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# Studies on the Terpenoids and Related Alicyclic Compounds. XXVI.[1] Total Syntheses of highly Oxygenated Furanoeremophilanes: (±)-6β-Hydroxy-1,10-dehydrofuranoeremophilan-9-one, (±)-Decompositin, (±)-Dihydrodecompositin, (±)-Adenostylone, (±)-3β,6β-Dipropionyloxyeuryopsin-9-one, (±)-3β,6β-Dihydroxy-10βH-furanoeremophilan-9-one, and (±)-3β,6β-Dihydroxy-10αH-furanoeremophilan-9-one

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The total syntheses of several highly oxygenated, 1,10-dehydrofuranoeremophilanes [(±)-6β-hydroxy-1,10-dehydrofuranoeremophilan-9-one (**1a**), (±)-decompositin (**1b**), (±)-dihydrodecompositin (3), (±)-adenostylone (**1c**), (±)-3β,6β-dipropionyleuryopsin-9-one (**2b**)] and polyoxy compounds [(±)-3β,6β-dihydroxy-10βH-furanoeremophilan-9-one (**4**), (±)-3β,6β-dihydroxy-10αH-furanoeremophilan-9-one (**5**), and 3β-acetoxy-6β-isobutyroxy-furanoeremophilan-9-one (**28b**)] from a bicyclic enone (**6a**) are described. Treatment of 10α-hydroxy-6,9-dioxo compounds (**8a**, **18** and **23**) with $SOCl_2$–pyridine gave the corresponding 1,10-dehydro-6,9-dioxo compounds (**11**, **20** and **24**, respectively). $NaBH_4$ reduction of **11**, **20** and **24** afforded the 6β-hydroxy derivatives (**12a**, **1a** and **2a**, respectively) regio- and stereoselectively. (±)-**1a** was converted into (±)-**1b**, (±)-**1c**, and (±)-**3**. (±)-**2a** was also converted into (±)-**2b**. Catalytic reduction of **12a** with $H_2$/Pd gave the 10α-H and 10β-H compounds (**25** and **26a**). Deketalization of **25** and **26a** with aq. AcOH followed by reduction with $NaBH_4$ gave (±)-**5** and (±)-**4**, respectively. Esterification of **26a** with 2-methylbutyric anhydride–pyridine gave the ester (**26b**), which was converted to (±)-**28a** and **28b**.

**Keywords**——sesquiterpenes; furanoeremophilanes; total synthesis; 6β-hydroxy-1,10-dehydrofuranoeremophilan-9-ones; 3β,6β-diacyloxyfuranoeremophilan-9-ones; dehydration; stereoselective reduction; hydroxylation, benzeneseleninic anhydride

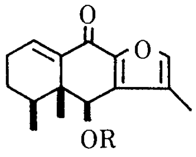
In previous papers, the authors have been reported[2-4] total syntheses of many kinds of 10H-furanoeremophilanes at various levels of oxidation for example, (±)-furanofukinol,[4] (±)-ligularone,[2] (±)-furanoeremophilone,[3] (±)-furanoeremophilane,[3] *etc.*, from 3,6,9-trioxofuranoeremophilane (**6a**)[2] by means of regio- and stereoselective reduction.

Recently, we reported[5] a novel hydroxylation of acyclic and alicyclic ketone derivatives using benzeneseleninic anhydride.[6] In this paper, we wish to report the application of this hydroxylation reaction to the total syntheses of various highly oxygenated 1,10-dehydrofuranoeremophilanes [(±)-6β-hydroxy-1,10-dehydrofuranoeremophilan-9-one (**1a**), (±)-decompositin (**1b**), (±)-dihydrodecompositin (**3**), (±)-adenostylone (**1c**) and (±)-3β,6β-dipropionyloxyeuryopsin-9-one -(**2b**)] and polyoxyfuranoeremophilanes [(±)-3β,6β-dihydroxy-10βH-furanoeremophilan-9-one (**4**) and (±)-3β,6β-dihydroxy-10αH-furanoeremophilan-9-one (**5**)] starting from the key intermediate (**6a**).

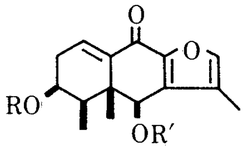
## Syntheses of 6β-Hydroxy Compounds

Many naturally occurring furanoeremophilanes have 6β-hydroxy or 6β-acyloxy groups,[7] and stereoselective syntheses of 6β-hydroxy compounds present a significant problem. It is well known that the reduction of 6-oxofuranoeremophilanes with metal hydrides affords 6α-hydroxy compounds.[8] It is expected that the reduction of 1,10-dehydro-6-oxo compounds with metal hydrides will yield 6β-hydroxy compounds, because the metal hydrides should attack the C-6 carbonyl group from the less hindered α-side due to the steric hindrance of the C-5 angular methyl group. On the basis of this consideration, syntheses of 1,10-dehydro-6-oxofuranoeremophilanes were investigated.

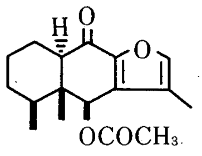
Hydroxylation of the 6,9-dione (**6b**) with benzeneseleninic anhydride gave the 10β-hydroxy compound (**7**) as the major product and the 10α-hydroxy epimer (**8a**) as a minor product, as reported previously.[5b] Treatment of **8a** with thionyl chloride in pyridine at 0°C for 15 min gave a 1,10-dehydro compound (**11**) in quantitative yield, whereas treatment of **7** with thionyl chloride under the same conditions gave only unchanged starting material.



**1a** : R=H
**1b** : R=COCH$_3$
**1c** : R=COCH(CH$_3$)$_2$



**2a** : R=COCH$_2$CH$_3$; R′=H
**2b** : R=R′=COCH$_2$CH$_3$



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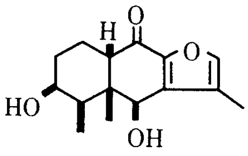
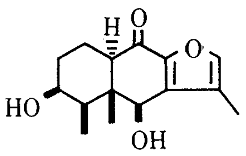
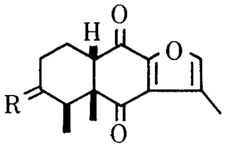


**4**

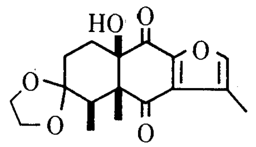


**5**

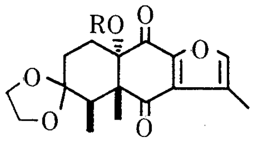


**6a** : R=O

**6b** : R= $\begin{matrix}CH_2O- \\ | \\ CH_2O-\end{matrix}$



**7**



**8a** : R=H
**8b** : R=COCH$_3$

On the other hand, reduction of **7** with sodium borohydride gave a ketol (**9a**) in quantitative yield, and **9a** was converted to the corresponding acetate (**9b**). The stereoformula of the ketol was deduced from spectroscopic data and the reduction mode. The ultraviolet (UV) spectrum of **9a** showed $\lambda_{max}$ 266 nm, which was consistent with a 6-oxofuran moiety.[7a] Sodium borohydride should attack the C-9 carbonyl group of **9a** from the less hindered side to form the 9β-hydroxy compound. Compound **9a** and its epimer 9α,10β-dihydroxyfuranoeremophilan-6-one[9] were compared. The stereoformula of **9a** should be 9β,10β-dihydroxyfuranoeremophilan-6-one. The acetate (**9b**) was treated with thionyl chloride in pyridine at 0°C for 20 min to afford a 1,10-dehydro compound (**10b**) in good yield. Hydrolysis of **10b** with methanolic potassium carbonate afforded a ketol (**10a**), which was oxidized with activated manganese dioxide to give the 1,10-dehydro compound (**11**) in 70% overall yield from **7**.

Reduction of **11** with sodium borohydride in methanol gave a hydroxy compound (**12a**), mp 190—193°C, in 99% yield. **12a** was converted to the corresponding acetate (**12b**), mp 176—178°C. The stereoformula of **12b** was confirmed by consideration of its spectroscopic data. The UV spectrum of **12b** showed $\lambda_{max}$ 300 nm, which was consistent with the presence of a 9-oxofuran moiety.[7a] All spectral data of **12b** were different from those of 6α-acetoxy-1,10-dehydrofuranoeremophilan-9-one (**14**) which was prepared from the known 6α-acetoxy-10α-hydroxyfuranoeremophilan-9-one (**13**)[5b] by treatment with thionyl chloride in pyridine. From these results, **12b** was confirmed to be an epimer of the 6α-acetate (**14**), 6β-acetoxy-1,10-dehydrofuranoeremophilan-9-one.

