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SESQUITERPENE ESTERS AND SESQUITERPENE-COUMARIN ETHERS FROM *FERULA JAESKEANA*

T. K. RAZDAN*, B. QADRI, M. A. QURISHI, M. A. KHUROO and P. K. KACHROO

Phytochemistry Division, Centre of Research for Development, University of Kashmir, Naseem Bagh, Srinagar-190 006, India

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Key Word Index—*Ferula jaeskeana*; Umbelliferae; sesquiterpene alcohol esters; sesquiterpene-coumarin ethers.

Abstract—Five new sesquiterpene esters, together with the known esters of jaeskeanadiol, were isolated and characterized from the roots of *Ferula jaeskeana*. Two sesquiterpene-coumarin ethers were isolated for the first time from this plant.

INTRODUCTION

The genus *Ferula* is well documented as a source of sesquiterpene alcohol esters, most of which are aromatic esters of jaeskeanadiol. This sesquiterpene was first isolated and stereochemically characterized [1], as a free alcohol, from *F. jaeskeana*. The salicyloyl and angeloyl esters of this alcohol, together with 3-hydroxy-4,5-methylene-dioxypropiophenone, were reported from *F. elaeochytis* [2]. A new carotane-γ-lactone derivative has recently been isolated from *F. jaeskeana* [3]. There are several reports [4–8] on the presence of sesquiterpene-coumarin ethers, mostly derived from umbelliferone, in some species of the genus.

A reinvestigation of the chemistry of the roots of *F. jaeskeana* afforded five new sesquiterpene alcohol esters, designated as jaeskeanin (**1**), ferutinone (**2**), jaeskeanidin (**3**), ferutinianin (**4**) and angeloyl ferutinianin (**5**), in addition to the five known aromatic esters of jaeskeanadiol. Also two known sesquiterpene-coumarin ethers were isolated, for the first time, from these roots.

RESULTS AND DISCUSSION

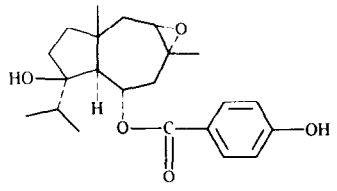
Extensive column chromatography and TLC of the ethyl acetate extract of the roots of *Ferula jaeskeana* afforded 12 compounds which were characterized mainly by spectroscopic methods, including off-resonance and decoupled ^{13}C NMR, some chemical transformations and comparison of the spectral data with literature [3, 9–12]. The UV, IR and ^{1}H NMR of the compounds showed that all, except one compound, carried an aromatic moiety.

The resemblances in the spectral patterns of compounds **1**–**10** suggested that they were structurally related with the differences residing in the nature or the position of their functional groups. The compounds were shown to be related to jaeskeanadiol (**10**) by the characteristic upfield methyl doublets in the ^{1}H NMR spectra centred at δ0.83–0.85 and 0.95–0.97 ($J=7$ Hz, H-13 and H-14). The ^{1}H NMR spectra also suggested that like jaeskeanadiol, all the compounds carried a hydroxyl at C-4. The IR and ^{13}C NMR data of compounds **1**–**9** revealed the presence of an ester function, δ_C 168.2–168.9, which was placed at the usual C-6 position on the basis of the chemical shift and multiplicity of the carbinylic proton, δ5.32–5.50 (1H, *t*, $J=3$, 10 Hz). The ^{1}H NMR spectra of compounds **2**–**10** contained the signal due to a vinylic proton at δ5.56 (1H, *t*, $J=6.5$–7 Hz, H-9) showing the presence of a trisubstituted double bond as in compound **10**. This was further confirmed by the ^{13}C NMR data (Table 1) of compounds **2**–**5**. Further information about the structures of the compounds was derived from a detailed study of their ^{1}H NMR and mass spectra.

Compound **1**, $[M]^+$ at *m/z* 374.1976, $C_{22}H_{30}O_5$, was shown to possess an epoxy function IR ν_{max}^{KBr} cm^{-1}: 3040, 1250, 870. Its ^{1}H NMR spectrum contained no signal due to the vinylic proton. Instead, a single proton resonance signal at δ3.39 (*dd*, $J=9.8$, 6 Hz) suggested the presence of an epoxy function situated, most probably, between C-8 and C-9. This was substantiated by the small downfield shift of the resonance signal due to H-11 to δ1.36, as compared to **10**, and the ^{13}C NMR signals at δ_C 57.2 (*s*) and 58.2 (*d*). In the downfield region, the ^{1}H NMR spectrum of the compound accounted for only four aromatic protons. The mass spectrum of the compound showed the base peak at *m/z* 121, due to the ester moiety and a prominent peak at *m/z* 137, indicating that the aromatic moiety carried only one hydroxyl. The chemical shift and multiplicity of aromatic protons suggested that compound **1** carried a *p*-hydroxybenzoic acid moiety. Other prominent peaks in the MS were observed at *m/z* 356, 331, 253, 237, 236 and 191. To confirm the presence of the epoxy function, **1** was treated with boron trifluoride-ethereate to yield a mixture from which the major product was recovered by column chromatography. It was directly acetylated with pyridine–acetic anhydride, resulting in the formation of two products, the major being a diacetate (**12**), in which the acetoxyls, δ2.03 and 2.05 (3H each, *s*), were shown to be secondary in nature by the presence of the carbinylic proton signals at δ5.10 (1H, *t*, $J=3$, 10 Hz, H-6) and δ4.16 (1H, *br q*, $J=10$, 3 Hz, H-9). The compound was thus characterized as 8,9-epoxyferutinin. The compound is reported for the first time in nature.

