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NEW DAUCANE AND GERMACRANE ESTERS FROM *FERULA ORIENTALIS* VAR. *ORIENTALIS*

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ASTRACT.—Twelve sesquiterpenoid esters, including two new daucane and four new germacrane esters, were isolated from the roots of *Ferula orientalis* var. *orientalis*. Structures for all compounds were elucidated by spectral methods and chemical transformations.

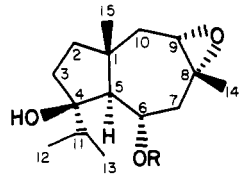
Ferula orientalis L. var. *orientalis* (Apiaceae), a medicinal plant (1) from the subgenus *Peucedanoides* (Boiss.) Korovin, is, according to Dioscorides, a source of "ammoniacum" (2), a well-known medicinal gum-resin. We previously reported a number of sesquiterpene esters from two other possible sources of "ammoniacum": *Ferula tingitana* L. (3-5) and *Ferula communis* L. ssp. *communis* (6,7). In continuation of our investigations of potential sources of "ammoniacum," we report here a series of daucane and germacrane alcohols esterified with vanillic and *p*-hydroxybenzoic acids, obtained from the C_6H_6 extract of the roots of *F. orientalis* var. *orientalis*.

RESULTS AND DISCUSSION

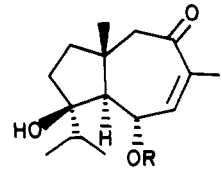
The known daucane esters were identified as jaeschkeanadiol *p*-hydroxybenzoate (8), jaeschkeanadiol vanillate (9), epoxyjaeschkeanadiol *p*-hydroxybenzoate [**1**] (10), and lancerodiol *p*-hydroxybenzoate [**3**] (10) by comparison of their spectral and physical data with those reported previously and, except for **3**, by comparison with authentic samples.

The ^{1}H-nmr spectrum of the new compound **2** (Table 1) showed close similarity to the spectrum of metabolite **1** except that it exhibited signals for a vanillate group instead of a *p*-hydroxybenzoate acyl moiety. The ir, uv, and mass spectra of **2** confirmed this difference. Finally, epoxidation of jaeschkeanadiol vanillate with *m*-CPBA proved **2** to be epoxyjaeschkeanadiol vanillate.

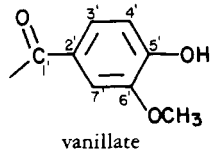
Except for different signals in their side chain acyl groups, the ^{1}H-nmr spectra of metabolites **3** and **4** were essentially identical (Table 1). Just as **2** differed from **1**, all



1 R=*p*-hydroxybenzoate
2 R=vanillate



3 R=*p*-hydroxybenzoate
4 R=vanillate



vanillate

TABLE 1. ^{1}H-nmr Spectra of **2** and **4**[a]

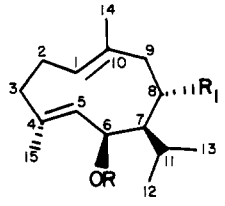
Proton	Compounds	
	2	**4**
H-5	2.28 d (11.3)	2.48 d (11)
H-6	5.43 dt (1.7; 11.3)	6.09 ddd (2; 2.4; 11)
H-7		6.19 dd (2; 2.4)
H-9	2.87 t (7.2)	
H-10a	2.25 dd (7.2; 14.2)	2.74 d (15.6)
H-10b	1.28 dd (7.2; 14.2)	2.62 d (15.6)
H-12	0.94 d (6.8)	0.97 d (6.8)
H-13	0.85 d (6.8)	0.85 d (6.8)
H-14	1.49 s	1.89 t (1.7)
H-15	1.26 s	1.26 s
H-3′	7.56 dd (1.9; 8.4)	7.69 dd (1.9; 8.4)
H-4′	6.94 d (8.4)	6.96 d (8.4)
H-7′	7.50 d (1.9)	7.58 d (1.9)
OCH_3	3.92 s	3.95 s

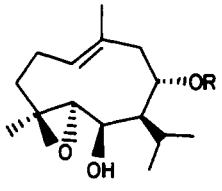
[a]δ ppm, *J* Values in Hz (in parentheses).

spectral data for **4** indicated that it contained a vanillate group in contrast to the *p*-hydroxybenzoate group of **3**. The structure of **4** is, thus, assigned as lancerodiol vanillate.

