3β,6β-Bis(acyloxy)furanoeremophilan-14-als and -14-oic Acids from *Syneilesis palmata* (THUNB.) MAXIM.[1]

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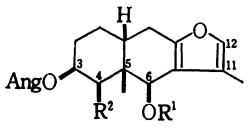
Structural studies of four new sesquiterpenes, 3β-angeloyloxy-6β-(3-methylbutanoyloxy)- and 3β,6β-bis(angeloyloxy)furanoeremophilan-14-als and 3β-angeloyloxy-6β-(3-methylbutanoyloxy)- and 3β-angeloyloxy-6β-(3-methylpentanoyloxy)furanoeremophilan-14-oic acids, together with 3β,6β-bis(angeloyloxy)furanoeremophilan-14-oic acid from *Syneilesis palmata* (THUNB.) MAXIM. are described.

Investigations on sesquiterpenes in the plants of the genera *Ligularia*,[2] *Eupatorium*,[3] *Farfugium*,[4] and *Cacalia*[5] (Compositae) have been carried out in our laboratory. Furanoeremophilane derivatives have been shown to be main sesquiterpenes for plants of the genera *Ligularia* and *Farfugium*,[6] but benzofuran derivatives[5,7] together with furanoeremophilanes[8] for those of the genus *Cacalia*.[9] In connection with these studies, *Syneilesis palmata* (THUMB.) MAXIM. (Japanese name: Yaburegasa) (Compositae) was now examined. Only a constitutional investigation of *S. palmata* has been reported by Hikichi and Furuya[10] and three alkaloids, syneilesine, acetylsyneilesine, and senecionine have been isolated. While *S. palmata* is classified morphologically into the genus *Syneilesis*, it is also classified taxonomically into the genus *Cacalia* and named *Cacalia Krameri* MAKINO. Therefore, examination on sesquiterpene constituents of this plant is interested from the chemotaxonomical viewpoint.

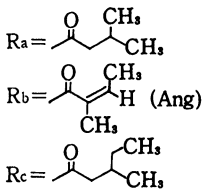
Chromatographic separation of the ethereal extract of the roots of *S. palmata* afforded two main components **A** and **B**, which were positive to the Ehrlich test.

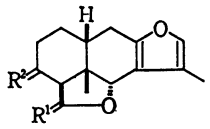
It was found that the component **A** gave two peaks in high performance liquid chromatographic examination. Since the component **A**, obtained as an oil, crystallized from pentane on standing, separation by fractional crystallization was attempted but was unsuccessful. High performance liquid chromatography (HPLC) was successfully applied to the separation to afford an aldehyde (**1**) and an ether (**2**) in a ratio of 1 : 1. On treatment of the component **A** with sodium borohydride, the ether (**2**) remained unchanged and separated easily from the reaction mixture. The ether (**2**; content: 0.02%), mp 97—98 °C, was found to be a known 3β-angeloyloxy-6α,14-epoxyfuranoeremophilane.[11]

The aldehyde (**1**; content: 0.03%), mp 82—83 °C, was found to be a mixture of two components **1a** and **1b** by appearance of two molecular ions at *m/e* 430.2334 ($C_{25}H_{34}O_6$) and *m/e* 428.2175 ($C_{25}H_{32}O_6$) in the high resolution mass spectrum. HPLC was applied to further separation of **1** into **1a** and **1b** without success,

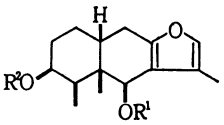


1a $R^1=R_a$; $R^2=CHO$
1b $R^1=R_b$; $R^2=CHO$
3a $R^1=R_a$; $R^2=CH_2OH$
3b $R^1=R_b$; $R^2=CH_2OH$
7a $R^1=R_a$; $R^2=COOH$
7b $R^1=R_b$; $R^2=COOH$
7c $R^1=R_c$; $R^2=COOH$
8a $R^1=R_a$; $R^2=COOCH_3$
8b $R^1=R_b$; $R^2=COOCH_3$
8c $R^1=R_c$; $R^2=COOCH_3$

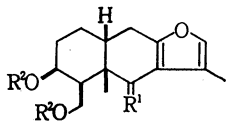




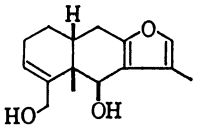
2 $R^1=H_2$; $R^2=\alpha$-H, β-OAng
10 $R^1=O$; $R^2=\alpha$-H, β-OAng
11 $R^1=O$; $R^2=H_2$
13 $R^1=H_2$; $R^2=\alpha$-H, β-OH
14 $R^1=H_2$; $R^2=H_2$
15 $R^1=H_2$; $R^2=O$



4 $R^1=H$; $R^2=H$
6 $R^1=Ac$; $R^2=Ang$



9 $R^1=\alpha$-H, β-OH; $R^2=H$
12 $R^1=\alpha$-OH, β-H; $R^2=H$
16 $R^1=\alpha$-H, β-OAc; $R^2=Ac$



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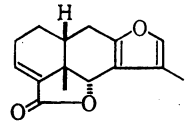

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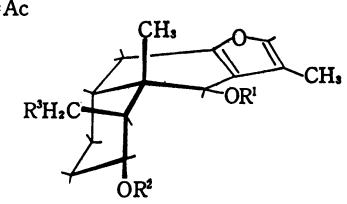

6a $R^1=Ac$; $R^2=Ang$; $R^3=H$
9a $R^1=R^2=H$; $R^3=OH$

because each retention time was nearly the same due to their structural similarity. Separation by gas-liquid chromatography (GLC) was not available because of thermal unstability of these compounds. Therefore we were obliged to analyze the mixture (**1**) in order to obtain the information for structure determination of **1a** and **1b**.

The IR and ^1H NMR spectra of the mixture **1** (**1a** and **1b**) showed the presence of a β-methyl-substituted furan with an α-hydrogen, a tertiary methyl, and an

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aldehyde group, together with protons on carbon atoms bearing acyloxyl groups [δ 5.47 (br signal, 1H; $C_{(3)}$–H), 6.28 (m, *ca.* 0.7H; $C_{(6)}$–H of **1a**), and 6.36 (m, *ca.* 0.3H; $C_{(6)}$–H of **1b**)]. Reduction of **1** with sodium borohydride afforded a mixture (**3**) of alcohols, **3a** and **3b**, whose ^{1}H NMR spectrum showed the presence of $-C\underline{H}_2OH$. The mixture of alcohols (**3a** and **3b**) was treated with methanesulfonyl chloride to afford a mixture of mesylates (δ 2.86; $-SO_2CH_3$), which, on reduction with lithium aluminium hydride gave two diols, **4** and **5** in 12% and 57% yields, respectively. The diol (**4**) was identified with a known furanofukinol[12] (furanoeremophilane-3β,6β-diol) by direct comparison with an authentic sample.