*Author to whom correspondence should be addressed.

Compound **2**, $[M]^+$ at *m/z* 372.1969, $C_{22}H_{28}O_5$, exhibited IR absorptions at ν_{max}^{KBr} cm^{-1}: 1685 and 1705, suggesting the presence of two carbonyls, one of which was probably a ring carbonyl. Its ^{1}H NMR spectrum contained a two proton broad doublet at δ2.62 (J = 10 Hz) due to the methylene protons adjacent to the carbonyl group. The ^{13}C NMR signals at δ_C 168.3 and 217.3 confirmed the presence of an ester and a ring carbonyl in the compound. In the downfield region, the ^{1}H NMR spectrum accounted for four protons of the *p*-hydroxybenzoic acid moiety. Its presence in the compound was further confirmed by the mass spectrum of **2** which contained the base peak at *m/z* 121 and a prominent peak at *m/z* 137.



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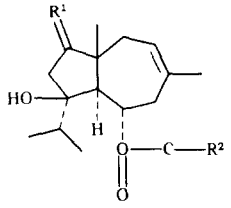

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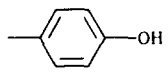
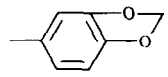
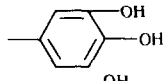
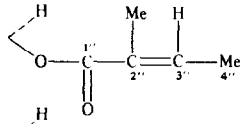
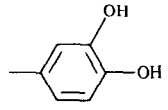
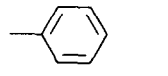
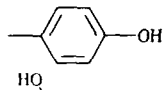
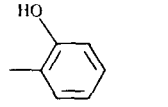
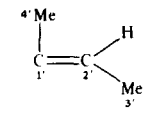
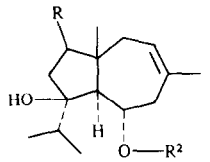
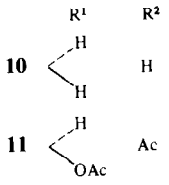
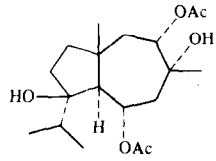
2	O	
3		
4		
5		
6		
7		
8		
9		





10 R^1 = H, R^2 = H

11 R^1 = H, R^2 = Ac



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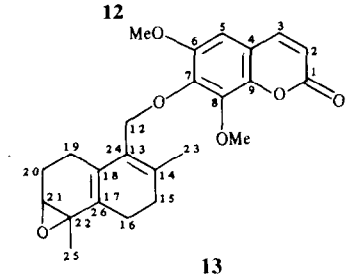

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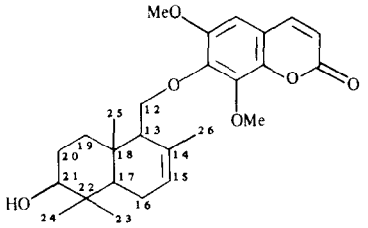

14

As the resonance signal due to the C-15 methyl of the compound was downfield at δ1.91 and there was no observed shift in the resonance signals of the vinylic and the ester carbinylic proton, as compared to ferutinin (**7**) [11], the position of the carbonyl was fixed at C-2. On reduction with lithium aluminium hydride and subsequent acetylation compound **2** formed a hydroxy diacetate (**11**), IR ν_{max}^{KBr} cm^{-1}: 3410 (OH), 1710, 1720 (ester carbonyls), in which the acetoxyls at δ2.03 and 2.05 (3H each, *s*), were shown to be secondary in nature by the carbinylic proton signals at δ4.90 (1H, *m*, H-2) and 5.12 (1H, *t*, J = 10, 3 Hz, H-6). The compound was thus identified as ferutinin-2-one.

Compound **3** $[M]^+$ at *m/z* 386.2094, $C_{23}H_{30}O_5$, in its ^{1}H NMR revealed a two proton singlet at δ6.08 and only three aromatic proton signals, in addition to other signals exhibited by compound **7**. This indicated the presence of a methylenedioxy group, δ_C 100.5 (-O-CH_2-O-), in the acylium moiety which was confirmed by the base peak at *m/z* 151 and the prominent peak at *m/z* 167, in the mass spectrum of the compound. The chemical shift, multiplicity and coupling constants of the aromatic protons (see Experimental) revealed the presence of 3',4'-methylenedioxybenzoic acid moiety in the compound. On hydrolysis, with 5% aq. potassium hydroxide, compound **3** gave jaeskeanadiol (**10**).

