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Studies on Terpenoids and Related Alicyclic Compounds. XVI.[1] Total Syntheses of Furanosesquiterpenes; (±)-Furanoeremophilane, (±)-Furanoligularane, (±)-9,10-Dehydrofuranoeremophilane, (±)-3β-Hydroxyfuranoeremophilane, and (±)-3β-Furanoligularanol

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Total syntheses of (±)-furanoeremophilane (**34**), (±)-furanoligularane (**37**), (±)-9,10-dehydrofuranoeremophilane (**32**), (±)-ligularone (**1**), (±)-3β-hydroxyfuranoeremophilane (**25**), and (±)-3β-furanoligularanol (**31**) are described. Reduction of *cis*-annulated 6,9-dioxo-3-ketal (**9**) with $NaBH_4$ gave ketols (**10a** and **11a**). **11a** was desketalized and subjected to selective reduction with P–I_2 to give 3,6-diketone (**13**), which was already converted into (±)-**1**. Reduction of 3,9-dioxo-6α-ol (**14**), derived from **10a**, with P–I_2 afforded a mixture of **17**—**20**. Both 3,9-diketones (**18** and **19**) were converted into 3,9-diol acetates (**24b** and **30b**), respectively. The Birch reductions were effected for deacetoxylation of α′-acetoxy-α-substituted furan, *e.g.* (**26**) and the results are shown in Table I. Reductive deacetoxylation of **24b** and **30b** by the Birch procedure gave (±)-**25** and (±)-**31**, respectively. (±)-Hydroxyfuranoeremophilane (**6**), derived from **18**, was treated with $POCl_3$-pyridine to give (±)-**32**. Reductive deacetoxylation of acetate (**33**) by the Birch procedure gave (±)-**34**. *trans*-Annulated 3,9-diketone (**19**) was derived to the acetate (**36b**), which was converted by the Birch procedure into (±)-**37**.

Keywords——total synthesis; furanosesquiterpenoid; eremophilanes; furanoeremophilane; furanoligularane; 9,10-dehydrofuranoeremophilane; 3β-hydroxyfuranoeremophilane; 3β-furanoligularanol; Birch reduction; reductive dehydroxylation

Furanosesquiterpenoids[3] possessing the eremophilane skeleton are widely distributed in *Petasites*, *Senecio*, and *Ligularia* species in Compositae. Positions 3, 6, and 9 of eremophilane structure are most frequently oxygenated, for example, in ligularone (**1**),[4] furanoeremophilone (**2**),[5] furanoligularenone (**3**),[6] furanofukinol (**4**),[7] and kablicin (**5**).[8]

In the previous papers, the authors reported total syntheses of (±)-ligularone (**1**),[9] (±)-furanoeremophilone (**2**),[10] and (±)-9-hydroxyfuranoeremophilane (**6**)[10] starting from 6,9-diketo diene adduct (**7**) which was prepared by the Diels-Alder reaction of 3-ethoxy-1,3-pentadiene and 3,5-dimethylbenzofuran-4,7-quinone.[9] The diene adduct (**7**) is an important key intermediate toward the total syntheses of several oxygenated furanoeremophilanes. For these purposes, regioselective reduction of oxygen functions at 3, 6, and 9 positions is

1) Part XV: K. Yamakawa, K. Nishitani, and K. Kasahara, *Tetrahedron*, submitted for publication.
2) Location: *12-Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.*
3) For review see H. Hikino and C. Konno, *Heterocycles*, **4**, 817 (1976).
4) *a*) H. Ishii, T. Tozyo, and H. Minato, *Tetrahedron*, **21**, 2605 (1965); *b*) M. Tada, Y. Moriyama, Y. Tanahashi, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **47**, 1999 (1974).
5) *a*) L. Novotny, Z. Samek, J. Harmatha, and F. Sorm, *Coll. Czech. Chem. Comm.*, **34**, 336 (1969); *b*) Z. Samek, J. Harmatha, L. Novotny, and F. Sorm, *ibid.*, 34, 2792 (1969).
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8) L. Novotny, Z. Samek, V. Herout, and R. Sorm, *Tetrahedron Lett.*, **1968**, 1401.
9) K. Yamakawa and T. Satoh, *Chem. Pharm. Bull.* (Tokyo), **25**, 2535 (1977).
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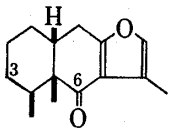
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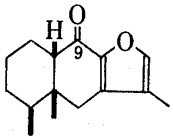
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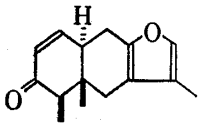
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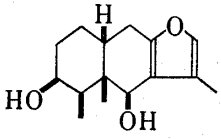
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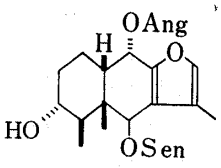
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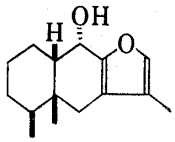
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necessary. The authors wish to report here the total syntheses of (±)-furanoeremophilane (**34**), (±)-furanoligularane (**37**), (±)-9,10-dehydrofuranoeremophilane (**32**), (±)-3β-hydroxyfuranoeremophilane (**25**), and (±)-3β-furanoligularanol (**31**). The synthetic procedure involves an effective deacetoxylation of α'(C-9)acetoxy α-substituted furan.

Syntheses of (±)-Ligularone, (±)-3β-Hydroxyfuranoeremophilane, and (±)-3β-Furanoligularanol

Treatment of *cis*-annulated triketone (**8**), which was previously prepared from the diene adduct (**7**),[9] with ethylene glycol in the presence of *p*-toluenesulfonic acid in benzene gave 6,9-dioxo-3-ketal (**9**), mp 180—181°, in 88% yield. Reduction of **9** with sodium borohydride afforded a mixture of ketols (**10a**), mp 169—171°, and (**11a**), mp 198—201°, in 52% and 42% yield, respectively. Both ketols (**10a** and **11a**) were converted with acetic anhydride-pyridine into the corresponding ketol acetates (**10b**), mp 135—137°, and (**11b**), mp 146—147°, respectively. The ketol (**11a**) was treated with aqueous acetic acid to afford hydroxy diketone (**12**), mp 172—174°, in 94% yield. Reduction of **12** with red phosphorus and iodine in acetic acid gave diketone (**13**), quantitatively. The spectral data of diketone (**13**) were identical

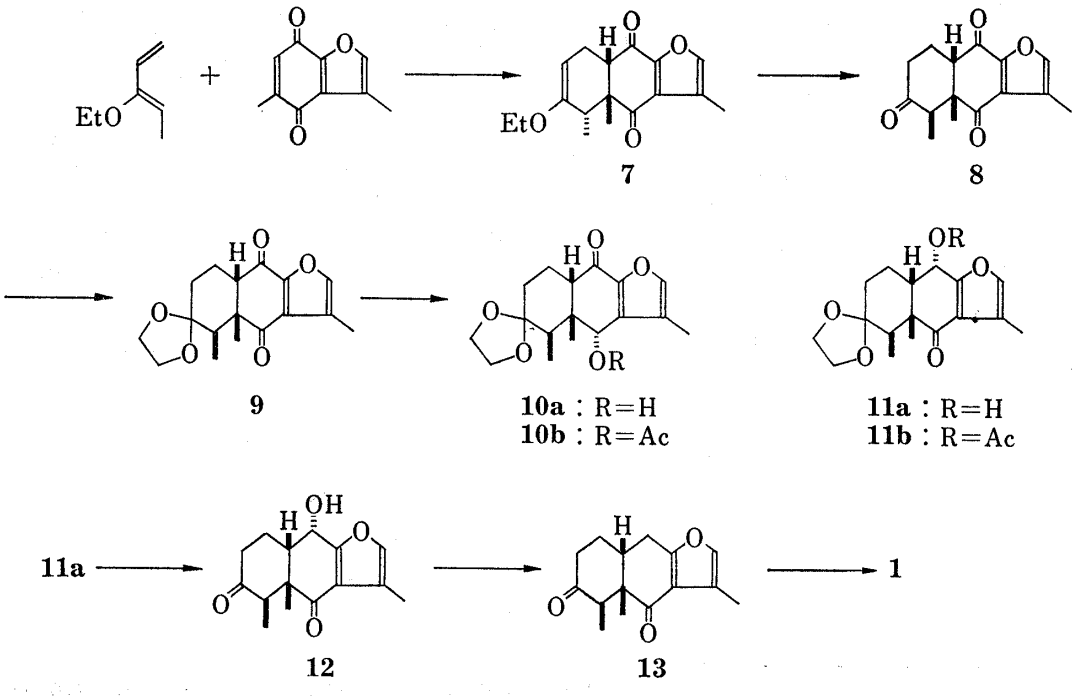

Chart 1

with those of authentic diketone which was previously reported.[9] The authors already synthesized (±)-ligularone (**1**) from **13**, so an alternative total synthesis of (±)-**1** has been achieved.