In the ^{1}H NMR spectrum of **1**, a doublet signal characteristic of a secondary methyl at C-4 of furanoeremophilanes was not observed, suggesting the formyl group must be attached to the C-4. This was supported by a doublet signal (J=5 Hz) due to the aldehydic proton at δ 9.97. Therefore, **1a** and **1b** were deduced to be 3β,6β-bis(acyloxy)furanoeremophilan-14-als.

The diol (**5**), $C_{15}H_{20}O_3$ (*m/e* 248.1482), was determined to be furanoeremophil-3-ene-6β,14-diol, supporting above conclusion. The presence of a secondary hydroxyl group at C-6 was shown by appearance of a multiplet signal at δ 4.77[13] and a *retro*-Diels Alder fragment ion at *m/e* 124.0518 ($C_7H_8O_2$) as a base peak.[14] The partial structure of 3-en-14-ol for **5** was supported by appearance of a broad signal at δ 5.40 ($C_{(3)}$–H) and an AB quartet signal due to a CH_2OH group attached to a carbon atom carrying no hydrogen atom.

The locations and structures of two acyloxyl groups were determined as follows. The component **A** (a mixture of **1** and **2**) was hydrolyzed with alkali. The carboxylic acids derived from the acyloxyl groups were methylated with diazomethane to give a mixture of methyl esters, which was examined by gas chromatography-mass spectrometry (GC-MS) measurement. Methyl angelate and methyl 3-methylbutanoate were detected in a ratio of *ca.* 3 : 1. From these observations together with the high resolution mass spectral data of **1a** and **1b**, a structure of 3β,6β-bis(angeloyloxy)-furanoeremophilan-14-al was suggested for **1b** and either 3β-angeloyloxy-6β-(3-methylbutanoyloxy)- or 6β-angeloyloxy-3β-(3-methylbutanoyloxy)furanoeremophilan-14-al for **1a**.

It is shown that when mass spectrum of 3β-angeloyloxy-6β-acetoxyfuranoeremophilane (**6**) was measured by direct inlet system, peaks at *m/e* 314 and *m/e* 274 due to fragment ions (M—AcOH)$^+$ and (M—Angelic acid)$^+$, respectively, were observed in an intensity ratio of 9 : 2, but when measured by indirect inlet system, only the former peak at *m/e* 314 due to (M—AcOH)$^+$ by elimination of the acetoxyl group on C-6 was observed.[15] These observations mean that an acid moiety at C-6 of 6-acyloxyfuranoeremophilane derivatives is easily eliminated to give the corresponding fragment ion by indirect inlet measurement. Table 1 gives the mass spectral data of **3** measured by the two inlet systems. The mass spectrum measured by indirect inlet system of **3** showed a peak at *m/e* 330 due to elimination of carboxylic acids (3-methylbutanoic acid for **3a** and angelic acid for **3b**) derived from the acyloxyl groups at C-6 with a relative intensity 8.7% but no peak at *m/e* 332 due to elimination of angelic acid, suggesting the presence of the angeloyloxyl group on C-3 for both **3a** and **3b**.

Table 1. Mass spectral data for **3**

m/e	Intensity/% Direct	Indirect	Assignment of ion
432	1.7	—	M$^+$(**3a**)
430	1.0	—	M$^+$(**3b**)
348	4.5	—	(M−R^1+H)$^+$
347	1.6	—	(M−R^1)$^+$
332	2.5	—	(M−AngOH)$^+$(derived from **3a**)
330	22[a,b]	8.7[a]	[a](M−R^{1}OH)$^+$ (derived form **3a** and **3b**) [b](M−AngOH)$^+$ (derived from **3b**)
248	6.4	—	(M−R^{1}OH−Ang+H)$^+$
247	7.5	—	(M−R^{1}OH−Ang)$^+$
230	37	14	(M−R^{1}OH−AngOH)$^+$
161	—	24	
159	34	21	
124	22	—	
100	—	24	(AngOH)$^+$
99	29	—	(AngO)$^+$
83	100	36	(Ang)$^+$
55	74	100	(CH$_3$CH=CCH$_3$)$^+$

In conclusion, **1** is shown to consist of 3β-angeloyloxy-6β-(3-methylbutanoyloxy)furanoeremophilan-14-al (**1a**) and 3β,6β-bis(angeloyloxy)furanoeremophilan-14-al (**1b**) in a ratio of *ca.* 7 : 3.

Component **B** (**7**) was obtained in 0.18% yield as a pale yellow oil and positive to the Ehrlich test. The ^{1}H NMR and mass spectral examination revealed that the component **B** consisted of three carboxylic acids, **7a**, **7b**, and **7c** (deuterium-exchangeable broad singlet at δ 10.05 and molecular ions at *m/e* 446, 444, and 460) and the presence of a β-methyl-substituted furan with an α-hydrogen, a tertiary methyl, and protons [δ 6.28 (*ca.* 0.2H), δ 6.37 (*ca.* 0.7H), and δ 6.48 (*ca.* 0.1H); each assigned to $C_{(6)}$–H, and δ 5.37; $C_{(3)}$–H)] on carbon atoms bearing acyloxyl groups, containing an angeloyloxyl group.

On esterification with diazomethane, **7** gave a mixture (**8**) of **8a** (*m/e* 460.2419, $C_{26}H_{36}O_7$), **8b** (*m/e* 458.2296, $C_{26}H_{34}O_7$), and **8c** (*m/e* 474.2818, $C_{27}H_{38}O_7$). Since HPLC separation of neither the mixture (**8**) nor the mixture (**7**) gave satisfactory results, analysis of the mixture (**8a**, **8b**, and **8c**) was carried out by the same procedures as in the case of **1**.

