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DAUCANE ESTERS FROM *FERULA COMMUNIS* SUBSP. *COMMUNIS*

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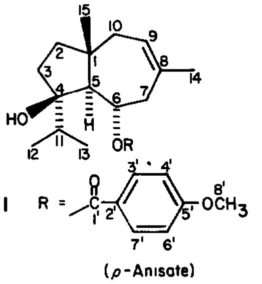
Key Word Index—*Ferula communis* subsp. *communis*; Umbelliferae; sesquiterpenoids; daucane esters.

Abstract—Fourteen daucane esters together with a known propiophenone 3,4-methylenedioxy-5-hydroxypropiophenone, were isolated from *Ferula communis* subsp. *communis*. Except for the 6-(*p*-anisic acid) ester of jaeschkeanadiol all these esters are new. Structures were elucidated using spectral properties of the esters and their partial hydrolysis products. X-ray diffraction analysis of one of the compounds confirmed its structure including the stereochemical assignments made on the basis of spectral data.

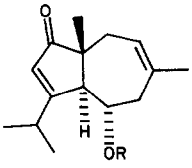
INTRODUCTION

In continuation of our studies of members of the genus *Ferula* which are indigenous to Anatolia [1, 2], we investigated *Ferula communis* L. subsp. *communis*. This species, which belongs to subgenus *Euferula* Boiss, is the type species for the genus *Ferula*. *F. communis*, already well known as a medicinal plant in ancient times [3], has, for example, been used as an antihysteric and for the treatment of dysentery [4]. Previously, several sesquiterpene esters some of different skeletal types but most containing a 1,5-*trans*-fused daucane ring system were reported from other *Ferula* species [5–10].

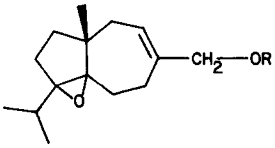


1 R =

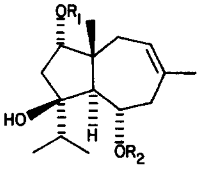
1a R = Ac



2 R = *p*-Anisate



3 R = *p*-Anisate



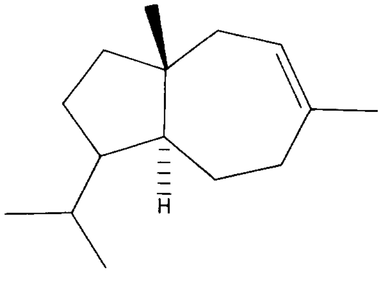
4 R_1 = Ac, R_2 = Benzoate
5 R_1 = Ac, R_2 = *p*-Anisate
6 R_1 = Ac, R_2 = H
7 R_1 = R_2 = H

RESULTS AND DISCUSSION

From the benzene extract of the dried roots of *Ferula communis*, we obtained one known and 13 new sesquiterpene esters and the known propiophenone **20** [1]. Each of these esters is discussed separately below.

Compound **1** ($[M]^+$ at m/z 372, $C_{23}H_{32}O_4$) was identified as the *p*-anisic acid ester of jaeschkeanadiol (ferutidin) by spectral data and direct comparison with an authentic sample [1].

Compound **2** ($[M]^+$ at m/z 368, $C_{23}H_{28}O_4$) exhibited IR absorptions characteristic for a cyclopentenone ring [1720 (sh) and 1710 cm^{-1}], as well as bands for an aromatic acyl group. In addition to the signals of the *p*-anisate portion the ^{1}H NMR spectrum of **2** corresponded to a daucane-type sesquiterpene nucleus, being similar to that of dehydrated-oxytingitanol (**22**) [2]. However, since the signal for H-10 appeared in the upfield region and H-9 (a broad triplet at δ5.59) was clearly coupled to two protons it was evident that **2** was not oxygenated at C-10; thus, the *p*-anisate moiety must be the C-6α acyl group.



Trans-fused dauc-8-ene

The ^{1}H NMR spectrum of compound **3** ($[M]^+$ at m/z 370, $C_{23}H_{30}O_4$) indicated that **3** also had an anisate, but showed that the C-14 methyl group present in **1** and **2** had been oxidized to a primary alcohol which is esterified with *p*-anisic acid. This finding was corroborated by a signal for C-14 at δ69.3 (*t*) in the ^{13}C NMR spectrum of **3** (see Table 1). The $[M]^+$ in the mass spectrum of **3** ($[M]^+$ at m/z 370) indicated the presence of an additional oxygen atom, which on the basis of the absence of a hydroxyl band in the IR spectrum and the presence of two signals at

Table 1. ^{13}C NMR data of **1**, **3**, **5**, **10**, **11**, **14** and **17**