Compound **4**, $[M]^+$ at *m/z* 374, 1979, $C_{22}H_{30}O_5$, showed a close resemblance to the compound **3** in its

upfield ^{1}H NMR region. In the downfield region, the spectrum accounted for only three aromatic protons. The mass spectrum of the compound contained the base peak at *m/z* 137 and a prominent peak at *m/z* 153, which together with the multiplicity and coupling constant of the aromatic proton resonance signals confirmed the presence of 3′,4′-dihydroxybenzoic acid moiety in **4**. The compound on heating with acetone–potassium carbonate gave compound **3**, thus confirming that **4** was the 3′,4′-dihydroxybenzoic acid ester of **10**.

Compound **5**, $[M]^+$ at *m/z* 472.4795, $C_{27}H_{36}O_7$, was shown to be a diester, IR ν_{max}^{KBr} cm^{-1}: 1710, 1730. Its ^{1}H NMR spectrum contained all the signals exhibited by compound **4** with additional signals at δ2.00 and 2.04 (3H each, *s*), and 6.13 (1H, *q*, *J* = 7.5, 7.5 Hz) corresponding to an angeloyl moiety. The carbinylic proton geminal to the angeloyl group resonated at δ4.50 (1H, *m*). The presence of the angeloyl group was confirmed by the strong MS peak at *m/z* 83, due to the angelate acylium ion. The MS exhibited a base peak fragment at *m/z* 137 with a prominent peak at *m/z* 153, due to the 3″,4″-dihydroxybenzoate acylium ion. The downfield chemical shift of the C-15 methyl resonance signal, δ1.57 (3H, *s*), together with the absence of a shift in the vinylic and the ester carbinylic proton signals fixed the position of the angelate function at C-2. The ^{13}C NMR data (Table 1) agreed well with structure **5**.

Compounds **6**–**10** were characterized as teferidine (**6**), ferutinin (**7**), jaeskeanadiol salicylate (**8**), jaeskeanadiol angelate (**9**) and jaeskeanadiol (**10**) by comparing their spectral data with the literature [**3**, **8**–**12**].

Compounds **13** and **14** were found to be coumarins by their colour reaction with alkaline hydroxylamine followed by ferric chloride [13], and their UV and IR absorptions [14]. The downfield ^{1}H NMR spectral patterns of the compounds were identical. The spectra exhibited two doublets near δ6.33 and 7.59 (*J* = 9.5 Hz) due to H-2 and H-3, and a singlet near δ6.65, due to H-5 suggesting that the compounds were 6,7,8-trisubstituted coumarins. The presence of two methoxyls in both the compounds was evident from the resonance signals close to δ3.87 and 4.00 (3H, each, *s*). The information regarding the sesquiterpene moieties was gathered from a detailed study of the ^{1}H NMR and MS of the compounds and was substantiated by ^{13}C NMR.

Compound **13**, $[M]^+$ at *m/z* 442.2360, $C_{26}H_{34}O_6$, in its ^{1}H NMR spectrum showed the presence of two trisubstituted double bonds, δ5.54 (1H, *br t*, *J* = 7 Hz, H-13) and 5.13 (1H, *br t*, J = 7.5 Hz, H-17), an oxymethylene group, δ4.66 (2H, ABq, *J* = 7 Hz), and two vinylic methyls, δ1.69 and 1.60 (3H each *s*, H-23 and H-24). The spectrum contained a six proton multiplet at δ2.00–2.12, attributable to the allylic methylene protons, and two methyl singlets at δ1.25 and 1.29. A single proton triplet at δ2.69 (*J* = 7 Hz) could be assigned to a proton of an epoxide ring. The mass spectrum contained the base peak at *m/z* 222 with prominent peaks at *m/z* 220 and 205 indicating that the ether-*O*-*C*(aryl) bond was cleaved followed by

Table 1. ^{13}C NMR spectral data of compounds **1**–**5** and **10** (δ_C: ppm)

C	1	2	3	4	5	10
1	45.3	43.2	45.2	45.2	43.7	45.2
2	32.8	217.3	32.3	32.4	75.5	32.3
3	41.2	40.3	42.1	42.2	40.3	42.1
4	87.2	87.5	87.5	87.5	87.5	87.1
5	37.3	36.2	36.1	36.2	36.1	36.1
6	79.3	79.3	79.8	79.8	79.2	67.9
7	39.2	42.4	42.2	42.2	43.0	43.0
8	57.2	133.9	133.6	133.6	133.4	133.6
9	58.2	129.4	129.3	129.3	128.2	129.1
10	38.1	41.8	41.2	41.4	40.3	41.2
11	29.1	29.7	29.3	29.3	29.2	27.7
12	61.9	61.9	61.7	61.7	61.6	61.9
13	17.2	17.2	17.3	17.2	17.4	17.2
14	18.4	18.4	18.4	18.5	18.5	18.4
15	19.7	29.9	19.8	19.8	18.2	19.8
1′	147.2	147.2	147.2	147.0	147.0	—
2′	128.7	128.7	112.2	116.2	116.2	—
3′	109.5	109.5	132.1	132.1	132.2	—
4′	147.1	147.1	149.1	133.2	133.2	—
5′	113.2	113.2	101.8	104.1	104.1	—
6′	127.9	127.9	101.8	101.8	101.8	—
Ester C=O	168.2	168.3	168.9	168.7	168.7	—
O-CH_2-O	—	—	100.5	—	—	—
Ester C=O	—	—	—	—	165.8	—
1″	—	—	—	—	126.3	—
2″	—	—	—	—	141.1	—
3″	—	—	—	—	25.6	—
4″	—	—	—	—	30.2	—

loss of a methyl radical. The upfield and chemical shift of the terminal methyl protons and of H-20 and H-21, as compared to those of isofraxidin [15, 16], indicated that the epoxide was at the terminal bond. The spectral evidence, including the ^{13}C NMR shifts, were in agreement with those reported for epoxyfarnochrol [17].