### Syntheses of (±)-Decompositin, (±)-Dihydrodecompositin, (±)-Adenostylone, (±)-3β,6β-Dipropionyloxyeuryopsin-9-one

Deketalization of the 10α-hydroxy-3-ketal (**8a**) with aqueous acetic acid gave a triketone

(**15a**), mp 257—260°C, in 96% yield. Acetylation of **15a** with acetic anhydride–pyridine–dimethylaminopyridine (DMAP)[10] gave an acetate (**15b**), mp 178—181°C, in 92% yield. The alcohol (**8a**) was acetylated to give **8b**, mp 189—190°C, which was deketalized to afford the same acetate (**15b**) in 57% overall yield from **8a**. The acetate (**15b**) was treated with ethanedithiol-borotrifluoride etherate complex gave a dithioketal (**16b**), mp 186—187°C, in 91% yield. Desulfurization of **16b** with W-2 Raney nickel catalyst in refluxing ethanol for 10 min gave the known diketone (**17**)[5b] in 54% yield. Then, hydrolysis of **16b** with methanolic potassium carbonate afforded the 10α-hydroxy compound (**16a**), mp 218—221°C, quantitatively. Desulfurization of **16a** with W-2 Raney nickel catalyst in dioxane gave a mixture of **18** and an olefin (**19**) in 90% yield. The mixture was reduced with palladium charcoal under a hydrogen atmosphere in ethyl acetate gave 10α-hydroxy-6,9-diketone (**18**), mp 189—190.5°C, in 97% yield. Dehydration of **18** with thionyl chloride in pyridine gave an enone (**20**), mp 89—90°C, in 95% yield. Reduction of **20** with sodium borohydride in methanol afforded the desired (±)-6β-hydroxy compound (**1a**), as an oil, quantitatively. The nuclear magnetic resonance (NMR) spectrum of (±)-**1a** was in good agreement with that of (−)-6β-hydroxy-1,10-dehydrofuranoeremophilan-9-one isolated from *Senecio lanceus* by Bohlmann *et al.*[11]

Acetylation of (±)-**1a** with acetic anhydride–pyridine–DMAP gave the acetate (**1b**), mp 145.5—147°C, in 85% yield. The NMR, infrared (IR), and UV spectra of (±)-**1b** were in good agreement with those of (+)-decompositin isolated from *Cacalia decomposita* by Hahn *et al.*[12] and Sorm *et al.*[13] Catalytic reduction of (±)-**1b** with palladium charcoal in ethyl acetate under a hydrogen atmosphere gave the 10α-H compound (**3**), mp 137—138°C, in 86% yield, whereas the 10βH epimer was not detected. The NMR spectrum of (±)-**3** was identical with that of natural dihydrodecompositin isolated from *Euryops othonnoides* reported by Bohlmann *et al.*[14]

Esterification of (±)-**1a** with isobutyric anhydride and DMAP gave the isobutyl ester (**1c**), mp 96—97°C. The NMR, IR, and UV spectra of (±)-**1c** were in good agreement with those of (−)-adenostylone isolated from *Adenostyles alliariae* by Sorm *et al.*[13]

Treatment of the 3β-hydroxy compound (**21a**),[5b] which was previously reported by us, with propionic anhydride gave a propionate (**21b**), mp 113—115°C, in 91% yield. Hydroxylation of **21b** with benzeneseleninic anhydride in toluene gave the 10β-hydroxy compound

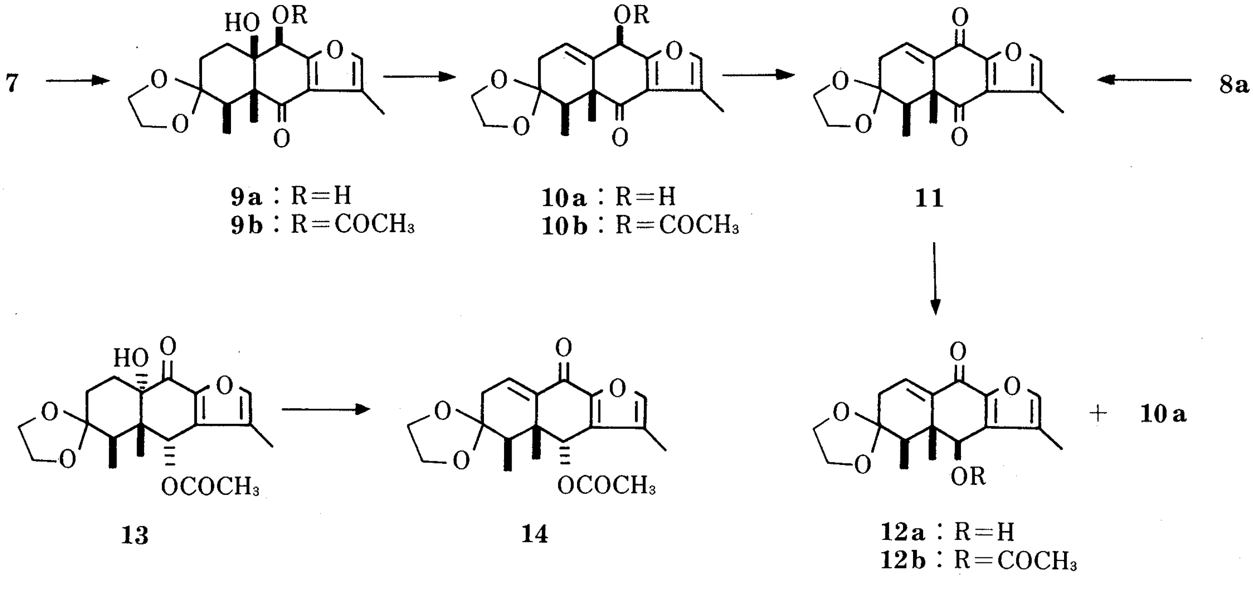


Chart 1

(**22**), mp 123—125°C, and 10α-hydroxy compound (**23**), mp 174—176°C, in 59% and 22% yields, respectively. The stereochemistries of **22** and **23** were confirmed by their spectral data in comparison with those of the corresponding 3β-acetates, which were previously reported.[5b)] Treatment of **23** with thionyl chloride in pyridine at 0°C for 10 min gave an enone (**24**), mp 152—154°C, in 91% yield, whereas the 10β-hydroxy epimer (22) was not dehydrated under the same conditions, and unchanged starting material was recovered. Reduction of **24** in methanol with sodium borohydride gave the 6β-hydroxy compound (**2a**), which was converted to the corresponding dipropionate (**2b**), mp 83—85°C, by treatment with propionic anhydride, quantitatively and stereoselectively. The NMR, IR, and UV spectral

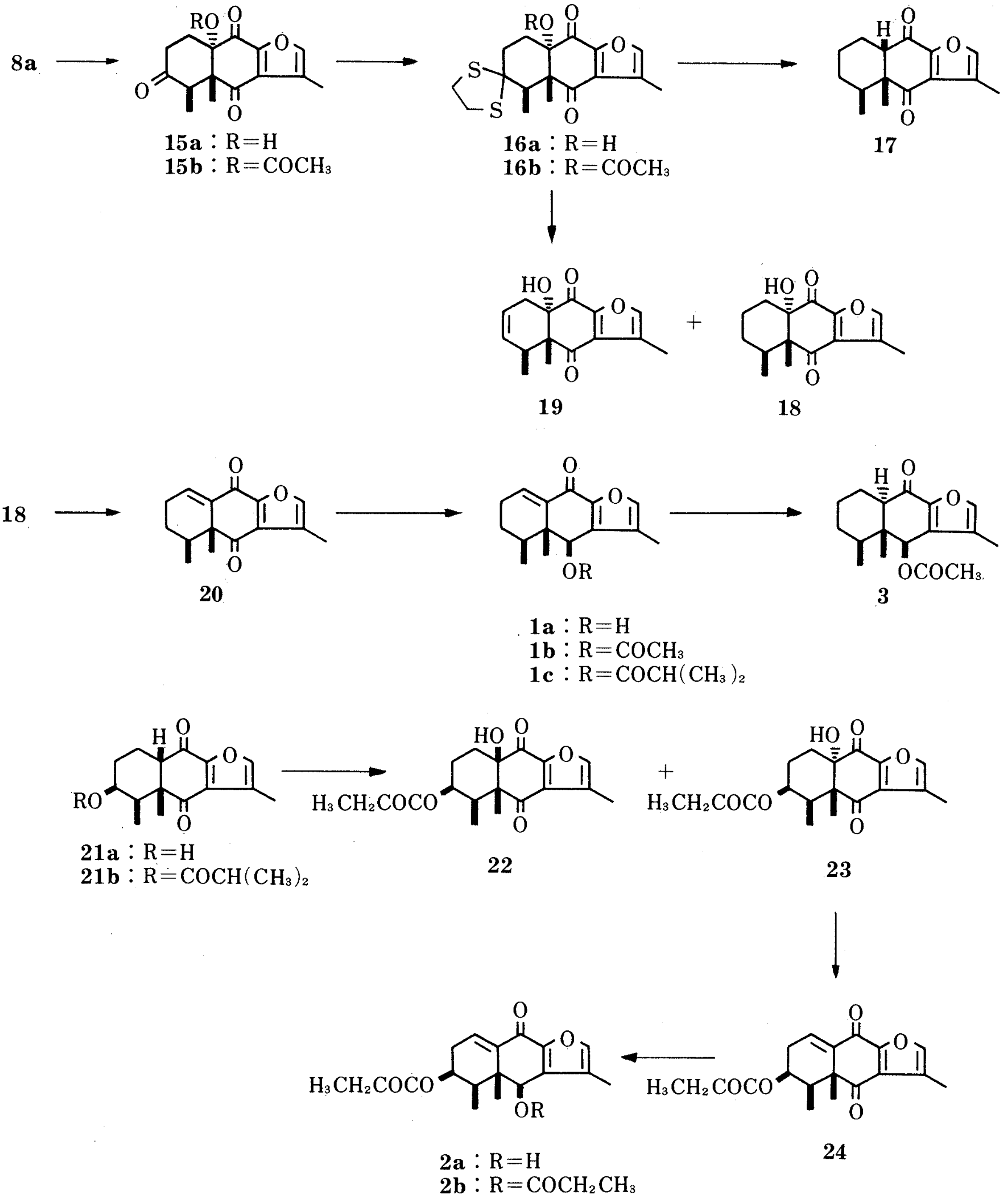


Chart 2

data of (±)-**2b** were in good agreement with those of natural 3$\beta$,6$\beta$-dipropionyloxyeuryopsin-9-one isolated from *Euryops lateriflorus* by Bohlmann *et al.*[15]

