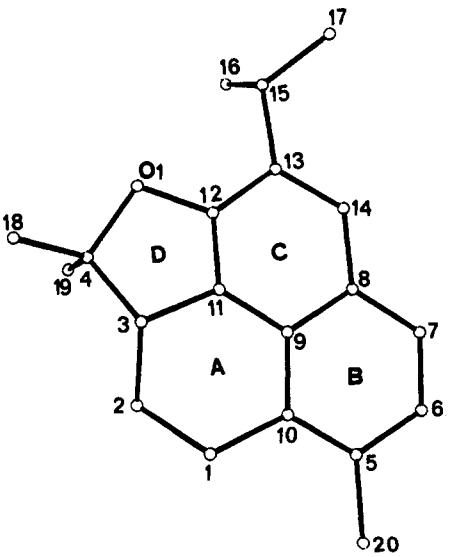

Figure 1. Computer-generated perspective drawing (ORTEP) of compound 2. (Hydrogens are omitted for clarity.)

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Chart I

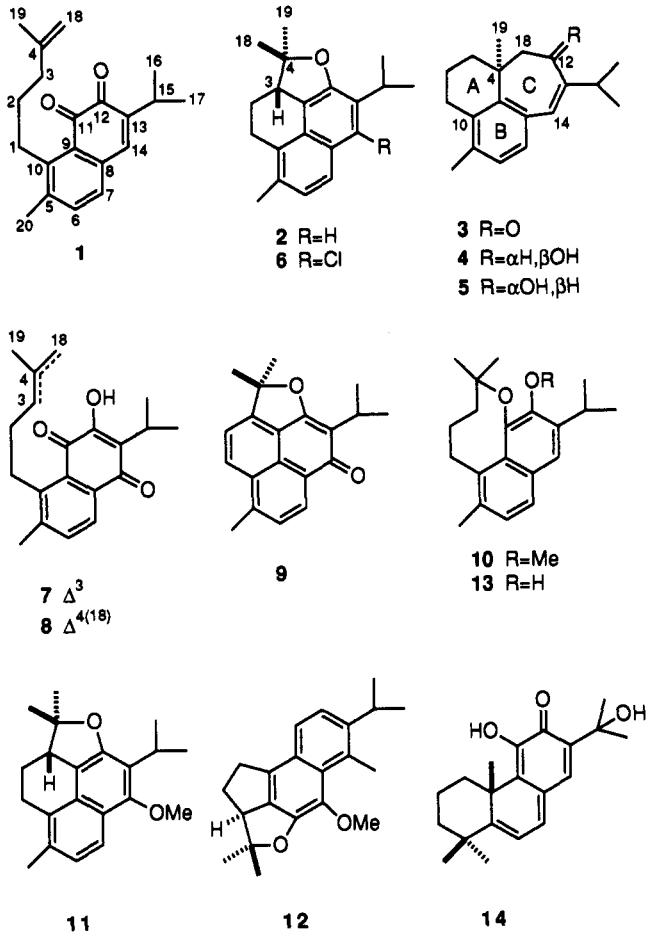

Table II. ^{13}C NMR Spectra of Compounds 2, 6, and 11[a]

C	2	6	11
1	26.56 t[b]	26.63 t	26.60 t
2	23.70 t	23.58 t	23.67 t
3	48.32 d	47.92 d	47.70 d
4	93.58 s	93.65 s	93.60 s
5	121.62 s	121.34 s	120.83 s
6	126.28 d	127.31 d	126.10 d
7	124.37 d	122.47 d	119.99 d
8	132.74 s	131.36 s	124.90 s
9	130.23 s	130.25 s	130.84 s
10	129.11 s	129.39 s	129.49 s
11	127.31 s	127.32 s	127.34 s
12	152.27 s	152.85 s	152.16 s
13	127.06 s	127.45 s	118.11 s
14	122.08 d	124.78 s	153.26 s
15	29.36 d	29.97 d	25.65 d
16[c]	22.54 q	20.57 q	21.50 q
17[c]	22.16 q	20.42 q	21.30 q
18	28.03 q	27.97 q	28.05 q
19	21.95 q	21.87 q	21.92 q
20	18.74 q	18.82 q	18.86 q
OMe			62.87 q

[a] At 50.3 MHz, in $CDCl_3$ solution. Chemical shifts are reported in ppm downfield from internal TMS. Assignments of carbons bearing hydrogen atoms were confirmed by heteronuclear ^1H–^{13}C 2D COSY spectra. Quaternary carbons were assigned by series of selective INEPT experiments.[15] [b] SFORD multiplicity. [c] Interchangeable assignments.

of compound 2. It is of interest to note that the two methyl groups attached to the C-4 position (Me-18 and Me-19) in 2 adopt a different spatial relationship with respect to the plane of the naphthalene part; Me-18 deviates from this plane by only 0.26 Å, whereas Me-19 deviates by 1.94 Å. This structural feature is clearly reflected in the ^1H NMR chemical shifts of these methyl groups, one of them (Me-18) appears downfield shifted (δ 1.73) with respect to the other one (Me-19, δ 1.18) as a consequence of the magnetic anisotropism of the naphthalene moiety.[16]

The formation of compound 2 may arise by a mechanistic pathway related to that proposed for compounds 6 and 11 (see below, Scheme II), where aethiopinone (1) may act as the reducing agent. This assumption is in agreement with the appreciable amount of unrecovered material observed in these reactions (see the Experimental Section).