Compound **14**, $[M]^+$ at *m/z* 442.2358, $C_{26}H_{34}O_6$, in its ^{1}H NMR spectrum exhibited resonance signal for only one vinylic proton and a vinylic methyl at δ5.54 (1H, *br* ill defined *t*, $W_{\frac{1}{2}}=9$ Hz) and 1.80 (3H, *s*), respectively. The spectrum contained signals for three methyls at δ0.92, 1.00 and 1.04, a carbinylic proton at δ3.36 (1H, *t*, $J\simeq9.4$ Hz, H-21) and a -CH_2-O-group at δ3.90 and 4.15 (2H, ABq, $J=10$ Hz). The mass spectrum exhibited the base peak at *m/z* 222 which represented the coumarin moiety. The information on the terpenoid moiety was derived from the prominent peak at *m/z* 203. This confirmed that the fragmentation took place at the -O−C terpenic bond. The mass fragmentation revealed that the terpene moiety was bicyclic in nature. The ^{1}H NMR spectral pattern was characteristic of a drimanol [18]. The spectral data, including the ^{13}C NMR, agreed well with that reported for drimatol-B [18] isolated from *Achillea orchroleuca*. This is the first report on the presence of isofraxidin ethers in the genus *Ferula*.

EXPERIMENTAL

^{1}H NMR: 60, 90 or 250 MHz, $CDCl_3$, with TMS as int. standard; ^{13}C NMR: 62.89 MHz; HRMS at 70 eV.

The air-dried roots of the plant, collected fresh from Gulmarg (Voucher no: 003725), were extracted with hot EtOAc. The extract was exhaustively chromatographed on silica gel and $AgNO_3$–silica gel columns, using solvent gradients of petrol–C_6H_6, C_6H_6, C_6H_6–EtOAc. The fractions collected were monitored by TLC on silica gel G. The crystalline compounds were purified by crystallization.

Jaeskeanin (**1**). Mp 83–85°, $[M]^+$ at *m/z* 374. 1970 (Calcd. for $C_{22}H_{30}O_5$ 374.4782). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 2960, 2855, 1705 (ester C=O), 3040, 1250, 870 (epoxy), 1645, 1450, 1270, 1150, 940, 705; ^{1}H NMR, (90 MHz) $CDCl_3$: δ0.85 (3H, *d*, $J=7$ Hz, H-14), 0.94 (3H, *d*, $J=7$ Hz, H-13), 1.36 (3H, *br s*, H-11), 1.87 (3H, *s*, H-15), 2.40 (2H, *dd*, $J=11$, 9 Hz, H-10), 3.39 (1H, *dd*, $J=9.8$, 6 Hz, H-9), 5.40 (1H, *t*, $J=3$, 10 Hz, H-6), 6.8 (2H, *d*, $J=8$ Hz, H-3′ and H-5′), 7.8 (2H, *d*, $J=8$ Hz, H-2′ and H-6′). MS *m/z*: 374 $[M]^+$, 359 $[M-Me]^+$, 356 $[M-H_2O]^+$, 331 $[M-C_3H_7]^+$, 253 $[M-C_7H_5O_2]^+$, 237 $[M-C_7H_5O_3]^+$, 236 $[M-C_7H_6O_3]^+$, 137 $[C_7H_5O_3]^+$, 121 (100%) $[C_6H_5OCO]^+$, 193, 165, 53, 43 and 28.

Ferutionone (**2**). Mp 93–94°, $[M]^+$ at *m/z* 372. 1969 (Calc. for $C_{22}H_{28}O_5$ 372.4624) IR ν_{max}^{KBr} cm^{-1}: 3410 (OH), 1685 (C=O), 2960, 2860, 1705 (ester C=O), 1645, 1440, 1260, 1145, 940; ^{1}H NMR (60 MHz), $CDCl_3$: δ0.85 (3H, *d*, $J=7$ Hz, H-14), 0.95 (3H, *d*, $J=7$ Hz, H-13), 1.54 (3H, *s*, H-11), 1.91 (3H, *s*, H-15), 2.62 (2H, *br d*, $J=10$ Hz, H-3), 5.56 (1H, *t*, $J=6.5$ Hz, H-9), 5.32 (1H, *t*, $J=10$, 3 Hz, H-6), 6.8 (2H, *d*, $J=8$ Hz, H-3′ and H-7′), 7.8 (2H, *d*, $J=8$ Hz, H-2″ and H-6′): MS *m/z*: 372 $[M]^+$, 354 $[M-H_2O]^+$, 329 $[M-C_3H_7]^+$ 234 $[M-C_7H_5O_2]^+$ 191 $[M-C_7H_5O_2-C_3H_7]^+$, 163 $[M-C_7H_5O_2-C_3H_7-CO]^+$, 137 $[C_7H_5O_3]^+$, 135 $[163-CO]^+$ 121 (100%, $[C_7H_5O_2]$)$^+$, 107, 93, 77, 55, 28.

