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Studies on the Terpenoids and Related Alicyclic Compounds. XXIII.[1] Total Syntheses of (±)-Phomenone, (±)-3-Epiphomenone, (±)-Ligularenolide, and (±)-Furanoligularanone

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Total syntheses of (±)-phomenone (**5a**), (±)-3-epiphomenone (**12**), (±)-ligularenolide (**27**), and (±)-furanoligularanone (**34**) are described. Dehydration of **6** followed by epoxidation gave the epoxide (**8**), which was treated with lithium diethylamide to afford the alcohol (**9**). Epoxidation of **9** gave the α-epoxide (**10**), which was deketalized to give the diketone (**11**). Reduction of **11** with $NaBH_4$ gave (±)-3-epiphomenone (**12**) as a major product. Stereoselective synthesis of (±)-**5a** starting from **7** was examined. Deketalization of **7** gave the triene-dione (**13**) which was reduced with $NaBH_4$ to afford the alcohols **14a** and **14b**. Epoxidation of 3α-ol (**14a**) gave the epoxide (**15**), which was treated with lithium diethylamide to afford the diol (**16**). Epoxidation of **16** with hydrogen peroxide gave (±)-phomenone (**5a**) regio- and stereoselectively. Treatment of **17** with lithium diisopropylamide followed by condensation with methyl pyruvate gave the hydroxy ester (**19**), which was treated with acetic acid to give the ketone (**24**). **24** was thioketalized to give **25**, which was treated with *p*-toluenesulfonic acid to afford the unsaturated lactone (**26**). **26** was transformed to (±)-ligularenolide (**27**) and (±)-tetrahydroligularenolide (**28**) in good yield. Condensation of **17** with acetol pyranyl ether followed by catalytic hydrogenation gave **33**. Treatment of **33** with *p*-toluenesulfonic acid gave (±)-furanoligularanone (**34**), which was transformed to (±)-3β-furanoligularanol (**36**).

Keywords——total synthesis; sesquiterpene; eremophilane; eremophilenolide; furanoeremophilane; phomenone; 3-epiphomenone; ligularenolide; furanoligularanone; aldol condensation

In previous papers,[3] the authors have reported syntheses of some eremophilane-type sesquiterpenoids, (±)-isopetasol (**1a**),[3] (±)-3-epiisopetasol (**1b**),[3] (±)-warburgiadione (**2**),[3] and (±)-petasitol (**3**),[3b] starting from the bicyclic intermediate (**4**) which was prepared by the Robinson annulation of 2,3-dimethylcyclohexane-1,4-dione and methyl vinyl ketone.[3b]

In this paper, we describe in detail total syntheses of (±)-phomenone (**5a**),[4] (±)-3-epiphomenone (**12**),[4] (±)-ligularenolide (**27**), and (±)-furanoligularanone (**34**) starting from the intermediate (**4**). This represents an elaboration of bicyclic eremophilanes into tricyclic eremophilenolides and furanoeremophilanes. On the other hand, some furanoeremophilanes have also been synthesized *via* Diels-Alder reactions by us (K.Y. and T.S.).[5] New total syntheses of some furanoeremophilanes have been achieved in two routes in our laboratory.

Syntheses of (±)-Phomenone (5a) and (±)-3-Epiphomenone (12)[4]

Phomenone, a phytotoxic metabolite from the fungus *Phoma exigua*, was found by Bousquet *et al.*[6] Phomenone was established as an eremophilane-type sesquiterpenoid (**5a**) by

1) Part XXII. K. Yamakawa, T. Satoh, N. Ohba, R. Sakaguchi, S. Takita, and N. Tamura, *Tetrahedron*, in press.
2) Location: *Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.*
3) *a*) K. Yamakawa, J. Izuta, H. Oka, and R. Sakaguchi, *Tetrahedron Lett.*, **1974**, 2187; *b*) K. Yamakawa, I. Izuta, H. Oka, R. Sakaguchi, M. Kobayashi, and T. Satoh, *Chem. Pharm. Bull.*, **27**, 331 (1979).
4) A part of this work has been published as a communication: K. Yamakawa, M. Kobayashi, S. Hinata, and T. Satoh, *Tetrahedron Lett.*, **1979**, 3871.
5) K. Yamakawa and T. Satoh, *Chem. Pharm. Bull.*, **26**, 3704 (1978).
6) C. Riche, C. Pascard-Billy, M. Devys, A. Gaudemer, M. Barbier, and J.-F. Bousquet, *Tetrahedron Lett.*, **1974**, 2765.

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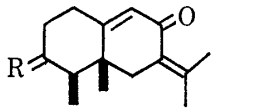
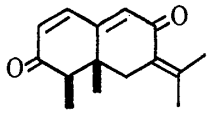


1a : R= H, OH
1b : R= OH, H



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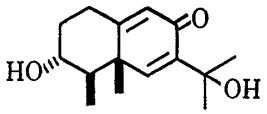

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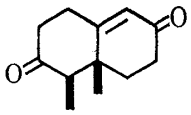

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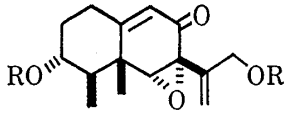
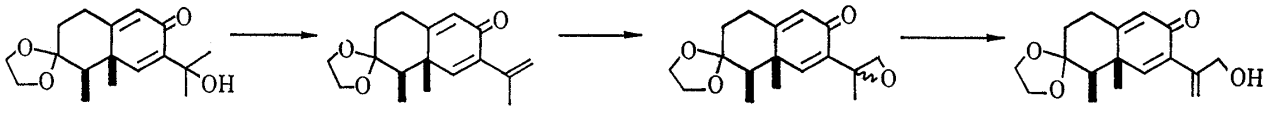


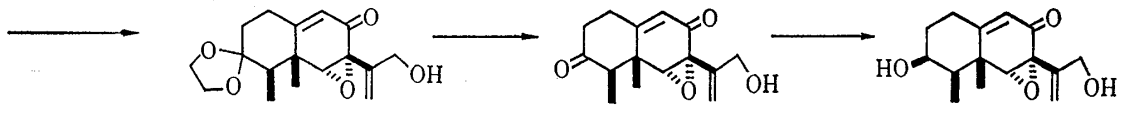
5a : R=H
5b : R=$COCH_3$

physico-chemical analysis and single crystal X-ray analysis.[6] We report the first total syntheses of (±)-phomenone (**5a**) and (±)-3-epiphomenone (**12**) from the bicyclic enone (**4**).[4]

3,3-Ethylenedioxy-11-hydroxyeremophila-6,9-dien-8-one (**6**),[3b] which was previously derived from **4** in our synthesis of (±)-petasitol (**3**), was chosen as a starting material. The preparation of **6**, which was previously reported[3b] (55% yield by the use of DDQ), was improved (74% yield) by the use of benzeneseleninic anhydride. Treatment of **6** with methyl (carboxysulfamoyl)triethylammonium hydroxide inner salt gave a trienone (**7**), mp 55—58°. Treatment of **7** with *m*-chloroperbenzoic acid gave a mixture of epoxides (**8**). The epoxides without separation were treated with lithium diethylamide (LDEA) in refluxing ether for 1.5 hr to afford the trienone alcohol (**9**) as an oil, in 70% yield. Regio- and stereoselective epoxidation of **9** with 30% hydrogen peroxide in the presence of sodium carbonate gave the α-epoxide (**10**), mp 135—136°, in 56% yield. Deketalization of **10** with 75% acetic acid at room temperature for 3 days afforded the ketone (**11**) in 75% yield. Reduction of **11** with sodium borohydride gave (±)-3-epiphomenone (**12**), mp 130—132°, in 85% yield together with a small amount of minor products. The stereochemistry of **12** was confirmed by its spectroscopic data. We attempted to purify the minor products by high performance liquid chromatography (HPLC), but (±)-**5a** could not be obtained in pure form.



