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Mass Spectra of Furanoeremophilane Derivatives[1)]

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Mass spectral fragmentations of furanoeremophilane derivatives bearing oxygen-function on B ring were investigated. It was found that mass spectra measured by direct inlet system gave characteristic *retro*-Diels-Alder fragmentations, while indirect introduction of the samples afforded intense peaks at *m/e* 159 and *m/e* 145 containing the furan moiety. Fragmentation patterns of other poly-functional derivatives were examined by measurements of accurate masses and metastable ions.

In the course of structure determination of sesquiterpenes in plants of the genera *Farfugium*,[2)] *Ligularia*,[3)] and *Syneilesis*,[4)] mass spectra of furanoeremophilane derivatives have been investigated. We now wish to report their characteristic fragmentations which provide useful information for structural studies of furanoeremophilane derivatives.

The *retro*-Diels-Alder fragmentation induced by electron-impact[5)] is one of the most important processes occurring in many sesquiterpenes of a furanoeremophilane type (Fig. 1). However in the case of furanoeremophilane derivatives possessing oxygen-function(s), such as hydroxyl, acyloxyl, and alkoxyl groups, on ring B, the *retro*-Diels-Alder fragmentation was predominant only when the direct introduction of the sample was employed. The spectra of these compounds measured by use of the indirect inlet system showed intense peaks at either *m/e* 159 or *m/e* 159 and 145 and the *retro*-Diels-Alder fragmentation was scarcely observed. The fragmentations leading to the ions at *m/e* 159 and *m/e* 145 are discussed below.

The mass spectra of ligularol (**1**),[6)] epiligularol (**2**),[6)] furanoeremophilan-9α-ol (**3**),[7)] 6β-methoxyfuranoeremophilane (**4**),[8)] 6β-ethoxyfuranoeremophilane (**5**), ligularol acetate (**6**),[6)] and 6β-senecioyloxyfuranoeremophilane (**7**),[2c)] exhibited characteristic peaks at *m/e* 216 (ion **a**), *m/e* 201 (ion **b**), *m/e* 159 (ion **c**), and *m/e* 145 (ion **d**) when the indirect introduction of the sample was employed. The ion **a** must arise by pyrolysis of these compounds prior to ionization at the surface of the heated inlet system. This is supported by comparison of the mass spectrum of 9-dehydrofuranoeremophilane (**8**), a dehydration product of **1**, **2**, and **3**, with those of **1**, **2**, and **3** (Figs. 2 and 3 and Table 1).

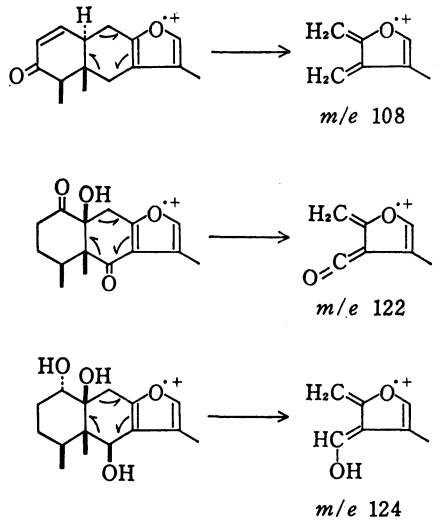

Fig. 1.

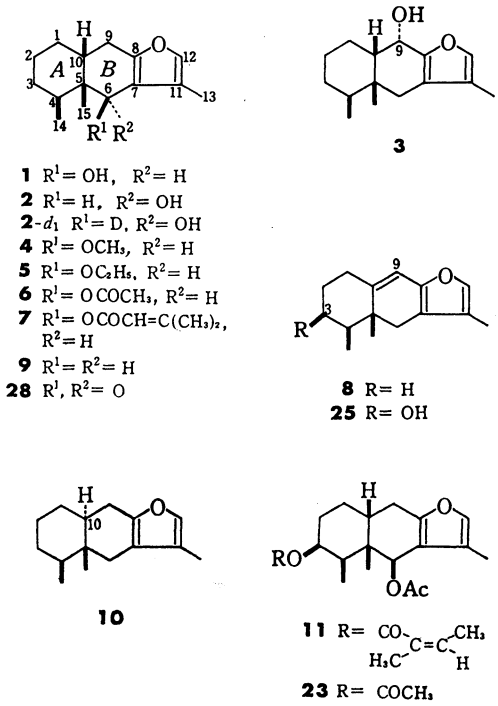

Fig. 2.