Jaeskeanidin (**3**). Mp 123–124°, $[M]^+$ at *m/z* 386.2094 (Calcd. for $C_{23}H_{30}O_5$ 386.4893). IR ν_{max}^{KBr} cm^{-1}: 3405 (OH), 2900, 1680 (ester C=O), 1845, 1680, 1640, 1270, 1170, 720; ^{1}H NMR (90 MHz) $CDCl_3$: δ0.85 (3H, *d*, $J=7$ Hz, H-14), 0.94 (3H, *d*, $J=7$ Hz, H-13), 1.16 (3H, *br s*, H-15), 1.91 (3H, *s*, H-11), 5.32 (1H, *t*, $J=10$, 3 Hz, H-6) 5.56 (1H, *t*, $J=6$, 5 Hz, H-9) 6.08 (2H, *s*, -CH_2-), 7.35 (1H, *d*, $J=3.5$ Hz, H-2′), 7.68 (1H, *t*, $J=7$, 2.5 Hz, H-6′), 8.02 (1H, *d*, $J=7$ Hz, H-5′); MS *m/z*: 386 $[M]^+$, 368 $[M-H_2O]^+$, 353 $[M-H_2O-Me]^+$, 343 $[M-C_3H_7]^+$, 310 $[M-H_2O-C_3H_7-Me]^+$, 161 $[310-C_8H_5O_3]^+$, 149 (100%) $[C_8H_5O_3]^+$, 121, 119, 91, 28.

Ferutinianin (**4**). Mp 193–195°, M^+ at *m/z* 374.1979 (Calcd. for $C_{22}H_{30}O_5$ 374.4782). IR ν_{max}^{KBr} cm^{-1}: 3410 (OH), 2960, 2860, 1705, 1645, 1450, 1270, 1150, 940. UV λ_{max}^{EtOH} nm: 275 (Sh), 260, 240, 210; ^{1}H NMR (250 MHz) $CDCl_3$: δ0.83 (3H, *d*, $J=7$ Hz, H-13), 0.97 (3H, *d*, $J=7$ Hz, H-14), 1.12 (3H, *s*, H-15), 1.89 (3H, *s*, H-11), 5.32 (1H, *t*, $J=10$, 3 Hz, H-6), 5.56 (1H, *t*, $J=7$ Hz, H-9), 7.20 (1H, *d*, $J=8$ Hz, H-5), 7.9 (2H, *d*, $J=8$ Hz, H-2′, H-6′), 4.98 (3H, *br s*, exch.D_2O, 3 × OH); MS *m/z*: 374 $[M]^+$, 356 $[M-H_2O]^+$, 331 $[M-C_3H_7]^+$, 313 $[M-C_3H_7-H_2O]^+$, 237 $[M-C_7H_5O_3]^+$, 219 $[M-C_7H_5O_3-H_2O]^+$, 193 $[M-C_7H_5O_3-C_3H_7]^+$, 153 $[C_7H_5O_4]^+$, 137 $[C_7H_5O_3]^+$, 109 $[C_7H_5O_2]^+$, 55, 43, 28.

Angeloylferutinianin (**5**). Mp 210–212°, M^+ at *m/z* 472.4795 (Calcd, for $C_{27}H_{36}O_7$, 472.5799). UV λ_{max}^{EtOH} nm: 280 (Sh.), 260, 240; IR ν_{max}^{KBr} cm^{-1}: 3410, 3425 (OH), 2960, 2860, 1730 (ester C=O), 1710 (ester C−O) 1645, 1440, 1270, 1150, 940 and 820; ^{1}H NMR (250 MHz) $CDCl_3$: δ0.85 (3H, *d*, $J=7$ Hz, H-13), 0.97 (3H, *d*, $J=7$ Hz, H-14), 1.57 (3H, *s*, H-15), 1.91 (3H, *s*, H-11), 2.00 (3H, *s*, H-4″), 2.04 (3H, *s*, H-5″), 2.20 (1H, *dd*, $J=10$ Hz, H-5), 2.45 (2H, *dd*, $J=9.4$ Hz, H-3), 4.50 (1H, *m*, H-2), 5.32 (1H, *t*, $J=10$, 3 Hz, H-6), 5.56 (1H, *t*, $J=6.5$ Hz, H-9), 6.13 (1H, *q*, $J=7.5$ Hz, H-3″), 7.20 (1H, *d*, $J=8$ Hz, H-5″), 7.9 (2H, *d*, $J=8$ Hz, H-2″). MS *m/z*: 472 $[M]^+$, 454 $[M-H_2O]^+$, 429 $[M-C_3H_7]^+$, 389 $[M-C_5H_7O]^+$, 372 $[M-C_5H_7O_2]^+$, 335 $[M-C_7H_5O_3]^+$, 318 $[M-C_7H_5O_4]^+$, 248 $[M-C_7H_5O_4-C_5H_7O]^+$, 232 $[M-C_7H_5O_4-C_5H_7O_2]^+$ 214 $[M-C_7H_5O_4-C_5H_7O_2-H_2O]^+$, 153 $[C_7H_5O_4]^+$, 137 $[C_7H_5O_2]^+$, 109 $[C_7H_5O_2-CO]^+$, 99 $[C_5H_7O_2]^+$, 53, 28.