Reduction of **8** with lithium aluminium hydride afforded a triol (**9**), mp 139—140 °C, which was found to be identical with a triol obtained from **1** by treatment with lithium aluminium hydride. The structure of triol (**9**) was determined to be furanoeremophilane-3β,6β,14-triol by ^{1}H NMR and mass spectral measurements together with the fact that **9** was also derived from **1**. The detail of the structure elucidation of **9** was described below. In the ^{1}H NMR spectrum of **7**, a doublet signal characteristic of a secondary methyl at C-4 is absent. The carboxyl group, therefore, must be

located on C-4 and the acyloxyl groups on C-3β and C-6β for **7**.

Alkaline hydrolysis of **7** gave a mixture of carboxylic acids derived from the acyloxyl moieties. The mixture was methylated with diazomethane and examined by GC-MS measurement. Methyl angelate, methyl 3-methylbutanoate, and methyl 3-methylpentanoate were detected in a ratio of *ca.* 6 : 4 : 1. These observations together with high resolution mass spectral data suggest that 3β,6β-bis(angeloyloxy)furanoeremophilan-14-oic acid could be proposed for **7b**, 3β-angeloyloxy-6β-(3-methylpentanoyloxy)- or 6β-angeloyloxy-3β-(3-methylpentanoyloxy)furanoeremophilan-14-oic acid for **7c**, and 3β-angeloyloxy-6β-(3-methylbutanoyloxy)- or 6β-angeloyloxy-3β-(3-methylbutanoyloxy)furanoeremophilan-14-oic acid for **7a**. The alternatives for **7a** and **7c** were determined by mass spectrum of **8** measured by indirect inlet system (Table 2) and this conclusion was confirmed by the formation of 3β-angeloyloxyfuranoeremophilan-14,6α-olide (**10**) (*vide infra*). Based on arguments developed for **1**, appearance of a fragment peak at *m/e* 358 due to elimination of the acid moieties at C-6 suggests the presence of the angeloyloxyl group on C-3 for **8a**, **8b**, and **8c**. Thus the component **B** (**7**) is shown to consist of 3β-angeloyloxy-6β-(3-methylbutanoyloxy)furanoeremophilan-14-oic acid (**7a**), 3β,6β-bis(angeloyloxy)furanoeremophilan-14-oic acid (**7b**),[11,16] and 3β-angeloyloxy-6β-(3-methylpentanoyloxy)furanoeremophilan-14-oic acid (**7c**) in a ratio of *ca.* 7 : 1 : 2.

TABLE 2. MASS SPECTRAL DATA FOR **8**

m/e	Intensity/%		Assignment
	Direct	Indirect	
474	0.7	—	M^+(**8c**)
460	2.7	—	M^+(**8a**)
458	0.9	—	M^+(**8b**)
376	17	—	$(M-R^1+H)^+$
375	8.7	—	$(M-R^1)^+$
374	0.2	—	$(M-AngOH)^+$ (derived from **8c**)
360	1.5	—	$(M-AngOH)^+$ (derived from **8a**)
358	19[a,b]	1.4[a]	[a] $(M-R^1OH)^+$ (derived from **8a**, **8b**, and **8c**) [b] $(M-AngOH)^+$ (derived from **8b**)
276	25	—	$(M-R^1OH-Ang+H)^+$
275	23	—	$(M-R^1OH-Ang)^+$
258	9.3	2.2	$(M-R^1OH-AngOH)^+$
161	—	8.6	
159	39	15	
124	25	—	
83	100	35	$(Ang)^+$
55	49	100	$(CH_3CH=CCH_3)^+$

Bohlmann *et al.*[16] isolated 3β,6β-bis(angeloyloxy)-furanoeremophilan-14-oic acid (**7b**) and related compounds from plants of the genus *Othonna* (Compositae) and these compounds were transformed into the triol (**9**; furanoeremophilane-3β,6β,14-triol) by methylation and reduction with lithium aluminium hydride. The ^{1}H NMR spectrum of our triol (**9**) derived from **8** was kindly measured and compared with that of the specimen (**9**)[11,16] by Professor Bohlmann. However, we were informed that the two compounds are not identical. The physical and ^{1}H NMR spectral data of **9** reported by Bohlmann *et al.*[11,16] were not coincident with those of ours as shown in Experimental. Therefore the structure of triol (**9**) derived from **8** was investigated closely. Treatment of **7** with a mixture of acetic acid and benzene under reflux afforded a lactone (**10**), mp 112—116 °C, IR 1765 cm^{-1}, the purity of which was confirmed by appearance of a single peak on GLC (column: H523, 200 °C, carrier gas: N_2) and a single molecular ion peak at *m/e* 344.1679 ($C_{20}H_{34}O_5$). The mass spectrum of **10** together with ^{1}H NMR spectrum reveals the presence of an angeloyloxyl moiety and the absence of the other two acyloxyl groups, suggesting the angeloyloxyl group remains at C-3β for **10**. The configuration of $C_{(6)}$–H could be established by NOE measurement. It has been reported that the signal due to $C_{(6\beta)}$–H resonated at δ 5.08 shows increase by 28% on irradiation at δ 1.26 assigned to a signal of $C_{(5\beta)}$–Me of furanoeremophilan-14,6α-olide (**11**).[6b] On saturation of a signal due to $C_{(5\beta)}$–Me resonating at δ 1.21, a signal at δ 4.58 due to the $C_{(6)}$–H of **10** resulted in increase by 25%, indicating the structure 3β-angeloyloxyfuranoeremophilan-14,6α-olide for **10**.

Reduction of **10** with lithium aluminium hydride yielded a triol (**12**), mp 170—172 °C [^{1}H NMR ($CDCl_3$) δ 1.21 (s; $C_{(5)}$–Me), 2.06 (d, J=1.5 Hz; $C_{(11)}$–Me], 4.34 [m; $C_{(6)}$–H, and 7.09 (m; $C_{(12)}$–H)], which was *not identical* with the triol (**9**) (*cf.* Experimental). The triol (**12**) is inferred to be furanoeremophilane-3β,6α,14-triol.