Treatment of 6α-hydroxy compound (**10a**) with aqueous acetic acid followed by silica gel preparative thin-layer chromatography (TLC) separation afforded diketo-ol (**14**), mp 166—175°, and a cyclic ether (**15**), an oily compound, in 75% and 22% yield, respectively. The structure of **15** was assumed by mass, infrared spectrum (IR) and nuclear magnetic resonance (NMR) spectral data, and the conformation could be shown to be non-steroidal (**15a**). Reductive dehydroxylation of the *cis*-dimethyl diketo-ol (**14**), according to the same condition previously described for *trans*-dimethyl diketo-ol (**16**),[10] with red phosphorus and iodine in acetic acid was carried out. The products were separated by silica gel preparative TLC to give a benzofuran derivative (**17**), mp 185—189°, in 8% yield and diketones (**18**; 20% yield), mp 166—170°, (**19**; 20% yield), mp 199—202°, and (**20**; 30% yield), as an oil. The structures of compounds (**17**—**20**) are presumed by their spectral properties. Ultraviolet (UV) spectrum of **17** showed very similar curve to that of 3,5-dimethyl-4-hydroxybenzofuran (**21**)[9] and NMR spectrum of **17** showed three methyl signals at δ 1.37 (d, J=7 Hz), 2.37 (d, J=1 Hz), and 2.47 (s). Mass spectrum of **17** showed molecular ion peak at m/e 244. Based on these spectral data, the structure of **17** was assumed to be a benzofuran derivative (**17**). The diketones (**18**—**20**) showed the same molecular ion peak at m/e 246 in their mass spectra. IR, UV and NMR data of the diketones (**18** and **19**) were in good agreement with those of authentic 10β-H- and 10α-H-furanoeremophilane-3,9-dione respectively, derived from natural products reported by Takahashi *et al.*[11] and Rivett *et al.*[12] A solution of the isomeric diketone (**20**) in benzene containing *p*-toluenesulfonic acid was refluxed for 2 hr to afford diketones (**18**), (**19**), and (**20**) in 23%, 18%, and 41% yield, respectively. Structure of **20** should be shown to be 4-epi-10β-H-furanoeremophilane-3,9-dione. Surprisingly, these reduction products (**17**)—(**20**) are identical with those obtained from the *trans*-dimethyl

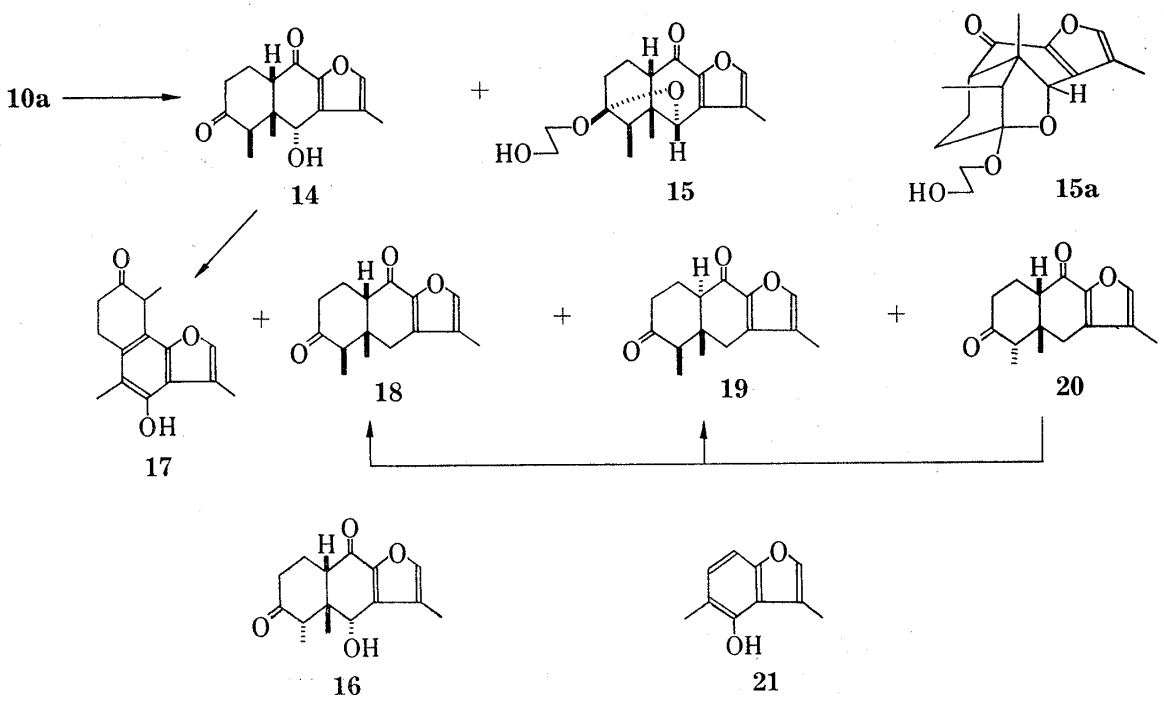

Chart 2

11) H. Nagano, Y. Tanahashi, Y. Moriyama, and T. Takahashi, *Bull. Chem. Soc. Jpn.*, **46**, 2840 (1973).
12) D.E.A. Rivett and G.R. Woolard, *Tetrahedron*, **23**, 2431 (1967).

compound (**16**)[10] under the same reaction conditions and the ratios of each product were nearly equal.

Reduction of *cis*-annulated *cis*-dimethyl-3,9-dione (**18**) with sodium borohydride gave 3β-ol (**22**), mp 137—138°, in 81% yield together with a minor product 3α-ol (**23**), mp 183—185°, in 7% yield. IR and NMR spectral data of 3β-ol (**22**) were identical with those of optical active **22** derived from 3β-angeloyloxy-9β-senecioyloxyfuranoeremophilane reported by Takahashi *et al.*[11] and also spectral data of 3α-ol (**23**) were identical with those of optical active **23** derived from kablicin (**5**) reported by Novotny *et al.*[8] 9-Oxo-3β-ol (**22**) was reduced by lithium aluminum hydride to give 3β,9α-diol (**24a**), mp 199—202°, in 93% yield. NMR spectrum of **24a** was identical with that of optical active (**24a**) derived from 3β-angeloyloxy-9β-senecioyloxyfuranoeremophilane reported by Takahashi *et al.*[11]