Teferidine (**6**). $[M]^+$ at *m/z* 342.3580 (Calcd. for $C_{22}H_{30}O_3$, 342.5794). UV λ_{max}^{MeOH} nm: 280, 250; IR ν_{max}^{KBr} cm^{-1}: 3360 (OH), 2980, 2870, 1670, 1610, 1585, 1375, 1295, 1235, 1160, 1095, 950 and 750; ^{1}H NMR (60 MHz) $CDCl_3$: δ0.85 (1H, *d*, $J=7$ Hz, H-14), 0.96 (1H, *d*, $J=7$ Hz, H-13), 1.12 (3H, *s*, H-15), 1.85 (3H, *s*, H-11), 5.32 (1H, *t*, $J=10$, 3 Hz, H-6), 5.56 (1H, *t*, $J=6.5$ Hz, H-9), 7.46 (2H, *t*, $J=2$, 9 Hz, H-2′ and H-6′), 7.60 (1H, *t*, $J=2$, 9 Hz. H-4′). 8.03 (2H, *d*, $J=2$, 9 Hz, H-3′ and H-5′); MS *m/z*: 342 $[M]^+$, 324 $[M-H_2O]^+$, 299 $[M-C_3H_7]^+$, 237 $[M-C_7H_5O]^+$, 221 $[M-C_7H_5O_2]^+$, 219 $[M-H_2O-C_7H_5O]^+$, 194 $[M-C_3H_7-C_7H_5O]^+$, 121 $[C_7H_5O_2]^+$, 105 $[C_7H_5O]^+$, 77 $[C_7H_5O-CO]^+$, 45, 28.

Ferutinin (**7**). M^+ at *m/z* 358.3798 (Calcd. for $C_{22}H_{30}O_4$, 358.4788). UV λ_{max}^{MeOH} nm: 325, 280, 250; IR ν_{max}^{KBr} cm^{-1}: 3450 (OH), 3360 (OH), 2970, 2870, 1670, 1610, 1580, 1370, 1295, 1230, 1160 and 950; ^{1}H NMR (60 MHz) $CDCl_3$: δ0.83 (3H, *d*, $J=7$ Hz, H-14), 0.96 (1H, *d*, $J=7$ Hz, H-13), 1.12 (3H, *s*, H-15), 1.85 (3H, *s*, H-11), 5.32 (1H, *t*, $J=10$, 3 Hz, H-6), 5.56 (1H, *t*, $J=6$, 5 Hz, H-9), 6.8 (2H, *d*, $J=8$ Hz, H-2′ and H-6′), 7.8 (2H, *d*, $J=8$ Hz, H-3′ and H-5′); MS *m/z*: 358 $[M]^+$, 340 $[M-H_2O]^+$, 315 $[M-C_3H_7]^+$, 237 $[M-C_7H_5O_2]^+$, 221 $[M-C_7H_5O_3]^+$, 219 $[M-C_7H_5O_2-H_2O]^+$, 203 $[M-C_7H_5O_3-H_2O]^+$, 194 $[M-C_7H_5O_2-C_3H_7]^+$, 121 (100%) $[C_7H_5O_2]^+$, 93 $[C_7H_5O_2-CO]^+$.

Jaeskeanadiol salicylate (**8**). Mp 210–213°, $[M]^+$ at *m/z* 358.3825 (Calcd. for $C_{22}H_{30}O_4$, 358.4788). UV λ_{max}^{MeOH} nm: 340, 280, 249, 220; IR ν_{max}^{KBr} cm^{-1}: 3470 (OH), 3360 (OH), 2980, 2880, 1680, 1610, 1585, 1550, 1375, 1235, 1160, 950, 750 and 700; ^{1}H NMR (250 MHz) $CDCl_3$: δ0.85 (1H, *d*, $J=7$ Hz, H-14), 0.96 (1H, *d*, $J=7$ Hz, H-13), 1.12 (3H, *s*, H-15), 1.85 (3H, *s*, H-11), 5.32 (1H, *t*, $J=3$, 10 Hz, H-6), 5.56 (1H, *t*, $J=6.5$ Hz, H-9) 7.07 (1H, *dt*, $J=2$, 8 Hz, H-4′), 7.52 (1H, *dt*, $J=2$, 8 Hz, H-5′), 7.94 (1H, *dd*, $J=2$, 9 Hz, H-3′), 8.65 (1H, *dd*, $J=2$, 9 Hz, H-6′); MS *m/z*: 358 $[M]^+$, 340 $[M-H_2O]^+$, 315 $[M-C_3H_7]^+$, 220 $[M-C_7H_5O_2$

$-H_2O]^+$, 202 $[M-C_7H_5O_2-2\times H_2O]^+$, 137 $[C_7H_5O_3-1]^+$, 121 $[C_7H_5O_2]^+$.