On treatment with dilute hydrochloric acid, **9** and **12** gave the same hydroxy ether (**13**), mp 136—138 °C, which was also obtained from the known 3β-angeloyloxy-6α,14-epoxyfuranoeremophilane (**2**)[11] by reduction with lithium aluminium hydride. The presence of a skeletal structure, 6α,14-epoxyfuranoeremophilane (**14**), was confirmed for **2** and **13** by the observed $J_{4,14}$-values (11 and 11.5 Hz, respectively)[6b] and the appearance of the 6β-H signal at δ 4.58 and 4.55 (in $CDCl_3$),[6b] respectively. The $C_{(5\beta)}$–Me of **13** resonates at lower field δ 1.44 (in $CDCl_3$) compared with that (δ 1.16) of **14**[6b] due to deshielding of the 3β(axial)-hydroxyl group. Based on the correlation of **12** with **10** and **13**, the 3β,6α,14-triol structure was shown for the triol (**12**).

From these evidence, the structure of the triol (**9**) derived from **1** and **7**, was unambiguously established to be furanoeremophilane-3β,6β,14-triol. The ^{1}H NMR spectral data[11] of "Bohlmann's triol" are practically identical with those (in $CDCl_3$) of 6α,14-epoxyfuranoeremophilan-3β-ol (**13**) (*cf.* Experimental). This suggests that "the triol" would be **13**, a dehydrated product of the 3β,6β,14-triol (**9**). The epoxy derivative (**13**) can be formed easily from **9** as shown before.

The $C_{(3\alpha)}$–H signal of our triol (**9**) appears as a quintet ($J_{2\beta,3\alpha}$=10, $J_{2\alpha,3\alpha}$=5, and $J_{3\alpha,4\alpha}$=5 Hz; in $CDCl_3$–D_2O) as in the case of 3β-angeloyloxy-6β-acetoxyfuranoeremophilane (**6** and **6a**).[12] This shows that **9** preferentially adopts a non-steroidal-like conformation depicted as in **9a**.

Some compounds (**15**, **16**, and **17**) derived from **13**,

9, and **10**, respectively, are also described.

The fact that benzofuran derivatives are not isolated from *S. palmata* suggests that plants of the genus *Syneilesis* would be chemotaxonomically related to those of the genus *Ligularia* rather than the genus *Cacalia*. Among four new sesquiterpenes (**1a**, **1b**, **7a**, and **7c**), **1a** and **1b** constitute the first examples of natural furanoeremophilanes with a formyl group at C-4.

Experimental

General Procedures. All melting points were measured on a Mel-temp capillary melting point apparatus (Laboratory Devices) and uncorrected. Optical rotations were determined on a JASCO polarimeter DIP-SL. Ultraviolet absorption (UV) spectra and infrared (IR) spectra were measured on a Hitachi EPS-3 and a Hitachi EPI-G2 spectrometer, respectively. Mass (MS) spectra were run on a Hitachi RMU-6 Tokugata mass spectrometer and high resolution mass spectra on a Hitachi RMH-2 or a JEOL JMS-D300 mass spectrometer operating at 70 eV. Gas chromatography-mass spectrometry (GC-MS) was carried out on a Hitachi RM-50 or a Hitachi 063 gas chromatograph connected with a Hitachi RMS-4 mass spectrometer. The relative intensities were expressed in % in parentheses. Proton nuclear magnetic resonance (^{1}H NMR) spectra (60 MHz) were taken using a Hitachi R-20B or a JEOL JNM FX-60 spectrometer. Chemical shifts were expressed in ppm downfield from tetramethylsilane as an internal standard (δ value) and coupling constants in Hz. Gas-liquid chromatography (GLC) was carried out using a Shimadzu GC-4APF or GC-6A equipped with a hydrogen flame ionization detector. Liquid Chromatograph Model ALC/GPC 202/401 (Waters Assoc.) was used for high performance liquid chromatography (HPLC). Thin layer chromatography (TLC) was carried out on Kieselgel 60 PF_{254} or Kieselgel GF_{254} in 0.25 mm- or 0.5 mm-thickness. Wakogel C-200 (Wako) was used for column chromatography.

Plant Material. *Syneilesis palmata* (Thunb.) Maxim. was collected in August 1977 in University Forest at Chichibu, the University of Tokyo.

Extraction and Separation. Extraction of the air-dried roots (7.5 kg) with ether was carried out for 5 d at room temperature. The extract was concentrated to give an oily residue (32 g), which was subjected to separation by silica gel (900 g) column chromatography and eluted (each fraction: 400 ml) with the following solvents: hexane, 100 ml; 5%-ether in hexane, 1000 ml; 10%-, 1500 ml; 20%-, 2500 ml; 25%-, 1000 ml; 50%-, 2000 ml; ether, 1000 ml; and acetone, 500 ml. Fractions 11—14 and fractions 16—18 were subjected to further purification.

Fractions 11—14 (component **A**), containing **1** and **2**, were combined and evaporated to give an oil (4.27 g), which crystallized from pentane. Separation of **1** and **2** was not attained by fractional crystallization, but was successful by HPLC (column; μ-Porasil, solvent: hexane–ether 4 : 1, flow rate: 0.6 ml/min). The mixture afforded **1** (R_t 8.7 min) and **2** (R_t 9.5 min) in a ratio of *ca.* 1 : 1.

Isolation of **2** from the mixture in a large scale was achieved as follows: the mixture (950 mg) in ethanol (100 ml) was treated with sodium borohydride (1.07 g) for 4 h at room temperature and the reaction mixture, after usual work-up, was purified by silica gel column chromatography. Elution with hexane–ether (1 : 1) afforded **2**[11] (387 mg) and **3** (a mixture of **3a** and **3b**; 345 mg).

Fractions 16—18 (component **B**) gave **7** (13.6 g), mp 124—134 °C (decomp.) (from hexane).

*3β-Angeloyloxy-6β-acyloxyfuranoeremophilan-14-als (**1**, a Mixture of **1a** and **1b**).* Mp 82—83 °C (from hexane), one spot on TLC, IR (Nujol) 1725, 1715, 1640, 1565, 1230, and 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.04 (3H, s, $C_{(5)}$–CH_3), 1.83 (3H, d, J=1.5 Hz, $C_{(11)}$–CH_3), 5.47 (1H, br signal, $W_{1/2}$=*ca.* 16 Hz, $C_{(3)}$–H), 6.00 (*ca.* 1.3H, br q, J=7 Hz, $\underline{H}C(CH_3)=C(CH_3)COO-$), 6.28 (*ca.* 0.7H, m, $C_{(6)}$–H of **1a**), 6.36 (*ca.* 0.3H, m, $C_{(6)}$–H of **1b**), 6.97 (1H, m, $C_{(12)}$–H), and 9.97 (1H, d, J=5 Hz, –CH–CHO); MS *m/e* (%) 430 (M$^+$ of **1a**; 0.9), 428 (M$^+$ of **1b**; 0.5), 346 (8), 345 (1.7), 330 ([**1a** –AngOH]$^+$ [17]; 1.8), 328 ([**1**–R^{1}OH]$^+$ [17] and [**1b**–AngOH]$^+$; 12), 246 (20), 245 (16), 228 (25), 159 (46), 124 (25), 85 (26), 83 (100), 57 (33), and 55 (56); Found for **1a**: *m/e* 430.2334. Calcd for $C_{25}H_{34}O_6$: M 430.2354. Found for **1b**: *m/e* 428.2175. Calcd for $C_{25}H_{32}O_6$: M 428.2197.