The structure of 2 is closely related to phenalen-8-one derivatives such as compound 9, which have already been obtained from abietane diterpenoids[14c,d] by a rearrangement reaction catalyzed by acids. A mechanistic pathway previously proposed[17] for this reaction postulates 4,5-seco-20(10→5)-*abeo*-abietane derivatives, like aethiopinone (1), as key intermediates for this transformation.

Combustion analysis and low-resolution mass spectrometry indicated a molecular formula $C_{19}H_{24}O$ for compound 3. Its IR spectrum showed strong absorption for a conjugated ketone function (1655 cm^{-1}) together with characteristic bands of an aromatic moiety (3050, 1625, 1590 cm^{-1}). Intense absorptions in the UV spectrum at λ_{max} (log ε) 209 (4.37), 218 (3.90), 238 (3.89), 243 (3.89), and 317 (4.16) nm suggested[18] the presence of a substituted cinnamoyl chromophore in the molecule of 3. The ^1H NMR spectrum (see Table I) of this substance indicated the presence of an isopropyl group (δ 1.16, 6 H, d, J = 6.9 Hz; δ 3.22, 1 H, septet of d, J_1 = 6.9 Hz, J_2 = 0.7 Hz), an aromatic methyl (δ 2.25 br s), and another methyl group (δ 1.21) attached to a fully substituted sp^3 carbon atom and long-range coupled (d, J = 0.6 Hz) with a methylene proton (δ 2.89 dd, J_{gem} = 15.0 Hz, $J_{long\text{-}range}$ = 0.6 Hz) whose proton partner resonated at δ 2.55 as a doublet (J = 15.0 Hz). Moreover, this spectrum also showed signals of two ortho aromatic protons (δ 7.16 br d, and 7.06 br d, J = 7.7 Hz) and an olefinic proton (δ 7.03 d, J = 0.7 Hz). Extensive decoupling experiments, together with the homonuclear COSY spectrum of compound 3, allowed the establishment of the partial structure of rings B and C of formula 3 (Chart I). On the other hand, from the above data and the degree of unsaturation it was apparent that the molecule possessed three condensed rings and that the remaining three carbons and six hydrogens were involved in the third ring, closed at the C-4 and C-10 positions, thereby establishing structure 3 for this substance. This conclusion was also supported by a one-proton signal at δ 2.76 (ddd, J_1 = 15.0 Hz, J_2 = 4.9 Hz, J_3 = 4.2 Hz) which was assigned to the pseudoequatorial C-1α benzylic proton, coupled with the C-2 methylene grouping of compound 3. The C-1β, C-2, and C-3 methylene protons appeared overlapped[19] in the ^1H NMR spectrum of 3, but its homonuclear COSY spectrum showed a coupling pattern only compatible with three consecutive methylene groups.

In addition, sodium borohydride reduction of 3 yielded two C-12 epimeric alcohols[20] (compounds 4 and 5), the ^1H

(16) In the crystalline state, the naphthalene moiety of compound 2 (rings B and C, see Figure 1) is almost planar, with maximum deviations of 0.04 Å. Rings A and D present envelope conformations with the flap at C-2 and C-4, respectively. The dihedral angles between rings A/B, A/C, A/D, B/C, and C/D are 8°, 9°, 11°, 3°, and 11°, respectively. There are no unusually short intermolecular contacts in this crystalline structure.

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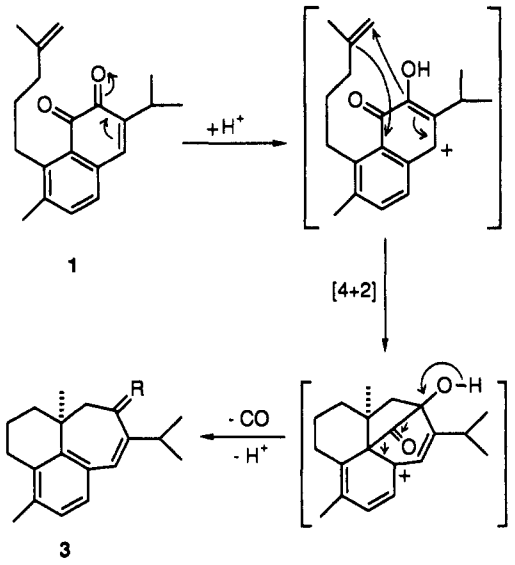
(19) The C-2 and C-3 methylene protons resonated as a complex 4 H signal between δ 1.60 and 1.95, whereas H-1β appeared overlapped with the H-18α proton at δ 2.55.