Epiligularol (**2**) was treated with *p*-toluenesulfonyl chloride in pyridine under reflux to give 9-dehydrofuranoeremophilane (**8**)[9)] as a major product, formation of which would be explicable by conjugate 1,4-elimination of water followed by [1,5]-hydride shift. The dehydration product (**8**), on hydrogenation over 10% palladium-charcoal, gave an inseparable epimeric mixture, which was revealed to consist of furanoeremophilane (**9**)[10)] and 10-epifuranoeremophilane (**10**)[3a)] in a ratio of 1 : 1 on the basis of comparison of ^{1}H NMR, UV, IR, and mass spectra.

Dehydration of ligularol (**1**) and furanoeremophilan-

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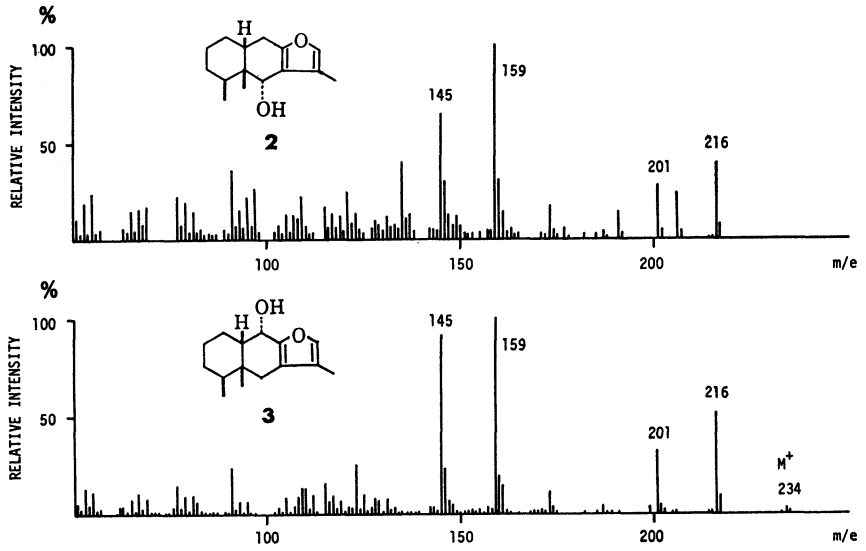

Fig. 3.

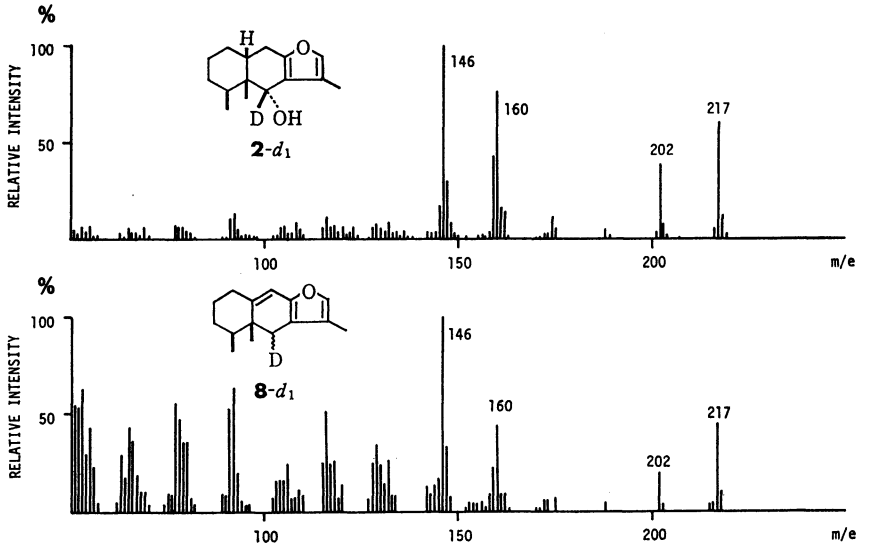

Fig. 4.