6 **7** **8** **9**



10 **11** **12**

Chart 1

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In order to obtain pure (±)-phomenone (**5a**), an alternative synthetic route was investigated. Treatment of **7** with 75% acetic acid at 100° for 1 hr gave the diketone (**13**), mp 82—83° (mp 64.5—66° as dimorph forms). Reduction of **13** with sodium borohydride afforded the 3α-ol (**14a**), as an oil, and the 3β-ol (**14b**), mp 88—90°, in 15% and 75% yields, respectively. In the ^{1}H-NMR spectra, the C-3 proton signals of **14a** and **14b** showed half-width values of 28 Hz and 7 Hz, respectively. The C-3 configurations of **14a** and **14b** were confirmed to be 3α-ol and 3β-ol, respectively, by their NMR spectra. Oxidation of **14b**, the major product, with Cornforth's reagent[7] gave the ketone (**13**) in 82% yield. The yield of the 3α-ol (**14a**) could be increased by recycling of this reduction and oxidation procedure. Epoxidation of **14a** with *m*-chloroperbenzoic acid in methylene chloride in the presence of sodium bicarbonate solution gave a mixture of epoxide (**15a** and **15b**) in 86% yield. Treatment of the mixture of epoxides (**15**) with LDEA under the conditions used for **8** afforded a dihydroxy-trienone (**16**) in 26% yield, as an oily product. Epoxidation of **16** with 30% hydrogen peroxide in refluxing ethanol in the presence of a catalytic amount of sodium bicarbonate solution for 3 hr afforded (±)-phomenone (**5a**) stereoselectively; it was isolated as an oil by HPLC. (±)-**5a** was acetylated with acetic anhydride and pyridine to give the corresponding (±)-phomenone diacetate (**5b**) as an oil. The NMR, mass, UV and IR spectral data for (±)-**5a** and **5b** were in good agreement with those of phomenone and phomenone diacetate, respectively, reported by Bousquet *et al.*[6]

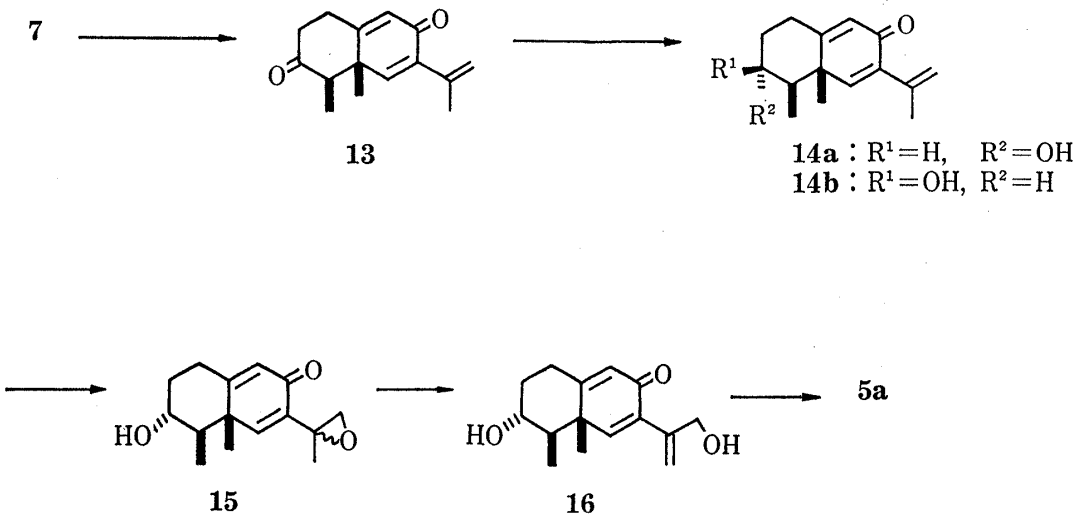

Chart 2

Synthesis of (±)-Ligularenolide (27)

In order to introduce a side chain for the formation of butenolide and furan rings, the reactions of ethyl 2-bromoacetate, ethyl 2-iodopropionate, methyl pyruvate, and acetol pyranyl ether at the C-7 position of the enone (**17**)[3b] derived from **4** were examined. Treatment of **17** with lithium diisopropylamide (LDA) followed by condensation of ethyl 2-bromoacetate and ethyl 2-iodopropionate gave **18a** and **18b**. However, the yields were unsatisfactory (20—24%). Condensation of **17** with methyl pyruvate under the same conditions gave a mixture of isomeric hydroxy esters in good yield. Preparative thin-layer chromatographic (TLC) separation of the products gave the hydroxy esters (**19a**), mp 116—118°, and (**19b**), mp 186—187°, in 34% and 50% yields, respectively. Treatment of **19a** with phosphorus oxychloride in pyridine gave two enone carboxylic esters (**20**) and (**21**), and an unsaturated

7) R.H. Cornforth, J.W. Cornforth, and G. Popjak, *Tetrahedron*, **18**, 1351 (1962).

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lactone (**22**), mp 151—152°, in 11%, 8%, and 16% yields, respectively. Similar results were obtained from **19b** under the conditions used for **19a**. However, the stereochemistries of **20** and **21** were not determined by the spectral data. Further treatment of **20** with phosphorus oxychloride in pyridine gave the unsaturated lactone (**23**) as an unstable oil in 38% yield. Treatment of **19a** and **19b** with 75% acetic acid at room temperature for 2 days gave the 3-ketones (**24a**), mp 116—117°, and (**24**), mp 151—152°, respectively. **24a** and **24b** were dissolved in methylene chloride and treated with ethanedithiol in the presence of a small amount of boron trifluoride etherate at room temperature for 1 hr to give the 3,3-ethylenedithioketals (**25a**), mp 170—172°, and (**25b**), mp 177—179°, in 84% and 86% yields, respectively. Benzene solutions of **25a** and **25b** were refluxed in the presence of *p*-toluenesulfonic acid for 3 hr to afford the same enolide (**26**), mp 190—192°, in 60% yield. Desulfurization of **26** with W-2 Raney nickel catalyst in a stirred solution of dioxane and ethanol (2: 1) at 0° for 1 hr afforded (±)-ligularenolide (**27**), mp 84—87°, in 70% yield. The NMR, IR, and UV spectra of (±)-**27** were identical with those of (−)-ligularenolide (**27**), which was isolated from "San-Shion" (the root of *Ligularia* species) by Takahashi *et al.*[8] When **26** was desulfurized with W-2 Raney nickel in refluxing ethanol, (±)-tetrahydroligularenolide (**28**), mp 92—93°, was obtained quantitatively.