Table III. Nuclear Overhauser Effect Experiments on Compounds 2, 6, 10, and 11[a]

no.	irradiation δ (proton)	observed NOE enhancement[b] H-1α	H-2α	H-6	H-7	H-14	H-15	Me-16, Me-17	Me-18	Me-19	Me-20	OMe
2	7.36 (H-14)				++		++	+++				
	2.37 (Me-20)	+		++		–[c]						
	1.18 (Me-19)		+						+		–[c]	
6	7.85 (H-7)			+++								
	7.14 (H-6)				+++						++	
	2.37 (Me-20)	+		+								
10	3.96 (OMe)						+	+	+	+		
11	3.88 (OMe)				+		+	++				
	2.37 (Me-20)	+		+								+[c]

[a] Measured at 300 MHz, by the FT difference method. [b] The signs (+), (++), and (+++) denote weak (1–4%), medium (4–7%), and strong (>8%) positive NOE enhancements, respectively. The sign (–) denotes a weak negative (<3%) NOE enhancement. [c] These weak NOE enhancements could be caused by transference NOE.

Scheme I



NMR spectra of which (Table I) showed their C-12 protons as double doublets at δ 4.36 (J_1 = 6.9 Hz, J_2 = 5.3 Hz) and δ 4.44 (J_1 = 8.4 Hz, J_2 = 8.0 Hz), respectively, whereas the C-18 methylene protons displayed the typical pattern of an ABX system (see Table I). Finally, the ^{13}C NMR spectra of compounds 3 and 4 (see the Experimental Section) were in complete agreement with the proposed structures.

The formation of a compound such as 3 starting from aethiopinone (1) is not surprising and should be rationalized as the addition of a pentadienyl cation moiety, arising from the *o*-quinone ring of aethiopinone, to the 2π electron alkene group in the side chain and subsequent loss of carbon monoxide, as it is outlined in Scheme I. An identical [4 + 2] cycloaddition has been proposed[21] to explain the thermal rearrangement of perezone into the pipitzols.[22]

On the other hand, when a solution of aethiopinone (1) in dioxane was treated with concentrated hydrochloric acid at 80 °C for 3 h, five substances (2, 6–9) were obtained, together with major quantities of several unidentified decomposition products. The previously synthesized phenalene derivative 2 (see above) was a minor constituent (4.7% yield), but its 14-chloro derivative 6 was the most abundant product (29.5% yield) of this reaction, which also gave an inseparable 1:2 mixture (7.9% yield) of the naturally occurring *p*-benzoquinone salvipisone[11b] (8) and its isomer 7, respectively (see the Experimental Section). In addition, this reaction also yielded minute amounts of the phenalen-8-one 9 (3% yield), previously known as a synthetic[14c,d] and natural[14a,b] product (salvilenone[14b]).

Compound 6 ($C_{20}H_{23}OCl$) had ^1H and ^{13}C NMR spectra almost identical to those of derivative 2 (see Tables I and II), and the observed differences [e.g. downfield shift of the C-15 proton in 6 (δ 3.74) with respect to 2 (δ 3.14), absence of the signal of the aromatic C-14 proton in 6, a higher upfield resonance of the C-16 and C-17 carbons in 6 than in 2] clearly revealed that these compounds were identical except for the substituent at the C-14 position, namely an hydrogen in 2 and a chlorine atom in compound 6. Scheme II shows a plausible mechanistic pathway for the formation of the derivative 6 starting from aethiopinone (1).

We next turned our attention to the striking similarity of the ^1H and ^{13}C NMR spectra of compound 6 with those previously reported[15] for prionitin, a diterpene isolated from the root of *S. prionitis*, to which structure 12 was attributed on the basis of spectroscopic studies. In fact, these spectra are identical, apart from small differences in the chemical shift values, and the absence in the spectra of compound 6 of the signals corresponding to the methoxyl group of prionitin (12). Consequently, we decided to obtain the C-14 methoxyl derivative of compound 2 by a nucleophilic aromatic substitution reaction on its 14-chloro derivative 6. Unfortunately, several attempts for achieving this transformation were unsuccessful, even when the derivative 6 was fused with sodium methoxide or treated with this reagent in HMPA solution.[23] However, when a methanolic solution of aethiopinone (1) was treated with boron trifluoride etherate at room temperature for 24 h, two compounds (10 and 11) were obtained in 34% and 3% yields, respectively. The major product possessed structure 10, supported by its IR, UV, ^1H and ^{13}C NMR, and mass spectra data (see the Experimental Section) as compared with those of compound 13, a rearranged derivative[24a] of the abietane diterpenoid fuerstione (14), found in *Fuerstia africana* (Labiatae).[24] In particular, the result of the NOE experiment shown in Table III clearly established the

(20) The C-12 epimeric alcohols 4 and 5 were obtained in a 7:1 ratio, respectively. We suppose that the major alcohol (4) is the 12β isomer, because the ring C of compound 3 adopts an envelope conformation in which the C-12 keto function is the flap, in a trans spatial relationship with the C-19 methyl group. In this conformation the β face of the carbonyl group shows a strong steric hindrance with ring B and, consequently, a most favored exo attack of the reducing reagent from the α side can be expected. (See the Dreiding's molecular model of 3.)

