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6β-Acetoxyfuranoeremophilan-3α-yl Angelate and 6β-Hydroxyfuranoeremophilan-3α-yl Angelate.[1] New Furanoeremophilane Derivatives from *Farfugium hiberniflorum* Kitamura

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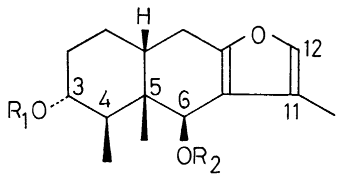
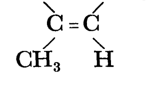
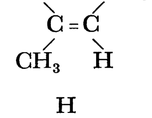
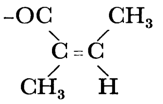
In connection with the structural studies of farfugin A and farfugin B isolated from *Farfugium japonicum* Kitamura (=*Ligularia tussilaginea* Makino; Tsuwabuki in Japanese),[2] we have examined the constituents of *Farfugium hiberniflorum* Kitamura (=*Liguralia hiberniflora* Makino; Kan-tsuwabuki in Japanese) and isolated 6β-acetoxyfuranoeremophilan-3α-yl angelate (I) and 6β-hydroxyfuranoeremophilan-3α-yl angelate (II),[1] which constitute two new furanoeremophilane derivatives related to furanofukinol (III).[3]

Compound I, $C_{22}H_{30}O_5$ (M^+ at m/e 374), a viscous oil, was positive to the Ehrlich test. IR, UV, PMR, and mass spectra (see Experimental) suggest the presence of a furan, a secondary and a tertiary methyl, and also that of partial structures: 
$CH_3COO\text{-}\overset{|}{\underset{|}{C}}H$



	R_1	R_2
(I)		Ac
(II)		H
(III)	H	H
(IV)	H	

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[1] The structures refer to those of relative configurations.

[2] H. Nagano, Y. Moriyama, Y. Tanahashi, T. Takahashi, M. Fukuyama, and K. Sato, *Chem. Lett.*, **1972**, 13.

[3] K. Naya, M. Nakagawa, M. Hayashi, K. Tsuji and M. Naito, *Tetrahedron Lett.*, **1971**, 2961.

and $CH_3CH{=}C(CH_3)COO{-}\overset{|}{\underset{|}{C}}H$. The latter moiety was determined as angelyl group by benzene induced solvent shift[4] ($\delta^{CDCl_3} - \delta^{C_6D_6} = 0.44$ ppm) of the olefinic proton found to be *trans* to the ester group. Reduction of I with lithium aluminum hydride gave a diol $C_{15}H_{22}O_3$ identical (IR, PMR, and tlc) with furanofukinol (III)[3] (3α,6β-dihydroxyfuranoeremophilane) isolated by Naya *et al.* from *Petasites japonicus* Maxim. Thus, compound I is either 6β-acetoxyfuranoeremophilan-3α-yl angelate (I) or 3α-acetoxyfuranoeremophilan-6β-yl angelate.[1]

Acetylation of II, $C_{20}H_{28}O_4$, an oil, with acetic anhydride and pyridine afforded a monoacetate identical (IR, vpc and tlc) with I. On reduction with lithium aluminum hydride, II gave III. However, spectral data of II differ from those of 6-angelylfuranofukinol (IV)[3] (3α-hydroxyfuranoeremophilan-6β-yl angelate).

Thus substances I and II should be represented by 6β-acetoxyfuranoeremophilan-3α-yl angelate and 6β-hydroxyfuranoeremophilan-3α-yl angelate,[1,5] respectively.

Experimental

Isolation. The dried roots of *Farfugium hiberniflorum* Kitamura (100 g) were extracted three times with boiling benzene (each 400 m*l*). The roots were then powdered and further extracted with boiling benzene. The combined extracts (1.6 g) were chromatographed on silica gel (Wakogel, C-200; 120 g) with light petroleum-ether (5 : 1) as eluent to give a pale yellow oil containing I. Successive elution with light petroleum-ether (3 : 1) afforded crude II. Pure I (60 mg) and II (100 mg) were obtained by repeated chromatography of each crude oil on silica gel.

