spectrum, m/z (relative intensity) 418 (M^+, 4.1), 376 (2), 228 (17), 131 (100), 105 (49).

Intramolecular Diels–Alder Reaction of 3f. Synthesis of Zeylena Acetate (1b). A solution of **3f** (120 mg, 0.29 mmol) in toluene (2.5 mL) was heated in a sealed tube at 70 °C for 4 days. The mixture was concentrated, and the residue was chromatographed on a silica gel column (6 g) with 2:5 ethyl acetate–hexane to give 113 mg (94%) of zeylena acetate (**1b**) as an amorphous solid: $[\alpha]^{21}_D$ −71° (*c* 1.30, $CHCl_3$). The ^1H NMR spectral data were in good accord with those described for an authentic sample.[1] Anal. Calcd for $C_{25}H_{22}O_6$: C, 71.77; H, 5.26. Found: C, 71.83; H, 5.41.

O-Deacetylation of 1b. A mixture of **1b** (110 mg, 0.26 mmol), *p*-toluenesulfonic acid (80 mg, 0.42 mmol), dichloromethane (2 mL), and methanol (12 mL) was stirred at ambient temperature for 3 days. TLC showed the disappearance of **1b** (R_f 0.54) and the formation of one major (R_f 0.34) and two minor components (R_f 0.42 and 0.07) in 1:1 ethyl acetate–hexane. The mixture was neutralized with an excess of sodium hydrogen carbonate and filtered. The filtrate was concentrated, and the residue was fractionated on a silica gel column (5 g) with 1:2 ethyl acetate–hexane as eluant to give first 10 mg (8%) of **methyl (1*S*)-*exo*-5-acetoxy-4-[(benzoyloxy)methyl]-*endo*-6-hydroxy-*exo*-3-phenylbicyclo[2.2.2]oct-8-ene-*endo*-2-carboxyalte (4a)** as a syrup, $[\alpha]^{20}_D$ −68° (*c* 2.0, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.10–7.98 (m, 2, benzoyloxy phenyl) 7.60–7.46 (m, 3, benzoyloxy phenyl), 7.19 (br s, 5, C-phenyl), 6.61 (dd, 1, $J_{1,7}$ = 6.8, $J_{7,8}$ = 8.3 Hz, C_7 H), 5.95 (d, 1, C_8 H), 4.63 (s, 1, C_5 H), 4.50 (d, 1, CH_2OBz), 3.76 (d, 1, J_{gem} = 11.3 Hz, CH_2OBz), 3.88 (d, 1, $J_{2,3}$ = 6.8 Hz, C_3 H), 3.67 (s, 3, ester methyl), 3.60–3.38 (m, 2, C_1 H, C_6 H), 3.10 (br s, 1, OH), 2.67 (dd, 1, $J_{1,2}$ = 2.6 Hz, C_2H), 1.98 (s, 3, OAc); mass spectrum, m/z (relative intensity) 418 (M^+ − 32) (8.0), 376 (4.2), 228 (20), 167 (19), 131 (100), 105 (90). The fraction eluted third was 10 mg (9%) of the dihydroxy ester (**4b**) as a syrup; mass spectrum, m/z (relative intensity) 376 (M^+ − 32) (4.2), 209 (31), 167 (70), 131 (48), 105 (100). The fraction eluted second was 54 mg (54%) of **1a** as a white solid, which was identified with the compound obtained before.

Both compounds **4a** and **4b** were convertible by treatment with acetic anhydride in pyridine into the diacetate (**4c**) quantitatively: syrup, $[\alpha]^{20}_D$ −82° (*c* 1.01, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.11–8.01 (2, m, benzoyloxy phenyl), 7.57–7.48 (m, 3, benzoyloxy phenyl), 7.22 (br s, 5, C-phenyl), 6.67 (dd, 1, $J_{1,7}$ = 7.5 $J_{7,8}$ = 7.8 Hz, C_7 H), 6.05 (d, 1, C_8 H), 5.16 (s, 1, C_5 H), 4.71 (d, 1, $J_{1,6}$ = 3.2 Hz, C_6, H), 4.41 (d, 1, CH_2OBz), 3.75 (d, 1, J_{gem} = 11.5 Hz, CH_2OBz), 3.77 (d, 1, $J_{2,3}$ = 7.5 Hz, C_3, H), 3.67 (s, 3, ester methyl), 3.60 (br m, 1, C_1 H), 2.69 (d, 1, C_2 H), 2.04 (s, 3, OAc), 1.95 (s, 3, 2 OAc); mass spectrum m/z (relative intensity) 492 (M^+, 1.2), 461 (4.5), 419 (10), 330 (12), 270 (9), 228 (75), 105 (100).