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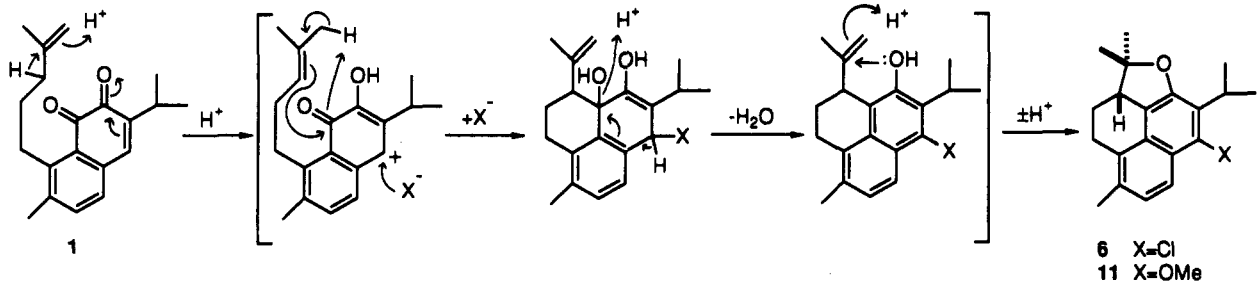
Scheme II



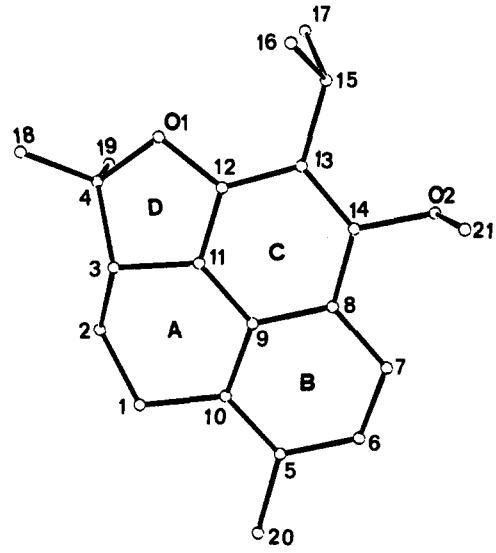


Figure 2. Computer-generated perspective drawing (ORTEP) of one of the enantiomers of racemic prionitin (11). (Hydrogens are omitted for clarity.)

attachment of the methoxyl group to the C-12 position of compound 10.

The other product obtained in the reaction of aethiopinone with $BF_3{\cdot}Et_2O$ in methanol solution (11) showed IR, UV, ^1H and ^{13}C NMR, and mass spectra absolutely identical[25] with those reported for prionitin (see Tables I and II, Experimental Section, and ref 15), although it was devoid of optical activity {$[\alpha]^{18}_D$ 0° (*c* 1.34, $CHCl_3$); prionitin:[15] $[\alpha]_D$ −11.9° (*c* 0.042, MeOH)} because 11 is a racemate. However, in the light of the sure structures of compounds 2 and 6 discussed above, all the spectroscopic data of the racemic compound (Tables I–III and Experimental Section) are in complete agreement with structure 11, whose plausible formation from aethiopinone is outlined in Scheme II. This conclusion was corroborated by the molecular structure obtained for the synthetic samples of compound 11 by a single-crystal X-ray diffraction[26] (see Figure 2).

The need to revise the structure of prionitin was also established through an examination of the heteronuclear multiple bond connectivity (HMBC) spectrum[27] obtained on a sample (1.7 mg) of the racemic material. Using a *J* value of 7 Hz, three bond correlations were observed between the OCH_3 and C-14 and between the isopropyl methyl groups and C-13. Similarly, the aromatic protons H-6 and H-7 showed correlations with C-8 and C-10, and C-5 and C-9, respectively. With these relationships established, the crucial observations were the correlations observed between H_3-20 and C-6, and C-10, and even more importantly, the unambiguous correlations observed between H-15 and the two oxygenated carbons C-12 and C-14 in 11. The latter are key in distinguishing 11 from 12 and in affirming that 11 is indeed the correct structure of prionitin.

Finally, comparison (TLC behavior as well as ^1H and ^{13}C NMR spectral comparison) of natural prionitin and its synthetic racemic form (11) confirmed the identity. From all the above data, it was evident that structure 12 previously assigned to prionitin should be changed to 11.