	1	**3**	**5**	**10**	**11**	**14**	**17**
C-1	44.0 *s*	41.9 *s*	47.3 *s*	46.8 *s*	46.7 *s*	51.1 *s*	49.1 *s*
C-2	31.6 *t*	23.4 *t*	82.8 *d*	31.2 *t*	30.9 *t*	79.3 *d*	80.6 *d*
C-3	41.1 *t*	28.0 *t*	40.8 *t*	40.5 *t*	40.5 *t*	41.1 *t*	39.9 *t*
C-4	86.2 *s*	76.8 *s*	85.1 *s*	86.2 *s*	86.1 *s*	85.7 *s*	84.0 *s*
C-5	60.0 *d*	76.0 *s*	55.9 *d*	51.5 *d*	51.5 *d*	55.5 *d*	49.1 *d*
C-6	71.0 *d*	24.7 *t*	70.4 *d*	71.5 *d*	71.0 *d*	69.5 *d*	70.0 *d*
C-7	41.4 *t*	22.2 *t*	39.7 *t*	37.4 *t*	37.3 *t*	39.4 *t*	39.0 *t*
C-8	133.6 *s*	138.1 *s*	133.9 *s*	137.4 *s*	137.4 *s*	131.6 *s*	135.4 *s*
C-9	125.3 *d*	127.2 *d*	124.6 *d*	124.6 *d*	124.5 *d*	128.6 *d*	125.5 *d*
C-10	41.4 *t*	33.3 *t*	34.9 *t*	74.5 *d*	74.4 *d*	75.1 *d*	75.1 *d*
C-11	37.2 *d*	33.9 *d*	37.0 *d*	37.4 *d*	37.3 *d*	37.1 *d*	36.8 *d*
C-12	18.5 *q*	18.2 *q*	18.2 *q*	18.5 *q*	18.5 *q*	18.1 *q*	18.2 *q*
C-13	17.5 *q*	17.8 *q*	17.6 *q*	17.4 *q*	17.4 *q*	17.5 *q*	17.6 *q*
C-14	26.4 *q*	69.3 *t*	25.9 *q*	27.3 *q*	27.3 *q*	26.0 *q*	26.0 *q*
C-15	20.3 *q*	20.3 *q*	20.5 *q*	21.0 *q*	21.0 *q*	21.0 *q*	21.2 *q*
Arom. Subst.							
C-1′	166.4 *s*	165.6 *s*	166.7 *s*	167.2 *s*	167.2 *s*	166.6 *s*	166.7 *s*
C-2′	123.0 *s*	122.3 *s*	122.8 *s*	130.7 *s*	122.8 *s*	122.5 *s*	122.5 *s*
C-3′	131.7 *d*	131.0 *d*	131.8 *d*	129.8 *d*	131.8 *d*	131.8 *d*	131.8 *d*
C-4′	113.8 *d*	113.1 *d*	113.9 *d*	128.6 *d*	113.9 *d*	114.0 *d*	114.0 *d*
C-5′	163.6 *s*	162.9 *s*	163.8 *s*	133.2 *s*	163.8 *s*	163.9 *s*	163.9 *s*
C-6′	113.8 *d*	113.1 *d*	113.9 *d*	129.8 *d*	113.9 *d*	114.0 *d*	114.0 *d*
C-7′	131.7 *d*	131.0 *d*	131.8 *d*	128.6 *d*	131.8 *d*	131.8 *d*	131.8 *d*
C-8′	55.3 *q*	54.7 *q*	55.5 *q*	—	55.4 *q*	54.5 *q*	55.4 *q*
Angelate							
C-1″	—	—	—	166.6 *s*	166.4 *s*	—	—
C-2″	—	—	—	128.1 *s*	127.9 *s*	—	—
C-3″	—	—	—	138.5 *d*	138.7 *d*	—	—
C-4″	—	—	—	20.7 *q*	20.6 *q*	—	—
C-5″	—	—	—	15.8 *q*	15.8 *q*	—	—
Acetate(s)							
C-1″	—	—	170.5 *s*	—	—	170.5 *s**	170.2 *s*
C-2″	—	—	19.8 *q*	—	—	21.0 *q*	21.1 *q*
C-1‴	—	—	—	—	—	170.2 *s**	170.2 *s*
C-2‴	—	—	—	—	—	21.0 *q*	21.1 *q*

*Interchangeable.

δ76.8 (*s*) and 76 (*s*) in the ^{13}C NMR spectrum could be assigned to an epoxy group connected to two tertiary carbon atoms: i.e. either at C-4,C-5 or C-4,C-11. The latter possibility for the epoxide was eliminated since the ^{1}H NMR spectrum of **3** exhibited doublets for the 12 and 13-methyl groups, establishing the presence of a proton on C-11.

Spectral properties demonstrated that compounds **4** and **5** had both a nonaromatic and an aromatic acyl function. The ^{1}H NMR spectra of **4** and **5** exhibited nearly identical signals for the sesquiterpene nucleus, including a doublet at δ4.89 (1H, J = 5 Hz, H-2) coupled with a multiplet at δ2.12 for cyclopentane ring protons; the corresponding ^{13}C NMR signals for this ring indicated that one of the acyl groups must be located at the C-2α position. A *dt* signal for one proton (J = 2.5, 9.5 and 10.5 Hz) in the ^{1}H NMR spectrum at *ca* δ5.4 is characteristic for the C-6β acyl geminal proton of *trans*-fused daucane skeletons [1, 2] and thus located the second acyl group at C-6α in **4** and **5**.