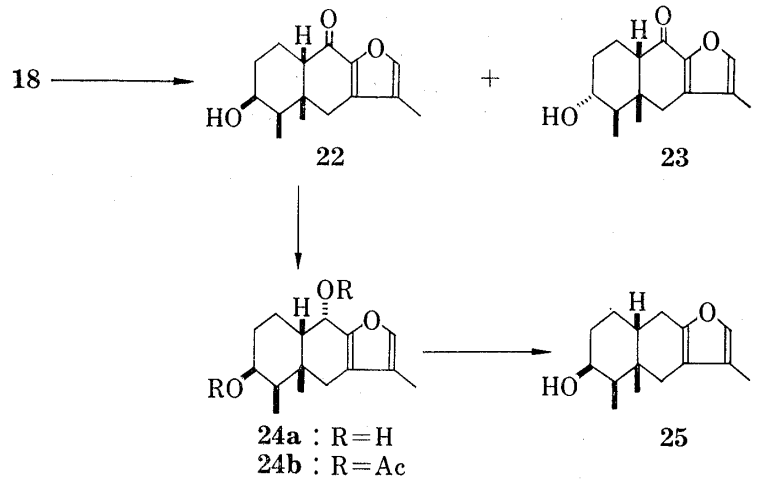

Chart 3

In general, a solution of 6- or 9-deoxo-furanoeremophilanes is unstable in air especially under acidic conditions. Therefore, for the purpose of syntheses toward furanoeremophilanes by dehydroxylation procedure described above, red phosphorous and iodine in acetic acid, can not be applied. The reaction conditions may be desired under neutral of alkaline conditions. Deacetoxylation of β'(C-6) acetoxy β-substituted furan by the Birch procedure has been reported by Takeda *et al.*,[13] and dehydroxylation of the same position by Bohlmann *et al.*,[14] and by the authors.[10] However, direct removal of acetoxyl groups of α'(C-9)acetoxy α-substituted furan has not yet been reported.

The Birch type reduction, with alkaline metal in liquid ammonia, of model compound 2-(1′-acetoxypentyl)furan (**26**) was investigated. Birch[15] has reported that reduction of 2-(1′-hydroxypentyl)furan (**28**) with dissolving lithium metal in liquid ammonia afforded 2-pentylfuran (**27**) as a hydrogenolysis product in a low yield (3.5% yield) together with 82% yield of the unchanged starting material. Hydrogenolysis of **26** with excess amount of alkaline metals in liquid ammonia under several conditions was carried out. When lithium metal was used, 2-pentylfuran (**27**) was obtained in good yield (80% yield), whereas on using sodium and calcium metal, formation of 2-(1′-hydroxypentyl)furan (**28**) as by-product was increased. These results are summarized in Table I.

13) H. Ishii, T. Tozyo, M. Nakamura, and K. Takeda, *Tetrahedron*, **24**, 625 (1968).
14) F. Bohlmann, H-J. Forster, and C-H. Fischer, *Liebig Ann. Chem.*, **1976**, 1487.
15) A.J. Birch, *J. Chem. Soc.*, **1945**, 809.

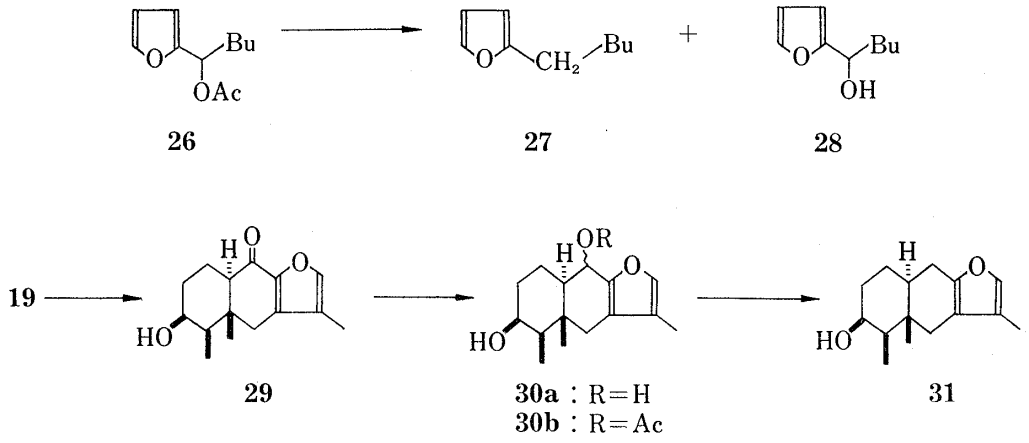

Chart 4

Table I. The Reduction Results of 2-(1′-Acetoxypentyl)furan (**26**) with Various Metals in liq. -NH_3

Metal	Atomic ratio for **26**	Product ratio (%)[a]		
		26	**27**	**28**
Li	2	13	83	4
	4	5	92	3
	6	0	95	5
Na	2	0	71	29
	6	0	83	17
Ca	2	0	50	50
	6	0	69	31
Mg	2	100	0	0

a) Products ratio (%) of **26**—**28** were indicated by NMR spectroscopy.

3β,9α-Dihydroxyfuranoeremophilane (**24a**) was treated with acetic anhydride in pyridine to give 3β,9α-diacetate (**24b**) which was reduced with lithium in liquid ammonia by the Birch procedure to afford (±)-3β-hydroxyfuranoeremophilane (**25**), mp 77—80°, quantitatively. IR and NMR spectra of **25** were in good agreement with those of the authentic product derived from 3β-angeloyloxyfuranoeremophilane isolated from *Farfugium japonicum* by Takahashi *et al.*[11]

According to the same way as described above, reduction of *trans*-annulated 3,9-dione (**19**) with sodium borohydride gave 3β-ol (**29**), mp 192—193°, in 93% yield. IR, UV and NMR spectral data of **29** were in good agreement with those of 3-epieuryopsonol reported by Takahashi *et al.*[11] Lithium aluminum hydride reduction of **29** afforded an epimeric mixture of 9-hydroxy compounds (**30a**), which was converted without purification to the corresponding acetates (**30b**) and subjected to reduction by the Birch procedure, lithium in liquid ammonia, to afford (±)-3β-furanoligularanol (**31**), mp 78—79.5°. IR, mass and NMR spectral data were in good agreement with those of optical active-**31** which was derived from furanoligularenone isolated from *Othonna Filicalis* reported by Ourisson and Takahashi *et al.*[6b,11]

Syntheses of (±)-9,10-Dehydrofuranoeremophilane, (±)-Furanoeremophilane and (±)-Furanoligularane

The total syntheses toward mother skeleton of furanoeremophilanes, (±)-furanoeremophilane (**34**), (±)-furanoligularane (**37**) and (±)-9,10-dehydrofuranoeremophilane (**32**), starting from the key intermediate (**7**) by reductive deoxygenation were investigated. We have previously reported[10] the total synthesis of (±)-9-hydroxyfuranoeremophilane (**6**) from the

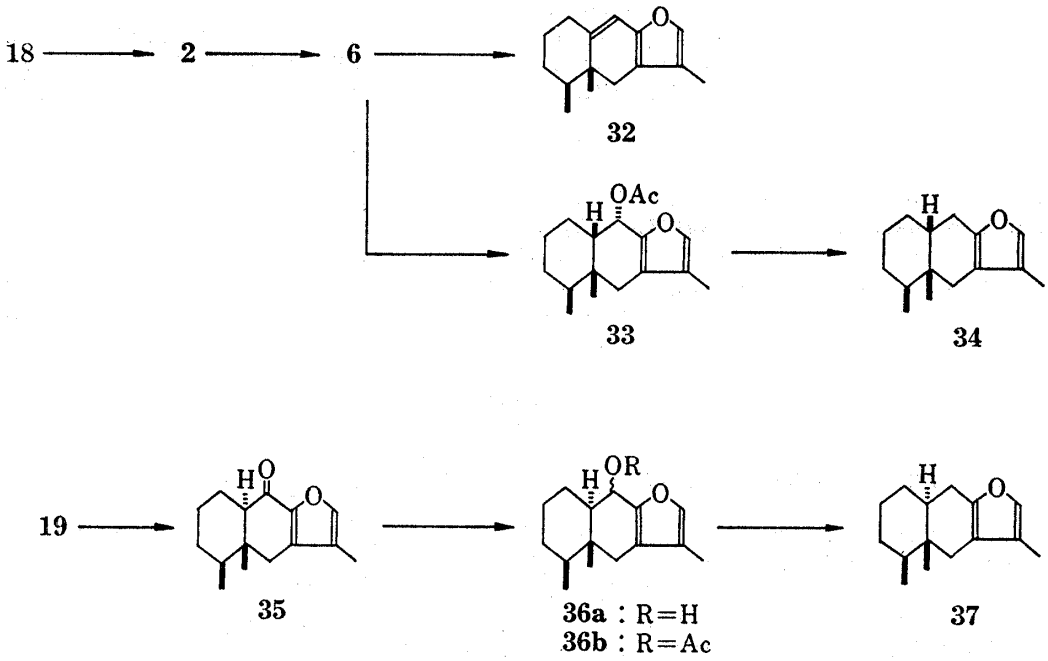

Chart 5

diketone (**18**). Treatment of **6** with phosphorus oxychloride in pyridine at 100° for 20 min. gave an unstable oily product of olefin (**32**), in 64% yield. UV and NMR spectral data of **32** were identical with those of 9,10-dehydrofuranoeremophilane isolated from *Senecio teretifolius* reported by Bohlmann and Zdero.[16]