## Synthesis of (±)-3$\beta$-Acetoxy-6$\beta$-(2-methylbutyryloxy)-10$\beta$H-furanoeremophilan-9-one

Recently, Bohlmann and his coworkers reported the isolation and structure determination of several 3$\beta$,6$\beta$-diacyloxy derivatives of 10$\beta$H-furanoeremophilan-9-one[16,17] and 3$\beta$,6$\beta$-diacyloxy derivatives of 10$\alpha$H-furanoeremophilan-9-one.[17b] We describe here a stereoselective total synthesis of (±)-3$\beta$-acetoxy-6$\beta$-(2-methylbutyryloxy)-10$\beta$H-furanoeremophilan-9-one (**28b**)[16] and its mother skeleton 3$\beta$,6$\beta$-dihydroxy-10$\beta$H-furanoeremophilan-9-one (**4**) and 3$\beta$,6$\beta$-dihydroxy-10$\alpha$H-furanoeremophilan-9-one (**5**).

Catalytic reduction of the 6$\beta$-hydroxy-1,10-dehydro compound (**12a**) in ethyl acetate with palladium charcoal under a hydrogen atmosphere gave a 10$\alpha$-H compound (**25**), mp 205—208°C, and 10$\beta$-H compound (**26a**), as an oil, in 87% and 10% yields, respectively. Treatment of **25** with ethanolic sodium ethoxide gave the epimer **26a** in 90% yield. Esterification of **26a** with racemic 2-methylbutyric anhydride in pyridine solution in the presence of DMAP gave an epimeric mixture at the secondary methyl center of the ester (**26b**), as an oil, in 96% yield. Attempted separation of the mixture of **26b** by preparative TLC was unsuccessful. Treatment of **26b** with aqueous acetic acid gave an isomeric mixture of a ketone (**27**), quantitatively. Reduction of **27** with sodium borohydride afforded the 3$\beta$-hydroxy derivative (**28a**), an oil, in 93% yield, and it was converted to the corresponding acetate (±)-**28b**, as an epimeric mixture at the secondary methyl center, exhibiting spectroscopic properties identical to those reported for the natural 3$\beta$-acetoxy-6$\beta$-(2-methylbutyryloxy)-10$\beta$H-furanoeremophilan-9-one isolated from *Senecio medley-woodii* HUTCH by Bohlmann *et al.*[16]

Deketalization of **26a** and **25** with aqueous acetic acid gave ketones (**29**), mp 176—180°C, and (**30**), mp 172—177°C, in 60% and 92% yields, respectively. Reduction of **29** with sodium borohydride afforded (±)-3$\beta$,6$\beta$-dihydroxy-10$\beta$H-furanoeremophilan-9-one (**4**), mp 154—156°C, stereoselectively and quantitatively. Reduction of **30** with sodium borohydride gave (±)-

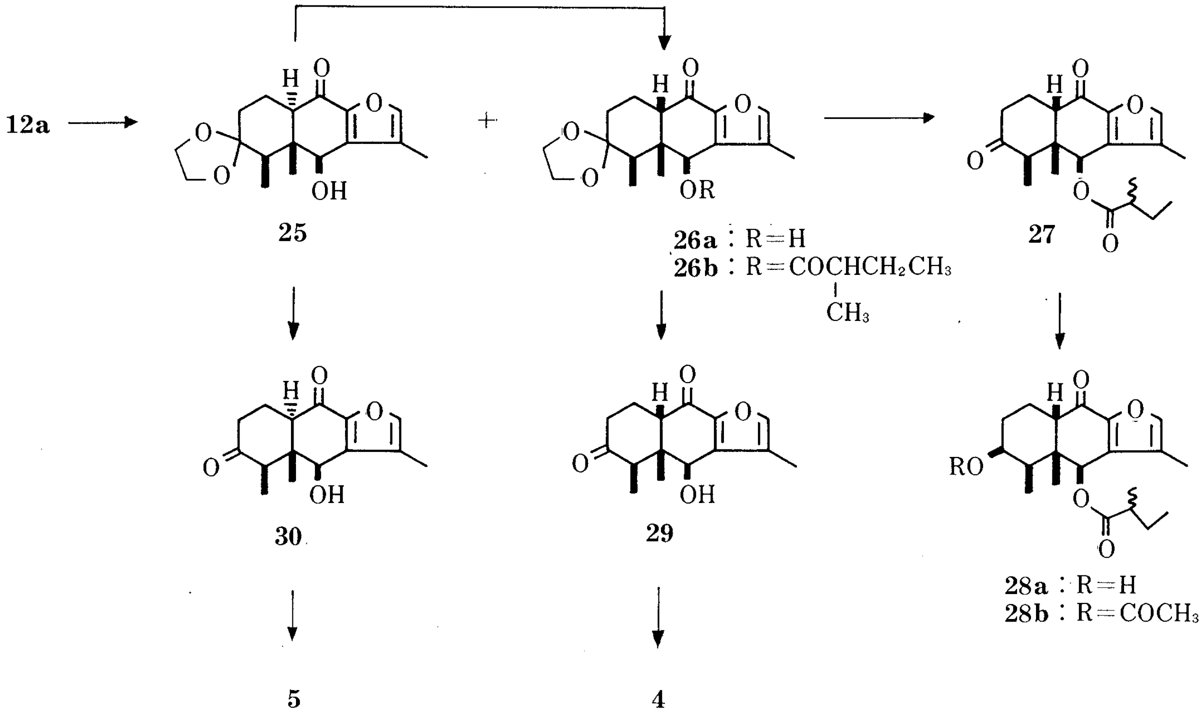


Chart 3

3$\beta$,6$\beta$-dihydroxy-10$\alpha$H-furanoeremophilan-9-one (**5**), mp 264—265°C, in 64% yield. Both 3$\beta$,6$\beta$-dihydroxy derivatives (**4** and **5**) are polyfunctional skeletons of naturally occurring furanoeremophilane derivatives.

## Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured in KBr disks with a Hitachi 215 spectrometer. Ultraviolet (UV) spectra were measured with a Hitachi 200 spectrometer. Nuclear magnetic resonance (NMR) spectra were measured in $CDCl_3$ solution on a JEOL JNM-FX-100 pulse Fourier transform spectrometer (100 MHz) 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.

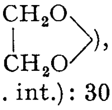
Wako silica gel C-200 (200 mesh) containing 2% fluorescence reagent 254 was used incolumn chromatography. Preparative thin-layer chromatography (TLC) was carried out using Merck silica gel $HF_{254}$.

**3,3-Ethylenedioxy-1,10-dehydrofuranoeremophilan-6,9-dione (11)**——A stirred solution of 96 mg of the 10$\alpha$-hydroxy compound (**8a**)[5b)] in dry pyridine (6 ml) was treated with $SOCl_2$ (5 drops) and the reaction mixture was stirred at 0°C for 15 min. The mixture was diluted with ether, and 6 ml of sat. aq. $NaHCO_3$ was added. The organic layer was concentrated *in vacuo* and the residue was separated by silica gel column chromatography to afford 90 mg (99%) of **11** as colorless plates, mp 142.5—144°C (from AcOEt–hexane). *Anal.* Calcd for $C_{17}H_{18}O_5$: C, 67.53; H, 6.00. Found: C, 67.51; H, 6.07. IR cm$^{-1}$: 1700, 1680 (CO), 1630 (C=C). UV $\lambda_{max}^{EtOH}$ nm ($\varepsilon$): 226 (13300), 313 (11500). NMR $\delta$: 1.19 (3H, d, $J$=7 Hz; 4-$CH_3$), 1.48 (3H, s, 5-$CH_3$), 2.26 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.80, 9-H, q, $J$=7 Hz, 4-H), 3.8—4.2 (4H, m, $\left.\begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\right\rangle$), 6.68 (1H, t, $J$=4 Hz, 1-H), 7.46 (1H, q, $J$=1 Hz, 12-H). MS $m/z$: (% Rel. int.): 302 ($M^+$, 9), 273 (17), 216 (17), 100 (100).

