

EIGHT NEW EREMOPHILANE DERIVATIVES FROM
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ABSTRACT.—Two known eremophilanodioides [1,2] and four new compounds of this class [3–6], a new eremophilanolide [7], two eremophilane epimers [9,10], and a noreremophilane derivative [8], were isolated in a phytochemical investigation of the roots of *Ligularia przewalskii*. Their structures were elucidated by nmr spectroscopic methods and by chemical transformations.

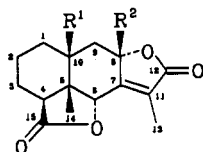
Ligularia przewalskii (Maxim.) Diels (Compositae) is mainly distributed in damp, shaded areas of the western regions of the People's Republic of China. It has been used traditionally in folk medicine for the treatment of asthma, hemoptysis, hepatitis, and pulmonary tuberculosis (1). We have previously reported the isolation of four new furans (2-acetyl-5,6-dimethoxybenzofuran, 2-propenyl-5-acetyl-7-hydroxy-2,3-dihydroxybenzofuran, 5-acetyl-7-methoxybenzofuran, and 1,3-dimethoxy-4,6,11-trimethylnaphthofuran) from this plant (2). Further study has provided ten other structurally unrelated eremophilane derivatives [1–10], two of which [1,2] were previously reported by Moriyama *et al.* (3). The present investigation also afforded a noreremophilane derivative with a rare skeleton [8]. Details of the isolation, structure determination, and the proposed biogenesis of these components are the subject of this report.

RESULTS AND DISCUSSION

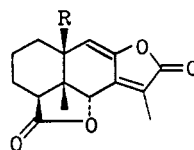
Compounds **1** and **2**, both obtained as colorless crystals, had identical ¹H-nmr data to those of two known eremophilanodioides previously isolated by Moriyama *et al.* from *Ligularia faurie* (3).

The nmr data of **3** (Tables 1 and 2) showed close resemblance to those of **1** and **2**. However, the C-8 hydroxyl absorption of dilactone **2** was absent in the ¹H-nmr and ir spectra of **3**, with instead, a methoxy group present, as suggested by signals at δ 3.20 (3H, s) and δ 50.47 (q) in the ¹H- and ¹³C-nmr spectra, respectively. The nearly identical nmr data of **3** and **2** implied that **3** had the same stereochemistry as **2**. The eims of **3** showed a molecular ion peak at *m/z* 292 (14 mass units higher than that of **2**), consistent with **3** being the 8-*O*-methyl ether of **2**.

Compound **4** has been reported previously as an artifact by Moriyama *et al.* (3), but appeared to be a natural component in *L. przewalskii*.



- 1 R¹=R²=H
2 R¹=H, R²=OH
3 R¹=H, R²=OMe



- 4 R=H
5 R=OH

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TABLE 1. ¹H-Nmr Data of Compounds 3–11 (400 MHz, *J* values in Hz in parentheses).