Acetylation of **6** with acetic anhydride in pyridine gave the acetate (**33**). Without purification of **33**, reduction with lithium in liquid ammonia according to the Birch procedure afforded (±)-furanoeremophilane (**34**), as colorless oil in quantitative yield from **6**. NMR spectrum of **34** was in good agreement with that of natural furanoeremophilane isolated from *Ligularia Fischeri* Turcz reported by Ishii *et al.*[17]

Reduction of (±)-10α*H*-furanoeremophilone (**35**),[10] which was previously synthesized from *trans*-annulated diketone (**19**), with lithium aluminum hydride gave an epimeric mixture of 9-ols (**36a**). Acetylation of (**36a**) afforded the corresponding acetates (**36b**). The Birch reduction of **36b** afforded a colorless oily compound, (±)-furanoliqularane (**37**), in 90% yield from ketone (**35**). IR and NMR spectra of **37** were in good agreement with those of (±)-furanoligularane derived from furanoligularenone reported by Ourisson and Takahashi *et al.*[6b]

Experimental

All melting points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi 215 or Hitachi Perkin-Elmer 225 spectrophotometer. Ultraviolet (UV) spectra were measured with a Hitachi 323 or 200 spectrophotometer. Nuclear magnetic resonance (NMR) spectra are for solution in $CDCl_3$ unless otherwise cited and they were measured on a JEOL JNM-4H 100, JEOL JNM-FX 100 pulse FT (100 MHz), or Hitachi R-24 (60 MHz) spectrometer. Low and high-resolution mass spectra were taken on a Hitachi RMU-7M double focusing spectrometer connected with data lyser 002 system.

3,3-Ethylenedioxy-furanoeremophilane-6,9-dione (9)——A mixture of furanoeremophilane-3,6,9-trione[9] (**8**) (520 mg), ethylene glycol (2.0 g), *p*-toluenesulfonic acid monohydrate (200 mg) and 80 ml of benzene was placed in a flask fitted with a water separator and condenser. The reaction mixture was refluxed for 4 hr and then was washed with sat. aq-$NaHCO_3$. Evaporation of solvent left a residue which was purified by

16) F. Bohlmann and C. Zdero, *Phytochemistry*, **16**, 135 (1977).
17) H. Ishii, T. Tozyo, and H. Minato, *J. Chem. Soc* (*C*), **1966**, 1545.

silica gel column chromatography to give crystals. Recrystallization from EtOAc–hexane gave colorless prisms of ketal (**9**) (534 mg; 88% yield), mp 180—181°. *Anal.* Calcd. for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62; Mol. Wt. 304.1308. Found: C, 67.36; H, 6.73; M$^+$ 304.1302. IR cm^{-1}: 1675 (CO); UV λ_{max}^{EtOH} nm (ε): 243 (5500), 302 (8100). NMR δ: 0.88 (3H, d, J=7 Hz, 4-CH_3), 1.28 (3H, s, 5-CH_3), 2.24 (3H, d, J=1 Hz, 11-CH_3), 2.41 (1H, q, J=7 Hz, 4-H), 2.74 (1H, dd, J=8, 5 Hz, 10-H), 3.7—4.1 (4H, m, ), 7.40 (1H, m, $W1/2$=5 Hz, 12-H). MS *m/e* (rel. intensity %): 304 (M$^+$, 13), 99 ([M–$C_{12}H_{13}O_3$],$^+$ 100).

Reduction of Diketone (9) with $NaBH_4$——To a solution of diketone (**9**) (91 mg) in tetrahydrofuran (THF) (1 ml) and MeOH (20 ml) was added $NaBH_4$ (12 mg) with stirring at 0° and stirring was continued for 40 min. NH_4Cl was added to the reaction mixture and then the solution was evaporated *in vacuo*. The residue was extracted with $(C_2H_5)_2O$ and washed with H_2O and dried. After removal of $(C_2H_5)_2O$, the residue was separated to two bands by preparative TLC.

Band 1: Recrystallization from EtOAc–hexane gave 9-oxo-6α-ol (**10a**) (48 mg; 52% yield), mp 169—171°, as colorless needles. *Anal.* Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24; Mol. Wt. 306.1466. Found: C, 66.89; H, 7.30; M$^+$ 306.1488. IR cm^{-1}: 3435 (OH), 1662 (CO); UV λ_{max}^{EtOH} 285.5 nm (ε 14500); NMR δ: 1.05 (3H, d, J=7 Hz, 4-CH_3), 1.26 (3H, s, 5-CH_3), 2.13 (3H, d, J=1 Hz, 11-CH_3), 3.8—4.1 (4H, m, ), 4.79 (1H, d, J=5 Hz, 6-H), the signal changed to a singlet on addition of D_2O, 7.37 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 306 (M$^+$, 12), 99 [(M–$C_{12}H_{15}O_3$]$^+$, 100).

Band 2: Recrystallization from EtOAc-hexane gave 6-oxo-9α-ol (**11a**) (39 mg; 42% yield), mp 198—201°, as colorless granular form. *Anal.* Calcd. for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24; Mol. Wt. 306.1465. Found: C, 66.57; H, 7.16; M$^+$ 306.1465. IR cm^{-1}: 3400 (OH), 1666 (CO); UV λ_{max}^{EtOH} 265.5 nm (ε 3700): NMR δ: 1.00 (3H, d, J=7 Hz, 4-CH_3), 1.07 (3H, s, 5-CH_3), 2.21 (3H, d, J=1 Hz, 11-CH_3), 2.74 (1H, q, J=7 Hz, 4-H), 3.6—4.2 (4H, m, ), 5.22 (1H, t, J=5.5 Hz, 9-H), when D_2O was added, the signal changed to a doublet, 7.17 (1H, m, $W1/2$=4 Hz, 12-H). MS *m/e* (rel. intensity %): 306 (M$^+$, 17), 99 ([M–$C_{12}H_{15}O_3$]$^+$, 100).

Ketol (**10a**) was converted with Ac_2O–pyridine in the usual manner to the corresponding acetate (**10b**), quantitatively, mp 135—137°, as colorless prisms. *Anal.* Calcd. for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94; Mol. Wt. 348.1572. Found: C, 65.62; H, 7.02; M$^+$ 348.1593. IR cm^{-1}: 1741, 1678 (CO), 1234 (COC); UV λ_{max}^{EtOH} 282 nm (ε 14800); NMR δ: 0.96 (3H, d, J=7 Hz, 4-CH_3), 1.27 (3H, s, 5-CH_3), 1.97 (3H, d, J=1 Hz, 11-CH_3), 2.19 (3H, s, $COCH_3$), 3.6—4.1 (4H, m, ), 6.22 (1H, s, 6-H), 7.37 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 348 (M$^+$, 7), 99 ([M–$C_{14}H_{17}O_4$]$^+$, 100).