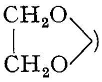
**3,3-Ethylenedioxy-9$\beta$,10$\beta$-dihydrofuranoeremophilan-6-one (9a)**——A stirred solution of 320 mg of the diketone (**7**)[5b)] in MeOH (30 ml) was treated with $NaBH_4$ (38 mg) and the mixture was stirred at 0°C for 30 min. $NH_4Cl$ was added to the reaction mixture and then the solution was concentrated *in vacuo*. The residue was extracted with AcOEt and the organic layer was washed with sat. aq. $NH_4Cl$ and dried. After removal of the AcOEt, recrystallization from AcOEt–hexane afforded 315 mg (98%) of **9a** as colorless prisms, mp 240—243°C. *Anal.* Calcd for $C_{17}H_{22}O_6$: C, 63.34; H, 6.88%. Mol. Wt. 322.1415. Found: C, 63.17; H, 6.92; $M^+$ 322.1419. IR cm$^{-1}$: 3430, 3325 (OH), 1675 (CO). UV $\lambda_{max}^{EtOH}$ 266 nm ($\varepsilon$ 3400). NMR $\delta$: 1.18 (3H, s, 5-$CH_3$), 1.20 (3H, d, $J$=7 Hz, 4-$CH_3$), 2.22 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.86 (1H, dq, $J$=1.5, 7 Hz, 4-H), 3.7—4.1 (4H, m, $\left.\begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\right\rangle$), 5.03 (1H, s, 9-H), 7.20 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 332 ($M^+$, 3), 304 ($[M-H_2O]^+$, 4), 275 ($[M-C_2H_7O]^+$, 7), 138 ($[M-C_{10}H_{16}O_3]^+$, 13), 99 (100).

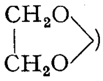
**3,3-Ethylenedioxy-9$\beta$-acetoxy-10$\beta$-hydroxyfuranoeremophilan-6-one (9b)**——**9a** (360 mg) was treated with acetic anhydride (5 g) and pyridine (20 g) at room temperature for 16 h. After work-up in the usual manner, the crude acetate was purified by silica gel column chromatography to give 410 mg (93%) of **9b** as colorless prisms, mp 211—212°C (from AcOEt–hexane). *Anal.* Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64. Found: C, 62.70; H, 6.65. IR cm$^{-1}$: 3540 (OH), 1760, 1725, 1680 (CO), 1260 (COC). UV $\lambda_{max}^{EtOH}$ 264.5 nm ($\varepsilon$ 3700). NMR $\delta$: 1.18 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.24 (3H, d, 5-$CH_3$), 2.20 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.27 (3H, s, $COCH_3$), 2.85 (1H, dq, $J$=2, 7 Hz, 4-H), 3.7—4.1 (4H, m, $\left.\begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\right\rangle$), 6.13 (1H, s, 9-H), 7.16 (1H, q, $J$=1 Hz, 12-H).

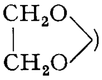
**3,3-Ethylenedioxy-9$\beta$-acetoxy-1,10-dehydrofuranoeremophilan-6-one (10b)**——A solution of **9b** (364 mg) in dry pyridine (15 ml) was treated with $SOCl_2$ (240 mg) at 0°C and the reaction mixture was stirred at 0°C for 20 min. Saturated aq. $NaHCO_3$ (4 ml) was added, and the whole was extracted with ether. The ether layer was washed with sat. aq. $NaHCO_3$ and dried. The solvents were evaporated off *in vacuo* and the residue was purified by silica gel column chromatography to give 326 mg (94%) of **10b** as colorless prisms, mp 162—165°C (from AcOEt–hexane). *Anal.* Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.72; H, 6.36. IR cm$^{-1}$: 1760, 1690 (CO), 1670 (C=C), 1230 (COC). UV $\lambda_{max}^{EtOH}$ 264 nm ($\varepsilon$ 2800). NMR $\delta$: 1.03 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.29 (3H, s, 5-$CH_3$), 2.19 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.27 (3H, s, $COCH_3$), 2.89 (1H, dq, $J$=1.5, 7 Hz, 4-H), 3.7—4.1 (4H, m, $\left.\begin{matrix}CH_2O\\ |\\ CH_2O\end{matrix}\right\rangle$), 5.75 (1H, m, $W^1/_2$=12 Hz, 1-H), 6.61 (1H, bs, 9-H), 7.11 (1H, d, $J$=1 Hz, 12-H); MS $m/z$ (% Rel. int.): 346 ($M^+$, 6), 287 (95), 214 (53), 201 (48), 100 (47), 86 (100).

**3,3-Ethylenedioxy-9$\beta$-hydroxy-1,10-dehydrofuranoeremophilan-6-one (10a)**——$K_2CO_3$ (166 mg) was added to a stirred solution of **10b** (277 mg) in MeOH (20 ml) and the mixture was stirred at room temperature for 30 min. $NH_4Cl$ was added to the reaction mixture and then the solvent was removed *in vacuo*. The residue was extracted with ether and the organic layer was washed with sat. aq. $NH_4Cl$ and dried. After removal of the ether, recrystallization from AcOEt–hexane gave 240 mg (99%) of **10a** as colorless plates, mp 194—196°C. *Anal.* Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62; Mol. Wt. 304.1308. Found: C, 66.84; H, 6.60; $M^+$ 304.1282. IR $cm^{-1}$: 3470 (OH), 1690 (CO), 1670 (C=C). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 265.5 nm ($\varepsilon$ 3300). NMR $\delta$: 1.02 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.22 (3H, s, 5-$CH_3$), 2.18 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.86 (1H, dq, $J$=2, 7 Hz, 4-H), 3.6—4.1 (4H, m,  $\left.\begin{matrix}CH_2O\\|\\CH_2O\end{matrix}\right>$), 5.42 (1H, bs, 9-H), 5.92 (1H, m, $W^1/_2$=10 Hz, 1-H), 7.12 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 304 ($M^+$, 6), 86 (100).

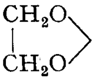
**$MnO_2$ Oxidation of 10a**——Freshly prepared activated $MnO_2$ (77 mg) was added to a solution of **10a** (11 mg) in $CHCl_3$ (4 ml), and the reaction mixture was stirred at room temperature for 15 min. The $MnO_2$ was filtered off and the filtrate was concentrated *in vacuo*. The residue was recrystallized from AcOEt–hexane to give 9 mg (82%) of **11**, mp 142—143.5°C, as colorless prisms. This product was identical with an authentic specimen.

**3,3-Ethylenedioxy-6β-hydroxy-1,10-dehydrofuranoeremophilan-9-one** (**12a**)——A stirred solution of **11** (15 mg) in MeOH (5 ml) was treated with $NaBH_4$ (2 mg) and the mixture was stirred at 0°C for 5 min. $NH_4Cl$ was added to the mixture and then the solvent was evaporated off *in vacuo*. The residue was extracted with ether and the organic layer was washed with sat. aq. $NH_4Cl$ and dried. The ether was evaporated off and the residue was recrystallized from AcOEt–hexane to give 15 mg (99%) of **12a** as colorless prisms, mp 190—193°C. *Anal.* Calcd for $C_{17}H_{20}O_5$: C, 67.09; H, 6.62. Found: C, 66.91; H, 6.57. IR $cm^{-1}$: 3510 (OH), 1685 (CO), 1645 (C=C). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 245 nm ($\varepsilon$ 4900), 303.5 nm ($\varepsilon$ 17000). NMR $\delta$: 1.19 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.20 (3H, s, 5-$CH_3$), 2.16 (3H, d, $J$=1 Hz, 11-$CH_3$), 3.9—4.1 (4H, m,  $\left.\begin{matrix}CH_2O\\|\\CH_2O\end{matrix}\right>$), 5.30 (1H, d, $J$=7 Hz, 6-H) the signal changed to a singlet on addition of $D_2O$, 6.62 (1H, t, $J$=4 Hz, 1-H), 7.38 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 304 ($M^+$, 42), 201 (23), 137 (29), 100 (100).

**3,3-Ethylenedioxy-6β-acetoxy-1,10-dehydrofuranoeremophilan-9-one** (**12b**)——**12a** was acetylated in the usual way to give the acetate (**12b**) as colorless plates, mp 176—178°C (from AcOEt–hexane), quantitatively. High-resolution mass spectrum for $C_{19}H_{22}O_6$: Mol. Wt. 346.1417. Observed: $M^+$, 346.1387. IR $cm^{-1}$: 1755, 1685 (CO), 1645 (C=C), 1230 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 242 nm ($\varepsilon$ 4800), 300 nm ($\varepsilon$ 17000). NMR $\delta$: 1.03 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.25 (3H, s, 5-$CH_3$), 1.93 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.23 (3H, s, $COCH_3$), 3.9—4.0 (4H, bs,  $\left.\begin{matrix}CH_2O\\|\\CH_2O\end{matrix}\right>$), 6.65 (1H, t, $J$=4 Hz, 1-H), 6.74 (1H, s, 6-H), 7.36 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 346 ($M^+$, 7), 317 (7), 304 (3), 287 (20), 100 (100).