(1*R*)-6-[(Benzoyloxy)methyl]-*exo*-10-[(*E*)-cinnamoyloxy]-*exo*-5-phenyl-2-oxatricyclo[4.3.1.0^{4,9}]dec-7-en-3-one [Zeylena (*E*)-Cinnamate] (1c). A solution of **3d** (159 mg, 0.31 mmol) in toluene (4 mL) was heated in a sealed tube at 70 °C for 4 days. The mixture was concentrated, and the residue was purified on a silica gel column (7 g) with 2:3 ethyl acetate–hexane to give 127 mg (80%) of **1c** as an amorphous solid: $[\alpha]^{17}_D$ +26.8° (*c* 1.36, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.10–8.00 (m, 2, phenyl), 7.61–6.97 (m, 13, phenyl), 7.63 (d, 1, *J* = 15.5 Hz, COCH=C*H*Ph), 6.56 (dd, 1, $J_{7,8}$ = 8, $J_{8,9}$ = 6.5 Hz, C_8 H), 6.31 (d, 1, COC*H*=CHPh), 6.04 (d, 1, C_7 H), 5.36 (s, 1, C_{10} H), 4.47 (d, 1, CH_2OBz), 4.01 (d, 1, (J_{gem} = 11.5 Hz, CH_2OBz), 4.42 (dd, 1, $J_{1,4}$ = 1, $J_{1,9}$ = 5 Hz, C_1, H), 3.73 (br q, 1, C_9 H), 3.45 (d, 1, $J_{4,5}$ = 2 Hz, C_5 H), 2.83 (ddd, 1, $J_{4,9}$ = 4.5 Hz, C_4 H); mass spectrum, m/z (relative intensity) 506 (M^+, 15), 356 (6.3), 325 (7.8), 131 (100), 105 (34).

(1*R*)-9-[(Benzoyloxy)methyl]-*exo*-10-hydroxy-*exo*-5-phenyl-2-oxatricyclo[4.3.1.0^{4,9}]dec-7-en-3-one (5a). A solution of **3b** (43 mg, 0.11 mmol) in toluene (2 mL) was heated in a sealed tube at 100 °C for 3 days. The mixture was concentrated, and the product was purified on a silica gel column (2 g) with 1:3 ethyl acetate–hexane to give 28 mg (65%) of **5a** as a colorless syrup: $[\alpha]^{21}_D$ +134° (*c* 0.41, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.12–8.02 (m, 2, 7.67–7.00 (m, 8, phenyl), 6.33–6.27 (m, 2, C_7 H, C_8 H), 4.70 (s, 2, CH_2OBz), 4.23 (s, 1, C_1 H), 4.13 (d, 1, $J_{6,10}$ = 3 Hz, C_{10} H), 3.37–3.23 (m, 2, C_5H, C_6 H), 2.73 (s, 1, C_4 H), 2.15 (br s, 1, OH); mass spectrum, m/z (relative intensity) 376 (M^+, 1.6), 167 (50), 131 (30), 105 (100).

Compound **5a** was converted in the usual way into the acetate (**5b**) in quantitative yield: syrup; $[\alpha]^{24}_D$ +57° (*c* 1.25, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 8.12–8.02 (m, 2, phenyl, 7.67–7.00 (m, 8, phenyl), 6.25–6.18 (m, 2, C_7 H, C_8 H), 5.08 (d, 1, $J_{6,10}$ = 3 Hz, C_{10} H), 4.70 (s, 2, CH_2OBz), 4.28 (s, 1, C_1 H), 347–3.33 (m, 2, C_5 H, C_6 H), 2.77 (s, 1, C_4 H), 2.00 (s, 3, OAc); mass spectrum, m/z (relative intensity) 418 (M^+, 1.6), 358 (3.1), 328 (5.1), 236 (24), 223 (30), 167 (24), 131 (58), 105 (100).

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Total Synthesis of (±)-Perezone

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A total synthesis of (±)-perezone (1) proceeding in 18% overall yield is described. The sequence starts from 5-bromopiperonal (2) and proceeds by way of 7, making use of an AgO-assisted oxidative dealkylation step to unmask the hydroxy-*p*-quinone-type system characteristic of 1.