Ketol (**11a**) was converted in the same manner for **10a** to the corresponding acetate (**11b**), quantitatively, as colorless prisms, mp 146—147°. *Anal.* Calcd. for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94; Mol. Wt. 348.1571. Found: C, 65.82; H, 7.02; M$^+$, 348.1576. IR cm^{-1}: 1750, 1664 (CO), 1235 (COC); UV λ_{max}^{EtOH} 263.5 nm (ε 3500); NMR δ: 1.00 (3H, d, J=7 Hz, 4-CH_3), 1.14 (3H, s, 5-CH_3), 2.21 (3H, d, J=1 Hz, 11-CH_3), 2.21 (3H, s, $COCH_3$), 2.75 (1H, q, J=7 Hz, 4-H), 3.6—4.2 (4H, m, ), 6.25 (1H, d, J=5 Hz, 9-H), 7.16 (1H, m, $W1/2$=4 Hz, 12-H); MS *m/e* (rel. intensity %): 348 (M$^+$, 18), 99 ([M–$C_{14}H_{17}O_4$]$^+$, 100).

Treatment of Ketal (11a) with Aqueous Acetic Acid——A solution of ketal (**11a**) (30 mg) in 6 ml of AcOH–H_2O (3:1) was allowed to stand at room temperature for 20 hr. The solvent was evaporated *in vacuo* to leave a crude product which was purified by preparative TLC. Recrystallization from EtOAc–hexane gave 24 mg (94% yield) of 3,6-dioxo-9α-ol (**12**), mp 172—174°, as colorless plates. *Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; Mol. Wt. 262.1204. Found: C, 68.68; H, 6.89; M$^+$ 262.1223. IR cm^{-1}: 3390 (OH), 1705, 1654 (CO); UV λ_{max}^{EtOH} 269 nm (ε 3100); NMR δ: 1.04 (3H, d, J=7 Hz, 4-CH_3), 1.17 (3H, s, 5-CH_3), 2.18 (3H, d, J=1 Hz, 11-CH_3), 2.99 (1H, d, J=5 Hz, 9-OH), on addition of D_2O, this signal disappeared, 3.25 (1H, q, J=7 Hz, 4-H), 5.25 (1H, t, J=5 Hz, 9-H), on addition of D_2O, this signal is changed to a doublet, 7.20 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 262 (M$^+$, 15), 244 ([M–H_2O]$^+$, 17), 138 [(M–$C_8H_{12}O$]$^+$, 100).

Furanoeremophilane-3,6-dione (13)——To a suspension of red phosphorus (300 mg) and iodine (100 mg) in AcOH (2 ml) was added a solution of **12** (14 mg) in AcOH (2 ml) and the reaction mixture was allowed to stand with stirring at room temperature for 2.5 hr. The red phosphorus was filtered out and washed with $(C_2H_5)_2O$. 10% aq.-$Na_2S_2O_3$ was added to the organic layer to remove the excess iodine. The mixture was neutralized by K_2CO_3 and was extracted with $(C_2H_5)_2O$, washed with H_2O and dried. Evaporation of $(C_2H_5)_2O$ afforded the crystalline residue which was purified by preparative TLC to give diketone (**13**) mp 176—178° as colorless needles, quantitatively. Melting points and all spectral data of (±)-**13** were identical with those of an authentic specimen of diketone (**13**) which was previously synthesized and described by the authors.[9]

Treatment of Ketol (10a) with Aqueous Acetic Acid——A solution of ketol (**10a**) (45 mg) in 6 ml of AcOH–H_2O (3: 1) was allowed to stand at room temperature for 3 hr. The solvent was evaporated *in vacuo* to leave crude products which were separated to two bands by silica gel preparative TLC.

Band 1: Recrystallization from EtOAc–hexane gave 29 mg (75% yield) of 3,9-dioxo-6α-ol (**14**), mp 166—175°, as colorless needles. *Anal.* Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; Mol. Wt. 262.1203. Found: C, 68.45; H, 7.02; M^+ 262.1201. IR cm^{-1}: 3320 (OH), 1695, 1685 (CO); UV λ_{max}^{EtOH} nm (ε): 238 (3200), 282.5 (13400); NMR δ: 1.01 (3H, d, J=7 Hz, 4-CH_3), 1.01 (3H, s, 5-CH_3), 2.09 (3H, d, J=1 Hz, 11-CH_3), 3.28 (1H, s, OH), on addition of D_2O, this signal disappeared, 4.66 (1H, bs, 6-H), 7.43 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 262 (M^+, 24), 244 ([M–H_2O]$^+$, 25), 229 (20), 189 ([M–C_3H_5O]$^+$, 100).

Band 2: 10 mg (22% yield) of ether (**15**) as colorless oily product was obtained. MS *m/e* (rel. intensity %): 306 (M^+, 5), 244 (21), 229 (18), 189 (100); IR cm^{-1}: 3450 (OH), 1685 (CO); NMR δ: 0.90 (3H, d, J=7 Hz, 4-CH_3), 0.98 (3H, s, 5-CH_3), 2.06 (3H, d, J=1 Hz, 11-CH_3), 3.25 (4H, bs, –O–CH_2CH_2–OH), 4.60 (1H, bs, 6-H), 7.42 (1H, m, $W1/2$=3 Hz, 12-H).

Reduction of 6α-Hydroxyfuranoeremophilane-3,9-dione (14) with Red Phosphorus and Iodine——To a suspension of red phosphorus (600 mg) and iodine (200 mg) in AcOH (4 ml) was added a solution of **14** (26 mg) in AcOH (2 ml) and the reaction mixture was allowed to stand with stirring at room temperature for 48 hr. The red phosphorus was filtered out and washed with $(C_2H_5)_2O$. 10% aq.-$Na_2S_2O_3$ was added to the filtrate to remove excess iodine. The mixture was neutralized by K_2CO_3 and was extracted with $(C_2H_5)_2O$. Evaporation of solvent left the residue which was separated to bands 1—4 by preparative TLC.

Band 1: Compound **17** was obtained (2 mg; 8% yield), as colorless plates, mp 185—189° (from EtOAc–hexane). *Anal.* Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60; Mol. Wt. 244.1097. Found: C, 73.92; H, 6.63; M^+ 244.1066. IR cm^{-1}: 3315 (OH), 1695 (CO); UV λ_{max}^{EtOH} nm (ε): 253 (11300), 285 (2330), 296 (1640); NMR δ: 1.37 (3H, d, J=7 Hz, 9-CH_3), 2.37 (3H, d, J=1 Hz, 3-CH_3), 2.47 (3H, s, 5-CH_3), 3.81 (1H, q, J=7 Hz, 9-H), 7.27 (1H, m, $W1/2$=6 Hz, 2-H); MS *m/e* (rel. intensity %): 244 (M^+, 100), 229 ([M–CH_3]$^+$, 58), 202 ([M–C_2H_2O]$^+$, 53), 201 ([M–C_2H_3O]$^+$, 58).

Band 2: 10βH-Furanoeremophilane-3,9-dione (**18**) (5 mg; 20% yield) was obtained. Recrystallization from EtOAc–hexane afforded colorless plates, mp 166—170°. *Anal.* Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.94: H, 7.41. IR cm^{-1}; 1715, 1660 (CO). UV λ_{max}^{EtOH} 281.5 nm (ε 14050); NMR δ: 0.96 (3H, d, J=7 Hz, 4-CH_3), 1.09 (3H, s, 5-CH_3), 2.00 (3H, d, J=1 Hz, 11-CH_3), 7.42 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 246 (M^+, 54), 231 ([M–CH_3]$^+$, 5), 175 (100).