The known germacrane esters were identified as 8-*p*-hydroxybenzoyl-shiromodiol [**9**] and 8-vanilloyl-shiromodiol [**10**] by comparison of their spectral data with those recently reported for 8-angeloyl-shiromodiol (11,12). We present here full spectral data for **9** and **10** (see Tables 2 and 3, and Experimental section) because the previous report of these compounds from *Ferula rubroarenosa* Korovin (13) (also a member of the subgenus *Peucedanoides*) was based on limited data.

The eims of the new germacrane ester **5** exhibited a molecular ion at *m/z* 342 for a $C_{22}H_{30}O_3$ molecular formula. The presence of a *p*-hydroxybenzoyl acyl group in **5** was





5 R=*p*-hydroxybenzoate, R_1=H
6 R=vanillate, R_1=H
7 R=H, R_1=*p*-hydroxybenzoyloxy
8 R=H, R_1=vanilloyloxy

9 R=*p*-hydroxybenzoate
10 R=vanillate

TABLE 2. ^{1}H-nmr Spectra of **5-10**[a]

Proton	Compounds					
	5	**6**	**7**[b]	**8**	**9**[b,c]	**10**[b,c]
H-1	5.01 m	4.97 m	5.09 b d (10.6)	5.09 b d (10.6)	5.38 m	5.37 m
H-5	4.98 b d (7.6)	5.03 b d (7.6)	5.33 b d (7.6)	5.31 b d (5.6)	2.89 d (8)	2.85 d (8)
H-6	5.78 dd (1.7; 7.6)	5.78 dd (1.7; 7.6)	4.59 b d (7.6)	4.53 b d (5.6)	3.59 dd (2.3; 8)	3.56 dd (2.3; 8)
H-7			1.42 b d (10.5)	1.39 b d (10.7)	1.53 b d (10.2)	1.53 b d (10.2)
H-8			5.34 b dd (5.1; 6.8)	5.36 b dd (4.9; 6.5)	5.37 b	5.40 b dd (4.5; 12.4)
H-9a			2.62 dd (6.8; 13)	2.72 b dd (4.9; 12.8)	2.71 b dd (4.5; 12.2)	2.71 b dd 4.5; 12.2)
H-9b			2.18 dd (5.1; 13)	2.26 dd (6.5; 12.8)	2.30 t (12.2)	2.29 t (12.2)
H-11			1.64 dq (6.5; 10.5)	1.66 dq (6.5; 10.7)	1.86 dq (6.5; 10.2)	1.88 dq (6.5; 10.2)
H-12	0.99 d (6.6)	1.00 d (6.6)	1.14 d (6.5)	1.15 d (6.5)	1.19 d (6.5)	1.18 d (6.5)
H-13	0.96 d (6.6)	0.97 d (6.6)	1.03 d (6.5)	1.03 d (6.5)	0.96 d (6.5)	0.94 d (6.5)
H-14	1.58 s	1.62 s	1.71 b s	1.71 b s	1.81 b s	1.81 b s
H-15	1.58 s	1.60 s	1.49 s	1.48 d (0.8)	1.20 s	1.19 s
H-3′	7.87 d (8.7)	7.61 dd (1.9; 8.2)	7.90 dd (8.5)	7.62 dd (1.9; 8.4)	7.94 d (8.7)	7.65 dd (1.9; 8.3)
H-4′	6.87 d (8.7)	6.92 d (8.2)	6.86 d (8.5)	6.93 d (8.4)	6.88 d (8.7)	6.95 d (8.3)
H-6′	6.87 d (8.7)		6.86 d (8.5)		6.88 d (8.7)	
H-7′	7.87 d (8.7)	7.55 d (1.9)	7.90 d (8.5)	7.55 d (1.9)	7.58 d (8.7)	7.59 d (1.9)
OCH_3		3.92 s		3.93 s		3.95 s