It is important to note that, from a biosynthetic point of view, phenalene derivatives, such as prionitin (11), must be considered as compounds of natural origin, arising from abietane diterpenes via 4,5-seco-20(10→5)-*abeo*-abietane derivatives like aethiopinone (1), by an enzymatic process which controls the chirality, because natural prionitin[15] shows optical activity, thus excluding its formation as an artefact.

Experimental Section

Melting points were determined in a Kofler apparatus and are uncorrected. Low-resolution mass spectra were obtained at 70 eV (mode EI, solid probe).

Starting material (1, aethiopinone) was available from previous studies.[11b,13]

Compounds 2 and 3 from Aethiopinone (1). H_2SO_4 (80%, 120 mL), cooled at 0 °C, was added to aethiopinone (1, 2 g, without solvent), and the mixture was vigorously stirred at 0 °C for 5 min. Then, the reaction mixture was dropwise added to ice–water (500 mL) under vigorous stirring. After a further 0.5 h, the reaction mixture was extracted with Et_2O (5 × 200 mL). The organic extract was dried (Na_2SO_4), filtered, and evaporated to dryness. The residue (1.85 g) was chromatographed on a silica gel (deactivated with 15% H_2O, w/v) column eluted with *n*-hexane, yielding compound 2 (0.74 g, 39%). Further elution with *n*-hexane–EtOAc (49:1) successively gave compound 3 (255 mg, 14% yield) and starting material (1, 0.5 g, 25%).

To a benzene (200 mL) solution of aethiopinone (1, 2 g) was dropwise added $BF_3{\cdot}Et_2O$ (10 mL) under stirring at rt for 3 h. Then, the reaction mixture was diluted with H_2O (500 mL) and extracted with Et_2O (5 × 150 mL). Workup in the usual manner yielded, after column chromatography, compounds 2 (80 mg, 5.8% yield) and 3 (900 mg, 58% yield).

(3-*rac*)-4,12-Epoxy-3,11-cyclo-4,5-seco-20(10→5)-*abeo*-abieta-5(10),6,8,11,13-pentaene (2): mp 87–88 °C (MeOH); $[\alpha]^{18}_D$ 0° (*c*, 3.1, $CHCl_3$); IR (KBr) 3040, 2970, 2930, 1655, 1605, 1525, 1425, 1370, 1250, 1100, 875, 820, 780, 770 cm^{-1}; UV (MeOH) nm (log ϵ) 219 sh (4.45), 241 (4.78), 243 (4.79), 280 (3.59), 291 (3.73),

(25) In accordance with the SFORD spectrum of compound 11, the carbon atom resonances at δ 47.70 d and 62.87 q must be assigned to the C-3 methine and the methoxyl carbons, respectively. These assignments are reversed in ref 15, where the multiplicity of the carbons was established by the APT spectrum.

(26) In the crystalline state compound 11 possesses its rings B and C (Figure 2) almost planar (maximum deviations of 0.04 Å). Rings A and D present the same conformations that in compound 2 (see footnote 16) and the dihedral angles between rings A/B, A/C, A/D, B/C, and C/D are 9°, 10°, 11°, 3°, and 11°, respectively, identical with those found[16] in 2, except for the angles between rings A/B and A/C. Moreover, the deviations from the plane of the C-18 (0.26 Å) and C-19 (1.94 Å) methyl groups are identical in both compounds (2 and 11).

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303 (3.67), 326 (3.39), 340 (3.52); ^{1}H NMR see Table I; ^{13}C NMR, see Table II; MS m/z (rel intensity) 280 (M^+, 96), 265 (11), 237 (100), 207 (11), 179 (11), 165 (11). Anal. Calcd for $C_{20}H_{24}O$: C, 85.66; H, 8.63. Found: C, 85.40; H, 8.48.

12-Keto-11-nor derivative 3: thick oil; $[\alpha]^{19}_D$ 0° (*c* 4.7, $CHCl_3$); IR (NaCl) 3050, 2960, 2930, 1655 (ketone), 1625, 1590, 1465, 1260, 995, 930, 835, 810 cm^{-1}; UV (MeOH) nm (log ϵ) 209 (4.37), 218 sh (3.90), 238 (3.89), 243 (3.89), 317 (4.16); ^{1}H NMR, see Table I; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 27.75 t (C-1), 18.28 t (C-2), 40.05 t (C-3), 33.79 s (C-4), 132.93 d (C-6), 127.72 d (C-7), 199.08 s (C-12), 140.16 d (C-14), 28.22 d (C-15), 22.84 q (C-16), 22.05 q (C-17), 56.39 t (C-18), 20.99 q (C-19), 20.55 q (C-20), quaternary sp^2 carbons at δ 132.37, 134.64, 139.12, 143.77, and 144.07 (C-5, 8–10, and 13, without assignment); MS m/z (rel intensity) 268 (M^+, 100), 253 (30), 225 (27), 198 (26), 183 (34), 165 (21), 155 (18), 43 (18). Anal. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01. Found: C, 84.89; H, 9.17.