Band 3: 10αH-Furanoeremophilane-3,9-dione (**19**) (5 mg, 20% yield) was obtained. Recrystallization from EtOAc–hexane afforded colorless prisms, mp 199—202°. *Anal.* Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.95; H, 7.38. IR cm^{-1}: 1720, 1660 (CO). UV λ_{max}^{EtOH} 280 nm (ε 14300); NMR δ: 0.77 (3H, s, 5-CH_3), 1.07 (3H, d, J=6 Hz, 4-CH_3), 2.00 (3H, d, J=1 Hz, 11-CH_3), 2.94 (1H, dd, J=11, 3.5 Hz, 10-H), 7.39 (1H, m, $W1/2$=3 Hz, 12-H); MS *m/e* (rel. intensity %): 246 (M^+, 48), 231 ([M–CH_3]$^+$, 6), 175 (100).

Band 4: 10βH-4-Epifuranoeremophilane-3,9-dione (**20**) (7 mg; 30% yield) was obtained as colorless oil. MS *m/e* (rel. intensity %): 246 (M^+, 45), 175 (100). IR cm^{-1}: 1715, 1680 (CO); UV λ_{max}^{EtOH} 281 nm; NMR δ: 1.09 (3H, d, J=7 Hz, 4-CH_3), 1.20 (3H, s, 5-CH_3), 1.96 (3H, d, J=1 Hz, 11-CH_3), 7.40 (1H, m, $W1/2$=3 Hz, 12-H).

Reduction of 6α-Hydroxy-4-epifuranoeremophilane-3,9-dione (**16**) with red phosphorus and iodine under the same conditions as described for **14** gave the same compounds **17**, **18**, **19** and **20** in the yields 11, 20, 30 and 27%, respectively.

Epimerization of 20 to 18 and 19——A solution of 4-epi compound (**20**) (120 mg) and *p*-toluenesulfonic acid monohydrate (100 mg) in benzene (60 ml) was refluxed for 2 hr. The reaction mixture was washed with sat. aq.-$NaHCO_3$, and was evaporated *in vacuo*. The residue was separated to three bands by preparative TLC. Bands 1, 2, and 3 afforded compound **18** (28 mg; 23% yield), **19** (22 mg; 18% yield), and **20** (49 mg; 41% yield), respectively.

Reduction of Furanoeremophilane-3,9-dione (18) with $NaBH_4$——To a stirring solution of **18** (44 mg) in MeOH (20 ml) was added $NaBH_4$ (10 mg) under cooling in an ice bath. After 10 min, NH_4Cl was added to the reaction mixture and the solvent was evaporated *in vacuo*. The residue was extracted with $(C_2H_5)_2O$, washed with H_2O and dried. After removal of $(C_2H_5)_2O$, the residue was separated to two bands by preparative TLC.

Band 1: Recrystallization from EtOAc–hexane afforded 3β-hydroxy-9-oxofuranoeremophilane (**22**) as colorless granular crystals (**36** mg; 81% yield), mp 137—139°. *Anal.* Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12; Mol. Wt. 248.1411. Found: C, 72.53; H, 8.22; M^+ 248.1411. IR cm^{-1}: 3515 (OH), 1649 (CO); UV ν_{max}^{EtOH} 281 nm (ε 16300): NMR δ: 0.97 (3H, d, J=7 Hz, 4-CH_3), 1.08 (3H, s, 5-CH_3), 1.98 (3H, d, J=1 Hz, 11-CH_3), 2.21 (1H, d, J=17 Hz, 6-H), 3.02 (1H, d, J=17 Hz, 6-H), 4.14 (1H, m, $W1/2$=16 Hz, 3-H), 7.37 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 248 (M^+, 99), 230 ([M–H_2O]$^+$, 21), 215 (32), 177 ([M–C_4H_7O]$^+$, 31), 176 ([M–C_4H_8O]$^+$, 24), 175 ([M–C_4H_9O]$^+$, 44), 163 ([M–C_5H_9O]$^+$, 100), 162 [(M–$C_5H_{10}O$]$^+$, 58).

Band 2: Recrystallization from EtOAc–hexane gave 3 mg (7% yield) of colorless granular form of 3α-hydroxy-9-oxofuranoeremophilane (**23**), mp 183—185°. High-resolution mass spectrum of **23** for $C_{15}H_{20}O_3$: Mol. Wt. 248.1411. Observed: M^+ 248.1427. IR cm^{-1}: 3435 (OH), 1641 (CO); UV λ_{max}^{EtOH} 281.5 nm: FT-NMR δ: 0.97 (3H, d, J=6.5 Hz, 4-CH_3), 1.14 (3H, s, 5-CH_3), 1.98 (3H, d, J=1 Hz, 11-CH_3), 3.50 (1H, m, $W1/2$=

16 Hz, 3-H), 7.36 (1H, m, $W1/2=3$ Hz, 12-H). MS *m/e* (rel. intensity %): 248 (M^+, 43), 230 ($[M-H_2O]^+$, 41), 215 (39), 175 ($[M-C_4H_9O]^+$, 86), 163 ($[M-C_5H_9O]^+$, 36), 162 ($[M-C_5H_{10}O]^+$, 100).

3β,9α-Dihydroxyfuranoeremophilane (24a)——To a solution of ketol (**22**) (16 mg) in abs. Et_2O (14 ml) was added $LiAlH_4$ (23 mg) with stirring in an ice bath for 5 min and the reaction mixture was allowed to stand at room temperature for 2 hr. After decomposition of the excess $LiAlH_4$ with aq. $(C_2H_5)_2O$, the reaction mixture was shaken with sat. aq. NH_4Cl. The $(C_2H_5)_2O$ layer was separated and was evaporated to afford crystals. Recrystallization from AcOEt–hexane gave 15 mg (93% yield) of 3β,9α-diol (**24a**), mp 199—202°, as colorless needles. High-resolution mass spectrum of **24a** for $C_{15}H_{22}O_3$: Mol. Wt. 250.1568. Observed: M^+ 250.1581; IR cm^{-1}: 3370, 3280 (OH); NMR (CD_3OD) δ: 0.93 (3H, s, 5-CH_3), 0.97 (3H, d, $J=7$ Hz, 4-CH_3), 1.87 (3H, d, $J=1$ Hz, 11-CH_3), 2.79 (1H, bd, $J=16$ Hz, 6-H), 4.15 (1H, m, $W1/2=23$ Hz, 3-H), 4.70 (1H, m, 9-H), 7.12 (1H, m, $W1/2=3$ Hz, 12-H), MS *m/e* (rel. intensity %): 250 (M^+, 10), 232 ($[M-H_2O]^+$, 5), 124 ($[M-C_8H_{14}O]^+$, 100).

2-(1′-Acetoxypentyl)furan (26)——Acetylation of 2-(1′-hydroxypentyl)furan (**28**)[15] (1.07 g) with 23 g of a mixture of acetic anhydride-pyridine (1:3) at room temperature for 3 hr was carried out. After work up in the usual manner, the resulting product was purified by distillation to give pale yellow oil, bp_{51} 135—136°, (1.24 g; 90% yield). IR cm^{-1}: 1635 (CO), 1235 ($OCOCH_3$). NMR δ: 2.05 (3H, s, $COCH_3$), 5.82 (1H, t, $J=7$ Hz, 1′-H), 6.31 (2H, m, $W1/2=3$ Hz, 3,4-Ar–H), 7.36 (1H, m, $W1/2=4$ Hz, 5-H).

The Birch Reduction of 2-(1′-Acetoxypentyl)furan (26)——Acetate (**26**) (196 mg; 1 mmol) was dissolved in abs. $(C_2H_5)_2O$ (2 ml) and liq. NH_3 (20 ml) at −70°. To the solution was added Li metal (42 mg; 6 m atom) with stirring at −70° and the reaction mixture was stirred at the temperature for 30 min. NH_4Cl was added to the reaction mixture and then NH_3 was evaporated. The reaction residue was extracted with pentane, and the extract was washed and dried. Removal of the solvent gave 110 mg (*ca.* 80% yield) of a colorless oily product. The oily compound was mainly 2-pentylfuran (**27**) together with a trace amount of 2-(1′-hydroxypentyl)furan as shown by TLC analysis. Compound (**27**): IR cm^{-1}: 1600 (C=C). NMR δ: 2.16 (2H, t, $J=7$ Hz, 1′-H), 5.96 (1H, m, $W1/2=5$ Hz, 3-H), 6.26 (1H, m, $W1/2=7$ Hz, 4-H), 7.28 (1H, m, $W1/2=3$ Hz, 5-H).