[a]δ ppm, *J* Values in Hz (in parentheses).
[b]At 360 MHz.
[c]At 55°.

readily deduced from the spectral data (see Table 2 and Experimental section). Of the three degrees of unsaturation calculated for the sesquiterpene alcohol part of **5**, two could be accounted for by two carbon-carbon double bonds on the basis of ^{1}H-nmr data: a signal for two vinylic methyl groups appeared at δ 1.58 (6 H, br s, CH_3-14 and CH_3-15) and two vinylic proton signals appeared at δ 5.01 (H-1) and 4.98 (H-5). Therefore, the remaining degree of unsaturation must represent of carbocyclic ring. Because signals for the two isopropyl methyl doublets were present at δ 0.99 (CH_3-12) and 0.96 (CH_3-13) in addition to the above-mentioned endocyclic vinylic systems, a germacrane-type structure for **5** was suggested. Double resonance ^{1}H-nmr experiments involving the vinylic proton signal at δ 4.98 (1H, br, d, H-5) and the acyl geminal proton signal at δ5.78 (1H, br, dd, H-6) confirmed the presence of a large coupling between these protons, as well as the attachment of the acyl group at the C-6 position in metabolite **5**. The stereochemistry of the C-7 isopropyl group has been accepted as β in germacranes and biogenetically related sesquiterpenes based on Hendrickson's biogenetic rule (14-16), which has been confirmed by several X-ray crystallographic studies of germacranes and related sesquiterpenes including two shiromodiol esters (17,18). Consequently, the large coupling between H-6 and H-5 and the small coupling between H-6 and H-7α were used to determine a β stereochemistry for the C-6 acyl

TABLE 3. ^{13}C-nmr Data of **2**, **8**, and **9**[a]

Carbon Atom	Compounds		
	2	**8**	**9**
C-1	44.2 s	132.2 d	129.2 d
C-2	31.8 t	24.9 t	24.3 t
C-3	41.2 t	38.9 t	38.3 t
C-4	86.1 s	133.4 s	60.6 s
C-5	60.9 d	133.6 d	68.6 d
C-6	70.2 d	67.9 d	71.6 d
C-7	44.2 t	54.9 d	50.9 d
C-8	56.0 s	75.6 d	72.9 d
C-9	60.9 d	42.3 t	42.9 t
C-10	40.6 t	129.4 s	130.2 s
C-11	37.4 d	26.6 d	26.2 d
C-12	18.5 q	21.7 q	21.3 q
C-13	17.6 q	23.8 q	23.7 q
C-14	23.3 q	21.1 q	20.8 q
C-15	19.6 q	16.4 q	16.3 q
C-1′	166.0 s	167.8 s	168.4 s
C-2′	122.1 s	121.9 s	120.9 s
C-3′	124.1 d	124.2 d	115.8 d
C-4′	112.1 d	112.2 d	132.4 d
C-5′	146.2 s	146.5 s	162.0 s
C-6′	150.6 s	150.7 s	132.4 d
C-7′	114.3 d	114.5 d	115.8 d
OCH_3	56.1 q	56.1 q	

[a]δ ppm.

group in metabolite **5**. Spectral comparison of **5** with other esters of this same sesquiterpene alcohol, previously reported from species of *Verbesina* (Compositae) (19,20) and *Senecio* (Compositae) (21), support this assignment.