6β-Acetoxyfuranoeremophilan-3α-yl Angelate (I). Spectral data of I, $C_{22}H_{30}O_5$, an oil, are as follows; UV: λ_{max}^{EtOH} 215 nm (ε 17000); IR: $\nu_{max}^{CHCl_3}$ 1730, 1710, 1640, 1560, 1235, and 1160 cm^{-1}; PMR ($CDCl_3$): δ 0.97 (d, J=7 Hz, $C_{(4)}$-$C\underline{H}_3$), 1.03 (s, $C_{(5)}$-$C\underline{H}_3$), 1.87 (d, J=1.5 Hz, $C_{(11)}$-$C\underline{H}_3$), 1.87 [s, $CH_3CH{=}C(C\underline{H}_3)COO$-], 1.97[d,[6] J=7 Hz, $C\underline{H}_3CH{=}C(CH_3)COO$-], 2.12 (s, $C\underline{H}_3CO$-), 5.37 (m, $C_{(3)}$-$\underline{H}$), 6.01[q,[6] J=7 Hz, $CH_3C\underline{H}{=}C(CH_3)COO$-], 6.37 (br. s, $C_{(6)}$–H), and 7.05 ppm (m, $C_{(12)}$–H); PMR (C_6D_6): δ 0.90 (d, J=7 Hz, $C_{(4)}$–$C\underline{H}_3$), 0.95 (s, $C_{(5)}$–$C\underline{H}_3$), 1.76 (s, $C\underline{H}_3$-CO–), 1.8—2.2[$C_{(11)}$–$C\underline{H}_3$, $CH_3CH{=}C(C\underline{H}_3)COO$– and $C\underline{H}_3CH{=}C(CH_3)COO$–], 5.57[m, $C_{(3)}$–$\underline{H}$ and $CH_3C\underline{H}{=}C(CH_3)COO$–], 6.51 (br. s, $C_{(6)}$–$\underline{H}$) and 6.95 ppm (m, $C_{(12)}$–H); MS: *m/e* 374 (relative intensity 2%, M$^+$), *m/e* 124 (100%, *retro*-Diels-Alder fragment), *m/e* 83 (82%, $[CH_3CH{=}C(CH_3)CO]^+$), *m/e* 55 (70%, $[CH_3CH{=}CCH_3]^+$) and *m/e* 43 (80%, $[CH_3CO]^+$).

6β-Hydroxyfuranoeremophilan-3α-yl Angelate (II). Characterization of II, $C_{20}H_{28}O_4$, an oil, is as follows; IR: $\nu_{max}^{CHCl_3}$ 3450, 1700, 1640, 1560, 1240 and 1160 cm^{-1}; PMR ($CDCl_3$): 0.95 (s, $C_{(5)}$–$C\underline{H}_3$), 1.00 (d, J=7 Hz, $C_{(4)}$–$C\underline{H}_3$), 1.8—2.1 [$C_{(11)}$–$C\underline{H}_3$, $CH_3CH{=}C(C\underline{H}_3)COO$– and $C\underline{H}_3CH{=}C(CH_3)COO$–], 5.07 (br. s, $C_{(6)}$–$\underline{H}$), 5.30 (m, $C_{(3)}$–$\underline{H}$), 6.05 [m, $CH_3C\underline{H}{=}C(CH_3)COO$–] and 7.04 ppm (m, $C_{(12)}$–$\underline{H}$).

Reduction of 6β-Acetoxyfuranoeremophilan-3α-yl Angelate (I) with Lithium Aluminum Hydride. A solution of I (43 mg) in dry ether was added to a suspension of lithium aluminum hydride (50 mg) in dry ether and the reaction mixture was refluxed for 1.5 hr under nitrogen atmosphere. The usual treatment gave a crystalline material (34 mg), which was purified by chromatography on silica gel to afford furanofukinol (III), UV: λ_{max}^{EtOH} 219 nm (ε 6200); IR: ν_{max}^{Nujol} 3375 and 3320 cm^{-1}; PMR (DMSO-d_6): 0.77 (s, $C_{(5)}$–CH_3), 0.84 (d, J=7 Hz, $C_{(4)}$–CH_3), 1.98 (d, J=*ca.* 1 Hz, $C_{(11)}$–CH_3), and 7.14 ppm (m, $C_{(12)}$–H); MS: *m/e* 250 (3%, M$^+$) and *m/e* 124 (100%, *retro*-Diels-Alder fragment).

6β-Hydroxyfuranoeremophilan-3α-yl angelate (II) was reduced with lithium aluminum hydride to give furanofukinol (III) by the same procedure as abave.

The authors wish to thank Prof. K. Naya, Kwansei Gakuin University, for the gift of the authentic sample of furanofukinol, and also for the PMR and IR spectra of furanofukinol and its derivatives.

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[4] J. Ronayne and D. H. Williams, *J. Chem. Soc., C*, **1967**, 2642.

[5] Since no optical rotation data were described for furanofukinol (III),[2] absolute configurations of compounds I and II are left undetermined. From biogenetic considerations, absolute configurations of I and II are plausible for compounds I and II.

[6] Further long-range couplings are observed for these signals.