9α-ol (**3**) with *p*-toluenesulfonyl chloride in pyridine gave also 9-dehydrofuranoeremophilane (**8**) as a major product. The mass spectrum of **8** measured by direct introduction showed intense peaks at *m/e* 216 (M^+), 201, 159, and 145 and its resemblance to those of **1**, **2**, and **3** is illustrated by the spectra of deuterio compounds, **2**-d_1 and **8**-d_1 (*vide infra*) (Fig. 4 and Table 1).

A plausible mechanism for the fragmentations to afford ion **b**, ion **c**, and ion **d** is depicted in Fig. 5.

The elemental compositions of ion **a** (*m/e* 216.1520; calcd for $C_{15}H_{20}O$: *m/e* 216.1513), ion **b** (*m/e* 201.1297; calcd for $C_{14}H_{17}O$: *m/e* 201.1279), ion **c** (*m/e* 159.0832; calcd for $C_{11}H_{11}O$: *m/e* 159.0810), and ion **d** (*m/e* 145.0652; calcd for $C_{10}H_9O$: *m/e* 145.0655) were determined by the high resolution mass spectrum of epiligularol (**2**). Metastable ions were observed at *m/e* 187.0 (*m/e* 216→*m/e* 201), *m/e* 104.6 (*m/e* 201→*m/e* 145), and *m/e* 117.2 (*m/e* 216→*m/e* 159) in the spectra of epiligularol (**2**), furanoeremophilan-9α-ol (**3**), and ligularol acetate (**6**). These observations indicate that ion **c** arises from ion **a** in one step and ion **d** from ion **a** through ion **b**. The mass spectra of 6β-deuterioepiligularol (**2**-d_1) and its dehydration product (**8**-d_1) showed peaks due to ion **a** at *m/e* 217, ion **b** at *m/e* 202, ion **c** at *m/e* 160 and 159, and ion **d** at *m/e* 146, affording further information for the mechanism of the fragmentations (Table 1). Ion **c** must be derived from ion **a** by the favorable cleavage of $C_{(1)}$–$C_{(2)}$ and $C_{(4)}$–$C_{(5)}$ bonds, both locating β to the Δ^9-double bond. Alternatively, ion **a** loses a methyl radical most probably from the position C-5 to afford ion **b**, the position being allylic to the double bond. The ion **b** may undergo 1,2-hydrogen shift from C-6 to C-5 followed by cleavage of $C_{(1)}$–$C_{(2)}$ and $C_{(4)}$–$C_{(5)}$ bonds to give the fully con-

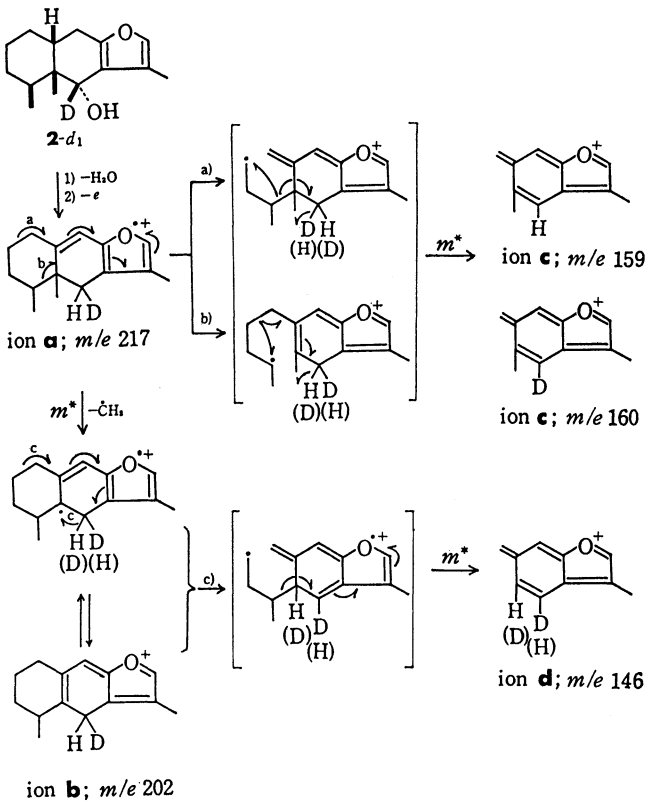

Fig. 5.