Proton(s)	Compound								
	3 ^a	4 ^a	5 ^b	6 ^b	7 ^c	8 ^a	(9/10) ^d		11 ^b
1	1.90 m	1.80 m	1.75 m	1.93 m	1.93 m	1.63 m	1.63 m	1.63 m	1.94 m
1'	1.76 m	1.87 m	1.90 m	1.84 m	1.87 m	1.40 m	1.38 m	1.38 m	1.86 m
2	1.42 m	1.38 m	1.36 m	1.53 m	1.56 m	1.58 m	1.48 m	1.48 m	1.55 m
2'	1.38 m	1.28 m	1.26 m	1.34 m	1.42 m	1.63 m	1.62 m	1.62 m	1.35 m
3	1.42 m	1.46 m	1.46 m	1.58 m	1.56 m	1.52 m	1.70 m	1.70 m	1.58 m
3'	1.83 m	2.03 m	1.98 m	1.81 m	1.76 m	1.73 m	1.78 m	1.78 m	1.82 m
4α	2.24 dd (12.2,3.2)	2.55 dd (12.0,3.0)	2.65 dd (12.0,3.5)	2.72 dd (11.6,3.1)	2.56 dd (12.8,4.2)	2.31 dd (12.0,3.6)	2.37 dd (13.0,4.0)	2.37 dd (13.0,4.0)	2.78 dd (11.7,2.9)
6	4.89 q (2.0)	5.15 q (1.9)	5.36 q (1.3)	5.04 q (1.8)	5.85 s	6.84 d (1.6)	6.45 br s	6.48 br s	5.13 q (1.8)
8α	—	—	—	—	—	2.50 br dd (16.0,8.0)	—	—	—
8β	—	—	—	—	—	2.43 ddd (16.0,8.0, 1.6)	—	—	—
9α	1.77 dd (13.4,13.4)	5.50 d (2.7)	5.69 s	3.58 s	1.85– 1.96 m	2.02 m	2.55 br d (10.6)	2.51 br d (10.6)	3.92 s
9β	2.28 dd (13.4,5.1)	—	—	—	2.20 dd (13.0,5.0)	—	2.64 dd (10.6,3.6)	2.65 dd (10.6,3.6)	—
10β	2.19 m	2.85 m	—	—	2.35 m	—	2.27 m	2.27 m	—
11	—	—	—	—	—	2.33 s	3.64 br q (7.2)	3.64 br q (7.2)	—
12	—	—	—	—	—	1.11 s	—	—	—
13	2.00 d (2.0)	2.02 br s	1.97 br s	1.85 d (1.8)	1.93 s	—	1.24 d (7.2)	1.26 d (7.2)	1.91 d (1.8)
14	1.27 s	1.30 s	1.28 s	1.32 s	1.26 s	—	1.23 s	1.23 s	1.33 s
OMe-8	3.20 s	—	—	—	—	—	—	—	—
OMe-12	—	—	—	—	—	—	3.63 s	3.62 s	—
OMe-13	—	—	—	—	—	3.69 s	—	—	—
OMe-15	—	—	—	—	—	—	3.66 s	3.66 s	—
OH	—	—	3.29 s	4.98 s	2.97 br s	—	—	—	—
OAc	—	—	—	—	—	—	—	—	2.11 s

^aMeasured in CDCl₃.^bMeasured in Me₂CO-*d*₆.^c°Ang: δ 2.00 (3H, dq, *J* = 7.5 and 1.4 Hz, =CH-Me), 1.91 (3H, br s, Me-CCOO), 6.14 (1H, qq, *J* = 7.5 and 1.4 Hz, =CH-Me).^dThe proton assignments for 9 and 10 for each position are interchangeable because they were analyzed as a mixture.

The molecular formula of **5** was established as C₁₅H₁₆O₅ on the basis of eims, elemental analysis, and ¹³C-nmr data (Table 2 and Experimental). Its ¹H- and ¹³C-nmr spectra exhibited a close similarity to those of **4**. However, the multiplet at δ 2.85 (1H) of H-10 in **4** (Table 1) was absent in the ¹H-nmr spectrum of **5**, and a quaternary carbon signal at δ 79.20 was observed, replacing the C-10 methine signal of **4** at δ 38.61 (d), in the ¹³C-nmr spectrum of **5** (Table 2). Moreover, an OH absorption band was visible at 3406 cm⁻¹ in the ir spectrum. This suggests that **5** is the OH-10β derivative of **4**, since a OH-10α substituent would not only fail to form the A/B ring system (as all eremophilane derivatives must have a Me-14β), but would also be expected to cause a marked low-field shift of the signal of H-4. Furthermore, nOe examination of **5** showed that the Me-14 signal had a clear nOe effect on H-6 (ca. 12%) and another correlation with OH-10 (8%), and was also in agreement with the structure proposed for this compound.

The elemental analysis and the molecular ion peak (*m/z* 292) of **6** revealed a molecular formula of C₁₅H₁₆O₆ (8 unsaturations). Considering the presence of two lactone rings and one double bond indicated by the ¹³C-nmr spectrum (Table 2), three additional rings were evident in the molecule. Although the ¹H- and ¹³C-nmr data of **6** showed similarities with those of **5**, some differences in the B ring were apparent. The ¹³C-nmr spectrum of **6** indicated that the 8,9-double bond of **5** was replaced by a ketal quaternary carbon (δ 100.5, s) and an oxygenated methine carbon (δ 63.7, d), and the

TABLE 2. ^{13}C -Nmr Data of Compounds 1–11 (100 MHz).