Catalytic hydrogenation of (±)-**27** in ethanol with 5% palladium charcoal gave (±)-tetrahydroligularenolide (**28**) stereoselectively. The NMR spectrum of (±)-**28** was in good agreement with that of (−)-tetrahydroligularenolide (**28**) recorded by Takahashi *et al.*[8b]

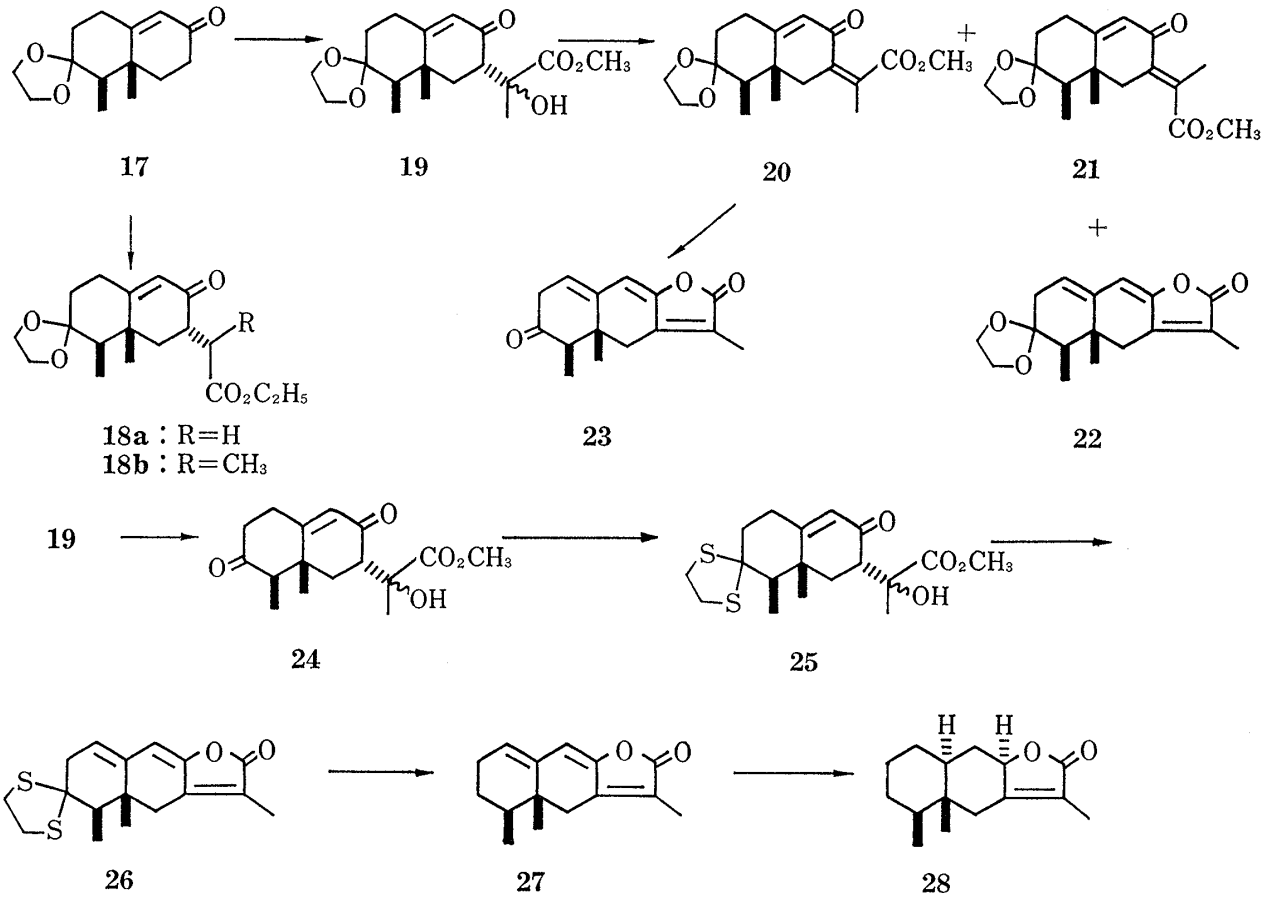

Chart 3

8) *a*) Y. Tanahashi, Y. Ishizaki, T. Takahashi, and K. Tori, *Tetrahedron Lett.*, **1968**, 3739; *b*) Y. Ishizaki, Y. Tanahashi, T. Takahashi, and K. Tori, *Tetrahedron*, **26**, 5387 (1970).

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Alternative total syntheses of (±)-**28** were previously reported by two groups, Piers and Geraghty (reported mp 91.5—92°),[9] and Takahashi *et al.*[10] (reported mp 83—84°).

Synthesis of (±)-Furanoligularanone (34)

The total synthesis of (±)-furanoligularanone (**34**) starting from the intermediate (**17**) was investigated. Hagiwara *et al.*[11] have recently reported that the aldol condensation of the keto enol ether (**29**) and acetol pyranyl ether gave the condensation product (**30**), which was treated with *p*-toluenesulfonic acid to give a furan derivative, 10α*H*-furanoeremophilone (**31**), which has already been synthesized *via* a Diels–Alder reaction by us.[5] Treatment of **17** with LDA followed by condensation of acetol pyranyl ether in the presence of zinc chloride, essentially according to Hagiwara's procedure,[11] gave the alcohol (**32**) in 88% yield. Catalytic hydrogenation of **32** in ethanol with palladium-charcoal gave **33** quantitatively. Treatment of **33** in a solution of tetrahydrofuran and a small amount of water with a catalytic amount of *p*-toluenesulfonic acid produced (±)-furanoligularanone (**34**) in 48% yield, this compound was very unstable. The IR and NMR spectra of (±)-**34** were identical with those of furanoligularanone derived from natural furanoligularenone (**35**) which was isolated from *Aster tataricus* L. by Takahashi *et al.*[12] Reduction of **34** with sodium borohydride gave (±)-3β-furanoligularanol (**36**) in 37% yield. All data (mp, NMR, and IR) for (±)-**36** were identical with those for (±)-3β-furanoligularanol previously synthesized by an alternative route starting from the diene adduct of 3-ethoxy-1,3-pentadiene and 3,5-dimethylbenzofuran-4,7-quinone by us (K.Y. and T.S.).[5]