Perezone (1), a well-known sesquiterpene quinone, was the first isolated from *Pereziae* sp. in 1852.[1] This rather simple molecule has been the subject of many scientific endeavors,[2] culminating in 1965 in its only reported[3] synthesis which, starting from 3,5-dimethoxytoluene, resulted in a very low overall yield.

In continuation of our research program dealing with the chemistry of sesquiterpene quinones[4–7] we now report

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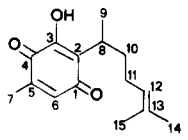
Table I. ^{13}C NMR Chemical Shifts of Intermediates 2–7 and (±)-Perezone (1)[a]

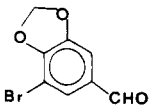
C atom or substituent	2	3	4	5	7	1
C-1	132.5	150.8	155.3	154.7	152.7	187.1
C-2	106.0	97.5	96.8	94.6	116.2	124.3
C-3	148.6	148.3	148.2	147.4	145.3	150.9
C-4	150.9	140.0	139.9	139.7	139.6	184.0
C-5	100.6	99.9	99.7	118.5	114.9	140.3
C-6	130.6	110.1	107.8	106.8	105.1	135.6
C-7				14.8	14.7	14.6
C-8					29.8	29.3
C-9					19.4	18.2
C-10					35.3	34.1
C-11					26.6	26.6
C-12					124.8	124.3
C-13					130.7	131.1
C-14					17.5	17.5
C-15					25.6	25.6
OCH_3			55.9	55.8	56.3	
OCH_2O	102.4	101.3	101.2	100.6	100.1	
CHO	188.6					

[a] Numbering of atoms is that normally followed for sesquiterpene quinones, see 1. Chemical shifts are given in parts per million down from internal tetramethylsilane (Me_4Si). All spectra were recorded in deuteriochloroform ($CDCl_3$) solutions.

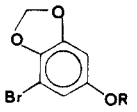
Scheme I



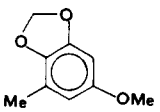
1



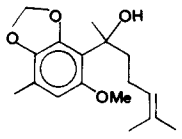
2



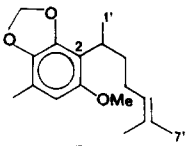
3, R = H
4, R = Me



5



6



7

an efficient total synthesis of (±)-perezone (1), based on utilization of the protected 5-methylsesamol derivative 5 (Scheme I) as a conveniently masked hydroxytoluquinoid synthon.[8] The eight-carbon side chain characteristic of these compounds can be derived from commercially available 6-methyl-5-hepten-2-one.[9]

Thus, reaction of 5-bromovanillin under Lange's conditions[10] furnished 5-bromo-3,4-dihydroxybenzaldehyde in 96% yield. Next, methylenation[11] via a modification of Cornforth's procedure[12] afforded 5-bromopiperonal (2) in 53% yield. The overall mildness of these modifications is a significant improvement over the method reported earlier.[13] All relevant intermediates (i.e., 2–7) were adequately characterized by ^{13}C NMR spectroscopy and the corresponding chemical shifts are collected in Table I.

Further transformation of 2 into the required phenolic derivative 3 in 93% yield was carried out by means of a Baeyer–Villiger oxidation[14] followed by acid hydrolysis of the resulting formate ester. Methylation under standard conditions afforded 5-bromo-3,4-(methylenedioxy)anisole (4), in 92% yield.

Reaction of bromo ether 4 with methyllithium[15] in the presence of excess iodomethane then gave a 90% yield of 5-methyl-3,4-(methylenedioxy)anisole (5).

Introduction, in a regiospecific manner, of an eight-carbon alkenyl side chain, was accomplished via reaction of the 2-lithio derivative of 5, prepared in ethyl ether solution,[16] with 6-methyl-5-hepten-2-one. This gave a 52% yield of the desired unstable carbinol 6.

We have recently found[6] that for the reductive removal of benzylic tertiary hydroxyls in electron-rich systems it is best to use the low-temperature boron trifluoride catalyzed reduction with triethylsilane.[8a] In this manner 7 was obtained in 80% yield from alcohol 6. The resulting racemic sample was identical, except for the optical rotation, with an authentic sample prepared from leucoperezone triacetate by consecutive reductive hydrolysis, methylenation, and O-methylation.[17]

(7) For a previous paper dealing with the total synthesis of (±)-curcuquinone, see: Sánchez, I. H.; Lemini, C.; Joseph-Nathan, P. *J. Org. Chem.* **1981**, *46*, 4666–4667.