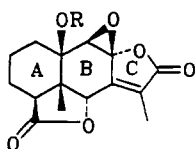
Carbon	Compound										
	1 ^a	2 ^b	3 ^c	4 ^c	5 ^b	6 ^b	7 ^{b,c}	8 ^c	(9/10) ^{a,d}		11 ^b
1	19.12	20.10	19.18	19.17	19.47	18.36	19.40	20.69	19.65	19.73	18.31
2	20.68	21.45	20.85	22.45	23.90	24.56	25.63	23.00	24.53	24.73	24.37
3	24.50	25.04	24.17	26.59	36.16	28.67	25.88	23.80	26.40	26.58	28.49
4	40.52	40.77	40.80	41.88	46.20	46.18	41.64	46.37	47.59	47.78	46.09
5	44.60	45.31	44.62	42.45	47.76	47.67	41.99	48.46	45.28	45.97	48.10
6	82.05	83.23	82.48	78.48	78.12	80.72	71.91	154.17	153.69	153.96	79.99
7	154.79	153.64	151.09	149.55	150.12	151.58	152.33	142.69	136.63	136.94	149.64
8	77.52	104.98	105.58	140.98	142.73	100.50	104.69	33.13	197.72	197.72	100.30
9	32.72	36.94	35.24	109.42	110.93	63.69	39.26	48.69	39.35	39.50	62.94
10	34.89	36.14	34.55	38.61	79.20	65.66	36.58	197.83	37.72	37.77	67.47
11	123.68	127.12	129.25	127.76	129.15	126.67	128.50	26.33	39.03	39.03	128.49
12	173.24	171.81	170.35	167.60	164.80	170.98	171.69	19.25	174.77	174.79	168.47
13	9.20	9.94	9.03	9.23	9.35	8.68	9.15	174.82	22.19	22.39	8.86
14	19.97	20.10	20.03	18.97	14.75	15.50	16.75	—	16.21	16.39	15.36
15	174.72	176.71	174.84	174.86	175.13	174.10	175.12	—	173.90	173.90	173.79
OMe	—	—	50.47	—	—	—	—	51.42	51.85	51.92	—
OAc	—	—	—	—	—	—	—	—	51.37	51.37	—
											20.53
											170.45

^aMeasured in CDCl_3 .^bMeasured in $\text{Me}_2\text{CO}-d_6$.^cOAng: δ 20.77 (q, $\text{MeCH}=\text{}$), 139.63 (d, $\text{MeCH}=\text{}$), 15.93 (q, MeCCOO), 129.58 (s, MeCCOO), 166.91 (s, COO).^dAssignments for each carbon of **9** and **10** are interchangeable, because they were analyzed as a mixture.

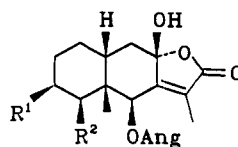
olefinic signal of H-9 in **5** was changed to a singlet (δ 3.58, s, 1H) in **6** when comparing the analogous data of the two compounds. These observations, in conjunction with the number of unsaturations, suggested the presence of an epoxy ring between C-8 and C-9. Acetylation of **6** yielded a mono-acetylated derivative, **11**. In the ^{13}C -nmr spectrum of **11**, the signal of the ketal carbon attributable to C-8 remained essentially unchanged (when compared with **6**), while that of the oxygenated quaternary carbon due to C-10 underwent a shift downfield from δ 65.66 to δ 67.47 (Table 2). NOe measurements for **11** indicated that the methyl protons of the OAc group were spatially close to Me-14 (ca. 12%), H-6 (8%), and one of the two hydrogens at C-1 (H-1 β) (8%), thus confirming the proposed structure.

Biogenetically, dilactone **6** is most likely formed by epoxidation of **5**. In fact, oxidation of **5** with *m*-chloroperbenzoic acid afforded **6** (see Experimental), which supported the notion that the epoxide ring is β (assistance of the OH group).