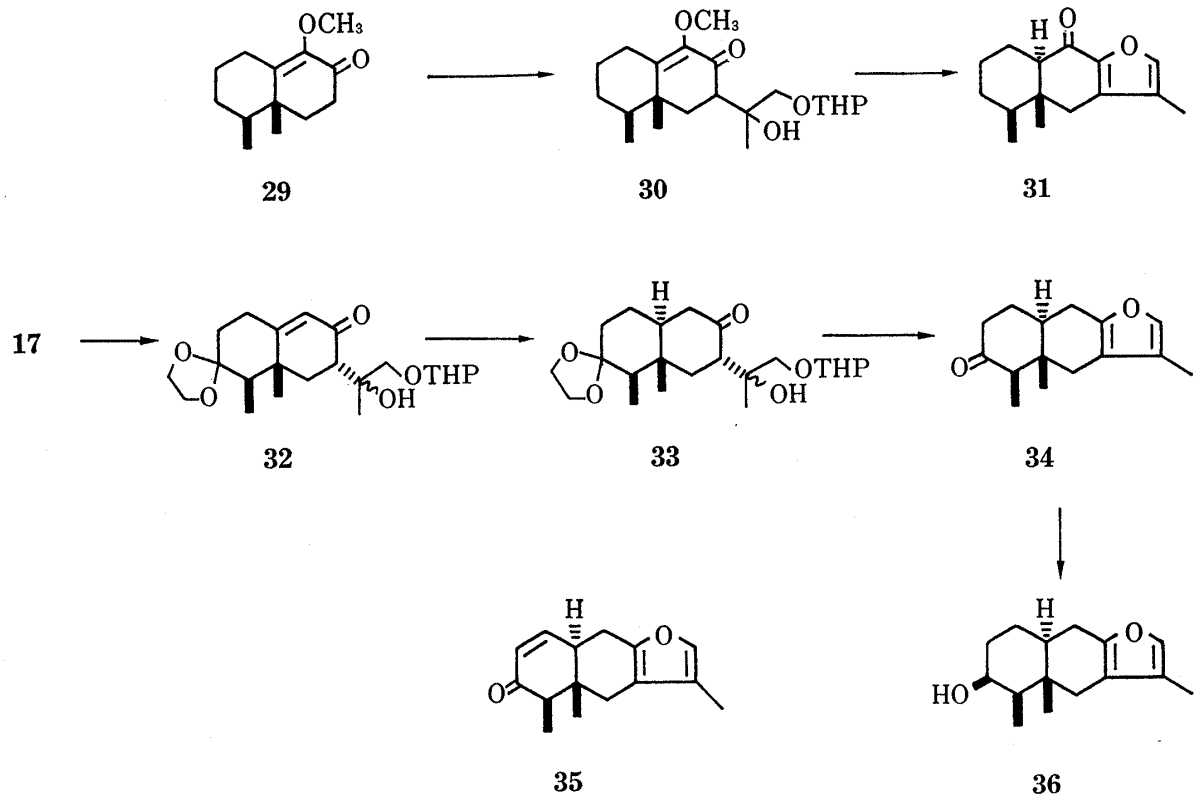

Chart 4

9) E. Piers and M.B. Geraghty, *Can. J. Chem.*, **52**, 2166 (1973).
10) T. Tatee and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **48**, 281 (1975).
11) H. Hagiwara, H. Uda, and T. Kodama, *J. Chem. Soc. Perkin-I*, **1980**, 963.
12) *a*) F. Patil, J.-M. Lehn, G. Ourisson, Y. Tanahashi, and T. Takahashi, *Bull. Soc. Chim. Fr.*, **1965**, 3085; *b*) F. Patil, G. Ourisson, Y. Tanahashi, M. Wada, and T. Takahashi, *ibid.*, **1968**, 1047.

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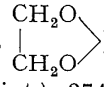
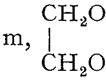
Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured in KBr disks with a Hitachi 215 or a Hitachi Perkin-Elmer 225 spectrophotometer. Ultraviolet (UV) spectra were measured with a Hitachi 323 or 200 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ solution on a JEOL JNM-FX 100 pulse FT (100 MHz), or a Hitachi R-24B (60 MHz) spectrometer using Me_4Si as an internal standard. Mass spectra (MS) were taken on a Hitachi RMU-7M double focusing spectrometer at 70 eV by direct insertion. High-resolution mass spectra were determined with a Hitachi datalyser 002 system connected on-line with the mass spectrometer. High performance liquid chromatography (HPLC) was performed on a Hitachi model 635A chromatograph with a porous polymer, Hitachi gel #3010.

3,3-Ethylenedioxy-11-hydroxyeremophila-6,9-dien-8-one (6)——A solution of 272 mg of 3,3-ethylenedioxy-11-hydroxyeremophil-9-en-8-one[3b] in toluene (60 ml) was treated with benzeneseleninic anhydride[13] (400 mg) and the mixture was refluxed for 18 hr. The reaction mixture was diluted with ether (60 ml) and the solution was washed and dried. The solvent was evaporated off *in vacuo* and the residue was separated by silica gel preparative TLC (hexane: AcOEt=2: 1) to afford 200 mg (74%) of **6**, mp 110—111°, as colorless needles. Melting point, IR, and NMR spectral data for **6** were identical with those for the dienone (**6**) reported previously.[3b]

3,3-Ethylenedioxyeremophila-6,9,11-trien-8-one (7)——A mixture of a solution of 220 mg of the dienone (**6**) in benzene (30 ml) and 358 mg of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt was heated at 50° for 3 hr. The mixture was diluted with 50 ml of ether and the organic layer was washed with saturated brine, dried and concentrated. The crude product was separated by silica gel preparative TLC (hexane: AcOEt=2: 1) to afford 180 mg (87%) of **7**, as colorless prisms, mp 55—58° (from pentane). High-resolution mass spectrum for $C_{17}H_{22}O_3$: Mol. Wt. 274.1570. Observed: 274.1580. IR cm^{-1}: 1660 (CO), 1630 (C=C); UV λ_{max}^{EtOH} 243 nm (ε 13000); NMR δ: 1.10 (3H, d, J=7 Hz, 4-CH_3), 1.31 (3H, s, 5-CH_3), 2.00 (3H, m, 11-CH_3), 4.00 (4H, m, ), 5.09, 5.20 (each 1H, m, ), 6.09 (1H, d, J=2 Hz, 9-H), 6.88 (1H, s, 6-H); MS *m/z* (% Rel. int.): 274 (M^+, 87), 213 (100).

11,12-Epoxy-3,3-ethylenedioxyeremophila-6,9-dien-8-one (8)——A solution of 139 mg of trienone (**7**) in CH_2Cl_2 (20 ml) was treated with 10 ml of sat. aq. $NaHCO_3$ and 134 mg of *m*-chloroperbenzoic acid, the mixture was stirred at room temperature for 12 hr. Work-up of the reaction mixture gave 140 mg (95%) of a diastereomeric epoxide mixture (**8a**, and **8b**) as an oil, which was separated by silica gel preparative TLC (hexane: AcOEt=5: 1). Epoxide (**8a**): IR cm^{-1}: 1670 (CO), 1635 (C=C); NMR δ: 1.08 (3H, d, J=7 Hz, 4-CH_3), 1.31 (3H, s, 5-CH_3), 1.56 (3H, s, 13-H), 2.59 (1H, d, J=5 Hz, 12-H), 2.87 (1H, d, J=5 Hz, 12-H), 3.8—4.2 (4H, m, ), 6.09 (1H, d, J=2 Hz, 9-H), 7.07 (1H, s, 6-H); MS *m/z* 290 (M^+). Epoxide (**8b**): IR cm^{-1}: 1670 (CO), 1635 (C=C); NMR δ: 1.12 (3H, d, J=7 Hz, 4-CH_3), 1.24 (3H, s, 5-CH_3), 1.57 (3H, s, 13-H), 2.59 (1H, d, J=5 Hz, 12-H), 2.88 (1H, d, J=5 Hz, 12-H), 3.8—4.2 (4H, m, ), 6.09 (1H, d, J=2 Hz, 9-H), 7.05 (1H, s, 6-H); MS *m/z* 290 (M^+).

3,3-Ethylenedioxy-13-hydroxyeremophila-6,9,11-trien-8-one (9)——Lithium diethylamide (LDEA) was prepared by addition of 0.6 mmol of *n*-BuLi (1.56 M in hexane) to 0.6 mmol of diethylamine at 0° under an N_2 atmosphere. A solution of 50 mg of epoxide (**8**) in dry ether (2 ml) was added to the LDEA solution and the mixture was refluxed for 1.5 hr. Sat. aq. NH_4Cl (5 ml) was added to the reaction mixture and the whole was extracted with ether. The organic layer was washed with water, dried, and concentrated. The residue was separated by silica gel preparative TLC (hexane: AcOEt=1: 1) to afford 35 mg (70%) of **9** as an oil. High-resolution mass spectrum for $C_{17}H_{22}O_4$: Mol. Wt. 290.1519. Observed: M^+ 290.1533. IR cm^{-1}: 3450 (OH), 1665 (CO), 1620 (C=C); UV λ_{max}^{EtOH} 244 nm; NMR δ: 1.10 (3H, d, J=7 Hz, 4-CH_3), 1.32 (3H, s, 5-CH_3), 4.00 (4H, m, ), 4.20 (2H, s, 13-H), 5.24, 5.31 (each 1H, m, ), 6.13 (1H, d, J=1.5 Hz, 9-H), 7.00 (1H, s, 6-H).

6α,7α-Epoxy-3,3-ethylenedioxy-13-hydroxyeremophila-9,11-dien-8-one (10)——A solution of 50 mg of **9** in EtOH (10 ml) was treated with 0.6 ml of 30% H_2O_2 and 10% aq. Na_2CO_3 (one drop) and the mixture refluxed. When the reaction was completed, the solvent was removed *in vacuo* and the residue was extracted with ether, washed and dried. The ether was evaporated off and the residue was separated by HPLC to give 28 mg (56%) of **10** as colorless prisms, mp 135—136° (from AcOEt–hexane). High-resolution mass spectrum for $C_{17}H_{22}O_5$: Mol. Wt. 306.1468. Observed: M^+ 306.1474. IR cm^{-1}: 3460 (OH), 1660 (CO), 1618 (C=C); UV λ_{max}^{EtOH} 242 nm (ε 14000); NMR δ: 1.12 (3H, d, J=8 Hz, 4-CH_3), 1.36 (3H, s, 5-CH_3), 3.30 (1H, s,

13) D.H.R. Barton, S.V. Ley, P.D. Magnus, and M.N. Rosenfeld, *J. Chem. Soc. Perkin-I*, **1977**, 567.