Sodium Borohydride Reduction of Compound 3: Alcohols 4 and 5. To a solution of compound **3** (200 mg) in MeOH (20 mL) was added an excess of $NaBH_4$, and the reaction mixture stirred at rt for 4 h. Workup in the usual way gave a residue (190 mg), which was subjected to column chromatography [silica gel, *n*-hexane–EtOAc (49:1) as eluent] giving compounds **4** (165 mg, less polar constituent, 82% yield) and **5** (23 mg, 11.7% yield).[20]

12β-Hydroxy-11-nor derivative 4: thick oil; IR (NaCl) 3450 (OH), 3050, 2930, 1660, 1645, 1590, 1465, 1380, 1070, 1045, 875, 810 cm^{-1}; UV (MeOH) nm (log ϵ) 208 (4.34), 245 sh (3.89), 264 (4.01), 295 (3.61); ^{1}H NMR, see Table I; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 28.50 t (C-1), 18.63 t (C-2), 41.77 t (C-3), 36.31 s (C-4), 124.56 d (C-6), 126.80 d (C-7), 71.06 d (C-12), 128.98 d (C-14), 30.43 d (C-15), 22.82 q (C-16), 22.75 q (C-17), 53.46 t (C-18), 26.67 q (C-19), 20.20 q (C-20), quaternary sp^2 carbons at δ 134.23, 134.88, 135.10, 143.22, and 147.83 (C-5, 8–10, and 13, without assignment); MS m/z (rel intensity) 270 (M^+, 12), 255 (6), 252 (1), 227 (100), 199 (29), 171 (11), 85 (20), 83 (31). Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.51; H, 9.42.

12α-Hydroxy-11-nor derivative 5: thick oil; IR (NaCl) 3340 (OH), 3050, 2930, 1660, 1590, 1465, 1385, 1035, 1015, 1000, 970, 945, 890, 810 cm^{-1}; UV (MeOH) nm (log ϵ) 215 (4.30), 260 sh (4.17), 267 (4.21), 277 (4.08); ^{1}H NMR, see Table I; MS m/z (rel intensity) 270 (M^+, 12), 255 (4), 252 (24), 237 (35), 227 (100), 199 (25), 171 (12), 165 (20), 57 (43). Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H, 9.69. Found: C, 84.43; H, 9.73.

Reaction of Aethiopinone (1) with Hydrochloric Acid: Compounds 2, 6, 7, 8 (Salvipisone[11b]), and 9 (Salvilenone[14]). To a solution of aethiopinone (1, 700 mg) in dioxane (150 mL) was added concentrated HCl acid (7 mL), and the mixture stirred at rt for 3 h. Then, the reaction mixture was diluted with H_2O (200 mL) and extracted with Et_2O (5 × 100 mL). The extract was dried (Na_2SO_4) and evaporated to dryness giving a residue (625 mg), which was chromatographed on a silica gel column. Elution with *n*-hexane gave **6** (220 mg, 29.5% yield, less polar constituent) and **2** (31 mg, 4% yield). Further elution with *n*-hexane–EtOAc (95:5) successively yielded a 2:1 mixture of **7** and **8** (58 mg, 7.9% yield) and **9** (21 mg, 3% yield).

(3-*rac*)-4,12-Epoxy-14-chloro-3,11-cyclo-4,5-seco-20(10→5)-*abeo*-abieta-5(10),6,8,11,13-pentaene (6): mp 130–132 °C (MeOH); $[\alpha]^{18}_D$ 0° (*c* 2.6, $CHCl_3$); IR (KBr) 3060, 2965, 2940, 1640, 1620, 1600, 1575, 1510, 1460, 1400, 1370, 1250, 1050, 855, 835, 785, 775 cm^{-1}; UV (MeOH) nm (log ϵ) 221 (4.39), 241 (4.57), 297 (3.71), 310 (3.72), 333 (3.48), 347 (3.60); ^{1}H NMR, see Table I; ^{13}C NMR, see Table II; MS m/z (rel intensity) 316 and 314 (M^+, 33 and 100, respectively), 273 (35), 271 (80), 221 (21), 205 (21), 189 (18), 165 (15), 43 (18). Anal. Calcd for $C_{20}H_{23}OCl$: C, 76.29; H, 7.36; Cl, 11.26. Found: C, 76.58; H, 7.15; Cl, 11.35.