**3,3-Ethylenedioxy-6α-acetoxy-1,10-dehydrofuranoeremophilan-9-one** (**14**)——A stirred solution of 29 mg of the 10α-hydroxy compound (**13**)[5b] in dry pyridine (4 ml) was treated with $SOCl_2$ (10 drops) at 0°C and the stirring was continued for 1 h. To the mixture was added 1 ml of sat. aq. $NaHCO_3$ and 50 ml of ether. The organic layer was washed with sat. aq. $NaHCO_3$ and dried. The ether and pyridine were evaporated off *in vacuo* and the residue was column chromatographed on silica gel to give 19 mg (70%) of **14** as colorless needles, mp 213°C (dec.) (from AcOEt–hexane). *Anal.* Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.70; H, 6.64%. IR $cm^{-1}$: 1740, 1680 (CO), 1635 (C=C), 1235 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 249 nm ($\varepsilon$ 4600), 302.5 nm ($\varepsilon$ 16800). NMR $\delta$: 1.00 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.17 (3H, s, 5-$CH_3$), 2.20 (3H, d, $COCH_3$), 2.08 (3H, d, $J$=1 Hz, 11-$CH_3$), 3.7—4.2 (4H, m,  $\left.\begin{matrix}CH_2O\\|\\CH_2O\end{matrix}\right>$), 5.83 (1H, s, 6-H), 6.95 (1H, t, $J$=4 Hz, 1-H), 7.40 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 346 ($M^+$, 3), 317 (3), 287 (18), 99 (100).

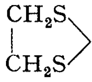
**10α-Hydroxyfuranoeremophilan-3,6,9-trione** (**15a**)——A solution of 64 mg of the ketal (**8a**) in 10 ml of a solution of AcOH–$H_2O$ (3 : 1) was allowed to stand at room temperature for 10 h. The solvent was evaporated off *in vacuo* and the residue was recrystallized from AcOEt–hexane to give 53 mg (96%) of triketone (**15a**), mp 257—260°C, as colorless prisms. High-resolution mass spectrum for $C_{15}H_{16}O_5$: Mol. Wt. 276.0997. Observed: $M^+$, 276.1000. IR $cm^{-1}$: 3480 (OH), 1715, 1680 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 244 nm (shoulder), 303 nm; NMR $\delta$ (DMSO-$d_6$): 0.94 (3H, s, 5-$CH_3$), 1.14 (3H, d, $J$=7 Hz, 4-$CH_3$), 2.16 (3H, d, $J$=1 Hz, 11-$CH_3$), 6.74 (1H, s, OH), 9.97 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 276 ($M^+$, 62), 248 (100).

**3,3-Ethylenedioxy-10α-acetoxyfuranoeremophilan-6,9-dione** (**8b**)——A solution of 16 mg of the 10α-hydroxy compound (**8a**) in $Ac_2O$ (0.5 ml), pyridine (1.5 ml) and $CH_2Cl_2$ (1 ml) was treated with 5 mg of DMAP. The mixture was allowed to stand at room temperature for 4 days. The mixture was evaporated to dryness *in vacuo* and the residue was purified by silica gel preparative TLC to afford 13 mg (72%) of **8b** as colorless needles, mp 189—190°C (from AcOEt–hexane). *Anal.* Calcd for $C_{19}H_{22}O_7$: C, 62.97; H, 6.12; Mol. Wt. 362.1363. Found: C, 63.17; H, 6.30; $M^+$, 362.1347. IR $cm^{-1}$: 1750, 1700 (CO), 1245 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 243 nm ($\varepsilon$ 4800), 302 nm ($\varepsilon$ 8600). NMR $\delta$: 1.19 (3H, d, $J$=7 Hz, 4-$CH_3$), 1.21 (3H, d, 5-$CH_3$), 1.93 (3H, s, $COCH_3$), 2.23 (3H, d, $J$=1 Hz, 11-$CH_3$), 2.84 (1H, q, $J$=7 Hz, 12-H), 3.8—4.1 (4H, m,  $\left.\begin{matrix}CH_2O\\|\\CH_2O\end{matrix}\right>$), 7.41 (1H, q, $J$=1 Hz, 12-H). MS $m/z$ (% Rel. int.): 362 ($M^+$, 3), 320 (8), 319 (6), 303 (14), 302 (19), 99 (100).

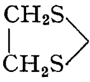
**10α-Acetoxyfuranoeremophilan-3,6,9-trione** (**15b**)——(a) A solution of 15 mg of the triketone (**15a**) in

$Ac_2O$ (1 ml), pyridine (3 ml) and $CH_2Cl_2$ (1 ml) was treated with 7 mg of DMAP. The mixture was allowed to stand overnight at room temperature. The mixture was concentrated *in vacuo* and the residue was purified by silica gel preparative TLC to afford 16 mg (92%) of **15b** as colorless plates, mp 178—181°C (from AcOEt–hexane). *Anal.* Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.27; H, 5.86%. IR $cm^{-1}$: 1760, 1710, (CO), 1245 (COC). UV $\lambda_{max}^{EtOH}$ 242 nm ($\varepsilon$ 4900), 303 nm ($\varepsilon$ 8300). NMR $\delta$: 1.03 (3H, s, 5-$CH_3$), 1.34 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.03 (3H, s, $COCH_3$), 2.25 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.43 (1H, q, $J=7$ Hz, 4-H), 7.48 (1H, q, $J=1$ Hz, 12-H). MS $m/z$ (% Rel. int.): 318 ($M^+$, 3), 258 (100), 230 (64).

(b) A solution of 22 mg of the ketal (**8b**) in 5 ml of AcOH–$H_2O$ (3: 1) was heated at 60°C for 5 h. The solution was concentrated *in vacuo* and the residue was purified by silica gel preparative TLC to afford 15 mg (77%) of the acetate (**15b**).

**3,3-Ethylenedithio-10$\alpha$-acetoxyfuranoeremophilan-6,9-dione (16b)**——Ethanedithiol (800 mg) and $BF_3 \cdot OEt_2$ complex (10 drops) were added to a solution of 101 mg of **15b** in $CH_2Cl_2$ (5 ml), and the mixture was allowed to stand at room temperature for 15 min. The mixture was diluted with ether (100 ml) and the ether solution was washed with sat. aq. $NaHCO_3$ and saturated brine. The ether was evaporated off and the residue was purified by silica gel column chromatography to give 114 mg (91%) of **16b** as colorless needles, mp 186—187°C (from AcOEt–hexane). *Anal.* Calcd for $C_{19}H_{22}O_5S_2$: C, 57.85; H, 5.62. Found: C, 58.02; H, 5.71. IR $cm^{-1}$: 1750, 1705 (CO), 1250 (COC). UV $\lambda_{max}^{EtOH}$ 241 nm ($\varepsilon$ 4800), 302 nm ($\varepsilon$ 8200). NMR $\delta$: 1.18 (3H, s, 5-$CH_3$), 1.51 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.94 (3H, s, $COCH_3$), 2.22 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.01 (1H, q, $J=7$ Hz, 4-H), 3.1—3.5 (4H, m,  $\begin{matrix}CH_2S\\ |\\ CH_2S\end{matrix}\rangle$), 7.41 (1H, q, $J=1$ Hz, 12-H). MS $m/z$ (% Rel. int.): 394 ($M^+$, 8), 334 (67), 305 (54), 131 (100), 118 (78).

**Desulfurization of 16b with Raney Ni**——W-2 Raney Ni (300 mg) was added to a solution of 15 mg of the thioketal (**16b**) in EtOH (5 ml), and the mixture was stirred and refluxed for 10 min. The Raney Ni was filtered off and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel preparative TLC to afford 5 mg (54%) of **17** as an oil. The NMR spectrum of **17** was identical with that of synthetic diketone (**17**) reported previously.[5b)]

**3,3-Ethylenedithio-10$\alpha$-hydroxyfuranoeremophilan-6,9-dione (16a)**——A solution of 114 mg of **16b** in MeOH (20 ml) was treated with 60 mg of $K_2CO_3$ and the mixture was stirred at room temperature for 30 min. Saturated aq. $NH_4Cl$ (1 ml) was added, and the solvent was evaporated off *in vacuo*. The residue was extracted with ether and the ether layer was washed with sat. aq. $NH_4Cl$ and dried. The ether was evaporated off and the residue was recrystallized from AcOEt–hexane to give 101 mg (99%) of **16a**, mp 218—221°C, as colorless prisms. High-resolution mass spectrum for $C_{17}H_{20}O_4S_2$: Mol. Wt. 352.0802. Observed: $M^+$, 352.0818. IR $cm^{-1}$: 3450 (OH), 1700, 1690 (CO); UV $\lambda_{max}^{EtOH}$ 244 nm ($\varepsilon$ 3500), 302 nm ($\varepsilon$ 7400). NMR $\delta$: 1.24 (3H, s, 5-$CH_3$), 1.48 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.23 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.03 (1H, q, $J=7$ Hz, 4-H), 3.1—3.5 (4H, m,  $\begin{matrix}CH_2S\\ |\\ CH_2S\end{matrix}\rangle$), 7.42 (1H, q, $J=1$ Hz, 12-H). MS $m/z$ (% Rel. int.): 352 ($M^+$, 4), 131 (100).