Jaeskeanadiol angelate (**9**). Oil, molecular ion peak not observed, but a peak at *m/z* 277 corresponding to $[M-C_3H_7]^+$ present. IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 2960, 2860, 1705 (ester C=O), 1645, 1450, 1270, 1150, 1030 and 940; ^1H NMR (90 MHz): $CDCl_3$: δ0.85 (3H, *d*, *J* = 7 Hz, H-13), 0.96 (3H, *d*, *J* = 7 Hz. H-14), 1.12 (3H, *s*, H-15), 1.85 (3H, *s*, H-11), 2.00 (3H, *s*, H-4′), 2.04 (3H, *s*, H-3′), 5.32 (1H, *t*, *J* = 3, 10 Hz, H-6), 5.56 (1H, *t*, *J* = 6.5 Hz, H-9′), 6.13 (1H, *dq*, *J* = 7.5 Hz, H-2′); MS *m/z* 277 $[M-C_3H_7]^+$, 220 $[M-C_5H_7O-H_2O]^+$, 202 $[M-C_5H_7O-2\times H_2O]^+$, 177 $[M-C_3H_7-H_2O]^+$, 83 $[C_5H_7O]^+$.

Jaeskeanadiol (**10**). $[M]^+$ at *m/z* 238, $C_{15}H_{26}O_2$. IR ν_{max}^{KBr} cm^{-1}: 3500 (OH), 1270 and 940; ^1H NMR (60 MHz) $CDCl_3$: δ0.85 (3H, *d*, *J* = 7 Hz, H-13), 0.96 (3H, *d*, *J* = 7 Hz, H-14), 1.12 (3H, *s*, H-15), 1.85 (3H, *s*, H-11), 3.92 (1H, *t*, *J* = 3, 10 Hz, H-6), 5.56 (1H, *t*, *J* = 6.5 Hz, H-9); MS *m/z*: 238 $[M]^+$, 220 $[M-H_2O]^+$, 202 $[M-2\times H_2O]^+$, 177 $[M-C_3H_7-H_2O]^+$.

Reduction and acetylation of **2**. Compound **2** (0.03 g) in 15 ml Et_2O was treated with 0.01 g $LiAlH_4$ at room temp. After usual work-up an oily product was recovered with Et_2O and subjected to acetylation with Ac_2O–pyridine, at room temp. After removing the pyridine the product was recovered with EtOAc. TLC showed it to be a mixture of 4 compounds. The mixture was chromatographed over silica gel when petrol–C_6H_6 (7:3) afforded a major product **11** (0.020 g) $[M]^+$ at *m/z* 322.4025, $C_{19}H_{30}O_4$, IR ν_{max}^{KBr} cm^{-1}: 3410 (OH), 1730, 1720 (ester carbonyls); ^1H NMR (60 MHz): $CDCl_3$: δ0.85 (3H, *d*, *J* = 7 Hz, H-13), 0.96 (3H, *d*, *J* = 7 Hz, H-14), 1.36 (3H, *s*, H-15), 1.85 (3H, *s*, H-11), 2.03 (3H, *s*, OAc), 2.05 (3H, *s*, OAc), 4.90 (1H, *m*, H-2), 5.12 (1H, *t*, *J* = 10.3 Hz, H-6) 5.56 (1H, *t*, *J* = 6.5 Hz, H-9); MS *m/z*: 322 $[M]^+$, 304 $[M-H_2O]^+$, 279 $[M-C_3H_7]^+$ 262 $[M-HOAc]^+$, 202 (100%), $[M-2\times HOAc]^+$, 184 $[M-2\times HOAc-H_2O]^+$, 166 $[M-2\times HOAc-2\times H_2O]^+$, 144 $[M-2\times HOAc-C_3H_7]^+$.

Hydrolysis of **1**. Compound 1 (0.25 g) in Et_2O was treated with BF_3-ethereate, at room temp. After allowing the reaction mixture to stand overnight, the product was treated with H_2O and isolated with EtOAc. The mixture thus obtained, on chromatography over silica gel afforded a major product which was acetylated with pyridine–Ac_2O, at room temp. for 36 hr. After usual work-up a binary mixture was recovered. The mixture was resolved by prep. TLC on silica gel (C_6H_6–EtOAc, 7:3) to afford the major product **12**, $[M]^+$ at *m/z* 356.4530 (Calcd for $C_{19}H_{32}O_6$, 356.4601). ^1H NMR (60 MHz) $CDCl_3$: δ0.85 (3H, *d*, *J* = 7 Hz, H-13), 1.00 (3H, *d*, *J* = 7 Hz, H-14), 1.12 (3H, *s*, H-15), 1.43 (3H, *s*, H-11), 2.03 (3H, *s*, OAc), 2.05 (3H, *s*, OAc), 2.89 (2H, *br*, *s*, exch, D_2O, 2 × OH), 4.16 (1H, *br q*, *J* = 10, 3 Hz, H-9), 5.10 (1H, *t*, *J* = 10, 3 Hz, H-6); MS: *m/s* at 356 $[M]^+$, 338 $[M-H_2O]^+$, 320 $[M-2\times H_2O]^+$, 297 $[M-H_2O-2\times HOAc]^+$, 176 $[M-H_2O-2\times HOAc-C_3H_7]^+$, 43 (100%) $[C_3H_7]^+$.