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6-H), 4.00 (4H, m, ), 4.25 (2H, d, J=5 Hz, 13-H), 5.36, 5.40 (each 1H, m, ), 5.80 (1H, *d*, J= 1.5 Hz, 9-H).

6α,7α-Epoxy-13-hydroxyeremophila-9,11-diene-3,8-dione (**11**)——A solution of 28 mg of the ketal (**10**) in 75% aq. AcOH (5 ml) was allowed to stand at room temperature for 3 days. The mixture was concentrated *in vacuo* and the residue was separated by silica gel preparative TLC (hexane: AcOEt=1: 2) to afford 18 mg (75%) of **11** as an oil. IR cm^{-1}: 3420 (OH), 1710, 1665 (CO), 1630 (C=C); NMR δ: 1.24 (3H, d, J=7 Hz, 4-CH_3), 1.27 (3H, s, 5-CH_3), 3.35 (1H, s, 6-H). 4.30 (2H, d, J=7 Hz, 13-H), 5.34, 5.42 (each 1H, m, ), 5.96 (1H, m, 9-H).

(±)-3-Epiphomenone (**12**)——A solution of 18 mg of **11** in EtOH (2 ml) was treated with 4 mg of $NaBH_4$ and the reaction mixture was stirred at 0°. When the reaction was completed, the solvent was removed *in vacuo* and the residue was extracted with ether, washed and dried. The ether was evaporated off and the residue was separated by silica gel preparative TLC (hexane: AcOEt=1: 2) to afford 15 mg (85%) of (±)-3-epiphomenone (**12**), mp 130—132°, and a trace amount of a mixture of (±)-phomenone (**5a**) and other products. **12**: High-resolution mass spectrum for $C_{15}H_{20}O_4$: Mol. Wt. 264.1362. Observed: M^+ 264.1338. IR cm^{-1}: 3445 (OH), 1650 (CO), 1615 (C=C); UV λ_{max}^{EtOH} 247 nm (ε 11200); NMR δ: 1.28 (3H, d, J=7 Hz, 4-CH_3), 1.44 (3H, s, 5-CH_3), 3.37 (1H, s, 6-H), 4.00 (1H, m, $W_{1/2}$=9 Hz, 3-H), 4.26 (2H, m, 13-H), 5.32, 5.41 (each 1H, m, ), 5.83 (1H, d, J=1.5 Hz, 9-H).

Eremophila-6,9,11-triene-3,8-dione (**13**)——A solution of 180 mg of the trienone (**7**) dissolved in 20 ml of AcOH–H_2O (3: 1) was heated at 100° for 1 hr. The solvent was evaporated off *in vacuo* and the residue was separated by silica gel preparative TLC (hexane: AcOEt=2: 1) to afford 137 mg (90%) of **13** as colorless prisms, mp 82—83° (from hexane). *Anal.* Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88; Mol. Wt. 230.1305. Found: C, 78.30; H, 7.85; M^+ 230.1295. IR cm^{-1}: 1710, 1660 (CO); UV λ_{max}^{EtOH} 241 nm (ε 14000); NMR δ: 1.16 (3H, s, 5-CH_3), 1.21 (3H, d, J=7 Hz, 4-CH_3), 2.01 (3H, m, 11-CH_3), 5.10 5.23 (each 1H, m, ), 6.21 (1H, d, J=1 Hz, 9-H), 6.76 (1H, s, 6-H); MS *m/z* (% Rel. int.): 230 (M^+, 45), 159 (100).

Reduction of Diketone (**13**) **with $NaBH_4$**——$NaBH_4$ (38 mg) was added to a stirred solution of 230 mg of the diketone (**13**) in EtOH (20 ml) and the solution was stirred at 0° for 15 min. Sat. aq. NH_4Cl was added to the reaction mixture and then the solution was concentrated *in vacuo*. The residue was extracted with ether and the organic layer was washed with water and dried. After removal of the ether, the residue was separated by silica gel preparative TLC (hexane: AcOEt=1: 1) to afford 34 mg (15%) of **14a** and 175 mg (75%) of **14b**. 3α-Hydroxyeremophila-6,9,11-trien-8-one (**14a**): oil, high-resolution mass spectrum for $C_{15}H_{20}O_2$: Mol. Wt. 232.1463. Observed: M^+ 232.1476. IR cm^{-1}: 3425 (OH), 1660 (CO), 1630 (C=C); UV λ_{max}^{EtOH} 243.5 nm; NMR δ: 1.17 (3H, s, 5-CH_3), 1.22 (3H, d, J=7 Hz, 4-CH_3), 1.98 (3H, m, 11-CH_3), 3.66 (1H, m, $W_{1/2}$=28 Hz, 3-H), 5.06, 5.17 (each 1H, m, ), 6.05 (1H, d, J=1 Hz, 9-H), 6.86 (1H, s, 6-H); MS *m/z* (% Rel. int.): 232 (M^+, 7), 199 (100). 3β-Hydroxyeremophila-6,9,11-trien-8-one (**14b**): colorless prisms, mp 88—90° (from AcOEt–hexane), *Anal.* Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; Mol. Wt. 232.1461. Found: C, 77.51; H, 8.71; M^+ 232.1439. IR cm^{-1}: 3370 (OH), 1650 (CO), 1615 (C=C); UV λ_{max}^{EtOH} 250 nm (ε 13000); NMR δ: 1.28 (3H, d, J=7 Hz, 4-CH_3), 1.38 (3H, s, 5-CH_3), 1.99 (3H, m, 11-CH_3), 3.92 (1H, m, $W_{1/2}$=7 Hz, 3-H), 5.05, 5.16 (each 1H, m, ), 6.09 (1H, d, J=2 Hz, 9-H), 6.87 (1H, s, 6-H); MS *m/z* (% Rel. int.): 232 (M^+, 15), 199 (100).

Oxidation of 14b with CrO_3–Pyridine–H_2O——A mixture of a solution of 300 mg of the 3β-hydroxy compound (**14b**) in pyridine (8 ml) and a solution of CrO_3 (400 mg) in H_2O (0.8 ml) was stirred at room temperature for 15 hr. The reaction mixture was diluted with ether (20 ml) and the resulting precipitate was filtered off. The filtrate was washed with water, and then dried and concentrated. The product was purified by silica gel preparative TLC (hexane: AcOEt=2: 1) to afford 245 mg (82%) of **13**.

11,12-Epoxy-3α-hydroxyeremophila-6,9-dien-8-one (**15**)——A solution of 64 mg of the 3α-hydroxy compound (**14a**) in CH_2Cl_2 (15 ml) was treated with 7.5 ml of sat. aq. $NaHCO_3$ and 90 mg of *m*-chloroperbenzoic acid. The reaction mixture was stirred at room temperature for 15 hr, then diluted with ether (100 ml), and the ether layer was washed with water, dried, and concentrated. The crude product was separated by silica gel preparative TLC (hexane: AcOEt=1: 2) to afford 59 mg (86%) of epoxide mixture (**15**) as an oil. IR cm^{-1}: 3450 (OH), 1670 (CO), 1630 (C=C); UV λ_{max}^{EtOH} 243.5 nm; MS *m/z* 248 (M^+).

