Extraction. Roots (5.6 kg) of young cultivated plants grown from seeds collected from a local (Himachal Pradesh, India) wild source, were cut into small pieces, dried at 30° and powdered. The powdered drug was soaked in aq. MeOH (50%) for 48 hr. The percolate was concd to dryness under red. pres. The residue (230 g) was dissolved in hot MeOH and the soln allowed to stand overnight at room temp. when a solid (5 g) separated out. The solid was charged on a column of Si gel and subjected to graded elution with C_6H_6–EtOAc. Elution with C_6H_6–EtOAc (4 : 1) gave a solid found to be homogenous on TLC (R_f 0.25; C_6H_6–EtOAc, 10 : 3). The solid on crystallization from C_6H_6 gave colourless needles (SM-I), mp 206°, MS 272.1096, $C_{16}H_{16}O_4$, m/z (rel. int.): 257 (78.4), 229 (20.8), UV λ_{max}^{EtOH} nm (ϵ): 210 (4000), 253 (7800), 263 (7500), 343 (2700), 351 (3000), 392 sh. IR ν_{max}^{KBr} cm^{-1}: 3400 (–OH), 1755 (γ-lactone C=O), 1635 (C=C). ^{1}H NMR, $(CD_3)_2CO$: δ 1.42 (6H, *d*, $J = 6$ Hz), 2.42 (3H, *s*, aromatic Me), 3.66 (1H, *sep*, $J = 6$ Hz), 4.3 (3H, *s*, –OMe), 7.07 and 7.57 (2 × 1H, *br s*, *meta*-coupled aromatic protons) and 9.8 (1H, *s*, –OH). Acetylation of the compound in pyridine with Ac_2O gave a colourless monoacetyl derivative (^{1}H NMR and IR) which was recrystallized from petrol, mp 165°.

Acknowledgements—Our thanks are due to scientists of the Instrumentation Division of this laboratory for recording the spectra.

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FURANOEREMOPHILANES FROM *LOPHOLAENA SPECIES**

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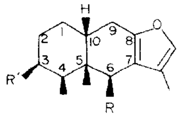
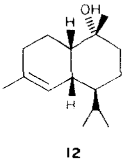
Key Word Index—*Lopholaena coriifolia*; *L. disticha*; *L. segmentata*; Compositae; sesquiterpenes; furanoeremophilanes.

Abstract—Three additional *Lopholaena* species afforded several furanoeremophilanes, two of them not reported previously.

Lopholaena, a genus with *ca* 20 taxa, is restricted to southern and tropical Africa. Only two species have been studied chemically[1] although we have now investigated three further species. The roots of *Lopholaena coriifolia* (Sond.) Phill. et C. A. Smith afforded caryophyllene and the furanoeremophilanes **1**[2], **2**[3], **3**[4], **5**[5], **6**[6] and **7**. The structure of the latter could be deduced from the ^{1}H NMR spectrum (Table 1) which was similar to that of **5**. The chemical shifts of H-3 and H-6 further showed that the ester group was at C-3. The aerial parts gave germacrene D, bicyclogermacrene, α-humulene, caryophyllene,



	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
R	H	OH	OAc	OAng	OH	OH	OH	OAng	OMeacr	OMeacr	H
R′	H	H	H	H	OAng	OSen	OMeacr	OAng	OMeacr	O Ang	OAng



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*Part 443 in the series "Naturally Occurring Terpene Derivatives". For Part 442 see Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 1989.

Table 1. ^1H NMR spectral data of compounds **7** and **10** (400 MHz, $CDCl_3$ TMS as internal standard)

	7	**10**
H-3	5.30 *ddd*	5.41 *ddd*
H-6	4.99 *brs*	6.42 *brs*
H-9	2.83 *brdd*	2.87 *brdd*
H-9'	2.24 *brd*	2.36 *brd*
H-10	2.07 *m*	2.15 *m*
H-12	7.05 *brs*	7.05 *brs*
H-13	2.07 *brs*	1.18 *brs*
H-14	0.95 *s*	1.05 *s*
H-15	0.99 *d*	0.98 *d*
OMeacr	6.11 *brs*	6.14 *brs*
	5.56 *dq*	5.58 *dq*
	1.95 *dd*	1.98 *dd*
OAng	—	6.02 *qq*
		1.92 *dq*
		1.88 *dq*

J (Hz): 2, 3 = 12; 2', 3 = 3, 4 ~ 4; 4, 15 = 7; 9, 9' = 17; 9, 10 = 6; OAng: 3', 4' = 7; 3', 5' = 4', 5' = 1.3; OMeacr: $3'_1$, $3'_2$ = $3'_2$, 4' = 1.5.