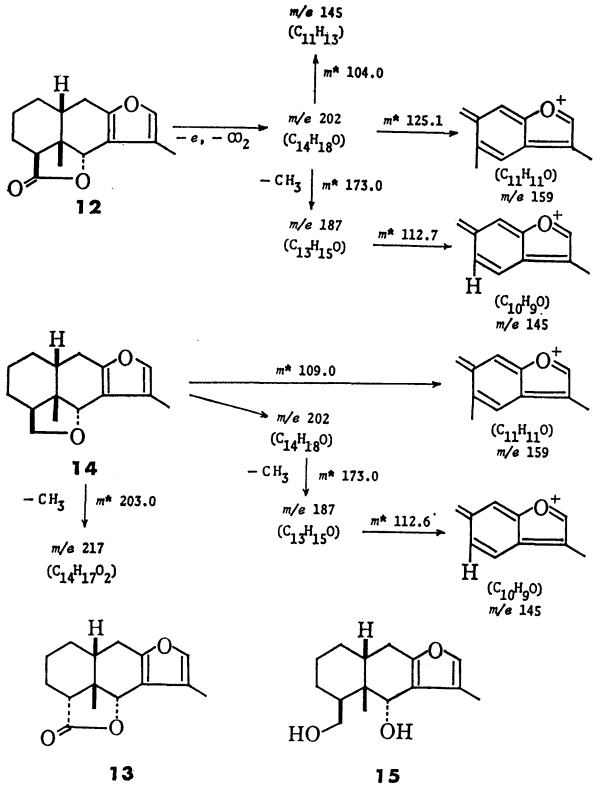

Fig. 6.

jugated ion **d** (Fig. 5).

Now it has been demonstrated that elimination of oxygen-function at C-6 in furanoeremophilane derivatives occurs with ease in mass spectral measurement by the indirect inlet system. A number of natural furanoeremophilanes with different acyloxyl groups at C-3 and C-6 positions have been reported.[11] The electron-impact mass spectral measurement by the indirect inlet method would provide a diagnostic technique for determination of the positions of acyloxyl groups based on the argument developed above.

Mass spectra of 6β-acetoxy-3β-angeloyloxyfuranoeremophilane (**11**)[2b] were then examined by two inlet methods. When mass spectrum of **11** was measured by indirect inlet method, a peak at *m/e* 314 due to elimination of acetic acid by preferential loss of the acetoxyl group at C-6 was observed; a peak at *m/e* 274 due to elimination of angelic acid by loss of the angeloyloxyl group at C-3 was absent. On the other hand, the direct inlet measurement afforded two peaks at *m/e* 314 and *m/e* 274 with an intensity ratio of 9 : 2 (Table 1). This method was successfully applied to determination of the structures of 3β,6β-diacyloxyfuranoeremophilane derivatives obtained from *Syneilesis palmata* (Thunb.) Maxim.[4]

Mass spectra of furanoeremophilan-14,6α-olide (**12**) and its derivatives, **13**, **14**, and **15**,[3b] also exhibited their characteristic ions at *m/e* 159 and *m/e* 145 even when they were measured by the direct inlet method. The fragmentation modes for **12** and **14** are shown in Fig. 6.

Accurate mass measurements for **12** and **14** revealed that the peak at *m/e* 145 splitted into a doublet, a peak at *m/e* 145.0649 (calcd for $C_{10}H_9O$: *m/e* 145.0655) and a peak at *m/e* 145.1001 (calcd for $C_{11}H_{13}$: *m/e* 145.1016). A metastable ion at *m/e* 104.0 for **12** may correspond to the process, $C_{14}H_{18}O^+$ (*m/e* 202)$\rightarrow C_{11}H_{13}^+$ (*m/e* 145). The ion at *m/e* 159 for **12** consists of two species, $C_{11}H_{11}O^+$ (*m/e* 159.0828; calcd: *m/e* 159.0810) and $C_{12}H_{15}^+$ (*m/e* 159.1182; calcd: *m/e* 159.1174). The ion at *m/e* 202 (*m/e* 202.1358; calcd for $C_{14}H_{18}O$: *m/e* 202.1358) for **14** is probably formed from its molecular ion (M^+ at *m/e* 232.1540; calcd: *m/e* 232.1463) by one-step elimination of CH_2O, although the appropriate metastable ion was not observed. In the case of **15**, its dehydration to give **14** dominates over the *retro*-Diels-Alder fragmentation.