As seen from the nmr data, compound **7** was structurally similar to an eremophilanolide [**12**], isolated previously from *Petasites japonicus* (4). However, the lack of the OH-3 of **12** was indicated in **7** by the ^{13}C -nmr data (Table 2). Additionally, the H-4 signal in **7** was a double doublet, thus requiring two hydrogens at C-3 (Table 1). The ir spectrum of **7** showed an absorption band at 1726 cm^{-1} attributable to a COOH group. This observation is consistent with the fact that the ^{13}C -nmr resonance of C-15 in **12** (δ 13.5, q) (4) was replaced in **7** by a quaternary carbon signal (δ 175.1, s),



6 R=H
11 R=Ac

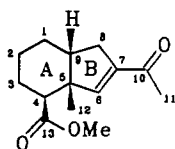
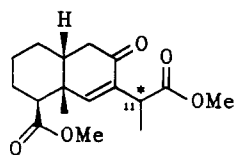


7 R¹=H, R²=COOH
12 R¹=OH, R²=Me

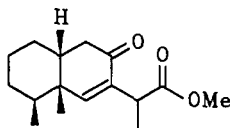
indicating the presence of a 15-COOH group. The methine hydrogen signal due to H-4 appeared at somewhat lower field (δ 2.56, 1H, dd) and followed from this assumption. The stereochemistry of **7** is proposed to be the same as that of **12**. The positive optical rotation value in each case required the presence of an OH-8 β group (5), while a 6 β -angeloyloxy group could be detected by the typical ^1H -nmr signals due to such a functionality and by the two singlets assigned to H-6 (δ 5.85, 1H) and to Me-13 (δ 1.93, 3H) (Table 1) (5). A nOe effect of H-10 on Me-14 (8%) was visible from nOe measurements, thus disclosing the presence of a 10 β -proton in **7**.

Only 14 carbon signals could be observed in the ^{13}C -nmr spectrum of compound **8**. Except for methoxy signals at δ 3.69 and δ 51.4 in the ^1H - and ^{13}C -nmr spectra, respectively, of **8** (Tables 1 and 2), only 13 skeletal carbon signals were apparent. The results of elemental analysis and the $[\text{M}]^+$ peak at m/z 236 allowed for a molecular formula of $\text{C}_{14}\text{H}_{20}\text{O}_3$. An ester group was present as deduced from its ir absorption band at 1738 cm^{-1} and the ^{13}C -nmr resonance at δ 174.8 (see Table 2 and the Experimental). Furthermore, the presence of a keto group followed from the ir absorption band at 1686 cm^{-1} and the ^{13}C -nmr resonance at δ 197.8 (Table 2), while the presence of a double bond could be inferred from the observed ^{13}C -nmr resonances at δ 142.7 (s) and 154.2 (d) (Table 2). The remaining two unsaturations could only be assigned to two rings. Considering that the ^1H -nmr spectrum exhibited only two methyl singlets at δ 1.11 and 2.33 (Table 1), together with two methyl signals at δ 19.25 and at δ 26.3 (methyl ketone) in the ^{13}C -nmr spectrum of **8**, a 6,5-fused AB ring system was assumed to be present, since only nine carbons remained to form the ring skeleton. The ^{13}C -nmr resonance of the keto carbonyl group at δ 197.8, the ir absorption band at 1686 cm^{-1} , and the olefinic hydrogen signal appearing as a doublet at δ 6.84 ($J=1.6\text{ Hz}$) (Table 1) in the ^1H -nmr spectrum, suggested that a keto group was conjugated with the double bond, which was in agreement with the uv absorption band observed at 235 nm. A pair of low-field methylene ^1H -nmr signals vicinal to a ketone group appeared at δ 2.50 (1H, br dd) and δ 2.43 (1H, ddd), and were assigned to H₂-8, which correlated with a methylene carbon signal at δ 33.1 (t) in a ^1H - ^{13}C COSY experiment. By irradiation of H-8, the signal at δ 6.84 (1H, d) changed to a singlet (elimination of an allylic coupling). Furthermore, simplification of the methine multiplet at δ 2.02 (1H) was observed, suggesting that H-8 was vicinal only with a single proton (H-9) in the B ring. This eliminated the possibility of a 5,6-fused AB ring system, and supported the idea that **8** possessed an indene skeleton with a 6,7-en-10-oxo moiety. From a biogenetic point of view, compound **8**, apparently a norremophilane derivative, should possess Me-12 β and COOMe-13 β functionalities, since all the remophilane derivatives isolated from plants in the Compositae have substituents (normally a Me, or a CH_2OH , or a COOMe) at C-4 and C-5, both in β -configurations. Comparison of a model and the coupling constants of **8** suggested that the configuration of H-9 should be in the β -orientation. Moreover, Me-14 exhibited nOe correlations with H-9 (8%) and with H-6 β (8%), further supporting the presence of a 9 β -proton in **8**.