The spectral data for natural product **6** indicated the presence of the same sesquiterpene alcohol as in compound **5** but with a different acyl moiety that, from ^{1}H-nmr, data, was a vanillate group (see Table 2 and Experimental section).

The aromatic acyl groups of **7** and **8** were also determined as *p*-hydroxybenzoate and vanillate, respectively, by spectral data. The similarity of the ^{1}H-nmr spectra of **7** and **8** clearly indicated the presence of the same sesquiterpene alcohol in both compounds. Comparison of the ^{1}H- and ^{13}C-nmr data (Table 2 and 3) for **7** and **8** with those for 8-*p*-hydroxybenzoyl-shiromodiol [**9**] and 8-vanilloyl-shiromodiol [**10**] suggested that **7** and **8** should be the 4,5-vinylic analogues of **9** and **10**. Selective epoxidation of **8** to **10** with *m*-CPBA under alkaline conditions confirmed this assignment. Different esters of this same sesquiterpene alcohol [6β,8α-dihydroxy-germacra-1(10),4-dione=tovarol] were recently reported from *Thapsia villosa* (Apiaceae) (11).

The co-occurence of daucanes and germacranes, sesquiterpenes of different biogenetic origin (22,23), in one species is rare. In addition to *F. orientalis* var. *orientalis*, the combined occurrence of these similar compounds is only known from *F. rubroarenosa* (13) and *Ferula tenuisecta* Korovin (24). *F. orientalis*, together with *F. rubroarenosa* and *F. tenuisecta*, have been placed into the *ovina* complex of the *xeronarthex* section of the subgenus *Peucedanoides* by Korovin (25). The association of these particular sesquiterpene metabolites, daucanes and germacranes, in these three species supports this taxonomical classification.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—^{1}H-nmr and ^{13}C-nmr spectra were recorded in $CDCl_3$ using TMS as an internal standard on Nicolet NT-200 (at 200 MHz) and NT-360 (at 90 MHz), respectively (unless otherwise stated). Ms spectra were obtained on a DuPont 21-491 spectrometer with a direct inlet system at 70 eV. Optical rotations were measured with a Perkin-Elmer, Model 241 MC polarimeter.

PLANT MATERIAL.—The roots of *F. orientalis* var. *orientalis* were collected from the Ağri province of Eastern Anatolia, Turkey. A voucher specimen is deposited in the Herbarium of Dicle University, Diyarbakir, Turkey (DUF) (Herb. no. SAYA 83-172).

ISOLATION AND IDENTIFICATION OF THE COMPOUNDS.—Air-dried and coarsely powdered roots of *F. orientalis* var. *orientalis* (90 g) were extracted with C_6H_6 in a Soxhlet apparatus. Concentration of the C_6H_6 extract provided a viscous oil (15 g). This oil was chromtographed on a Si gel column (5×60 cm) packed in hexane and eluted with a hexane-EtOAc gradient. Further purification of the compounds employed Sephadex LH-20 columns packed in cyclohexane-CH_2Cl_2-EtOH (7:4:1) and preparative Si gel tlc (1.5-mm thickness, developed with cyclohexane-EtOAc mixtures, 7:3 and 3:2).

EPOXYJAESCHKEANADIOL VANILLATE [**2**].—15 mg (0.1% of extractables); $[\alpha]^{23}D+52.9°$ (*c* 1.4, $CHCl_3$); uv λ max (MeOH) 293, 263 nm; ir ν max (NaCl) 3520, 3400, 2960, 2940, 2855, 1700, 1610 (sh), 1598, 1513, 1460, 1428, 1382, 1280, 1110, 1100, 1032, 960, 932, 877, 850, 782, 763, 738, 700 cm^{-1}; eims *m/z* (% rel. int.) 404 $[M]^+$ (0.3), 361 [M-isoprop.]$^+$ (.7), 237 [M-vanillic acid+H]$^+$ (3.7), 218 [M-vanillic acid-H_2O]$^+$ (3.4), 193 (13.1), 175 (19.2), 168 [vanillic acid]$^+$ (70.3), 151 [vanillate]$^+$] (100).