Mass spectral fragmentations of the following furanoeremophilane derivatives which have two or three oxygen-functions (Fig. 7) were examined; furanoeremophilane-3β,9β-diol (**16**),[2c] furanopetasine (**17**),[12] furanopetasol (**18**)[12] (Fig. 8), furanoeremophilane-3β,10β-diol (**19**)[2d] (Fig. 8), 3β-angeloyloxy-9β-senecioyloxyfuranoeremophilane (**20**),[2c] furanoeremophilane-6β,10β-diol (**21**)[3c] (Fig. 9), 6β-senecioyloxyfuranoeremophilan-10β-ol (**22**),[2c] 3β,6β-diacetoxyfuranoeremophilane (**23**),[2b] 6β-acetoxy-3β-angeloyloxyfuranoeremophilane (**11**) (*vide supra*), and furanoeremophilane-3β,9β,10β-triol (**24**).[2d] These compounds showed the same fragmentation modes as those of the compounds **1**—**7**; the characteristic fragment ions at *m/e* 159 and *m/e* 145 were observed by the indirect inlet measurement, while the *retro*-Diels-Alder fragmentation was predominant by the direct inlet method (Table 1). Among these compounds, **21**, **22**, and **24** which possess

TABLE 1. PRINCIPAL FRAGMENT PEAKS AND THEIR RELATIVE INTENSITIES

Compound		*m/e* 145 (%)	*m/e* 159 (%)	RDA fragment[b] *m/e* (%)	Other fragments *m/e*(%)
1	i	(48)	(100)		201(11), 216(25, $[M-H_2O]^+$)
	d			124(100)	
2	i	(65)	(100)		201(28), 216(40)
	d			124(100)	
2-d_1	i	(18) (100)[c]	(44) (77)[d]		202(38), 217(61)
	d			124(4.5) 125(100)	
3	i	(92)	(100)		201(32), 216(52), 234(3, M^+)
	d			124(100)	
4	i	(25)	(18)	138(100)	128(89), 248(13, M^+)
5	i	(84)	(100)		201(30), 216(47)
6	i	(100)	(97)		43(100), 60(60), 201(39), 216(53)
	d	(12)	(34)	124(100)	43(35), 216(21), 233(10), 276(2, M^+)
7	i	(29)	(77)		55(23), 83(100), 316(1, M^+)
8	d	(100)	(92)		201(34), 216(54)
8-d_1	d	(100)[c]	(45)[d]		202(20), 217(46)
11	i	(15)	(100)		55(76), 83(83), 199(21), 214(11), 232(18), 314(10)
	d	(10)	(48)	124(100)	43(21), 55(70), 83(82), 274(2), 314(9), 331(6), 374(2, M^+)
12	d	(54)	(41)		246(58, M^+)
13	d	(64)	(56)		95(100), 187(46), 202(46), 246(48, M^+)
14	i	(40)	(52)		187(16), 202(9), 217(5), 232(100, M^+)
15	d	(100)	(87)		232(97, $[M-H_2O]^+$)
16	i	(38)	(100)		199(78), 214(23), 250(1, M^+)
	d	(7)	(15)	124(100)	250(5, M^+)
17	i	(15)	(17)		55(44),83(27), 199(76), 214(100), 314(0.2, $[M-H_2O]^+$) 332(0.2, M^+)
	d	(19)	(18)	124(100)	55(71), 83(33), 109(43),199(61), 214(82), 232(20), 332(2, M^+)
18	i	(68)	(86)		173(98), 199(100), 214(30), 232(74), 250(2, M^+)
	d			124(100)	250(13, M^+)
19	i	(44)	(100)		199(75), 214(28),232(35,$[M-H_2O]^+$)
	d			108(64)	109(100), 250(10,M^+)
20	i	(27)	(94)		55(82), 83(45), 100(78), 314(33,$[M-C_5H_8O_2]^+$)
21	i	(8)	(95)		199(100), 214(67)
	d			124(100)	232(18), 250(2, M^+)
22	i	(8)	(100)		55(75), 100(88), 199(97), 214(64), 232(8)
	d				55(23), 83(100), 232(13), 332(1, M^+)
23	i	(19)	(100)		199(47), 214(18), 274(17, $[M-AcOH]^+$)
24	i	(12)	(100)		230(20, $[M-2H_2O]^+$)
	d			124(100)	
25	i	(44)	(100)		199(79), 214(22), 232(40, M^+)
26	i				199(100), 214(79, M^+)
27	i	(6)	(100)		214(37,M^+)