(8) For the use of sesamol or other trihydroxybenzene derivatives as hydroxy-*p*-quinoid synthons, see: (a) Kraus, G. A.; Neuenschwander, K. *Synth. Commun.* **1980**, *10*, 9–16. (b) Danishefsky, S.; Berman, E.; Cvetovich, R.; Minamikawa, J. *Tetrahedron Lett.* **1980**, *21*, 4819–4822. See also ref 6.

(9) This rather useful side chain precursor can also be readily prepared via base-catalyzed retroaldolization of citral, see: Cortés, E.; Walls, F. *Bol. Inst. Quim. Univ. Nac. Auton. Mex.* **1965**, *17*, 34–41.

(10) Lange, R. G. *J. Org. Chem.* **1962**, *27*, 2037–2039.

(11) There are several methods reported for the methylenation of substituted catechol derivatives, inter alia, see: (a) Sonn, A.; Benirschke, F. *Ber.* **1921**, *54*, 1733–1735. (b) Ghosh, B. N. *J. Chem. Soc.* **1915**, *107*, 1588–1605. (c) Perkin, W. H.; Trikojus, V. M. *J. Chem. Soc.* **1926**, 2925–2933. (d) Baker, W. *Ibid.* **1931**, 1765–1771. (e) Campbell, K. N.; Hopper, P. F.; Campbell, B. K. *J. Org. Chem.* **1951**, *16*, 1736–1741. (f) Bashall, A. P.; Collins, J. F. *Tetrahedron Lett.* **1975**, 3489–3490.

(12) Bonthrone, W.; Cornforth, J. W. *J. Chem. Soc. C* **1969**, 1202–1204.

(13) Tomita, M.; Aoyagi, Y. *Chem. Pharm. Bull.* **1968**, *16*, 523–526.

(14) Godfrey, I. M.; Sargent, M. V. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1353–1354.

(15) For a general review, see: (a) Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 339–366. See also: (b) Whitesides, G. M.; Fischer, W. F., Jr.; San Filippo, J., Jr.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* **1969**, *91*, 4871–4882. (c) Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911–3912.

(16) Inter alia, see: (a) Kraus, G. A.; Pezzanite, J. O. *J. Org. Chem.* **1979**, *44*, 2480–2482. (b) Ronald, R. C.; Lansinger, J. M.; Lillie, T. S.; Wheeler, C. J. *J. Org. Chem.* **1982**, *47*, 2541–2549. (c) Ronald, R. C.; Winkle, M. R. *Tetrahedron* **1983**, *39*, 2031–2042.

Use of the conditions recently developed for our curcuquinone synthesis,[7] namely, treatment of **7** with freshly prepared[18] silver(II) oxide in dioxane containing a small amount of 7 N nitric acid, furnished (±)-perezone (**1**), mp 72–73 °C (hexane) (lit.[3] mp 102–103 °C for natural (–)-perezone), in 56% yield. The synthetic sample was identical by spectroscopic and chromatographic comparison with authentic (–)-perezone isolated from *P. cuernavacana*.[17] Thus, the overall synthetic sequence proceeds in 18% yield from 5-bromopiperonal (**2**).

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane (Me_4Si). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; sex., sextet; m, multiplet; br, broad signal. Coupling constants (J) are given in hertz (Hz). All yields reported refer to isolated materials, homogeneous by TLC and NMR spectroscopy.