*3β-Angeloyloxy-6β-acyloxyfuranoeremophilan-14-oic Acids (**7**, a Mixture of **7a**, **7b**, and **7c**).* An oil (one spot on TLC), IR (liq) 3000, 1730, 1720, 1710, 1645, 1560, 1230, and 1160 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.13 (3H, s, $C_{(5)}$–CH_3), 1.81 (3H, d, J=1.5 Hz, $C_{(11)}$–CH_3), 5.37 (1H, br signal, $W_{1/2}$=*ca.* 15 Hz, $C_{(3)}$–H), 5.59 (*ca.* 1H, br q, J=7 Hz, $\underline{H}C(CH_3)=C(CH_3)COO-$), 6.28 (*ca.* 0.2H, m, $C_{(6)}$–H of **7c**), 6.37 (*ca.* 0.7H, m, $C_{(6)}$–H of **7a**), 6.48 (*ca.* 0.1H, m, $C_{(6)}$–H of **7b**), 6.97 (1H, q, J=1.5 Hz, $C_{(12)}$–H), and 10.05 (1H, br s, –COOH; disappeared on addition of D_2O); MS *m/e* (%) 460 (M$^+$ of **7c**; 0.05), 446 (M$^+$ of **7a**; 0.17), 444 (M$^+$ of **7b**; 0.07), 362 (0.8), 361 (0.4), 360 ([**7c** –AngOH]$^+$; 0.4), 346 ([**7a**–AngOH]$^+$; 0.2), 344 ([**7** –R^{1}OH]$^+$ and [**7b** –AngOH]$^+$; 2.7), 262 (5.5), 245 (2.3), 244 (3.7), 161 (13), 159 (11), 83 (75), and 55 (100).

*3β-Angeloyloxy-6α,14-epoxyfuranoereomphilane (**2**).* Mp 97—98 °C (from ether), $[\alpha]_D^{22}$ −18° (*c* 1.2, EtOH), IR (Nujol) 1710, 1635, 1560, 1235, and 1155 cm^{-1}; UV (EtOH) 218 nm (ε 28000); ^{1}H NMR ($CDCl_3$) δ 1.40 (3H, s, $C_{(5)}$–CH_3), 2.02 (3H, d, J=1.5 Hz, $C_{(11)}$–CH_3), 3.67 (1H, dd, $J_{4,14\beta}$=11 and $J_{14\alpha,14\beta}$=7.5 Hz, $C_{(14\beta)}$–H), 3.92 (1H, t, $J_{4,14\alpha}$=7.5 and $J_{14\alpha,14\beta}$=7.5 Hz, $C_{(14\alpha)}$–H), 4.58 (1H, m, $C_{(6)}$–H), 5.32 (1H, br s, $W_{1/2}$=*ca.* 7 Hz, $C_{(3)}$–H), 6.07 (1H, q-like, J=7 Hz, $\underline{H}C(CH_3)=C(CH_3)COO-$), and 7.01 (1H, m, $C_{(12)}$–H); MS *m/e* (%) 330 (M$^+$; 36), 230 (37), 159 (63), 83 (89), and 55 (100). The ^{1}H NMR and mass spectral data are in good agreement with those of **2** reported in lit.[11]

*3β-Angeloyloxy-6β-acyloxyfuranoeremophilan-14-ols (**3**, a Mixture of **3a** and **3b**).* An oil, IR (liq) 3450, 1720, 1710, 1640, 1560, 1230, and 1160 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.12 (3H, s, $C_{(5)}$–CH_3), 1.90 (3H, d, J=1.5 Hz, $C_{(11)}$–CH_3), 4.36 (1H, br signal, $W_{1/2}$=19 Hz, $C_{(3)}$–H), 4.34 (1H, dd, J=11.5 and J=6 Hz, $C_{(14)}$–H), 4.73 (1H, dd, J=11.5 and J=3 Hz, $C_{(14)}$–H), 5.75 (1H, br q, J=7 Hz, $\underline{H}C(CH_3)=C(CH_3)COO-$), 6.49 (*ca.* 0.6H, m, $C_{(6)}$–H of **3a**), 6.59 (*ca.* 0.4H, m, $C_{(6)}$–H of **3b**), 6.96 (1H, m, $C_{(12)}$–H); MS are given in Table 1.

*Treatment of **3** with Methanesulfonyl Chloride.* A solution of **3** (135 mg) in pyridine (4 ml) and methanesulfonyl chloride (15 drops) were allowed to stand overnight at room temperature and usual work-up gave a mesylate (crude, 177 mg) as an oil; IR (liq) 1720, 1705, 1635, 1560, 1340, 1230, and 1160 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.86 (3H, s, $-SO_2CH_3$); MS *m/e* (%) 510 (M$^+$ of a mesylate from **3a**; 0.4), 508 (M$^+$ of a mesylate from **3b**; 0.2), 426 (4.3), 408 (10), 326 (2.7), 325 (3.2), 308 (6.7), 159 (37), 83 (100), and 55 (96).

Reduction of the Mesylates with Lithium Aluminium Hydride.

A mixture of the crude mesylates (177 mg) dissolved in ether (20 ml) and lithium aluminium hydride (200 mg) was stirred at room temperature for 1.5 h and then heated under reflux for 1 h. The reaction mixture was worked up as usual, chromatographed on silica gel, and eluted with ether to give furanoeremophilane-3β,6β-diol (**4**;[12] 9 mg, 12% yield from **3**) and furanoeremophil-3-ene-6β,14-diol (**5**; 44 mg, 57% yield from **3**).