a) Mass spectra were measured on a Hitachi RMU-6-Tokugata mass spectrometer. Relative intensities are indicated in parentheses and i and d in the second column indicate indirect and direct introduction of samples, respectively. b) RDA fragment represents *retro*-Diels-Alder fragmentation. c) Observed at *m/e* 146. d) Observed at *m/e* 160.

two oxygen-functions at C-10 and either C-6 or C-9 on B ring, showed remarkable intense peak at *m/e* 159 compared with peak at *m/e* 145 by the indirect inlet measurement.

Thermal dehydration of furanoeremophilane-6β,10β-diol (**21**) has been reported to give benzofuran derivatives, farfugins A (**26**) and B (**27**).[2a] The mass spectral investigation showed that farfugin B (**27**) gave a dominant fragmentation due to benzylic cleavage, resulting in the formation of a benzyl (or tropylium) ion at *m/e* 159 (Fig. 9), while the principal peaks in the spectrum of farfugin A (**26**) were a molecular ion at *m/e* 214 and an ion at *m/e* 199 $[M-CH_3]^+$. These results suggest that **21**, **22**, and **24** undergo a facile aromatization into **26** and **27** on the heated surface of the inlet system prior to ionization and give the intense benzyl ion at *m/e* 159, a part of which, however, would be produced through the fragmentation analogous to that shown in Fig. 5. Thus the mass spectral investigation could be applied to the prediction of aptitude for the aromatiza-

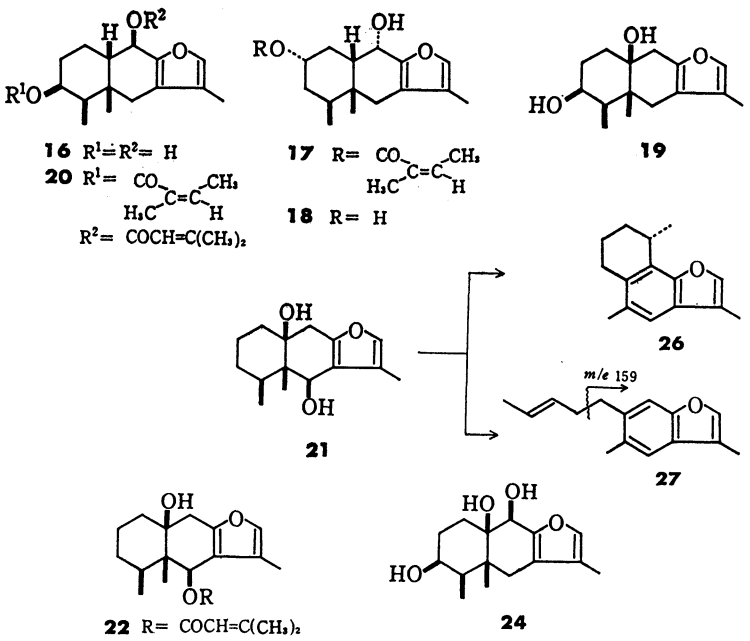

Fig. 7.