**10$\alpha$-Hydroxyfuranoeremophilan-6,9-dione (18)**——W-2 Raney Ni (800 mg) was added to a refluxing solution of 101 mg of **16a** in dioxane (8 ml), and the mixture was refluxed for 3 min. The Ni catalyst was filtered off and the filtrate was concentrated *in vacuo*. The residue was column chromatographed on silica gel to give 68 mg (90%) of a 1: 1 mixture of **18** and **19**. Catalytic reduction of the products in AcOEt (12 ml) with 10% Pd-charcoal (102 mg) under an $H_2$ atmosphere was carried out at room temperature for 5 h. Work-up of the mixture in the usual way yielded a product, which was purified by silica gel column chromatography to give 66 mg (97%) of **18** as colorless needles, mp 189—190.5°C (from AcOEt–hexane). *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; Mol. Wt. 262.1204. Found: C, 68.68; H, 6.83; $M^+$, 262.1183. IR $cm^{-1}$: 3480 (OH), 1690, 1975 (CO). UV $\lambda_{max}^{EtOH}$ 243 nm ($\varepsilon$ 4300), 301 nm ($\varepsilon$ 8950). NMR $\delta$: 1.09 (3H, s, 5-$CH_3$), 1.15 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.24 (3H, d, $J=1$ Hz, 11-$CH_3$), 7.42 (1H, q, $J=1$ Hz, 12-H). MS $m/z$ (% Rel. int.): 262 ($M^+$, 42), 244 ($[M-H_2O]^+$, 20), 229 ($[M-CH_3-H_2O]^+$, 38), 218 ($[M-CO_2]^+$, 100).

**1,10-Dehydrofuranoeremophilan-6,9-dione (20)**——A solution of 18 mg of **18** in dry pyridine (3 ml) was treated with $SOCl_2$ (2 drops) and the mixture was stirred at 0°C for 10 min. The mixture was diluted with ether and the organic layer was washed sat. aq. $NaHCO_3$ and dried. The solvent was evaporated off *in vacuo* and the residue was purified by silica gel preparative TLC to afford 16 mg (95%) of **20** as colorless prisms, mp 89—90°C (from AcOEt–hexane). High-resolution mass spectrum for $C_{15}H_{16}O_3$: Mol. Wt. 244.1099. Observed: $M^+$, 244.1105. IR $cm^{-1}$: 1700, 1680 (CO), 1630 (C=C). UV $\lambda_{max}^{EtOH}$ 226, 247 (shoulder), 314 nm. NMR $\delta$: 1.29 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.34 (3H, s, 5-$CH_3$), 2.26 (3H, d, $J=1$ Hz, 11-$CH_3$), 6.99 (1H, t, $J=4$ Hz, 1-H), 7.45 (1H, q, $J=1$ Hz, 12-H). MS $m/z$ (% Rel. int.): 244 ($M^+$, 100), 229 ($[M-CH_3]^+$, 51), 216 ($[M-CO]^+$, 21), 215 ($[M-CHO]^+$, 27), 201 ($[M-CH_3-CO]^+$, 32).

**6$\beta$-Hydroxy-1,10-dehydrofuranoeremophilan-9-one (1a)**——$NaBH_4$ (3 mg) was added to a solution of 20 mg of **20** in MeOH (6 ml), and the mixture was stirred at 0°C for 5 min. Work-up of the mixture in the usual way gave a crude products, which was purified by silica gel preparative TLC to afford 20 mg (quantitative yield) of **1a** as an oil. IR $cm^{-1}$: 3450 (OH), 1670 (CO), 1630 (C=C). UV $\lambda_{max}^{EtOH}$ 248, 304 nm. NMR $\delta$: 1.06 (3H, s, 5-$CH_3$), 1.23 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.16 (3H, d, $J=1$ Hz, 11-$CH_3$), 4.96 (1H, d, $J=8$ Hz, 6-H) the signal changed to a singlet on addition of $D_2O$, 6.92 (1H, t, $J=4$ Hz, 1-H), 7.37 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 246 ($M^+$, 100), 231 (15), 217 (20), 177 (33), 109 (54). IR and NMR data of (±)-**1a** were identical with those of (−)-6β-hydroxy-1,10-dehydrofuranoeremophilan-9-one reported by Bohlmann *et al.*[10]

**(±)-Decompositin (1b)**——A solution of 15 mg of **1a** in $Ac_2O$ (1 ml) and pyridine (4 ml) was treated with DMAP (7.5 mg), and the mixture was allowed to stand at room temperature for 1 h. The solvent was evaporated off *in vacuo* and the residue was purified by silica gel preparative TLC to afford 15 mg (85%) of (±)-**1b** as colorless needless, mp 145.5—147°C (from AcOEt–hexane). *Anal.* Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99; Mol. Wt. 288.1359. Found: C, 70.67; H, 6.92%; $M^+$, 288.1337. IR $cm^{-1}$: 1745, 1670 (CO), 1630 (C=C), 1240 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 244.5 nm ($\varepsilon$ 5050), 300 nm ($\varepsilon$ 18800). NMR $\delta$: 1.00 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.12 (3H, s, 5-$CH_3$), 1.94 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.22 (3H, s, $COCH_3$), 6.28 (1H, s, 6-H), 6.96 (1H, t, $J=4$ Hz, 1-H), 7.36 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 288 ($M^+$, 3), 246 ($[M-C_2H_2O]^+$, 14), 228 ($[M-CH_3CO_2H]^+$, 100), 213 ($[M-CH_3CO_2H-CH_3]^+$, 64). The NMR, IR, and UV spectral data of (+)-**1b** were in good agreement with those of (+)-decompositin reported by Hahn *et al.*[11] and Sorm *et al.*[12]

**(±)-Dihydrodecompositin (3)**——Catalytic reduction of 15 mg of **1b** in AcOEt (5 ml) with 10% Pd-charcoal catalyst (30 mg) under an $H_2$ atmosphere was carried out at room temperature for 50 min. Work-up of the mixture in the usual way yielded a product, which was purified by silica gel preparative TLC to afford 13 mg (86%) of (±)-**3** as colorless prisms, mp 137—138°C (from AcOEt–hexane). High-resolution mass spectrum of **3** for $C_{17}H_{22}O_4$: Mol. Wt. 290.1517. Observed: $M^+$, 290.1547. IR $cm^{-1}$: 1750, 1730, 1680 (CO), 1245 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 278.5 nm ($\varepsilon$ 13700). NMR $\delta$: 0.90 (3H, d, $J=7$ Hz, 4-$CH_3$), 0.92 (3H, s, 5-$CH_3$), 1.91 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.17 (3H, s, $COCH_3$), 6.29 (1H, s, 6-H), 7.30 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 290 ($M^+$, 11), 248 ($[M-C_2H_2O]^+$, 100), 230 ($[M-CH_3CO_2H]^+$, 50), 138 (95). The NMR spectrum of (±)-**3** was in good agreement with that of natural dihydrodecompositin reported by Bohlmann *et al.*[13]

**(±)-Adenostylone (1c)**——Treatment of the 6β-hydroxy compound (**1a**) with isobutyric anhydride and pyridine in the presence of DMAP at 40°C for 4 h gave (±)-**1c** as colorless prisms, mp 96—97°C (from AcOEt–hexane). IR $cm^{-1}$: 1745, 1675 (CO), 1630 (C=C), 1140 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 300 nm. NMR $\delta$: 0.99 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.15 (3H, s, 5-$CH_3$), 1.29, 1.30 (each 3H, d, $J=7$ Hz, $COCH(\underline{CH_3})_2$), 1.92 (3H, d, $J=1$ Hz, 11-$CH_3$), 6.32 (1H, s, 6-H), 6.94 (1H, t, $J=4$ Hz, 1-H), 7.36 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 246 ($[M-(CH_3)_2CCO]^+$, 39), 228 ($[M-C_4H_8O_2]^+$, 100), 213 (74). The NMR, IR, and UV spectral data of (±)-**1c** were in good agreement with those of (−)-adenostylone reported by Sorm *et al.*[12]

**3β-Propionyloxyfuranoeremophilan-6,9-dione (21b)**——3β-Hydroxyfuranoeremophilan-6,9-dione (**21a**)[5b] (93 mg) was dissolved in a solution of propionic anhydride (1.5 ml) and pyridine (4.5 ml) and the mixture was allowed to stand overnight at room temperature. Concentration of the mixture *in vacuo* gave a crude product, which was purified by silica gel column chromatography to give 103 mg (91%) of **21b** as colorless prisms, mp 113—115°C (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 68.06; H, 6.94. IR $cm^{-1}$: 1730, 1700, 1685 (CO), 1210 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 244.5 nm ($\varepsilon$ 5400), 304.5 nm ($\varepsilon$ 7600). NMR $\delta$: 0.96 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.16 (3H, t, $J=8$ Hz, $OCOCH_2\underline{CH_3}$), 1.31 (3H, s, 5-$CH_3$), 2.15 (2H, t, $J=8$ Hz, $O\underline{CH_2}CH_3$), 2.28 (3H, d, $J=1$ Hz, 11-$CH_3$), 4.84 (1H, m, $W_{1/2}=14$ Hz, 3-H), 7.44 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 318 ($M^+$, 5), 262 $[(M-CH_3CHCO]^+$, 70), 244 ($[M-CH_3CH_2CO_2H]^+$, 100).