4; Mp 176—179 °C (decomp) (from ether). **5**; An oil, $[\alpha]_D^{27}$ −14° (*c* 0.02, EtOH); IR (liq) 3430, 3250, 1645, and 1565 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.08 (3H, s, $C_{(5)}$-CH_3), 2.22 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 3.58 (1H, A part of an ABq, J=11 Hz, $C_{(14)}$-H_A), 4.08 (1H, B part of an ABq, J=11 Hz, $C_{(14)}$-H_B), 4.77 (1H, m, $C_{(6)}$-H), 5.40 (1H, br signal, $W_{1/2}$=*ca.* 7.5 Hz, $C_{(3)}$-H), and 7.04 (1H, m, $C_{(12)}$-H); MS *m/e* (%) 248 (M^+; 3.4), 230 (13), 141 (6.1), and 124 (100); Found: *m/e* 248.1482. Calcd for $C_{15}H_{20}O_3$: M 248.1411. Found: *m/e* 124.0518. Calcd for $C_7H_8O_2$: *m/e* 124.0523.

Alkaline Hydrolysis of 1. A mixture (53 mg) of **1** and **2** was dissolved in methanol (5 ml). Potassium hydroxide (250 mg) in water (1 ml) was added and the reaction mixture was refluxed for 1 h. After addition of water (50 ml), the solution was washed with ether. The aqueous layer was acidified with 2 M** hydrochloric acid to pH 1 and extracted with ether. The ethereal layer was dried (Na_2SO_4) and concentrated carefully. To the concentrated solution, diazomethane in ether was added and the solution was allowed to stand for 1 h. The mixture of methyl esters was analyzed by GC-MS measurement (column: PEG-20M, temperature: heated from 50 °C at a rate of 3 °C/min; carrier gas: He, 0.5 kg/cm^2) and found to be a mixture of methyl angelate (M^+ at *m/e* 114, R_t 15.3 min) and methyl 3-methylbutanoate (M^+ at *m/e* 116, R_t 12.2 min) in a ratio of *ca.* 3 : 1.

Esterification of 7 with Diazomethane. 3β-Angeloyloxy-6β-acyloxyfuranoeremophilan-14-oic acids (**7**; 32 mg) was treated with excess diazomethane in ether and the reaction product was purified by silica-gel column chromatography to give methyl 3β-angeloyloxy-6β-acyloxyfuranoeremophilan-14-oates (**8**; 28 mg) as an oil, IR (liq) 1740, 1720, 1640, 1565, 1230, and 1160 cm^{-1}; UV (EtOH) 217 nm (ε 22000); ^{1}H NMR (C_6D_6) δ 1.07 (3H, s, $C_{(5)}$-CH_3), 1.87 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 3.38 (3H, s, -COOCH_3), 5.69 (*ca.* 1H, br q, J=7 Hz, $\underline{H}$>C=C<(COO-, CH_3)), 5.81 (1H, br signal, $W_{1/2}$=13 Hz, $C_{(3)}$-H), 6.50 (*ca.* 0.7H, m, $C_{(6)}$-H of **8a**), 6.60 (*ca.* 0.2H, m, $C_{(6)}$-H of **8c**), 6.63 (*ca*, 0.1H, m, $C_{(6)}$-H of **8b**), and 6.95 (1H, m, $C_{(12)}$-H); MS as given in Table 2; Found for **8a**: *m/e* 460.2419. Calcd for $C_{26}H_{36}O_7$: M 460.2531. Found for **8b**: *m/e* 458.2296. Calcd for $C_{26}H_{34}O_7$: M 458.2442, and Found for **8c**: *m/e* 474.2818. Calcd for $C_{27}H_{38}O_7$: M 474.3021.

Furanoeremophilane-3β,6β,14-triol (9). *From 8*: Methyl 3β-angeloyloxy-6β-acyloxyfuranoeremophilan-14-oates (**8**; 276 mg) in ether (30 ml) was treated with lithium aluminium hydride (530 mg) at reflux temperature for 1.5 h to give **9** (99 mg).

From 1: A mixture (58 mg) of **1** and **2** was treated with lithium aluminium hydride (100 mg) as above and the reaction mixture was chromatographed on silica gel to yield **9** (16 mg) together with 6α,14-epoxyfuranoeremophilan-3β-ol (**13**).

9; Mp 139—140 °C (from ether; derived from **8**), 137—138 °C (from ether; derived from **1**), mp of the admixture 137—140 °C; lit,[14] 148 °C; lit,[11] 122 °C; $[\alpha]_D^{25}$ −12° (*c* 1.45, EtOH; derived from **8**), $[\alpha]_D^{26}$ −11° (*c* 0.63, EtOH; derived from **1**); lit,[14] $[\alpha]_D^{24}$ −36.9° (*c* 1.48, $CHCl_3$); IR (Nujol) 3250, 1635, and 1560 cm^{-1}; UV (EtOH) 218 nm (ε 8600); ^{1}H NMR [$(CD_3)_2CO$] δ 0.97 (3H, s, $C_{(5)}$-CH_3), 2.03 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 4.46 (1H, m, $C_{(6)}$-H), and 7.02 (1H, br s, $W_{1/2}$=4 Hz, $C_{(12)}$-H); ^{1}H NMR ($CDCl_3$-D_2O, determined by Prof. Bohlmann) δ 1.04 (3H, s, $C_{(5)}$-CH_3), 2.08 (3H, d, J=1.1 Hz, $C_{(11)}$-CH_3), 2.20 (1H, d-like, J=17.5 Hz, $C_{(9\alpha)}$-H), 2.81 (1H, m, $C_{(9\beta)}$-H), 3.89 (1H, dd, J=10.5 and J=3 Hz, $C_{(14)}$-H), 4.14 (1H, t, J=10.5 Hz, $C_{(14)}$-H), 4.45 (1H, quintet, $J_{2\beta,3\alpha}$=10, $J_{2\alpha,3\alpha}$=5, and $J_{3\alpha,4\alpha}$=5 Hz, $C_{(3\alpha)}$-H), 4.89 (1H, br s, $W_{1/2}$=*ca.* 5.5 Hz, $C_{(6)}$-H), and 7.05 (1H, br s, $W_{1/2}$=*ca.* 4 Hz, $C_{(12)}$-H); lit,[14] [$(CD_3)_2CO$] δ 1.48 (3H, s, $C_{(5)}$-CH_3), 2.06 (3H, d, J=1 Hz, $C_{(11)}$-CH_3), 3.95 (2H, d, J=9 Hz, $C_{(14)}$-H_2), 4.29 (1H, ddd, J=2.5, J=2, and J=2 Hz, $C_{(3)}$-H), 4.59 (1H, t, J=1 Hz, $C_{(6)}$-H), and 7.04 (1H, br s, $C_{(12)}$-H); lit,[11] ^{1}H NMR (solvent not registered, probably $CDCl_3$) δ 1.45 (3H, s, $C_{(5)}$-CH_3), 2.03 (3H, d, J=1 Hz, $C_{(11)}$-H), 3.92 (2H, m, $C_{(14)}$-H_2), 4.25 (1H, dd, J=5 and J=2 Hz, $C_{(3)}$-H), 4.57 (1H, t, J=1 Hz, $C_{(6)}$-H), and 7.01 (1H, br s, $C_{(12)}$-H); MS *m/e* (%) 266 (M^+; 4.7), 248 (2.3), 230 (2.5), and 124 (100); Found: C, 67.78; H, 8.63%. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33%.