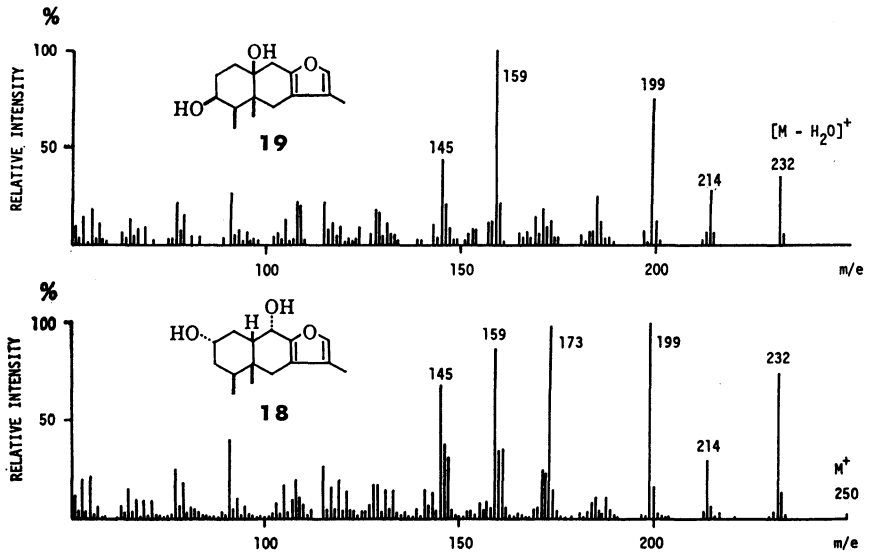

Fig. 8.

tion of furanoeremophilanediol, triol, and their acyl derivatives by elimination of the oxygen-functions to give **27** or its derivatives.[2a,13]

Experimental

Measurement of Mass Spectra. The low-resolution mass spectra were measured on a Hitachi RMU-6-Tokugata mass spectrometer using ionization energy 70 eV with source temperature of 180—230 °C (indirect inlet system) and 120—140 °C (direct inlet system). The high-resolution mass spectra were determined with a CEC 110B type mass spectrometer (indirect inlet system).

Dehydration of Epiligularol (2) with p-Toluenesulfonyl Chloride in Pyridine. *p*-Toluenesulfonyl chloride (100 mg) was added to a solution of **2** (91 mg) in pyridine (8 ml) and the mixture was heated at 120 °C (oil bath temperature) for 2 h under a nitrogen atmosphere. Evaporation of the solvent under reduced pressure gave a residue, which was immediately chromatographed on silical gel (5 g) using light petroleum as an eluent to give an oil (58 mg) containing **8** as the major component. The oil was unstable and therefore further purification was not carried out.

Hydrogenation of 9-Dehydrofuranoeremophilane (8) over Palladium-charcoal. The above product (**8**) prepared from epiligularol (**2**; 67 mg) was hydrogenated over 10% palladium-charcoal (50 mg) in ethanol with stirring for 9.5 h. Filtration of the catalyst and evaporation of the solvent gave a residue (45 mg), which was chromatographed on silica gel using light petroleum as an eluent to afford a mixture of furanoeremophilane (**9**) and 10-epifuranoeremophilane (**10**) in a ratio of 1:1. Spectral data of the mixture of **9** and **10** are as

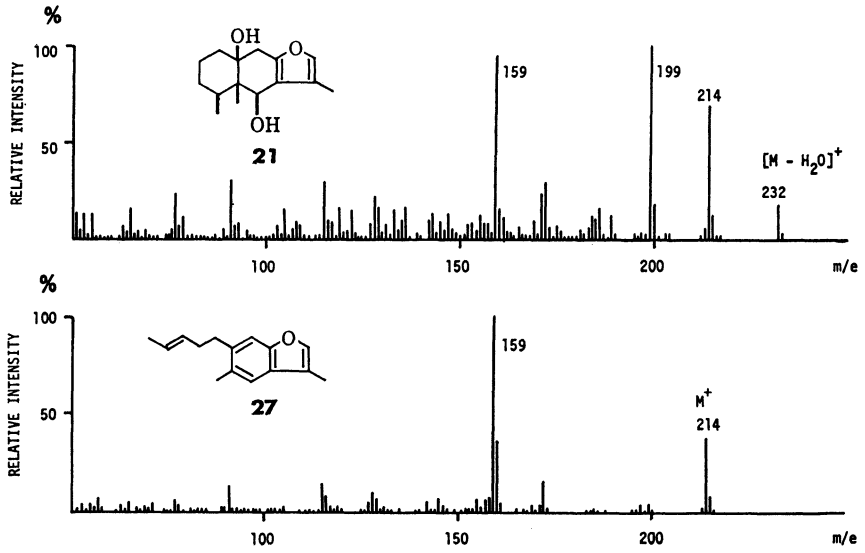

Fig. 9.