5-Bromo-3,4-(methylenedioxy)phenol (3). *m*-Chloroperoxybenzoic acid (11.3 g, 0.065 mmol) was added in one portion to a magnetically stirred solution of aldehyde **2** (5 g, 0.021 mmol) in dry chloroform (200 mL). After being heated to reflux for 90 min, the reaction mixture was allowed to cool down to room temperature, transferred to a separatory funnel, and washed with saturated sodium sulfite solution (2 × 100 mL), sodium bicarbonate solution (100 mL), and water (100 mL). The extract was dried (Na_2SO_4) and evaporated to dryness. The resulting oily residue was taken up in methanol (100 mL) and diluted with 6 N hydrochloric acid (100 mL). The reaction mixture was stirred at room temperature for 1 h, diluted with water (100 mL), concentrated under vacuum to approximately half-volume, and thoroughly extracted with chloroform (3 × 150 mL). The extracts were washed ($NaHCO_3$, H_2O, brine), dried (Na_2SO_4), and evaporated to a solid residue. Purification by column chromatography (SiO_2, 90:10 hexane–EtOAc) afforded **3** (4.4 g, 93%) as a colorless solid: mp 95–96 °C ($CHCl_3$–hexane); IR (KBr) 3400–3200, 930, 610 cm^{-1}; ^1H NMR δ 6.42 (d, J = 2.5 Hz, Ar H_6), 6.32 (d, J = 2.5 Hz, Ar H_2), 5.95 (s, OCH_2O), 4.84 (s, Ar OH); ^{13}C NMR, see Table I; MS (EI), m/e (relative intensity) ($C_7H_5BrO_3$ requires 216/218) 218 (100), 217 (72), 216 (97), 215 (64), 187 (5), 185 (4), 161 (15), 159 (16), 131 (3), 129 (2), 50 (21). Anal. ($C_7H_5BrO_3$) C, H.

5-Bromo-3,4-(methylenedioxy)anisole (4). Anhydrous potassium carbonate (15.92 g, 0.115 mol) was added to a solution of phenol **3** (5 g, 0.023 mol) and dimethyl sulfate (5.46 mL, 0.0575 mol) in dry acetone (200 mL). After being stirred for 5 h at room temperature, the reaction mixture was filtered, concentrated to a small volume (40–50 mL), diluted with water (125 mL), and exhaustively extracted with chloroform. The combined extracts were washed (H_2O, brine), dried (Na_2SO_4), and evaporated. The oily residue was purified by column chromatography (SiO_2, 95:5 hexane–EtOAc) to yield **4** (4.92 g, 93%) as colorless crystals: mp 48–49 °C ($CHCl_3$–hexane); IR (KBr) 2830, 925, 650 cm^{-1}; ^1H NMR δ 6.43 (d, J = 2.5 Hz, Ar H_6), 6.37 (d, J = 2.5 Hz, Ar H_2), 5.95 (s, OCH_2O), 3.73 (s, OCH_3); ^{13}C NMR, see Table I; MS (EI), m/e (relative intensity) ($C_8H_7BrO_3$ requires 230/232) 232 (98), 230 (100), 217 (72), 215 (72), 187 (27), 185 (25), 159 (19), 157 (21), 131 (11), 129 (9), 50 (7). Anal. ($C_8H_7BrO_3$) C, H.

5-Methyl-3,4-(methylenedioxy)anisole (5). Methyllithium (10.6 mL of a 1.5 M solution in ethyl ether, 0.016 mol) was slowly added to a cold (0 °C) solution of **4** (2.31 g, 0.01 mol) in dry ethyl ether (25 mL). After the mixture was stirred for 20 min under nitrogen atmosphere, iodomethane (2.74 mL, 0.044 mol) was added and the resulting yellowish suspension further stirred for 60 min. The reaction mixture was first quenched by the dropwise addition of cold saturated ammonium chloride solution (10 mL) and water (15 mL) and then thoroughly extracted with EtOAc. The extract was washed (H_2O, brine), dried (Na_2SO_4), and evaporated. The oily residue was purified by column chromatography (SiO_2, 95:5 hexane–EtOAc) to furnish **5** (1.5 g, 90%) as a colorless oil: bp 71–76 °C (3–4 mm); IR (neat) 2960, 2850, 920 cm^{-1}; ^1H NMR δ 6.31 (d, J = 2.5 Hz, Ar H_6), 6.13 (d, J = 2.5 Hz, Ar H_6), 5.86 (s, OCH_2O), 3.72 (s, OCH_2), 2.20 (s, CH_3); ^{13}C NMR, see Table I; MS (EI), m/e (relative intensity) ($C_9H_{10}O_3$ requires 166) 166 (80), 151 (100), 121 (43), 93 (43), 65 (18), 53 (19), 50 (10).