**Oxidation of 21b with Benzeneseleninic Anhydride**——Benzeneseleninic anhydride (277 mg) was added to a solution of 97 mg of **21b** in toluene (15 ml), and the mixture was refluxed for 4 h. The mixture was cooled to room temperature and the resulting crystalline precipitate was filtered off. The filtrate was concentrated *in vacuo* and the residue was separated by silica gel preparative TLC. A less polar band gave 60 mg (59%) of 3β-propionyloxy-10β-hydroxyfuranoeremophilan-6,9-dione (**22**) as colorless prisms, mp 123—125°C (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63. Found: C, 64.62; H, 6.43%. IR $cm^{-1}$: 3420, 3280 (OH), 1735, 1690 (CO), 1230 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 245 nm ($\varepsilon$ 5000), 305 nm ($\varepsilon$ 8000). NMR $\delta$: 1.15 (3H, t, $J=8$ Hz, $OCOCH_2\underline{CH_3}$), 1.18 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.21 (3H, s, 5-$CH_3$), 2.28 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.35 (2H, q, $J=8$ Hz, $OCO\underline{CH_2}CH_3$), 4.80 (1H, m, $W^1/_2=20$ Hz, 3-H), 7.51 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 334 ($M^+$, 100), 306 ($[M-C_2H_4]^+$, 5), 278 ($[M-CH_3CHCO]^+$, 16), 206 ($[M-CH_3CH_2CO_2H]^+$, 55). A polar band gave 22 mg (22%) of 3β-propionyloxy-10α-hydroxyfuranoeremophilan-6,9-dione (**23**) as colorless needles, mp 174—176°C (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{22}O_6$: C, 64.66; H, 6.63; Mol. Wt. 334.1415. Found: C, 64.56; H, 6.67%; $M^+$, 334.1428. IR $cm^{-1}$: 3420 (OH), 1745, 1700, 1690, 1680 (CO), 1200 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 244 nm ($\varepsilon$ 4000), 302 nm ($\varepsilon$ 8600). NMR $\delta$: 1.16 (3H, t, $J=8$ Hz, $OCOCH_2\underline{CH_3}$), 1.19 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.31 (3H, s, 5-$CH_3$), 2.23 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.35 (2H, q, $J=8$ Hz, $OCO\underline{CH_2}CH_3$), 5.05 (1H, m, $W_{1/2}=8$ Hz, 3-H), 7.42 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 334 ($M^+$, 23), 260 ($[M-CH_3CH_2CO_2H]^+$, 71), 245 (61), 242 (44), 227 (100).

**3β-Propionyloxy-1,10-dehydrofuranoeremophilan-6,9-dione (24)**——A solution of 21 mg of **23** in pyridine (3 ml) was treated with 2 drops of $SOCl_2$ and the mixture was stirred at 0°C for 10 min. The mixture was diluted with ether (50 ml) and the ether solution was washed with sat. aq. $NaHCO_3$ and dried. Removal of the solvent by evaporation *in vacuo* yielded a residue which was purified by silica gel preparative TLC to afford 18 mg (91%) of **24** as colorless prisms, mp 152—154°C (from AcOEt–hexane). *Anal.* Calcd for $C_{18}H_{20}O_5$: C, 68.34; H, 6.37; Mol. Wt. 316.1309. Found: C, 68.25; H, 6.36%; $M^+$, 316.1323. IR $cm^{-1}$: 1745, 1700, 1680 (CO), 1630, 1595 (C=C), 1190 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 227 nm ($\varepsilon$ 13000), 313 nm ($\varepsilon$ 11500). NMR $\delta$: 1.15

(3H, t, $J=8$ Hz, $OCOCH_2C\underline{H}_3$), 1.31 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.55 (3H, s, 5-$CH_3$), 2.26 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.34 (2H, q, $J=8$ Hz, $OCOC\underline{H}_2CH_3$), 5.10 (1H, m, $W^1/_2=6$ Hz, 3-H), 6.76 (1H, t, $J=4$ Hz, 1-H), 7.47 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 316 ($M^+$, 2), 242 ($[M-CH_3CH_2CO_2H]^+$, 53), 227 (100).

**3β-Propionyloxy-6β-hydroxy-1,10-dehydrofuranoeremophilan-9-one (2a)**——$NaBH_4$ (2.5 mg) was added to a solution of 20 mg of **24** in MeOH (10 ml), and the mixture was stirred at 0°C for 5 min. Work-up of the mixture in the usual way gave a crude product, which was purified by silica gel preparative TLC to afford 20 mg (quantitative yield) of **2a** as an oil. IR $cm^{-1}$: 3460 (OH), 1740, 1675 (CO), 1635, 1600 (C=C), 1200 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 243.5, 302 nm. NMR δ: 1.13 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.14 (3H, t, $J=8$ Hz, $OCOCH_2C\underline{H}_3$), 1.18 (3H, s, 5-$CH_3$), 2.16 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.35 (2H, q, $J=8$ Hz, $OCOC\underline{H}_2CH_3$), 5.04 (2H, m, 3-, 6-H), 6.56 (1H, t, $J=4$ Hz, 1-H), 7.37 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 318 ($M^+$, 12), 244 ($[M-CH_3CH_2CO_2H]^+$, 19), 229 (57), 226 (100).

**(±)-3β,6β-Dipropionyloxyeuryopsin-9-one (2b)**——A solution of 16 mg of **2a** in propionic anhydride (1 ml) and pyridine (3 ml) was treated with DMAP (4 mg), and the mixture was allowed to stand at room temperature for 1.5 h. The mixture was concentrated *in vacuo* and the residue was purified by silica gel preparative TLC to afford 19 mg (quantitative yield) of (±)-**2b** as colorless prisms, mp 83—85°C (from AcOEt–hexane). High-resolution mass spectrum for $C_{21}H_{26}O_6$: 374.1727. Observed: $M^+$, 374.1717. IR $cm^{-1}$: 1750, 1740, 1685 (CO), 1640, 1610 (C=C), 1195 (COC). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 242 nm (ε 5100), 298.5 nm (ε 18700). NMR δ: 1.04 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.13, 1.24 (each 3H, t, $J=8$ Hz, $OCOCH_2C\underline{H}_3$), 1.26 (3H, s, 5-$CH_3$), 1.93 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.32, 2.52 (each 2H, q, $J=8$ Hz, $OCOC\underline{H}_2CH_3$), 5.04 (1H, m, $W^1/_2=12$ Hz, 3-H), 6.35 (1H, s, 6-H), 6.71 (1H, t, $J=4$ Hz, 1-H), 7.38 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 374 ($M^+$, 1), 318 ($[M-CH_3CHCO]^+$, 4), 300 ($[M-CH_3CH_2CO_2H]^+$, 2), 244 (20), 226 ($[M-(CH_3CH_2CO_2H)_2]^+$, 100). The NMR, IR, and mass spectral data of (±)-**2b** were in good agreement with those of natural 3β,6β-dipropionyloxyeuryopsin-9-one reported by Bohlmann *et al.*[14]

**Catalytic Reduction of 12a**——Catalytic reduction of the enone (**12a**) (183 mg) with 10% Pd-charcoal (18 mg) in AcOEt (25 ml) under an $H_2$ atmosphere at room temperature for 40 min was carried out. The catalyst was filtered off and the filtrate was concentrated *in vacuo* to give a crystalline product. Fractional recrystallization from AcOEt–hexane gave 160 mg (87%) of **25**, and the mother liquor was purified by silica gel preparative TLC to afford 18 mg (10%) of **26a** as a colorless oil. Compound (**25**): colorless prisms, mp 205—208°C. *Anal.* Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.51; H, 7.23%. IR $cm^{-1}$: 3470 (OH), 1670 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 280 nm (ε 13500). NMR δ: 0.98 (3H, s, 5-$CH_3$), 1.20 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.14 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.7—4.2 (4H, m, $\left.\begin{array}{l}\mathrm{CH_2O}\\ \,|\\ \mathrm{CH_2O}\end{array}\right\rangle$), 4.92 (1H, d, $J=10$ Hz, 6-H) the signal changed to a singlet on addition of $D_2O$, 7.31 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 306 ($M^+$, 17), 99 (100). Compound (**26a**): IR $cm^{-1}$: 3460 (OH), 1665 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 283.5 nm. NMR δ: 0.94 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.16 (3H, bs, 5-$CH_3$), 2.13 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.92 (4H, s, $\left.\begin{array}{l}\mathrm{CH_2O}\\ \,|\\ \mathrm{CH_2O}\end{array}\right\rangle$), 5.40 (1H, bs, 6-H), 7.35 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (Rel. int.): 306 ($M^+$, 26), 178 (31), 99 (100).