Isomers **9** and **10** were obtained as a mixture (ca. 1:1 from the ^1H - and ^{13}C -nmr

**8****9** 11*R
10 11*S

spectral data). Their nmr data showed close similarities with those of **13**, which was isolated from *Petasites japonicus* by Sugama *et al.* (4). However, the Me-15 of **13** was absent in **9** and **10**, while a carbonyl resonance at δ 173.9 was visible in addition to the 12-carboxyl signal of **9** and **10** at δ 174.8 (Table 2). This observation, coupled with the additional methoxy signals at δ 3.66 (^1H nmr) and δ 51.4 (^{13}C nmr), strongly suggested the presence of a 15-COOMe group in **9** and **10**. Since the other ^1H - and ^{13}C -nmr data of **9** and **10** were nearly identical with those of **13**, compounds **9** and **10** were unambiguously determined as a pair of 15-carboxylic acid methyl ester derivatives of **13**. The eims data of **9** and **10** showed molecular ion peaks at m/z 308 and a series of fragments, supporting the proposed structure. A careful examination of the ^1H -nmr signals of **9** and **10** revealed slight differences between the pair, found mainly at H-6, H-9 α , H-13, and COOMe-12 (Table 1). This observation suggested that the compounds are epimeric at C-11, a stereogenic center prone to undergo facile epimerization.

**13**

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mps were determined on a Kofler hot-stage instrument and are uncorrected. ^1H - and ^{13}C -nmr spectra were measured on a Bruker AM 400 Ft-nmr spectrometer with TMS as internal reference. Ir spectra were recorded on a 5DX Ft-ir interferometer. Eims data were obtained on a VG ZAB-HS spectrometer at 70 eV. Optical rotations were measured with a Perkin-Elmer 241 polarimeter. Uv spectra were recorded in MeOH, employing a Shimadzu UV-260 instrument. Results of elemental analysis were given by a Carlo Erba MOD 1106 elemental analyzer. Prep. tlc was performed on Si GF₂₅₄ plates (Qingdao Marine, Qingdao, People's Republic of China).

PLANT MATERIAL.—As published previously by Jia and Zhao (2).

EXTRACTION AND ISOLATION.—The dried roots (7.5 kg) of *L. przewalskii* were powdered and extracted with petroleum ether (60–90°)-Et₂O-Me₂CO (1:1:1) at room temperature three times (3 days each). This yielded 135 g of crude extract, which was subjected to cc on 1400 g Si gel with a petroleum ether-Et₂O gradient (1:0→1:1). Four crude fractions (fractions 1 through 4) were obtained. Fraction 1 (24 g) was further separated by cc over Si gel with a petroleum ether (60–90°)-Me₂CO gradient (100:1→1:1). Elutes 3–5 were combined and purified by prep. tlc using petroleum ether-CH₂Cl₂-Et₂O (10:10:1, three developments) to yield 100 mg of euparin and 10 mg of 5-acetyl-7-methoxybenzofuran (2). Prep. tlc of eluates 8–9, using petroleum ether-Me₂CO (6:1), afforded 40 mg of **1**. Combination and recrystallization of eluates 11–14 gave 18 mg of **4**. Eluate 16 was dried and subjected to prep. tlc, and developed with petroleum ether-Me₂CO (6:1, three developments) to afford 15 mg of **3**. Fraction 2 (32 g) was re-chromatographed with petroleum ether-Me₂CO (10:1→1:1) mixtures to give eight fractions (fractions 2.1–2.8, tlc monitoring). Fraction 2.2 (2.8 g) was purified by prep. tlc with CHCl₃-Me₂CO (10:1, four developments), and 19 mg of **9** and **10** were obtained, while elution with CH₂Cl₂-Me₂CO (15:1, five developments) resulted in the isolation of 32 mg of **8**. Fraction 2.3 (2.2 g) was further purified by prep. tlc with petroleum ether-CH₂Cl₂-Et₂O (3:3:1, six developments) to afford 40 mg of 2-acetyl-5,6-dimethoxybenzofuran, 28 mg of platyphyllid, and 14 mg of 1,3-dimethoxy-4,6,11-trimethylnaphthofuran (2). Fraction 2.4 (4.4 g) was rechromatographed with CHCl₃-Me₂CO (10:1→3:1) and then recrystallized in CHCl₃ or MeOH to afford 16 mg of **2** (from eluates 8–9), 16 mg of **5** (from eluates 11–14), and 38 mg of **6** (from eluates 13–16). By repeated cc with CHCl₃-Me₂CO (3:1), 22 mg of **7** were obtained from fraction 3 (16 g), along with 12 mg of 2-propenyl-5-acetyl-7-hydroxy-2,3-dihydrobenzofuran, 50 mg of *p*-hydroxybenzaldehyde, and 45 mg of 2-hydroxyplatyphyllid (2).