Alkaline Hydrolysis of 7. A mixture of **7** (158 mg) in methanol (15 ml) and potassium hydroxide (700 mg) in water (3 ml) was heated under reflux for 1.5 h and the reaction product was treated and analyzed by the same procedures as in the case of the alkaline hydrolysis of **1** (*vide supra*) and was found to be a mixture of methyl 3-methylbutanoate (M^+ at *m/e* 116, R_t 12.2 min), methyl angelate (M^+ at *m/e* 114, R_t 15.3 min), and methyl 3-methylpentanoate (M^+ at *m/e* 130, R_t 15.6 min) in a ratio of *ca.* 4 : 6 : 1.

3β-Angeloyloxyfuranoeremophilan-14,6α-olide (10). A mixture (207 mg) of **7** in benzene (30 ml) and acetic acid (30 ml) was refluxed under a nitrogen atmosphere for 5 h. After addition of water, the reaction product was extracted with ether and the ethereal layer was washed with sodium hydrogencarbonate solution. The usual work-up gave 111 mg of **10**, mp 112—116 °C (from hexane–ether); $[\alpha]_D^{23}$ +18° (*c* 1.63, EtOH); IR (Nujol) 1765, 1720, 1645, 1635, 1565, 1235, and 1145 cm^{-1}; UV (EtOH) 216 (ε 16000); ^{1}H NMR (C_6D_6) δ 1.21 (3H, s, $C_{(5)}$-CH_3), 1.80 (3H, q, J=*ca.* 2 Hz, CH_3>C=C<(COO-, $\underline{CH_3}$)), 1.93 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 2.01 (3H, dq, J=7 and J=*ca.* 2 Hz, CH_3>C=C<(COO-, CH_3)), 4.58 (1H, m, $C_{(6)}$-H), 5.43 (1H, br s, $W_{1/2}$=7 Hz, $C_{(3)}$-H), 5.71 (1H, br q, J=7 Hz, CH_3>C=C<(COO-, CH_3)), and 6.88 (1H, m, $C_{(12)}$-H); MS *m/e* (%) 344 (M^+; 26), 262 (63), 245 (25), 244 (39), 83 (96), and 55 (100); Found: *m/e* 344.1679. Calcd for $C_{20}H_{24}O_5$: M 344.1622.

Furanoeremophilane-3β,6α,14-triol (12). 3β-Angeloyloxyfuranoeremophilan-14,6α-olide (**10**; 70 mg) in ether (10 ml) was treated with lithium aluminium hydride (200 mg) at reflux temperature for 1.5 h to give **12** (50 mg), mp 170—172 °C (from acetone); $[\alpha]_D^{17}$ ±0° (*c* 2.37, EtOH); IR (Nujol) 3300, 1645, and 1565 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, s, $C_{(5)}$-CH_3), 2.06 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 4.00 and 4.08 (2H, m, $C_{(14)}$-H_2), 4.34 (1H, m, $C_{(6)}$-H), 4.95 (1H, br signal, $W_{1/2}$=*ca.* 18 Hz, $C_{(3)}$-H), and 7.09 (1H, br s, $W_{1/2}$=*ca.* 3.5 Hz, $C_{(12)}$-H); ^{1}H NMR [$(CD_3)_2CO$] δ 1.18 (3H, s, $C_{(5)}$-CH_3), 2.00 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 3.90 (2H, br signal, $W_{1/2}$=*ca.* 12 Hz, $C_{(14)}$-H_2), 4.26 (1H, m, $C_{(6)}$-H), 4.70 (1H, br signal, $W_{1/2}$=*ca.* 12 Hz, $C_{(3)}$-H), and 7.10 (1H, br s, $W_{1/2}$=*ca.* 4 Hz, $C_{(12)}$-H); MS *m/e* (%) 266 (M^+; 1.7), 248 (2.5), 230 (1.1), 160 (3.4), 159 (2.9), and 124 (100).

6α,14-Epoxyfuranoeremophilan-3β-ol (13). *From 9*: Furanoeremophilane-3β,6β,14-triol (**9**; 30 mg) in methanol

** 1 M=1 mol dm^{-3}.

(a few drop) was stirred with 0.05 M hydrochloric acid (18 ml) at room temperature for 10 min under a nitrogen atmosphere. Extraction with ether and washing with sodium hydrogencarbonate solution afforded **13** (27 mg).

From 12: Furanoeremophilane-3β,6α,14-triol (**12**; 16 mg) in acetone (a few drop) was treated with 0.2 M hydrochloric acid (5 ml) under the same conditions as above to give **13** (9 mg).

From 2: A mixture of 3β-angeloyloxy-6α,14-epoxyfuranoeremophilane (**2**; 72 mg) in ether (10 ml) and lithium aluminium hydride (100 mg) was heated under reflux for 1 h to give **13** (63 mg).