The Birch reductions of **26** with other metals in liq. NH_3 under various conditions were summarized in Table I.

(±)-3β-Hydroxyfuranoeremophilane (25)——A solution of 3β,9α-diol (**24a**) (12 mg) in 2.5 ml of a mixture of Ac_2O–pyridine (1:4) was allowed to stand at room temperature for 20 hr. After evaporation of the solvent, the crude diacetate was dissolved in abs. $(C_2H_5)_2O$ (2 ml) and liq. NH_3 (20 ml) at −70° and then Li metal (14 mg) was added to the reaction mixture at −70° with stirring. After work up in the usual manner as described for **34**, an oily product was obtained which was chromatographed on alumina to give 11 mg of **25** in the quantitative yield from **24a**. Recrystallization from hexane gave colorless granular form of (±)-3β-hydroxyfuranoeremophilane (**25**), mp 77—80°. High-resolution mass spectrum of **25** for $C_{15}H_{22}O_2$: Mol. Wt. 234.1618. Observed: M^+ 234.1616. IR cm^{-1}: 3410 (OH); NMR (CCl_4) δ: 0.93 (3H, s, 5-CH_3), 0.94 (3H, d, $J=7$ Hz, 4-CH_3), 1.85 (3H, d, $J=1$ Hz, 11-CH_3), 4.08 (1H, m, $W1/2=21$ Hz, 3-H), 6.90 (1H, m, $W1/2=3$ Hz, 12-H). MS *m/e* (rel. intensity %): 234 (M^+, 20), 108 ($[M-C_8H_{14}O]^+$, 100).

The NMR spectrum of **25** was in good agreement with that of 3β-hydroxyfuranoeremophilane reported by Takahashi *et al.*[11]

(±)-3-Epieuryopsonol (29)——According to the procedure described above for diketone **18**, reduction of **19** (16 mg) with $NaBH_4$ (2.5 mg) under the same conditions was carried out. After purification of the resulting product by preparative TLC, recrystallization from AcOEt–hexane afforded colorless granular form of (±)-3-epieuryopsonol (**29**) (15 mg; 93% yield), mp 192—193°. *Anal.* Calcd. for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12; Mol. Wt. 248.1411. Found: C, 72.56; H, 8.22; M^+ 248.1405. IR cm^{-1}: 3455 (OH), 1641 (CO); UV λ_{max}^{EtOH} 279 nm (ε 14500); NMR δ: 1.01 (3H, s, 5-CH_3), 1.14 (3H, d, $J=7$ Hz, 4-CH_3), 1.98 (3H, d, $J=1$ Hz, 11-CH_3), 2.38 (1H, d, $J=16$ Hz, 6-H), 2.69 (1H, d, $J=16$ Hz, 6-H), 3.89 (1H, m, $W1/2=6$ Hz, 3-H), 7.34 (1H, m, $W1/2=3$ Hz, 12-H). MS *m/e* (rel. intensity %): 248 (M^+, 93), 230 ($[M-H_2O]^+$, 29), 215 (45), 162 ($[M-C_5H_{10}O]^+$, 71), 122 ($[M-C_8H_{14}O]^+$, 100).

The NMR spectrum of **29** was in good agreement with that of (−)-3-epieuryopsonol reported by Takahashi.[11]

(±)-3β-Furanoligularanol (31)——According to the procedure described for (±)-3β-hydroxyfuranoeremophilane (**25**), 3β-hydroxy-9-one (**29**) (16 mg) was dissolved in THF (2 ml) and abs. $(C_2H_5)_2O$ (12 ml). $LiAlH_4$ (23 mg) was added into the reaction mixture with stirring on an ice bath and then the stirring was continued at room temperature for 2 hr. After work up in the usual manner, the product was purified by preparative TLC to give 15 mg (93% yield) of a mixture of 3β,9α- and 3β,9β-diol (**30a**).

Acetylation of the mixture of diol (**30a**) with acetic anhydride-pyridine gave the corresponding mixture of acetates (**30b**).

The Birch reduction of the crude **30b** with Li-liq. NH_3 under the same conditions as described above for **24b** afforded crude crystals. Chromatographic purification on alumina and recrystallization from hexane gave 11 mg (79% yield from diol (**30a**)) of (±)-3β-furanoligularanol (**31**), as colorless granular form, mp 78—79.5°. High-resolution mass spectrum of **31**: $C_{15}H_{22}O_2$ Mol. Wt. 234.1619. Observed: M^+ 234.1622. IR cm^{-1}: 3360 (OH). NMR (CCl_4) δ: 0.85 (3H, s, 5-CH_3), 1.08 (3H, d, $J=7$ Hz, 4-CH_3), 1.84 (3H, d, $J=1$ Hz,

11-CH_3), 3.78 (1H, m, $W1/2=6$ Hz, 3-H), 6.87 (1H, m, $W1/2=3$ Hz, 12-H). MS *m/e* (rel. intensity %): 234 (M^+, 25), 108 ([M–$C_8H_{14}O$]$^+$, 100).

The NMR spectrum of **31** was in good agreement with that of authentic 3β-furanoligularanol reported by Ourison and Takahashi *et al.*[6b,11]

(±)-Furanoeremophilone (2)——To a solution of diketone (**18**) (33 mg) and ethanedithiol (400 mg) in abs. $(C_2H_5)_2O$ (5 ml) was added 25 drops of BF_3–$(C_2H_5)_2O$ and the reaction mixture was allowed to stand at room temperature for 4 days. Sat. aq. $NaHCO_3$ was added to the reaction mixture and was extracted with $(C_2H_5)_2O$, washed, and dried. After removal of $(C_2H_5)_2O$, the product was chromatographed on a column to give 3,3-ethanedithioketal, which was recrystallized from AcOEt–hexane to afford 32 mg (74% yield) of colorless needles, mp 177—179°. *Anal.* Calcd. for $C_{17}H_{22}O_2S_2$: C, 63.32; H, 6.88; Mol. Wt. 322.1059. Found: C, 63.34; H, 6.88; M^+ 322.1045. IR cm^{-1}: 1665 (CO); UV λ_{max}^{EtOH} 283 nm (ε 14700); NMR δ: 1.16 (3H, d, $J=$ 7 Hz, 4-CH_3), 1.31 (3H, s, 5-CH_3), 1.97 (3H, d, $J=1$ Hz, 11-CH_3), 2.9—3.4 (4H, m, $\begin{matrix}CH_2\text{–}S\\ |\quad\quad\rangle\\ CH_2\text{–}S\end{matrix}$), 7.37 (1H, m, $W1/2=3$ Hz, 12-H). MS *m/e* (rel. intensity %): 322 (M^+, 47), 199 (42), 131 (100).

A solution of the ethanedithioketal (36 mg) in abs. EtOH (10 ml) was refluxed for 15 min with Raney nickel (600 mg). After removal of nickel and evaporation of EtOH *in vacuo*, the residue was purified by preparative TLC to afford (±)-furanoeremophilone (**2**) (24 mg; 92% yield). Recrystallization from hexane gave colorless plates, mp 130.5—132°. *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; Mol. Wt. 232.1461. Found: C, 77.36; H, 8.68; M^+ 232.1443. IR cm^{-1}: 1661 (CO); UV λ_{max}^{EtOH} 281 nm (ε 14800); NMR δ: 0.88 (3H, d, $J=7$ Hz, 4-CH_3), 1.06 (3H, s, 5-CH_3), 1.97 (3H, d, $J=1$ Hz, 11-CH_3), 2.24 (1H, d, $J=17$ Hz, 6-H), 2.95 (1H, d, $J=17$ Hz, 6-H), 7.35 (1H, m, $W1/2=4$ Hz, 12-H); MS *m/e* (rel. intensity %): 232 (M^+, 59), 217 ([M–CH_3]$^+$, 29), 163 ([M–C_5H_9]$^+$, 79), 109 ([M–$C_7H_7O_2$]$^+$, 100).