3α,13-Dihydroxyeremophila-6,9,11-trien-8-one (**16**)——A solution of 30 mg of the epoxide (**15**) in dry ether (5 ml) was added to an LDEA solution (prepared from 1.4 mmol of *n*-BuLi and 1.4 mmol of diethylamine) and the reaction mixture was refluxed for 2 hr. Work-up of the reaction mixture in the manner

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described for **9** gave 8 mg (26%) of **16** as an oil. IR cm^{-1}: 3400 (OH), 1660 (CO), 1620 (C=C); UV λ_{max}^{EtOH} 246 nm; NMR δ: 1.20 (3H, s, 5-CH_3), 1.25 (3H, d, J=8.5 Hz, 4-CH_3), 3.70 (1H, m, $W_{1/2}$=23 Hz, 3-H), 4.21 (2H, bs, $W_{1/2}$=4 Hz, 13-H), 5.24, 5.33 (each 1H, m, = ), 6.13 (1H, d, J=1 Hz, 9-H), 7.02 (1H, s, 6-H); MS m/z 248 (M^+).

(±)-Phomenone (5a)——A solution of 12 mg of **16** in EtOH (5 ml) was treated with 0.2 ml of 30% H_2O_2 and sat. aq. $NaHCO_3$ (one drop), and the mixture was refluxed for 3 hr. The solvent was removed *in vacuo*, and the residue was extracted with ether, washed and dried. The ether was evaporated off and the residue was separated by HPLC to give 5 mg (40%) of (±)-phomenone (**5a**) as an oil. High-resolution mass spectrum for $C_{15}H_{20}O_4$: Mol. Wt. 264.1360. Observed: M^+ 264.1329. IR cm^{-1}: 3400 (OH), 1670 (CO); UV λ_{max}^{EtOH} 243 nm; NMR δ: 1.19 (3H, d, J=6 Hz, 4-CH_3), 1.26 (3H, s, 5-CH_3), 3.40 (1H, s, 6-H), 4.22 (2H, d, J=4 Hz, 13-H), 5.21, 5.24 (each 1H, m, = ), 5.71 (1H, d, J=2 Hz, 9-H); MS m/z 264 (M^+). IR, UV, NMR, and mass spectral data for (±)-**5a** were in good agreement with those for natural (+)-phomenone reported by Bousquet *et al.*[6]

(±)-Phomenone Diacetate (5b)——(±)-**5a** was acetylated in the usual way to give (±)-phomenone diacetate (**5b**) as an oil in quantitative yield. IR cm^{-1}: 1740, 1680 (CO), 1245 (COC); NMR δ: 1.12 (3H, d, J=7 Hz, 4-CH_3), 1.29 (3H, s, 5-CH_3), 2.03, 2.09 (each 3H, s, $COCH_3$), 3.31 (1H, s, 6-H), 4.76 (2H, bs, 13-H), 5.38 (2H, m, $W_{1/2}$=4 Hz, 12-H), 5.75 (1H, d, J=1.5 Hz, 9-H); MS m/z 288 ($[M-CH_3CO_2H]^+$).

3,3-Ethylenedioxy-4β,5β-dimethyloctalin-9-en-8-one (17)——A solution of 5.5 g of **4**[3b] in 10 ml of 3,3-ethylenedioxybutane was treated with 550 mg of $TsOH \cdot H_2O$ and the mixture was stirred at room temperature for 3 hr. The reaction mixture was diluted with ether (100 ml) and washed with sat. aq. $NaHCO_3$ and with sat. brine. The ether and 3,3-ethylenedioxybutane were evaporated off *in vacuo* and the residue was column chromatographed on Florisil to give 5.4 g (80%) of **17**, mp 80—82°, as colorless needles. Melting point, IR, and NMR data for **17** were identical with those for the ketal (**17**) reported previously.[3b]

3,3-Ethylenedioxy-4β,5β-dimethyl-7α-(ethoxycarbonyl methyl)octalin-9-en-8-one (18a)——Lithium diisopropylamide (LDA) was prepared by addition of 1.5 ml of *n*-BuLi (1.56 M in hexane) to 0.4 ml of diisopropylamine at −78° under an N_2 atmosphere, followed by stirring for 1 hr. A solution of 100 mg of **17** in dry THF (1 ml) was added to the LDA solution during a period of 1 hr and stirring was continued for 1 hr at −78°. A solution of 0.5 ml of HMPA and 0.2 ml of ethyl bromoacetate in dry THF (1 ml) was then added and the mixture was stirred at −20° for 30 min. Sat. aq. NH_4Cl was added and the whole was extracted with ether. The extract was washed with water and dried. The ether was evaporated off and the residue was separated by silica gel preparative TLC (hexane: AcOEt=3: 1) to afford 33 mg (24%) of **18a** as colorless crystals, mp 35—37° (from AcOEt–hexane). IR cm^{-1}: 1730, 1670 (CO), 1625 (C=C); NMR δ: 0.93 (3H, d, J=7 Hz, 4-CH_3), 1.28 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.33 (3H, d, 5-CH_3), 4.00 (4H, m, ), 4.17 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.76 (1H, d, J=1.5 Hz, 9-H).

3,3-Ethylenedioxy-4β,5β-dimethyl-7α-(1′-ethoxycarbonyl ethyl)octalin-9-en-8-one (18b)——A solution of 100 mg of **17** in dry THF (1 ml) was added to an LDA solution, prepared as described above, during a period of 1 hr, and stirring was continued for 1 hr at −78°. Next, a solution of 0.4 ml of HMPA and 0.26 ml of ethyl-α-iodopropionate in dry THF (1 ml) was added and the mixture was stirred at −20° for 30 min. Work-up of the reaction mixture as described above afforded 30 mg (20%) of **18b** as an oil. IR cm^{-1}: 1740, 1670 (CO), 1625 (C=C); NMR δ: 0.95 (3H, d, J=7 Hz, 4-CH_3), 1.13 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 5.76 (1H, d, J=1.5 Hz, 9-H).

3,3-Ethylenedioxy-4β,5β-dimethyl-7α-(1′-methoxycarbonyl-1′-hydroxyethyl) octalin-9-en-8-one (19)——A solution of 1 g (4 mmol) of **17** in dry THF (10 ml) was added to an LDA solution (prepared from 30 mmol of *n*-BuLi and 4 ml of diisopropylamine as described for **18a**) during a period of 1 hr, and stirring was continued for 1 hr at −78°. Next, a saturated ethereal solution of $ZnCl_2$ (6 ml) was added, followed by methyl pyruvate (3 ml), and the reaction mixture was stirred at −30° for 1 hr. Sat. aq. NH_4Cl was added and the whole was extracted with ether. The organic layer was washed with water and dried, then the ether was evaporated off. The residue was separated by silica gel preparative TLC (hexane: AcOEt: $CHCl_3$=3: 1: 5). **19a**: (490 mg, 34%), colorless prisms, mp 116—118° (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74; Mol. Wt. 338.1727. Found: C, 63.94; H, 7.75; M^+ 338.1707. IR cm^{-1}: 3400 (OH), 1740, 1650 (CO), 1610 (C=C); UV λ_{max}^{EtOH} 237.5 nm (ε 15800); NMR δ: 0.95 (3H, d, J=7 Hz, 4-CH_3), 1.27 (3H, s, 5-CH_3), 1.45 (3H, s, 11-CH_3), 3.72 (3H, s, OCH_3), 3.96 (4H, m, ), 5.71 (1H, d, J=1.5 Hz, 9-H); MS m/z (% Rel. int.): 338 (M^+, 8), 279 (100). **19b**: (710 mg, 50%), colorless needles, mp 186—187°, (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74; Mol. Wt. 338.1727. Found: C, 63.94; H, 7.71; M^+ 338.1711. IR cm^{-1}: 3550 (OH), 1745, 1670 (CO), 1630 (C=C); UV λ_{max}^{EtOH} 237 nm (ε 15000); NMR δ: 0.97

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(3H, d, J=7 Hz, 4-CH_3), 1.30 (3H, s, 5-CH_3), 1.35 (3H, s, 11-CH_3), 3.78 (3H, s, OCH_3), 3.96 (4H, m, ), 5.69 (1H, d, J=1.5 Hz, 9-H); MS m/z (% Rel. int.): 338 (M^+, 8), 279 (100).