13; Mp 136—138 °C (from ether); $[\alpha]_D^{25}$ −30° (*c* 0.49, EtOH; derived from **9**), $[\alpha]_D^{22}$ −27° (*c* 1.1, EtOH; derived from **12**), $[\alpha]_D^{23}$ −27° (*c* 0.88, EtOH; derived from **2**); IR (Nujol) 3470, 1635, and 1565 cm^{-1}; UV (EtOH) 210 nm (end absorption, ε 8800); ^1H NMR (C_6D_6) δ 1.40 (3H, s, $C_{(5)}$-CH_3), 2.14 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 3.56 (1H, br s, $W_{1/2}$=6 Hz, $C_{(3)}$-H), 3.70 (1H, t, $J_{4,14\alpha}$=7 and $J_{14\alpha,14\beta}$=7 Hz, $C_{(14\alpha)}$-H), 3.87 (1H, dd, $J_{4,14\beta}$=11.5 and $J_{14\alpha,14\beta}$=7 Hz, $C_{(14\beta)}$-H), 4.54 (1H, m, $C_{(6)}$-H), and 6.99 (1H, m, $C_{(12)}$-H); ^1H NMR ($CDCl_3$) δ 1.44 (3H, s, $C_{(5)}$-CH_3), 2.01 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 3.84 and 4.00 (2H, m, $C_{(14)}$-H_2), 4.26 (1H, br s, $W_{1/2}$=6 Hz, $C_{(3)}$-H), 4.55 (1H, m, $C_{(6)}$-H), and 7.02 (1H, br s, $C_{(12)}$-H); MS *m/e* (%) 248 (M^+; 100), 161 (23), 160 (30), 159 (38), and 108 (31); Found: C, 72.40; H, 8.40%. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12%.

6α,14-Epoxyfuranoeremophilan-3-one (15). Chromium trioxide (700 mg) was dissolved in a solution of pyridine (1 ml) and dichloromethane (20 ml) and stirred at room temperature for 15 min. 6α,14-Epoxyfuranoeremophilan-3β-ol (**13**; 246 mg) was added to the solution and the whole was stirred for 5 h. The reaction mixture was filtered, and the precipitate was washed with ether. The filtrate and washing were combined and washed with 5% sodium hydroxide solution, 1 M hydrochloric acid, 10% sodium hydrogencarbonate solution, and brine, in turn. The usual work-up gave **15** (103 mg), mp 172—175 °C (from ether); $[\alpha]_D^{24}$ −31° (*c* 1.29, $CHCl_3$); IR (Nujol) 1710, 1630, and 1560 cm^{-1}; ^1H NMR (C_6D_6) δ 0.78 (3H, s, $C_{(5)}$-CH_3), 2.06 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 3.85 (1H, t, $J_{4,14\alpha}$=8 and $J_{14\alpha,14\beta}$=8 Hz, $C_{(14\alpha)}$-H), 4.15 (1H, dd, $J_{4,14\beta}$=11 and $J_{14\alpha,14\beta}$=8 Hz, $C_{(14\beta)}$-H), 4.43 (1H, m, $C_{(6)}$-H), and 6.94 (1H, m, $C_{(12)}$-H); MS *m/e* (%) 246 (M^+; 100), 231 (16), 160 (51), 159 (37), and 145 (43); Found: *m/e* 246.1264. Calcd for $C_{15}H_{18}O_3$: M 246.1255.

3β,6β,14-Triacetoxyfuranoeremophilane (16). Treatment of furanoeremophilane-3β,6β,14-triol (**9**; 28 mg) in pyridine (4 ml) with acetic anhydride (1 ml) at room temperature gave a crude acetate, which was purified by silica-gel column chromatography. Elution with petroleum ether–ether (1 : 1) afforded **16** (33 mg) as an oil, $[\alpha]_D^{30}$ −35° (*c* 1.2, EtOH); IR liq) 1740, 1640, 1560, and 1240 cm^{-1}; UV (EtOH) 217 nm (ε 7700); ^1H NMR (C_6D_6) δ 1.09 (3H, s, $C_{(5)}$-CH_3), 1.68, 1.69, and 1.79 (each 3H, s, -OCOCH_3), 1.88 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 4.33 (2H, m, $C_{(14)}$-H_2), 5.43 (1H, br signal, $W_{1/2}$=*ca.* 16 Hz, $C_{(3)}$-H), 6.49 (1H, m, $C_{(6)}$-H), and 6.94 (1H, m, $C_{(12)}$-H); ^1H NMR [$(CD_3)_2CO$] δ 1.17 (3H, s, $C_{(5)}$-CH_3), 1.87 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 1.99, 2.02, and 2.12 (each 3H, s, -OCOCH_3), 4.29 (2H, d, J=5 Hz, $C_{(14)}$-H_2), 5.28 (1H, dt, J=8 and J=5 Hz, $C_{(3)}$-H), 6.28 (1H, m, $C_{(6)}$-H), and 7.18 (1H, m, $C_{(12)}$-H); MS *m/e* (%) 392 (M^+; 1.8), 350 (7.1), 332 (10), 290 (6.4), 272 (5.8), 230 (15), 212 (20), 166 (10), 159 (30), and 124 (100).

Furanoeremophil-3-en-14,6α-olide (17). Aqueous methanol (80%, 50 ml) and then sodium carbonate (900 mg) in water (10 ml) were added to a solution of 3β-angeloyloxyfuranoeremophilan-14,6α-olide (**10**; 70 mg) in methanol (3 ml), and the mixture was stirred at room temperature for 45 min under nitrogen. The usual work-up afforded **17** (34 mg), mp 103—107 °C (from ether); $[\alpha]_D^{18}$ −68° (*c* 0.96, EtOH); IR (Nujol) 1740, 1670, 1640, and 1560 cm^{-1}; UV (EtOH) 218 nm (ε 28000); ^1H NMR ($CDCl_3$) δ 1.43 (3H, s, $C_{(5)}$-CH_3), 2.05 (3H, d, J=1.5 Hz, $C_{(11)}$-CH_3), 5.25 (1H, m, $C_{(6)}$-H), 6.28 (1H, t-like, J=3 Hz, $C_{(3)}$-H), and 7.03 (1H, m, $C_{(12)}$-H); MS *m/e* (%) 244 (M^+; 59), 187 (48), 185 (27), and 121 (100).

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17) "Ang" represents an angeloyl group, $\begin{matrix}CH_3\\H\end{matrix}\!\!>\!C\!=\!C\!<\!\begin{matrix}CO-\\CH_3\end{matrix}$ and R^1 refers to acyl moieties as a part of the acyloxyl group at C-6.