follows: UV (EtOH) λ_{max} 220.5 nm (ε 6700); IR (liquid film) 1640, 1560, and 735 cm^{-1}; ^1H NMR (CCl_4) δ 0.69 (s, $C_{(5)}$-CH_3 for **10**), 0.91 (s, $C_{(5)}$-CH_3 for **9**), 1.86 (d, J=*ca.* 1 Hz, $C_{(11)}$-CH_3), and 6.90 (m, $C_{(12)}$-H); ^1H NMR ($CDCl_3$) δ 0.68 (s, $C_{(5)}$-CH_3 for **10**), 0.91 (s, $C_{(5)}$-CH_3 for **9**), 1.89 (d, J=*ca.* 1 Hz, $C_{(11)}$-CH_3), and 7.03 (m, $C_{(12)}$-H); ^1H NMR (C_6D_6) δ 0.61 (s, $C_{(5)}$-CH_3 for **10**), 0.79 (s, $C_{(5)}$-CH_3 for **9**), 1.80 (d, J=*ca.* 1 Hz, $C_{(11)}$-CH_3), and 7.05 (m, $C_{(12)}$-H); the chemical shifts of $C_{(5)}$-CH_3 for furanoeremophilane (**9**) and 10-epifuranoeremophilane (**10**) reported in the literatures[3a,10] are as follows: δ 0.90 ($CDCl_3$) for **9** and δ 0.69 (CCl_4) and 0.61 (C_6D_6) for **10**; MS *m/e* 218 (19%, M^+ ($C_{15}H_{22}O$)) and 108 (100%, *retro*-Diels-Alder fragment).

*6β-Deuterioepiligularol (**2**-d_1).* Ligularone (**28**: 43 mg) in dry ether was stirred with lithium aluminium deuteride (15 mg) for 1 h under a nitrogen atmosphere. The excess of the reagent was decomposed with water, and the reaction product was extracted with ether. The usual work-up gave a crystalline product (34 mg), which was recrystallized from light petroleum to give **2**-d_1. The molecular ion was observed at *m/e* 235.

*6β-Ethoxyfuranoeremophilane (**5**).* A solution of ligularol (**1**; 56 mg) in ethyl iodide (3 ml) was heated under reflux in the presence of silver(I) oxide (113 mg) and *N,N*-dimethylformamide (0.5 ml) for 3 h. After filtration the reaction mixture was evaporated to give an oily residue. The oil was chromatographed on silica gel (3 g) using light petroleum as an eluent to give 6β-ethoxyfuranoeremophilane (**5**; 18 mg).

Extraction of the roots of *Ligularia fischeri* TURCZ. with methanol and ethanol gave 6β-methoxyfuanoeremophilane (**4**) and 6β-ethoxyfuranoeremophilane (**5**), respectively. In the extract of the root of the plant with benzene **4** and **5** were not detected. This indicates that these compounds are artifacts derived from ligularol (**1**) by acid-catalyzed substitution reaction during the extraction procedure. Spectral data of **5**, mp 36—39 °C, are as follows: UV (MeOH) λ_{max} 221 nm (ε 5600); IR (Nujol) 1640 and 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (d, J=*ca.* 6 Hz, $C_{(4)}$-CH_3), 1.03 (s, $C_{(5)}$-CH_3), 1.17 (t, J=7.5 Hz, $-OCH_2\underline{C}H_3$), 2.03 (d, J=*ca.* 1 Hz, $C_{(11)}$-CH_3), 3.67 (q, J=7.5 Hz, $-OC\underline{H}_2CH_3$), 4.22 (br s, $C_{(6)}$-H), and 7.10 (m, $C_{(12)}$-H); Found: C, 77.79; H, 10.59%. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99%.

6ξ-Deuterio-9-dehydrofuranoeremophilane (8-d_1). 6β-Deuterioepiligularol (**2**-d_1) obtained from ligularone (**28**; 50 mg), was treated with *p*-toluenesulfonyl chloride (58 mg) in pyridine (7 ml) under the same conditions as in the case of **2** to afford 6ξ-deuterio-9-dehydrofuranoeremophilane (**8**-d_1).

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