polyisoprene, α-zingiberene, α-curcumene, caryophyllene 1,10-epoxide and the furanoeremophilanes **3**, **5–7** and T-muurolol (**12**)[7]. The roots of *L. disticha* (N.E.Br.) S. Moore afforded caryophyllene, **1**, **3**, **5** and **6**, while the aerial parts gave caryophyllene, germacrene D, bicyclogermacrene, α-humulene, **3**, **4**[8], **5**, **6** and **11**[4]. The aerial parts of *L. segmentata* (Oliv.) S. Moore afforded germacrene D and α-humulene, while the roots gave the furanoeremophilanes **5–7**, **8**[4], **9**[6] and **10**. The structure of **10** followed from the ^1H NMR spectral data (Table 1), which clearly showed that an angelate and a methacrylate residue were present, while typical signals of a β-furan methyl and a furan proton together with the methyl signals at 1.05 *s* and 0.98 *d* indicated a furanoeremophilane. All the other signals were similar to those of **8** and **9**. However, small differences in the chemical shifts of H-3 and H-6 as well as of the signals of the ester groups were visible. As usual the angelate residue caused a slightly more downfield shift of the signal of the proton under the ester function than a methacrylate group. Furthermore the signals of the ester part if situated at C-6 were slightly shifted downfield due to the deshielding effect of the furan moiety. Thus a clear decision concerning the relative positions of the ester groups was possible.

The chemistry of *Lopholaena* seems to be very uniform and may indicate a position in the *Gynuroide* group of the Senecioneae, as furanoeremophilanes of types **1–11** are widespread in *Gynura* and related *Senecio* species[9].

EXPERIMENTAL

The air-dried plant material, collected during February 1981 in Transvaal, was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material. Voucher specimens were deposited in the Botanic Research Institute, Pretoria.

L. coriifolia (*voucher* 81/20). The roots (170 g) gave 60 mg caryophyllene, 100 mg **1**, 400 mg **2**, 85 mg **3**, 200 mg **5**, 120 mg **6** and 80 mg **7** (Et_2O–petrol, 1:1), while the aerial parts (550 g) gave 350 mg germacrene D, 50 mg bicyclogermacrene, 80 mg α-humulene, 400 mg polyisoprene, 220 mg α-zingiberene, 170 mg α-curcumene, 90 mg caryophyllene, 30 mg caryophyllene 1,10-epoxide, 50 mg **3**, 300 mg **5**, 120 mg **6**, 120 mg **7** and 500 mg **12**.

L. disticha (*voucher* 81/77). The roots (80 g) gave 30 mg caryophyllene, 15 mg **1**, 20 mg **3**, 300 mg **5** and 100 mg **6**, while the aerial parts (250 g) afforded 50 mg caryophyllene, 50 mg germacrene D, 30 mg bicyclogermacrene, 50 mg α-humulene, 70 mg **3**, 500 mg **5**, 100 mg **6** and 20 mg **11**.

L. segmentata (*voucher* 81/103). The roots (45 g) gave 15 mg **5**, 3 mg **6**, 10 mg **7**, 6 mg **8**, 6 mg **9** and 4 mg **10** (Et_2O–petrol, 1:4), while the aerial parts afforded 3 mg germacrene D and 3 mg α-humulene.

3β - (*Methacryloyloxy*) - 6β - *hydroxy* - 10βH - *furanoeremophilane* (**7**). Colourless gum, not free from **5**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 318.183 $[M]^+$ (1) ($C_{19}H_{26}O_4$), 300 $[M - H_2O]^+$ (1), 214 $[300 - RCO_2H]^+$ (12), 69 $[C_3H_5CO]^+$ (100).

3β - *Angeloyloxy* - 6β - *methacryloyloxy* - 10βH - furanoeremophilane (**10**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1630 ($C{=}CCO_2R$); MS *m/z* (rel. int.): 400.225 $[M]^+$ (1) ($C_{24}H_{32}O_5$), 314 $[M - HOMeacr]^+$ (6), 300 $[M - HOAng]^+$ (20), 231 $[300 - C_3H_5CO]^+$ (25), 214 $[314 - HOAng]^+$ (8), 83 $[C_4H_7CO]^+$ (87), 69 $[C_3H_5CO]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \qquad 578 \qquad 546 \qquad 436\ nm}{-1 \qquad -1 \qquad -24 \qquad -88} (CHCl_3;\ c\ 0.3).$$

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