The known compounds were identified by comparing their corresponding properties (mp, ms, ir, and nmr) with literature values, and some were compared directly with authentic samples.

The ^1H -nmr data for compounds **3–8**, **9/10** (mixture), and **11** are given in Table 1. Table 2 summarizes the ^{13}C -nmr data for compounds **1–8**, **9/10** (mixture), and **11**.

8 β -Methoxyeremophil-7(11)-en-6 α ,15;8 α ,12-diolide [3].—Needles, mp 181–182° (CHCl₃); [α]²⁰_D +42.9° ($c=1.10$, CHCl₃); ir ν max (KBr) 1788, 1767, 1701, 1445, 1305, 1197, 991 cm⁻¹; eims m/z [M]⁺ 292.1314 (84) (calcd 292.1311), 277 [$\text{M}-\text{Me}$]⁺ (13), 261 (36), 248 (15), 247 (14), 232 (40), 220 (20), 205 (100), 195 (57), 183 (16), 159 (60), 140 (50), 109 (92), 99 (71), 77 (72); *anal.*, found C 65.79, H 6.87, calcd for C₁₆H₂₀O₅, C 65.75, H 6.85. R_f 0.75 (CHCl₃-Me₂CO, 10:1).

Eremophil-8(9),7(11)-dien-6 α ,15;8,12-diolide [4].—Needles, mp 190–191° (CHCl₃); [α]²⁰_D +113° ($c=1.31$, CHCl₃); ir ν max (KBr) 1786, 1668, 1068, 967 cm⁻¹; eims m/z [M]⁺ 260.1046 (60) (calcd 260.1049), 245 [$\text{M}-\text{Me}$]⁺ (18), 232 (34), 216 (18), 203 (80), 189 (26), 175 (28), 161 (83), 145 (36), 115 (36), 41 (100); *anal.*, found C 69.37, H 6.25, calcd for C₁₆H₁₆O₄, C 69.23, H 6.15. R_f 0.85 (CHCl₃-Me₂CO, 10:1).

10 β -Hydroxyeremophil-8(9),7(11)-dien-6 α ,15;8,12-diolide [5].—Prisms, mp 225–226° (dec) (Me₂CO); [α]²⁰_D +22° ($c=0.84$, Me₂CO); ir ν max (KBr) 3406 (OH), 1774 br, 1703 sh, 1337, 1005, 950 cm⁻¹; eims m/z [M]⁺ 276.1001 (26) (calcd 276.0998), 258 [$\text{M}-\text{H}_2\text{O}$]⁺ (8), 232 (8), 219 (41), 203 (11), 193 (17), 177 (100), 161 (20), 148 (15), 115 (30), 105 (38), 100 (40), 79 (52); *anal.*, found C 65.26, H 5.93, calcd for C₁₅H₁₆O₅, C 65.22, H 5.80. R_f 0.40 (CHCl₃-Me₂CO, 10:1).

A solution of 16 mg of **5** in 2 ml Me₂CO was oxidized with 12 mg *m*-chloroperbenzoic acid under a N₂ atmosphere. After stirring for 2 h at -10°, the solution was neutralized with 0.1 M Na₂CO₃ and extracted with Et₂O (8 ml×3). The Et₂O layer was washed, dried, and evaporated, and the residue (13 mg) purified by prep. tlc (CHCl₃-Me₂CO, 15:1, five developments) to afford 7 mg of **6** (identified by comparing their [α]²⁰_D, ir, and ^1H -nmr data; see below).