Dehydration of 19 with $POCl_3$——A solution of 130 mg of **19a** in pyridine (9 ml) at 0° was treated with 3 ml of $POCl_3$ and the reaction mixture was stirred at room temperature for 2 hr. Water was added, followed by ether, then the ether layer was washed with sat. aq. $NaHCO_3$ and dried. The ether and pyridine were evaporated off *in vacuo* and the residue was separated by silica gel preparative TLC (hexane: AcOEt=3: 1). **20**: (14 mg, 11%), oil, IR cm^{-1}: 1730, 1670 (CO), 1625 (C=C); NMR δ: 0.99 (3H, d, J=7 Hz, 4-CH_3), 1.16 (3H, s, 5-CH_3), 1.98 (3H, d, J=2 Hz, 11-CH_3), 3.76 (3H, s, OCH_3), 5.80 (1H, d, J=1.5 Hz, 9-H); MS m/z 320 (M^+). **21**: (10 mg, 8%), oil, high-resolution mass pectrum for $C_{18}H_{24}O_5$: Mol. Wt. 320.1623. Observed: M^+ 320.1647. IR cm^{-1}: 1730, 1665 (CO), 1630 (C=C); NMR δ: 0.92 (3H, d, J=7 Hz, 4-CH_3), 1.14 (3H, s, 5-CH_3), 2.18 (3H, bs, 11-CH_3), 3.79 (3H, s, OCH_3), 5.78 (1H, d, J=1.5 Hz, 9-H). **22**: (20 mg, 16%), yellow prisms, mp 151—152° (from AcOEt–hexane). High-resolution mass spectrum for $C_{17}H_{20}O_4$: Mol. Wt. 288.1361. Observed: M^+ 288.1388. IR cm^{-1}: 1765 (CO), 1630, 1620 (C=C); UV λ_{max}^{EtOH} 328.5 nm (ε 21000); NMR δ: 1.03 (3H, d, J=7 Hz, 4-CH_3), 1.12 (3H, d, J=1 Hz, 5-CH_3), 1.91 (3H, d, J=1.5 Hz, 11-CH_3), 3.8—4.0 (4H, m, ), 5.64 (1H, t, J=5 Hz, 1-H), 5.93 (1H, bs, 9-H).

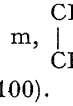
The alcohol (**19b**) was dehydrated with $POCl_3$ under the conditions described above to give **20**, **21**, and **22** in 9%, 11%, and 20% yield respectively.

The keto ester (**20**) was dehydrated with $POCl_3$ in pyridine to give **23** (38%) as an unstable oil. NMR δ: 0.91 (3H, s, 5-CH_3), 1.16 (3H, d, J=7 Hz, 4-CH_3), 1.95 (3H, d, J=1.5 Hz, 11-CH_3), 5.81 (1H, t, J=4 Hz, 1-H), 6.00 (1H, s, 9-H).

4β,5β-Dimethyl-7α-(1′-methoxycarbonyl-1′-hydroxyethyl)octalin-9-en-3,8-dione (**24**)——(a) A solution of 30 mg of the keto ester (**19a**) in 5 ml of 75% aq. AcOH was allowed to stand at room temperature for 48 hr. The aq. AcOH was evaporated off and the residue was purified by silica gel preparative TLC (hexane: AcOEt=3: 1) to give **24a** as colorless prisms, mp 116—117° (from AcOEt–hexane) in quantitative yield. *Anal.* Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53; Mol. Wt. 294.1465. Found: C, 65.14; H, 7.39; M^+ 294.1466. IR cm^{-1}: 3550 (OH), 1730, 1720, 1655 (CO), 1630 (C=C); UV λ_{max}^{EtOH} 235.5 nm (ε 16000); NMR δ: 1.07 (3H, d, J=7 Hz, 4-CH_3), 1.11 (3H, s, 5-CH_3), 1.47 (3H, d, J=1 Hz, 11-CH_3), 3.75 (3H, s, OCH_3), 5.88 (1H, bs, 9-H); MS m/z (% Rel. int.): 294 (M^+, 4), 235 (100).

(b) **19b** (30 mg) was treated under the conditions described above to give **24b** quantitatively as colorless needles, mp 151—152° (from AcOEt–hexane). *Anal.* Calcd for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53; Mol. Wt. 294.1468. Found: C, 65.22; H, 7.51; M^+ 294.1492. IR cm^{-1}: 4350 (OH), 1755, 1705, 1680 (CO), 1630 (C=C); UV λ_{max}^{EtOH} 235 nm (ε 16000); NMR δ: 1.09 (3H, d, J=7 Hz, 4-CH_3), 1.14 (3H, s, 5-CH_3), 1.36 (3H, s, 11-CH_3), 3.80 (3H, s, OCH_3), 5.85 (1H, bs, 9-H); MS m/z 294 (M^+).

3,3-Ethylenedithio-4β,5β-dimethyl-7α-(1′-methoxycarbonyl-1′-hydroxyethyl)octalin-9-en-8-one (**25**)——(a) A solution of 25 mg of **24a** in CH_2Cl_2 (5 ml) was treated with 50 mg of ethanedithiol and 6 drops of $BF_3 \cdot OEt_2$ at 0°. The reaction mixture was allowed to stand at room temperature for 1 hr. The mixture was diluted with ether (50 ml) and the ether layer was washed with sat. aq. $NaHCO_3$ and then with water. After removal of the solvent by evaporation the residue was purified by silica gel column chromatography (hexane: AcOEt=3: 1) to afford 26 mg (84%) of **25a** as colorless plates, mp 170—172° (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{26}O_4S_2$: C, 58.35; H, 7.07; Mol. Wt. 370.1271. Found: C, 58.44; H, 7.16; M^+ 370.1286. IR cm^{-1}: 3450 (OH), 1730, 1635 (CO); UV λ_{max}^{EtOH} 238.5 nm (ε 15000); NMR δ: 1.24 (3H, s, 5-CH_3), 1.27 (3H, d, J=7 Hz, 4-CH_3), 1.44 (3H, d, J=1 Hz, 11-CH_3), 3.27 (4H, m, ), 3.73 (3H, s, OCH_3), 5.69 (1H, d, J=1.5 Hz, 9-H); MS m/z (% Rel. int.): 370 (M^+, 32), 268 (100).

(b) **24b** (25 mg) was treated under the conditions described as above to afford 27 mg (86%) of **25b** as colorless needles, mp 177—179° (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{26}O_4S_2$: C, 58.35; H, 7.07; Mol. Wt. 370.1271. Found: C, 58.55; H, 7.15; M^+ 370.1285. IR cm^{-1}: 3550 (OH), 1735, 1665 (CO), 1625 (C=C); UV λ_{max}^{EtOH} 238 nm (ε 18000); NMR δ: 1.27 (3H, s, 5-CH_3), 1.31 (3H, d, J=7 Hz, 4-CH_3), 1.34 (3H, s, 11-CH_3), 3.26 (4H, m, ), 3.79 (3H, s, OCH_3), 5.68 (1H, d, J=1.5 Hz, 9-H); MS m/z (% Rel. int.): 370 (M^+, 76), 268 (100).