(±)-9α-Hydroxyfuranoeremophilane (6)——To a solution of **2** (13 mg) in abs. $(C_2H_5)_2O$ (5 ml) was added $LiAlH_4$ (3 mg) with stirring in an ice bath for 1 hr. After work up in the usual manner, the reaction product was purified by preparative TLC to afford (±)-9α-hydroxyfuranoeremophilane (**6**), as an oily compound (11 mg; 85% yield). IR cm^{-1}: 3420 (OH); NMR δ: 0.88 (3H, s, 5-CH_3), 1.03 (3H, d, $J=7$ Hz, 4-CH_3), 1.89 (3H, d, $J=1$ Hz, 11-CH_3), 2.08 (1H, bd, $J=16$ Hz, 6-H), 4.81 (1H, bd, $J=5$ Hz, 9-H), 7.12 (1H, m, $W1/2=$ 4 Hz, 12-H).

(±)-9,10-Dehydrofuranoeremophilane (32)——To a solution of 9α-ol (**6**) (13.5 mg) in dry pyridine (3 ml) was added $POCl_3$ (100 mg) and the mixture was allowed to stand at room temperature for 2 hr. Then the reaction mixture was heated at 100° for 20 min. The resulting reaction mixture was added with sat. aq. K_2CO_3 and was extracted with $(C_2H_5)_2O$, washed with H_2O, and dried. The solvent was evaporated under reduced pressure. The residue was chromatographed on an alumina column to afford a pale yellow oil of (±)-9,10-dehydrofuranoeremophilane (**32**) (8 mg; 64% yield). The NMR spectrum of **32** (in C_6D_6, 60 MHz) was identical with that of natural 9,10-dehydrofuranoeremophilane recorded by Bohlmann and Zdero.[16] UV λ_{max}^{EtOH} nm 290, 297, 313 (shoulder). (±)-**32** was very unstable in benzene even at −20°, it changed to dark due to decomposition.

(±)-Furanoeremophilane (34)——A solution of 9α-ol (**6**) (11 mg) in 2.5 ml of a mixture of acetic anhydride-pyridine (1: 4) was allowed to stand at room temperature for 10 hr. Removal of the solvent under reduced pressure gave 14 mg of crude acetate (**33**). The acetate was dissolved in abs. $(C_2H_5)_2O$ (2 ml) and liq. NH_3 (20 ml) and Li metal (8 mg) was added to the reaction mixture at −70° with stirring. After 15 min, NH_4Cl was added to the reaction mixture and NH_3 was evaporated. The residue was extracted with $(C_2H_5)_2O$, washed with H_2O and dried. After removal of $(C_2H_5)_2O$, the residue was chromatographed on alumina to give a colorless oil, 10 mg of (±)-furanoeremophilane (**34**), quantitatively. High-resolution mass spectrum of **34** for $C_{15}H_{22}O$: Mol. Wt. 218.1669. Observed M^+ 218.1669. NMR δ: 0.89 (3H, s, 5-CH_3), 0.95 (3H, d, $J=7$ Hz, 4-CH_3), 1.88 (3H, d, $J=1$ Hz, 11-CH_3), 2.2—2.8 (4H, m, 6-H, 9-H), 7.02 (1H, m, $W1/2=4$ Hz, 12-H). MS *m/e* (rel. intensity %): 218 (M^+, 16), 122 ([M–C_6H_8O]$^+$, 33), 108 ([M–C_8H_{14}]$^+$, 100). The NMR spectrum (60 MHz) of (±)-**34** was identical with that of (−)-furanoeremophilane isolated from *Ligularia Fischeri* Turcz reported by Ishii *et al.*[17]

(±)-10αH-Furanoeremophilone (35)——According to the procedure described above for (±)-**2**, the diketone (**19**) (44 mg) was treated with ethanedithiol and BF_3–$O(C_2H_5)$ in $(C_2H_5)_2O$ under the same conditions. Recrystallization from EtOAc–hexane gave 3,3-ethanedithioketal (34 mg; 59% yield) as colorless prisms, mp 202—205°. *Anal.* Calcd. for $C_{17}H_{22}O_2S_2$: C, 63.32; H, 6.88; Mol. Wt. 322.1060. Found: C, 63.14; H, 6.92; M^+ 322.1050. IR cm^{-1}: 1670 (CO). UV λ_{max}^{EtOH} 279.5 nm (ε 13900). NMR δ: 0.91 (3H, s, 5-CH_3), 1.31 (3H, d, $J=7$ Hz, 4-CH_3), 1.97 (3H, d, $J=1$ Hz, 11-CH_3), 3.1—3.4 (4H, m, $\begin{matrix}CH_2\text{–}S\\ |\quad\quad\rangle\\ CH_2\text{–}S\end{matrix}$), 7.33 (1H, m, $W1/2$ $=3$ Hz, 12-H). MS *m/e* (rel. intensity %): 322 (M^+, 54), 191 (58), 131 (100).

A solution of the ethanedithioketal (19 mg) in abs. EtOH (8 ml) was refluxed for 15 min with Raney nickel (480 mg). After work up in the usual manner, the resulting product was purified by preparative TLC to afford (±)-10αH-furanoeremophilone (**35**) (12 mg; 87% yield). Recrystallization from pentane gave colorless needles, mp 109—111°. *Anal.* Calcd. for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68; Mol. Wt. 233.1461.

Found: C, 77.27; H, 8.70; M^+ 232.1458. IR cm^{-1}: 1656 (CO); UV λ_{max}^{EtOH} 279 nm (ε 15600); NMR δ: 0.78 (3H, s, 5-CH_3), 0.93 (3H, d, J=7 Hz, 4-CH_3), 1.98 (3H, d, J=1 Hz, 11-CH_3), 2.43 (1H, d, J=16 Hz, 6-H), 2.70 (1H, d, J=16 Hz, 6-H), 7.32 (1H, m, $W1/2$=3 Hz, 12-H). MS *m/e* (rel. intensity %): 232 (M^+, 74), 217 ($[M-CH_3]^+$, 100), 161 ($[M-C_5H_{11}]^+$, 55), 122 (87), 109 (47).

The spectral data of **35** were identical with those of 10αH-furanoeremophilone isolated from *Petasites hybridus* L. by Novotny *et al.*[5]

(±)-Furanoligularane ((±)-10αH-Furanoeremophilane) (37)——According to the procedure as described above for (±)-furanoeremophilane (**34**), $LiAlH_4$ reduction of 10αH-furanoeremophilone (13 mg) under the same conditions gave 12 mg (92% yield) of a mixture of 9α- and 9β-ol (**36a**). **36a** was converted with acetic anhydride-pyridine to the corresponding acetates (**36b**). The Birch reduction of crude acetates (**36b**) with Li metal (10 mg) in liq. NH_3 (15 ml) at −70° with stirring was carried out. After work up in the usual manner, the resulting product was chromatographed on alumina to afford 11 mg (90% yield from **35**) of (±)-furanoligularane (**37**) as colorless oil. UV λ_{max}^{EtOH} 221 nm; NMR δ: 0.67 (3H, s, 5-CH_3), 0.92 (3H, bd, 4-CH_3), 1.88 (3H, d, J=1 Hz, 11-CH_3), 7.00 (1H, m, $W1/2$=4 Hz, 12-H). MS *m/e* (rel. intensity %): 218 (M^+, 30), 108 ($[M-C_8H_{14}]^+$, 100).

The spectral data of **37** were in good agreement with those of natural furanoligularane reported by Ourison and Takahashi *et al.*[6b,11]

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