Epoxyfarnachrol (**13**). $[M]^+$ at *m/z* 442.2360 (Calcd for $C_{26}H_{34}O_6$ 442.5536), $[\alpha]_D^{20}$ −9° (Me_2CO; *c* 0.7). IR ν_{max}^{KBr} cm^{-1}: 2960, 2940, 1745, 1560, 1485, 1420, 1375, 1290, 1195, 1125, 1080, 940 and 820; UV λ_{max}^{MeOH} nm: 339 (Sh), 297, 226, 207; ^1H NMR (250 MHz) $CDCl_3$: δ1.25 (3H, *s*, H-25), 1.29 (3H, *s*, H-26), 1.58 (2H, *m*, H-20), 1.60 (3H, *br s*, H-24), 1.69 (3H, *br s* H-23), 2.00–2.12 (6H, *m*, H-19, H-16 and H-15), 2.69 (1H, *t*, *J* = 7 Hz, H-21), 3.88 (3H, *s*, OMe), 4.02 (3H, *s*, OMe), 4.66 (2H, ABq, *J* = 7 Hz, H-12), 5.13 (1H, *t*, *br*, *J* = 7.5 Hz, H-17), 5.54 (1H, *t*, *J* = 7 Hz, H-13), 6.33 (1H, *d*, *J* = 9.5 Hz, H-2), 6.66 (1H, *s*, H-5). 7.62 (1H, *d*, *J* = 9.5 Hz, H-3); MS *m/z*: 442 $[M]^+$, 223, 222 (100%), 221, 220, 215, 207, 205, 173, 149, 128, 199, 115, 109, 107, 105, 97, 93; ^{13}C NMR ($CDCl_3$): δ_C160.5 (C-1), 115.3 (C-2), 143.5 (C-3). 114.5 (C-4), 103.8 (C-5), 150.7 (C-6), 145.1 (C-7), 141.9 (C-8) 143.2 (C-9), 56.4 (C-10), 61.7 (C-11), 70.3 (C-12), 119.9 (C-13) 142.3 (C-14), 39.6 (C-15), 26.3 (C-16), 124.4 (C-17), 134.6 (C-18), 346 (C-19), 27.6 (C-20), 64.2 (C-21), 58.2 (C-22), 16.4 (C-23), 16.0 (C-24), 24.9 (C-25), 18.8 (C-26).

Drimatrol B (**14**). Mp 148–149° [lit. mp 145–146°]. $[M]^+$ at *m/z* 442.2350 (Calcd for $C_{26}H_{34}O_6$ 442.5556). UV λ_{max}^{MeOH} nm 338 (sh) 297, 227, 207; IR ν_{max}^{KBr} cm^{-1}: 3630, 2930, 1740, 1555, 1455, 1430, 1290, 1040, 980 and 840; ^1H NMR (250 MHz) $CDCl_3$: δ0.92 (3H, *s*, H-23), 1.00 (3H, *s*, H-24), 1.04 (3H, *s*, H-25), 1.80 (H-26), 3.36 (1H, *t*, *J* = 9, 4 Hz, H-21), 3.90 and 4.15 (2H, ABq, *J* = 10 Hz, H-12), 2.00–2.15 (2H, *m*, H-16), 1.85 (1H, *m*, H-13), 3.87 (3H, *s*, OMe), 4.00 (3H, *s*, OMe) 5.54 (1H, *br t*, $W_{\frac{1}{2}}$ = 9 Hz, H-15), 6.65 (1H, *s*, H-5), 7.59 (1H, *d*, *J* = 9.5 Hz, H-3), 6.34 (1H, *d*, *J* = 9.5 Hz, H-2); MS *m/z*: 442 $[M]^+$, 223, 222 (100%), 221, 204, 203, 161, 147, 135, 133, 121, 109, 105, 95; ^{13}C NMR: δ_C160.4 (C-1), 115.2 (C-2), 143.3 (C-3), 114.5 (C-4), 104.1 (C-5), 150.5 (C-6), 145.4 (C-7), 141.7 (C-8), 143.2 (C-9), 56.3 (C-10), 61.8 (C-11), 73.4 (C-12), 55.7 (C-13), 131.6 (C-14), 123.1 (C-15), 23.7 (C-16), 42.5 (C-17), 35.8 (C-18), 34.0 (C-19), 27.6 (C-20), 79.4 (C-21), 38.7 (C-22), 22.6 (C-23), 21.7 (C-24), 15.2 (C-25), 27.9 (C-26).

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