12-Hydroxy-4,5-seco-20(10→5)-*abeo*-abieta-3,5(10),6,8,12-pentaene-11,14-dione (7) and Salvipisone[11b] (8). Several attempts at isolating compounds **7** and **8** were unsuccessful. The ^{1}H and ^{13}C NMR spectra of this mixture revealed that it was constituted by salvipisone[11b] (**8**) and its Δ^3 isomer (**7**) in a 1:2 ratio, respectively. These spectra showed all the signals previously reported[11b] for salvipisone and those corresponding to compound **7**, which were identical to those of **8**, except for the signals due to the 2-methyl-2-penten-5-yl side chain: δ_H 5.28 br t, J = 7.3 Hz (H-3), 1.72 d and 1.60 d, J = 0.9 Hz (Me-18 and Me-19); δ_C 27.80 t (C-1), 30.16 t (C-2), 123.72 d (C-3), 132.43 s (C-4), 25.68 q (C-18), 17.50 q (C-19). The MS of the mixture showed m/z (rel intensity) 312 (M^+, 20), 294 (12), 244 (82), 229 (17), 128 (15), 69 (100), 41 (32). $C_{20}H_{24}O_3$: M_r 312.

Salvilenone[14] (9): mp 140–141 °C (*n*-hexane); IR (KBr), UV (MeOH), ^{1}H NMR (300 MHz, $CDCl_3$), and MS identical with those previously reported for the synthetic[14c,d] and natural [14a,b] product (mp 141 °C).[14a–c]

Compounds 10 and 11 [*rac*-Prionitin[15]] from Aethiopinone (1). To a solution of aethiopinone (1, 2 g) in MeOH (150 mL) was added $BF_3{\cdot}Et_2O$ (10 mL), and the mixture was stirred at rt for 24 h. The reaction mixture was diluted with H_2O (500 mL) and extracted with Et_2O (6 × 100 mL). The extract was dried (Na_2SO_4) and evaporated to dryness. The residue (1.3 g) was subjected to column chromatography (silica gel deactivated with 15% H_2O, w/v, *n*-hexane as eluent) giving compounds **10** (725 mg, 34%, less polar constituent) and **11** (64 mg, after crystallization from MeOH, 3% yield).

4,11-Epoxy-12-methoxy-4,5-seco-20(10→5)-*abeo*-abieta-5(10),6,8,11,13-pentaene (10): thick oil; IR (NaCl) 3050, 2970, 1605, 1565, 1500, 1460, 1410, 1360, 1260, 1120, 1020, 945, 880, 825, 790 cm^{-1}; UV (MeOH) nm (log ϵ) 219 sh (4.73), 238 (5.19), 290 sh (4.08), 297 (4.10); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 br d, J = 8.3 Hz (H-7), 7.34 br s (H-14), 7.14 br d, J = 8.3 Hz (H-6), 3.96 s (OMe), 3.35 septet d, J_1 = 6.9 Hz, J_2 = 0.7 Hz (H-15), 2.43 br s (Me-20), 1.60 s and 1.13 s (Me-18 and Me-19), 1.29 d and 1.28 d, J = 6.9 Hz (Me-16 and Me-17); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 26.93 t (C-1), 23.02 t (C-2), 33.50 t (C-3), 83.96 s (C-4), 128.00 d (C-6), 125.66 d (C-7), 151.69 s (C-12), 120.45 d (C-14), 27.76 d (C-15), 23.46 q (C-16), 23.08 q (C-17), 26.37 q (C-18 or 19), 26.92 q (C-19 or 18), 19.95 q (C-20), 60.50 q (OMe), quaternary sp^2 carbons at δ 142.78, 140.63, 132.26, 131.36, 130.38, and 126.41 (C-5, 8–11, and 13, without assignment); MS m/z (rel intensity) 312 (M^+, 21), 243 (100), 215 (25), 185 (6), 68 (16). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.65; H, 9.09.

***rac*-Prionitin (11)**: mp 102–104 °C (MeOH); $[\alpha]^{18}_D$ 0° (*c* 1.02, $CHCl_3$); IR (KBr), UV (MeOH), ^{1}H and ^{13}C NMR (see Tables I and II, respectively), and MS superposable with those of natural (–)-prionitin[15] [mp 98–100 °C; $[\alpha]_D$ –11.9° (*c* 0.042, MeOH)]. Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.29, H, 8.39. Comparison (^{1}H and ^{13}C NMR, TLC) between compound **11** and natural prionitin[15] confirmed the identity.

Spectral Analysis of *rac*-Prionitin. A sample (1.7 mg) of **11** was dissolved in $CDCl_3$ (0.3 mL, 99.8% D) in a 5-mm NMR tube. Some NMR spectra were recorded at 25 °C on a GEΩ 500 spectrometer operating in the Fourier transform mode at 500.12 MHz for protons and 125.76 MHz for carbons, respectively. Chemical shifts were determined relative to TMS employing the residual solvent peak as a reference (7.26 ppm for proton and 77 ppm for carbon). All phase-sensitive 2D experiments were carried out in the hypercomplex mode.