(±)-2-(6′-Methyl-5′-hepten-2′-yl)-5-methyl-3,4-(methylenedioxy)anisole (7). (a) Coupling Step. *n*-Butyllithium (2.65 mL of a 1.7 M solution in hexane, 4.518 mmol) was added to a cold (0 °C) solution of **5** (500 mg, 3.012 mmol) in dry ethyl ether (10 mL). The reaction mixture was stirred at 0 °C for 10 min and then at room temperature for 24 h. The mixture was cooled again to 0 °C and 6-methyl-5-hepten-2-one (0.71 mL, 4.819 mmol) added dropwise over 10 min. After 30 min of being stirred, the reaction was quenched by careful addition of saturated NH_4Cl solution (10 mL), diluted with H_2O (10 mL), and extracted with EtOAc (3 × 50 mL). The combined extracts were washed (H_2O, brine), dried (Na_2SO_4), and evaporated. The oily residue was quickly purified by column chromatography (SiO_2, 90:10 hexane–EtOAc) to yield **6** (300 mg, 52%) as a pale yellow oil and recovered **12** (170 mg).

(b) Reductive Deoxygenation Step. A solution of **6** (292 mg, 1.0 mmol) and triethylsilane (0.192 mL, 1.2 mmol) in dry dichloromethane (10 mL) was cooled down to –78 °C and treated dropwise with freshly distilled boron trifluoride etherate (0.018 mL, 1.5 mmol). After 30 min of being stirred, the reaction mixture was quenched by the addition of solid $NaHCO_3$ (200 mg), allowed to warm up to 5 °C, diluted with H_2O (20 mL), and thoroughly extracted with chloroform (4 × 50 mL). The combined extracts were washed (H_2O), dried (Na_2SO_4), and evaporated. The oily residue was purified by column chromatography (SiO_2, 95:5 hexane–EtOAc) to furnish **7** (220 mg, 80%) as a colorless oil: IR (neat) 2960, 2880, 815 cm^{-1}; ^1H NMR δ 6.11 (s, Ar H_6), 5.85 (s, OCH_2O), 5.10 (m, 5′-H), 3.74 (s, OCH_3), 3.15 (sex., J = 7 Hz, 2′-H), 2.20 (s, Ar CH_3), 1.8 (m, 3′- and 4′-CH_2), 1.67 (s, 7′-CH_3), 1.55 (s, 6′-CCH_3), 1.25 (d, J = 7 Hz, 1′-CH_3); ^{13}C NMR, see Table I; MS (EI), m/e (relative intensity) $C_{17}H_{24}O_3$ requires 276) 276 (73), 193 (100), 178 (23), 166 (84), 151 (8), 147 (11), 121 (7), 93 (7), 53 (8). This material proved identical by spectroscopic and chromatographic comparison with a sample prepared directly from (–)-perezone.[17]

(±)-Perezone (1). Freshly prepared silver(II) oxide[18] (179.4 mg, 1.448 mmol) and 7 N nitric acid (0.42 mL) were added, in that order, to a solution of **7** (100 mg, 0.362 mmol) in peroxide-free dioxane (8 mL). The reaction mixture was stirred at room temperature for 10 min, quenched by the addition of cold water (40 mL), and exhaustively extracted with chloroform (4 × 40 mL). The combined extracts were washed (H_2O, brine), dried (Na_2SO_4), and evaporated. The solid residue was purified by column chromatography (SiO_2, 90:10 hexane–EtOAc) to provide pure **1** (50 mg, 56%) as yellow-orange crystals: mp 72–73 °C (hexane) (lit.[3] mp 102–103 °C for natural (–)-perezone); IR (KBr) 3285, 1655, 1645, 1620, 1610 cm^{-1}; ^1H NMR δ 6.95 (s, 3-OH, exchangeable with D_2O), 6.46 (q, J = 1.8 Hz, H_6), 5.05 (m, H_{12}), 3.10 (sex., J = 7 Hz, H_8), 2.06 (q, J = 1.8 Hz, 7-CH_3), 1.85 (m, 10- and 11-CH_2), 1.66, 1.55 (2 s, 14- and 15-CH_3), 1.21 (d, J = 7 Hz, 9-CH_3); ^{13}C NMR, see Table I; MS (EI), m/e (relative intensity) ($C_{15}H_{20}O_3$ requires 248) 248 (9), 192 (3), 191 (10), 166 (100), 165 (5), 138 (3), 137 (4), 109 (3).

Our synthetic sample of (±)-perezone proved identical by spectroscopic and chromatographic comparison with natural (–)-perezone.[17] The mp of (±)-perezone (**1**) was not reported in the original synthetic work.[3]

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(18) Hammer, R. N.; Kleinberg, J. *Inorg. Synth.* **1953**, *4*, 12–14.