**Epimerization of 25 with $NaOC_2H_5$**——To a solution of **25** (61 mg) in EtOH (15 ml) was added 0.4 ml of $NaOC_2H_5$ solution (prepared from 200 mg of Na and 10 ml of abs. EtOH), and the mixture was allowed to stand at room temperature for 1 h. $NH_4Cl$ was then added and the solvent was evaporated off *in vacuo*. The residue was diluted with ether, and 3 ml of $H_2O$ was added. The organic layer was washed with $H_2O$ and dried. Removal of the solvent left a residue, which was subjected to silica gel preparative TLC to afford 55 mg (90%) of **26a** and 6 mg (10%) of **25**.

**3,3-Ethylenedioxy-6β-(2-methylbutyryloxy)furanoeremophilan-9-one (26b)**——A solution of **26a** (18 mg) and 2-methylbutyric anhydride (200 mg) in pyridine (1.2 ml) was treated with 10 mg of DMAP. The mixture was allowed to stand at room temperature for 1 h. The mixture was concentrated *in vacuo* and the residue was purified by silica gel column chromatography to give 22 mg (96%) of **26b** as an oil. IR $cm^{-1}$: 1735, 1680 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 239, 283 nm. NMR δ: 2.04 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.6—4.1 (4H, m, $\left.\begin{array}{l}\mathrm{CH_2O}\\ \,|\\ \mathrm{CH_2O}\end{array}\right\rangle$), 6.12 (1H, bs, 6-H), 7.35 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 390 ($M^+$, 7), 306 ($[M-CH_3CH_2C(CH_3)CO]^+$, 6), 305 (9), 289 (9), 259 (16), 99 (100).

**6β-(2-Methylbutyryloxy)furanoeremophilan-3,9-dione (27)**——A solution of **26b** (18 mg) in 5 ml of AcOH–$H_2O$ (3:1) was allowed to stand at 70°C for 2.5 h. The solvent was evaporated off *in vacuo* and the residue was purified by silica gel preparative TLC to afford 16 mg (quantitative yield) of **27** as an oil. IR $cm^{-1}$: 1740, 1715, 1685 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ 237.5, 285 nm. NMR δ: 0.99 (3H, d, $J=6$ Hz, 4-$CH_3$), 1.05 (3H, s, 5-$CH_3$), 2.07 (3H, d, $J=1$ Hz, 11-$CH_3$), 5.99 (1H, s, 6-H), 7.42 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 346 ($M^+$, 8), 262 ($[M-CH_3CH_2C(CH_3)CO]^+$, 73), 85 (100).

**(±)-3β-Acetoxy-6β-(2-methylbutyryloxy)-10βH-furanoeremophilan-9-one (28b)**——$NaBH_4$ (1.5 mg) was added to a solution of **27** (14 mg) in MeOH (10 ml) with stirring at 0°C, and stirring was continued for 10 min. $NH_4Cl$ was added to the mixture and the solvent was evaporated off *in vacuo*. The residue was extracted with ether, washed with $H_2O$ and dried. After removal of the ether, the residue was purified by silica gel preparative TLC to give 13 mg (93%) of **28a** as an oil. IR cm$^{-1}$: 3460 (OH), 1740, 1680 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 281.5 nm. MS *m/z* 348 (M$^+$).

**28a** (12 mg) was treated with $Ac_2O$ (0.5 ml), pyridine (1.5 ml), and DMAP (3 mg) at room temperature for 20 min. The mixture was concentrated *in vacuo* and the residue was purified by silica gel preparative TLC to give 10 mg (74%) of **28b** as an oil. IR cm$^{-1}$: 1745, 1740, 1685 (CO), 1255, 1240 (COC). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 243, 282.5 nm. NMR $\delta$ ($C_6D_6$, 72°C): 0.76 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.15 (3H, s, 5-$CH_3$), 1.67 (3H, s, $COCH_3$), 1.81 (3H, d, $J=1$ Hz, 11-$CH_3$), 2.62 (1H, m, 10-H), 4.96 (1H, m, 3-H), 6.32 (1H, s, 6-H), 6.80 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 390 (M$^+$, 3), 306 ([M$-CH_3CH_2C(CH_3)CO$]$^+$, 32), 246 (30), 85 (67), 57 (100). The NMR spectral data of (±)-**28b** were identical with those of natural 3$\beta$-acetoxy-6$\beta$-(2-methylbutyryloxy)-10$\beta$-H-furanoeremophilan-9-one reported by Bohlmann *et al.*[15]

**6$\beta$-Hydroxyfuranoeremophilan-3,9-dione (29)**——A solution of the ketal (**26a**) (18 mg) in 6 ml of AcOH–$H_2O$ (3: 1) was allowed to stand at room temperature for 3 h. The solvent was evaporated off *in vacuo* and the residue was purified by silica gel preparative TLC to afford a crystalline compound. Recrystallization from AcOEt–hexane gave 9 mg (60%) of **29** as colorless needles, mp 176—180°C. IR cm$^{-1}$: 3490 (OH), 1710, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 239, 284 nm. NMR $\delta$: 0.96 (3H, d, $J=7$ Hz, 4-$CH_3$), 1.13 (3H, s, 5-$CH_3$), 2.13 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.04 (1H, t, $J=4$ Hz, 10-H), 4.66 (1H, bs, 6-H), 7.41 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 262 (M$^+$, 100), 191 (27), 138 (73), 110 (49).

**3$\beta$,6$\beta$-Dihydroxyfuranoeremophilan-9-one (4)**——$NaBH_4$ was added to a solution of **29** (8 mg) in MeOH (10 ml) with stirring at 0°C, and stirring was continued for 30 min. After work-up in the usual way, the oily product was purified by silica gel preparative TLC to give a crystalline compound. Recrystallization from AcOEt–hexane afforded 8 mg (quantitative yield) of **4** as colorless prisms, mp 154—156°. High-resolution mass spectrum of **4** for $C_{15}H_{20}O_4$: Mol. Wt. 264.1360. Observed: M$^+$, 264.1360. IR cm$^{-1}$: 3460, 3340 (OH), 1690 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 283 nm. NMR $\delta$ ($CD_3OD$): 0.94 (3H, d, $J=7$ Hz, 4-$CH_3$), 0.97 (3H, s, 5-$CH_3$), 2.16 (3H, d, $J=1$ Hz, 11-$CH_3$), 4.12 (1H, m, $W^1/_2=18$ Hz, 3-H), 5.25 (1H, bs, 6-H), 7.52 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 264 (M$^+$, 49), 246 ([M$-H_2O$]$^+$, 30), 138 ([M$-C_8H_{14}O$]$^+$, 100).

**6$\beta$-Hydroxy-10$\alpha$H-furanoeremophilan-3,9-dione (30)**——A solution of the ketal (**25**) (92 mg) in 10 ml of AcOH–$H_2O$ (3: 1) was allowed to stand at room temperature for 4 h. The solvent was evaporated off *in vacuo* and the residue was purified by silica gel column chromatography to afford a crystalline compound. Recrystallization from AcOEt–hexane gave 72 mg (92%) of **30** as colorless prisms, mp 172—177°C. *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92; Mol. Wt. 262.1203. Found: C, 68.49; H, 6.94%; M$^+$, 262.1186. IR cm$^{-1}$: 3550 (OH), 1710, 1660 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 280.5 nm ($\varepsilon$ 14000). NMR $\delta$: 0.80 (3H, s, 5-$CH_3$), 1.27 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.17 (3H, d, $J=1$ Hz, 11-$CH_3$), 5.18 (1H, d, $J=9$ Hz, 6-H) the signal changed to a singlet on addition of $D_2O$, 7.36 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 262 (M$^+$, 100), 138 ([M$-C_8H_{12}O$]$^+$, 87).

**3$\beta$,6$\beta$-Dihydroxy-10$\alpha$H-furanoeremophilan-9-one (5)**——$NaBH_4$ (1.8 mg) was added to a solution of **30** (11 mg) in MeOH (10 ml) with stirring at 0°C, and stirring was continued for 20 min. After work-up in the usual way, the crude crystalline compound was recrystallized from AcOEt to give 7 mg (64%) of **5** as colorless prisms, mp 264—265°C. High-resolution mass spectrum of **5** for $C_{15}H_{20}O_4$: Mol. Wt. 264.1360. Observed: M$^+$, 264.1368. IR cm$^{-1}$: 3480, 3390 (OH), 1680 (CO). UV $\lambda_{\text{max}}^{\text{EtOH}}$ 280 nm ($\varepsilon$ 13600). NMR $\delta$ ($CD_3OD$): 0.99 (3H, s, 5-$CH_3$), 1.35 (3H, d, $J=7$ Hz, 4-$CH_3$), 2.13 (3H, d, $J=1$ Hz, 11-$CH_3$), 3.72 (1H, m, $W^1/_2=6$ Hz, 3-H), 7.44 (1H, q, $J=1$ Hz, 12-H). MS *m/z* (% Rel. int.): 264 (M$^+$, 46), 246 ([M$-H_2O$]$^+$, 16), 138 ([M$-C_8H_{14}O$]$^+$, 100).

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