The ^{1}H-detected heteronuclear multiple bond ^{1}H–^{13}C correlation (HMBC) spectrum[27] was obtained using GE HMBCF3 pulse sequence. The data were collected in 1k × 512 data points, using a data acquisition of 64 scan × 512 increments in the t_1. The spectral widths of 4400 and 15600 Hz were employed in the F_2 (for ^{1}H) and F_1 (for ^{13}C) domains, respectively. The acquisition time was 13 h. Double Fourier transformation after zero filling yielded a data matrix of 1k × 1k with a resolution of 4.3 Hz in proton and 15.2 Hz in carbon. Sine bell windows shifted by 90° and 90° were applied for proton and carbon dimension, respectively, prior to Fourier transformation.

X-ray Structure Determination of Compounds 2 and 11. The crystal samples of both compounds are colorless flattened prisms. Table IV (see the supplementary material) summarizes the crystal data and data collection characteristics for compounds **2** and **11**. The data were corrected for Lorentz and polarization effects, but not absorption correction was applied. The structures were solved by direct methods, using MULTAN[28] and DIRDIF.[29] All

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non-hydrogen atoms were refined by full-matrix least squares with anisotropic temperature factors; H atoms were found from difference Fourier maps and not refined. The final difference maps showed maximum positive peaks of 0.53 e $Å^{-3}$ and $(\Delta/\sigma) < 0.80$ for compound 2, and 0.20 e $Å^{-3}$ and $(\Delta/\sigma) < 0.03$ for compound 11. For the calculations, a VAX 6410 computer and the "X-Ray 76 System"[30] program were used. Scattering factors were taken from the literature.[31]

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Supplementary Material Available: Crystal data and data collection characteristics (Table IV), tables of atomic coordinates, thermal parameters, bond lengths, bond angles, and torsion angles for compounds 2 and 11 (13 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.

Stereospecific Synthesis of a Novel Allenic Cyclohexanoid Epoxide from the Fungus *Eutypa lata*

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The stereospecific synthesis of the novel allenic cyclohexanoid epoxide **13** is reported. Key steps include Diels–Alder reaction between a 1,4-dioxygenatedbuta-1,3-diene **1** and a ketene equivalent **2** and the coupling of a mixed isopropenyl cuprate with propagylic sulfinate **10**.

Recently we reported the isolation of a novel allenic epoxycyclohexane **13**[1] from the fungus *Eutypa lata*, the pathogen responsible for the vineyard dieback observed in recent years in Switzerland and France.[2] The structure of **13** was elucidated by classic spectroscopic techniques and confirmed by an X-ray study. Due to the novel structure of **13** and the small quantity isolated, we thought it interesting to carry out its total synthesis, eventually with a view to assign its absolute configuration by carrying out the synthesis enantioselectively.

Compound **13** shows a large structural similarity to the recently isolated asperpentyn[3] and contains the same epoxy-1,4-diol system found in eupenoxide.[4] Our retrosynthetic analysis suggested a ketone of type **7** as a key intermediate, which we thought would be obtainable by a Diels–Alder reaction between a 1,4-dioxygenated butadiene and a ketene equivalent.[5] Most Diels–Alder reactions between dienes and ketene equivalents have been used to form bicyclic systems where the questions of double-bond migration and epimerization of the functionality α to the newly formed ketone have not posed problems. In our case, we needed to choose from among the wide range of available ketene equivalents one which would be transformed under conditions mild enough not to cause these problems. For the diene we chose the bis(silyloxy) diene **1** that Duke and Rickards used in their synthesis of eupenoxide.[4]

Results and Discussion

Heating the diene **1** with 1-acetoxy-1-cyanoethylene (**2**) in a sealed tube a 110 °C for 4 days gave the required cycloadducts **3a** and **3b** (ratio by NMR ca. 8:1). Recrystallization gave **3a** in 50–65% yield. In most cases both unreacted diene and dieneophile could be recovered and reused. The double bond of the cycloadduct proved unreactive to peracid under standard conditions (CH_2Cl_2, rt), probably due to the presence of two allylic oxygen functions, but heating **3a** under reflux in dichloroethane with *m*-CPBA in the presence of a radical inhibitor[6] gave a single epoxide **4** in quantitative yield. We were relying on the directing influence of the two bulky TBDMS groups to give the epoxidation on the rear face of the molecule. That the epoxidation had in fact taken place in the desired manner was proven by the following NMR experiments. A NOE difference experiment based on the irradiation of the signal centered at δ 1.75 led to a 7% enhancement of the signal at δ 4.12 (2-H) and an 8% enhancement of the triplet at δ 4.27 (5-H) leading its assignment as H-4endo. A second experiment irradiating the signal at δ 2.62 led to a 2% enhancement of the triplet at δ 4.27 (5-H) leading to its assignment as H-4exo. Irradiation of the signal at δ 3.21 (6-H) revealed a W-type coupling (J = 0.7 Hz) with the signal at δ 2.62 (H-4exo). This information taken with the very small coupling constants $J_{1,2}$ (0.5 Hz) and $J_{5,6}$ (1.3 Hz) show that epoxidation had occurred on the required face of the molecule. Further NMR experiments were

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