EPOXIDATION OF JAESCHKEANADIOL VANILLATE.—Jaeschkeanadiol vanillate (40 mg) was dissolved in 5 ml $CHCl_3$; 30 mg *m*-CPBA were added gradually while stirring the solution. After 2 h the reaction mixture was diluted with 20 ml CH_2Cl_2, transferred to a separatory funnel and washed with 5% $NaHCO_3$ solution (3×20 ml). The CH_2Cl_2 solution was dried with anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield epoxyjaeshkeanadiol vanillate (38 mg), identical with **2** by physical and spectral properties.

LANCERODIOL VANILLATE [**4**].—Compound **4**: 8 mg (0.054% of extractables); uv λ max (MeOH) 292, 263 nm; ir ν max 3380, 3080, 2960, 1710 (sh), 1690, 1655, 1610 (sh), 1598, 1516, 1450, 1385, 1275, 1100, 875, 850, 780, 760, 738 cm^{-1}; eims *m/z* (% rel. int.) 402 $[M]^+$ (0.2), 329 [M-isoprop.]$^+$ (0.6), 234 [M-vanillic acid]$^+$ (10.9), 216 [M-vanillic acid-H_2O]$^+$ (2.5), 191 (32.2), 168 [vanillic acid]$^+$ (20.1), 163 (17.9), 151 [vanillate]$^+$ (100), 148 (45.9).

6-β-*p*-HYDROXYBENZOYLOXY-GERMACRA-1(10),4-DIENE [**5**].—Compound 5: 60 mg (0.4% of extractables); $[\alpha]^{23}D-45.5°$ (*c* 5, $CHCl_3$); uv λ max (MeOH) 308 (sh), 258 nm; ir ν max (NaCl) 3380, 3080, 2960, 1710 (sh), 1688, 1610, 1595, 1515, 1450, 1375, 1280, 1163, 1112, 1100, 850, 772, 738, 700 cm^-; eims *m/z* (% rel. int.) 342 $[M]^+$ (10.5), 220 [M-*p*-hydroxybenzoate-H]$^+$ (6.5), 204 [M-*p*-hydroxybenzoic acid]$^+$ (30.8), 185 (11.2), 138 [*p*-hydroxybenzoic acid]$^+$ (27.1), 121 [*p*-hydroxybenzoate]$^+$ (100), 105 (40).

6-β-VANILLOYLOXY-GERMACRA-1(10),4-DIENE [**6**].—Compound **6**: 26 mg (0.18% of extractions); uv λ max (MeOH) 293, 263, nm; ir ν max (NaCl) 3430, 3100, 2970, 2860, 1710, 1610 (sh), 1598, 1510, 1460, 1430, 1370, 1280, 1210, 1025, 875, 850, 780 (sh), 760, 735 cm^{-1}; eims *m/z* (% rel. int.) 372 $[M]^+$ (0.4), 220 [M-vanillate-H]$^+$ (14.9), 204 [M-vanillic acid]$^+$ (16.5), 189 (12), 177 (32.2), 168 [vanillic acid]$^+$ (58.3), 159 (28.1), 151 [vanillate]$^+$ (100), 121 (33.7), 119 (39.3), 105 (46.9).

8-*p*-HDROXYBENZOYL-TOVAROL [**7**].—Compound **7**: 35 mg (0.24% of extractables); $[\alpha]^{23}D-54.2°$ (*c* 24, $CHCl_3$); uv λ max (MeOH) 310 (sh), 259 nm; ir ν max (NaCl) 3350, 3080, 2960, 2870, 1710 (sh), 1680, 1610, 1595, 1515, 1450, 1280, 1165, 1125, 110), 970, 850, 773, 740, 700 cm^{-1}; eims *m/z* (% rel. int.) 358 $[M]^+$ (0.3), 236 [M-*p*-hydroxybenzoate-H]$^+$ (2.5), 220 [M-*p*-hydroxybenzoic acid]$^+$ (4.1), 202 [M-*p*-hydroxybenzoic acid-H_2O]$^+$ (20), 177 (7.1), 159 (15.5), 138 [*p*-hydroxybenzoic acid]$^+$ (11.5), 136 (13.2), 121 [*p*-hydroxybenzoate]$^+$ (100).