3,3-Ethylenedithioligularenolide (**26**)——(a) A mixture of a solution of 39 mg of **25a** in benzene (10 ml) and $TsOH \cdot H_2O$ (10 mg) was refluxed for 3 hr. The reaction mixture was diluted with ether and the solution was washed with sat. aq. $NaHCO_3$ and dried. The solvent was evaporated off *in vacuo* and the residue was purified by silica gel preparative TLC (hexane: $CHCl_3$: AcOEt=10: 5: 1) to afford 21 mg (62%) of **26**, as yellow needles, mp 190—192° (from AcOEt–hexane). *Anal.* Calcd for $C_{17}H_{20}O_2S_2$: C, 63.71; H, 6.29; Mol. Wt. 320.0903. Found: C, 63.79; H, 6.43; M^+ 320.0897. IR cm^{-1}: 1765 (CO), 1645, 1630 (C=C); UV λ_{max}^{EtOH} 330 nm (ε 22000); NMR δ: 1.17 (3H, d, J=1 Hz, 5-CH_3), 1.38 (3H, d, J=7 Hz, 4-CH_3), 1.91 (3H, d,

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J=1.5 Hz, 11-CH_3), 5.69 (1H, t, J=4 Hz, 1-H), 5.94 (1H, s, 9-H); MS m/z (% Rel. int.): 320 (M^+, 22), 188 (100).

(b) **25b** (39 mg) was treated under the conditions described above to afford 20 mg (60%) of **26**, mp 190—192°.

(±)-Ligularenolide (27)——Raney nickel (0.3 g) was added to a solution of 20 mg of **26** in dioxane (2 ml) and ethanol (1 ml) at 0° and the reaction mixture was stirred for 1 hr. The nickel was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel preparative TLC (hexane: AcOEt=10: 1) to afford 10 mg (70%) of (±)-ligularenolide (**27**), mp 84—87°, as yellow prisms. High-resolution mass spectrum for $C_{15}H_{18}O_2$: Mol. Wt. 230.1306. Observed: M^+ 230.1308. IR cm^{-1}: 1760 (CO), 1645, 1625 (C=C); UV λ_{max}^{EtOH} 331 nm (ε 21000); NMR δ: 0.97 (3H, d, J=1 Hz, 5-CH_3), 1.00 (3H, d, J=5.7 Hz, 4-CH_3), 1.91 (3H, d, J=1.8 Hz, 11-CH_3), 2.86 (1H, d, J=16 Hz, 6-H), 5.77 (1H, t, J=4 Hz, 1-H), 5.90 (1H, s, 9-H); MS m/z (% Rel. int.): 230 (M^+, 100), 215 (82). NMR, IR, and mass spectral data for (±)-**27** were identical with those for natural (−)-ligularenolide reported by Takahashi *et al.*[8]

(±)-Tetrahydroligularenolide (28)——(a) (±)-Ligularenolide (**27**) (20 mg) was catalytically reduced with 10% Pd-C (10 mg) in EtOH (10 ml) at room temperature for 30 min. The catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel preparative TLC (hexane: AcOEt=5: 1) to afford (±)-tetrahydroligularenolide (**28**) in quantitative yield. Recrystallization from hexane gave **28**, mp 92—93°, as colorless needles. *Anal.* Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46; Mol. Wt. 234.1618. Found: C, 76.54; H, 9.23; M^+ 234.1610. IR cm^{-1}: 1730 (CO), 1680 (C=C); UV λ_{max}^{EtOH} 220.5 nm (ε 16200); NMR δ: 0.57 (3H, d, J=1 Hz, 5-CH_3), 0.90 (3H, d, J=5.7 Hz, 4-CH_3), 1.79 (3H, m, 11-CH_3), 2.77 (1H, d, J=14 Hz, 6-H), 4.62 (1H, m, 8-H); MS m/z (% Rel. int.): 234 (M^+, 48), 123 (100).

(b) A solution of 7 mg of thioketal (**26**) in EtOH (5 ml) was treated with 0.2 g of Raney nickel and the mixture was refluxed for 3 hr. After work-up as described above, the product was purified by silica gel preparative TLC (hexane: AcOEt=5: 1) to give (±)-tetrahydroligularenolide (**28**) quantitatively. Melting point and IR, NMR, UV, and mass spectral data for (±)-**28** were identical with those for synthetic tetrahydroligularenolide reported by Piers *et al.*[9]

Condensation of 17 with Acetol Pyranyl Ether——A solution of 500 mg (2 mmol) of **17** in dry THF (5 ml) was added to an LDA solution (prepared from 15 mmol of *n*-BuLi and 2 ml of diisopropylamine as described for **18a**) during a period of 1 hr, then stirring was continued for 1 hr at −78°. Next, a saturated ethereal solution of $ZnCl_2$ (3 ml) was added, followed by a solution of acetol pyranyl ether (1.75 ml) in dry THF (3 ml), and the reaction mixture was stirred at −40° for 1 hr. Sat. aq. NH_4Cl was added and the whole was extracted with ether. The organic layer was washed with water and dried, then the ether was evaporated off. The residue was separated by silica gel preparative TLC (hexane: AcOEt=3: 1) to afford 740 mg (88%) of **32** (diastereoisomeric mixture) as an oil. IR cm^{-1}: 3450 (OH), 1650 (CO); NMR δ: 0.94, 0.96 (each 3H, d, J=7 Hz, 4-CH_3); UV λ_{max}^{EtOH} 238.5 nm; MS m/z 309 ($[M-85]^+$).

Catalytic Hydrogenation of 32——The enone (**32**) (740 mg) in EtOH (10 ml) was catalytically reduced with 10% Pd-C (74 mg). After work-up, the crude product was purified by silica gel preparative TLC (hexane: AcOEt=3: 1) to afford the ketone (**33**) in quantitative yield as an oil. IR cm^{-1}: 1710 (CO); NMR δ 0.92 (3H, d, J=7 Hz, 4-CH_3); MS m/z 311 ($[M-85]^+$).

(±)-Furanoligularanone (34)——H_2O (2 drops) and $TsOH \cdot H_2O$ (30 mg) were added to a solution of 300 mg of ketone (**33**) in THF (10 ml) and the reaction mixture was warmed at 60°. When the reaction was completed, the reaction mixture was diluted with ether and the organic layer was washed with sat. aq. $NaHCO_3$ and dried. The ether was evaporated off *in vacuo* and the residue was column-chromatographed on alumina (hexane: AcOEt=20: 1) to give 84 mg (48%) of (±)-furanoligularanone (**34**) as colorless crystals, mp 86—88° (from hexane). High-resolution mass spectrum for $C_{15}H_{20}O_2$: Mol. Wt. 232.1462. Observed: M^+ 232.1458. IR cm^{-1}: 1715 (CO); NMR δ: 0.64 (3H, s, 5-CH_3), 1.07 (3H, d, J=7 Hz, 4-CH_3), 1.91 (3H, d, J=1 Hz, 11-CH_3), 6.92 (1H, q, J=1 Hz, 12-H); MS m/z (% Rel. int.): 232 (M^+, 29), 108 (100).

(±)-3β-Furanoligularanol (36)——A solution of 80 mg of furanoligularanone (**34**) in EtOH (5 ml) was treated with 13 mg of $NaBH_4$ at 0° and the reaction mixture was stirred for 4 hr. After work-up in the usual way, the product was column-chromatographed on alumina (hexane: AcOEt=5: 1) to give 30 mg (37%) of (±)-3β-furanoligularanol (**36**), mp 78—80° as colorless granules. Melting point and IR, NMR, and mass spectral data for (±)-**36** were identical with those for synthetic (±)-3β-furanoligularanol (**36**) reported previously.[5]

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