10 β -Hydroxy-8 β ,9 β -epoxyeremophil-7(11)-en-6 α ,15;8 α ,12-diolide [6].—Prisms, mp 178–179° (Me₂CO); [α]²⁰_D +14° ($c=1.20$, Me₂CO); ir ν max (KBr) 3451 (OH), 1797, 1738, 1748, 1664, 1372, 961 cm⁻¹; eims m/z [M]⁺ 292.0946 (6) (calcd 292.0947), 276 (5), 258 (4), 256 (6), 246 (8), 231 (10), 219 (14), 218 (15), 203 (12), 201 (11), 187 (14), 177 (14), 159 (16), 145 (23), 115 (20), 109 (28), 95 (52), 55 (100); *anal.*, found C 61.53, H 5.38, calcd for C₁₅H₁₆O₆, C 61.64, H 5.48. R_f 0.45 (CHCl₃-Me₂CO, 10:1).

Treatment of 20 mg of **6** with Ac₂O-pyridine (1:1) followed by prep. tlc (R_f 0.65, CHCl₃-Me₂CO, 10:1), afforded 16 mg of **11**. Ir ν max (KBr) 1788, 1706 sh, 1637, 1373, 1213, 1000, 958 cm⁻¹; eims m/z [M]⁺ 334 (14), 292 (100), 275 (52), 274 [$\text{M}-\text{AcOH}$]⁺ (20), 264 (19), 246 (52), 235 (40), 218 (52), 200 (25), 190 (21), 189 (24), 175 (19), 163 (13), 151 (42), 135 (11), 123 (30), 111 (27), 93 (23), 91 (39), 78 (31), 77 (30), 55 (21).

8 β -Hydroxy-6 β -angeloyloxyeremophil-7(11)-en-8 α ,12-olide-15-oic acid [7].—Prisms, mp 253–254° (MeOH); [α]²⁰_D +67° ($c=1.21$, Me₂CO); ir ν max 3161 br, 1726, 1649 sh, 1446, 1385, 1160, 1135 cm⁻¹; eims m/z [M]⁺ 378.1674 (6) (calcd 378.1679), 360 [$\text{M}-\text{H}_2\text{O}$]⁺ (43), 232 (46), 187 (12), 159 (8), 109 (17), 100 (15), 83 (100), 55 (78); *anal.*, found C 63.44, H 6.66, calcd for C₂₀H₂₆O₇, C 63.49, H 6.88; R_f 0.47 (C₆H₆-MeOH, 30:1).

2-Acetyl-3 α , β -methyl-3 α ,4,5,6,7,7a-hexahydroinden-4 β -carboxylic methyl ester [8].—Colorless gum; [α]²⁰_D +3.5° ($c=0.45$, CHCl₃); ir ν max (KBr) 2949, 1738, 1686, 1425, 1375, 1029 cm⁻¹; uv λ max (MeOH) 235 nm (ϵ 9780); eims m/z [M]⁺ 236.1416 (16) (calcd 236.1412), 221 [$\text{M}-\text{Me}$]⁺ (6), 205 (21), 204 (25), 189 (32), 177 (36), 176 [$\text{M}-\text{COOMe}$]⁺ (100), 161 (22), 117 (49), 116 (64), 88 (60); *anal.*, found C 71.17, H 8.45, calcd for C₁₄H₂₀O₃, C 71.19, H 8.41.

11(RS)-8-Oxoeremophil-6(7)-en-dimethyl-12,15-dioate [9 and 10].—Colorless gum, [α]²⁰_D -16° ($c=0.6$, Me₂CO); ir ν max (KBr) 2947, 1734, 1676, 1436, 1376, 1242, 1197, 1170, 1027 cm⁻¹; uv λ max (MeOH) 242 nm (ϵ 7900); eims m/z [M]⁺ 308.1620 (36) (calcd 308.1624), 293 [$\text{M}-\text{Me}$]⁺ (9), 276 [$\text{M}-\text{Me}$]⁺ (52), 261 [276-Me]⁺ (25), 249 [$\text{M}-\text{COOMe}$]⁺ (59), 248 [$\text{M}-\text{HCOOMe}$]⁺ (45), 232 (58), 189 (58), 188 [$\text{M}-2\times\text{HCOOMe}$]⁺ (50), 161 (100), 127 (54), 91 (83), 77 (65), *anal.*, found C 66.08, H 7.85, calcd for C₁₇H₂₄O₆, C 66.23, H 7.79.

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