8-VANILLOYL-TOVAROL [**8**].—Compound **8**: 52 mg (0.35% of extractables); [**a**]$^{23}D-48.2$ (*c* 5, $CHCl_3$); uv λ max (MeOH) 293, 262 nm; ir ν max (NaCl) 3400, 3080,, 2970, 2930, 2870, 1710 (sh), 1685, 1610 (sh), 1595, 1515, 1460, 1430, 1370, 1280, 1220, 1110, 1035, 970, 875, 855, 835, 790, 768, 735 cm^{-1}; eims *m/z* (% rel. int.) 388 $[M]^+$ (0.8), 236 [M-vanillate-H]$^+$ (3.7), 220 [M-vanillic acid]$^+$ (8), 202 [M-vanillic acid]$^+$ (20), 177 (16.4), 168 [vanillic acid]$^+$ (55), 159 (32.5), 151 [vanillate]$^+$ (100), 136 (16.6), 121 (28.1).

EPOXIDATION OF **8**.—Compound **8** (20 mg) was reacted with *m*-CPBA (10 mg) in the presence of

NaOAc (10 mg) in 3 ml $CHCl_3$ for 1 h. Work up as previously specified gave 16 mg of 8-vanilloylshiromodiol, identical by physical and chemical properties with **10**.

8-*p*-HYDROXYBENZOYL-SHIROMODIOL [**9**].—Compound **9**: 45 mg (0.3% of extractables), uv λ max (MeOH) 308 (sh), 258 nm; ir ν max (NaCl) 3350,3080, 2970, 2930, 2870, 1710 (sh), 1680, 1610, 1610, 1593, 1515, 1440, 1372, 1278, 1235, 1163, 1115, 1100, 850, 820, 772, 738, 700 cm^{-1}; eims *m/z* (% rel. int.) 374 $[M]^+$ (0.4), 356 $[M-H_2O]^+$ (1.5), 236 [M-*p*-hydroxybenzoic acid]$^+$ (16.2), 218 [M-*p*-hydroxybenzoic acid-H_2O]$^+$ (38.1), 203 (2.1), 200 [M-*p*-hydroxybenzoic acid-2×H_2O]$^+$ (10.6), 193 (22.6), 175 (65.4), 160 (44.2), 147 (27.9), 138 [*p*-hydroxybenzoic acid]$^+$ (41.1), 136 (53.6), 121 [*p*-hydroxybenzoic acid]$^+$ (100), 107 (37.1).

8-VANILLOYL-SHIROMODIOL [**10**].—Compound **10**: 18 mg (0.12% of extractables); uv λ max (MeOH) 293, 263 nm; ir ν max (NaCl) 3420, 3080, 2970, 2930, 2875, 1710 (sh), 1680, 1610, 1598, 1613, 1460, 1428, 1380, 1290, 1225, 1110, 1030, 880, 860,, 825, 785, 765, 735 cm^{-1}; eims *m/z* (% rel. int.) 404 $[M]^+$ (0.5), 386 $[M-H_2O]^+$ (0.9), 236 [M-vanillic acid]$^+$ (3.2), 218 [M-vanillic acid-H_2O]$^+$ (12.2), 200 [M-vanillic acid-2×H_2O]$^+$ (9.5), 175 (31.5), 168 [vanillic acid]$^+$ (54.8), 160 (18.9) 151 [vanillate]$^+$ (100), 136 (47.5).

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