Inspection of Dreiding models for **4** and **5** showed that relative to the C-2α acyl group, the C-6α acyl moiety is closer to the isopropyl side chain. This supported the ^{1}H NMR-observable effect of C-6α acyl groups on the isopropyl moiety. That is, when the isopropyl methyl doublets for **4** and **5** were compared with those for jaeschkeanadiol acetate (**1a**), tingitanol (**21**) and tingitanol acetate (**21a**) [1, 2], it was evident that **4** and **5** have these doublets separated more (*ca* Δ0.13 ppm) than do those compounds which do not have an aromatic acyl group at the C-6α position (i.e. for **1a**, **21** and **21a**, $\Delta \leq 0.07$ ppm). These comparisons indicate that nonaromatic substitution at C-6α would not give a separation of the doublet signals as large as 0.13 ppm for the two isopropyl methyl groups. In accord with these data the aromatic acyl substitution of **4** and **5** should be C-6α. This assignment of C-6 aromatic acyl groups for **4** and **5** was verified by the partial hydrolysis of **5**, which afforded mainly **6** and a small amount of **7**. In the ^{1}H NMR spectrum of **6**, the H-6 proton signal shifted to δ3.96 (1H, *dt*, J = 2.5, 10 and

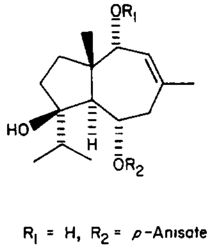
10.5 Hz, Δ1.37 ppm upfield), the aromatic group signals disappeared and, significantly, two doublets for the isopropyl methyls appeared near each other (δ0.93 and 0.91, each 3H, *d*, *J* = 6.5 Hz, Δ0.02 ppm).

The ^{1}H NMR spectrum of **5** contained the *p*-anisoyl signals similar to those observed for **1**–**3**; **4**, however, exhibited benzoyl signals in its spectrum. In addition, the ^{1}H NMR spectra of both **4** and **5** showed the acetyl methyl signal at δ2.07 (3H, *s*). Similar chemical shifts for the C-4 assymetric centre were observed for **1**, **4** and **5** when their ^{13}C NMR spectra were compared (see Table 1), suggesting the same stereochemistry at this centre (β-OH and α-isopropyl).

For compounds **8** ($[M]^+$ at *m/z* 388, $C_{23}H_{32}O_5$), **9** ($[M]^+$ at *m/z* 430, $C_{25}H_{34}O_6$), **10** ($[M]^+$ at *m/z* 440, $C_{27}H_{36}O_5$), **11** ($[M]^+$ at *m/z* 470, $C_{28}H_{38}O_6$) and **12** ($[M]^+$ at *m/z* 500, $C_{29}H_{40}O_7$), ^{1}H NMR spectra and spin decoupling experiments (as well as other spectral data) indicated that all had the same sesquiterpene nucleus. All ^{1}H NMR spectra (except for **8**) exhibited a doublet at *ca* δ4.95 for H-10 (*J* = 7 Hz) coupled with a broad doublet at *ca* δ5.8 (1H, *J* = 7 Hz, H-9); the first signal corresponds to an acyl geminal proton and indicated that C-10 was acylated in the α position for **9**–**12** and that **8** (δ3.86 for H-10) therefore represents the parent C-10 hydroxyl compound. As observed in the ^{1}H NMR spectra of **4** and **5**, the spectra of **8**–**12** contained a *dt* (1H, *J* = *ca* 2.5, 9.5 and 10.5 Hz) at *ca* δ5.45 assignable to a C-6β acyl geminal proton in a *trans*-fused daucene skeleton. In addition, well separated isopropyl methyl doublets (Δ0.15 ppm) indicated the presence of C-6α aromatic acyl groups in **8**–**12** This assignment was confirmed since the ^{1}H NMR and mass spectral differences between **11** and its partial hydrolysis product **13** are similar to those observed between the spectra of compounds **5** and **6**.

Spectra indicated that at C-6 **8**, **9** and **11** were anisates and **10** and **12** were benzoate and veratrate, respectively. In addition, **10**, **11** and **12** were clearly substituted at C-10α with an angeloyl moiety; in contrast, **9** was substituted with an acetyl group at this position.

Compounds **14** ($[M]^+$ at *m/z* 446, $C_{25}H_{34}O_7$) and **15** ($[M]^+$ at *m/z* 488, $C_{27}H_{36}O_8$) exhibited similar ^{1}H NMR spectra except for the signals of the C-10 moiety. Decoupling experiments for **14** and **15** showed that a broad singlet at δ5.4 (1H), which could be attributed to the H-9 vinylic proton, interacted with a broad singlet at δ5.23 (1H, H-10) in **14** and δ4.34 (1H, H-10) in **15**. The downfield position of these latter signals indicated that both **14** and **15** were oxygenated at C-10; furthermore, the 0.89 ppm greater downfield shift observed for H-10 in **14** established the presence of an acylated hydroxyl group at C-10. Inspection of Dreiding models of **14** and **15** confirmed that a small coupling between H-9 and H-10 was only possible when the proton at C-10 was α; therefore, the C-10 acyl groups in **14** and **15** must be β.



8 R_1 = H, R_2 = *p*-Anisate

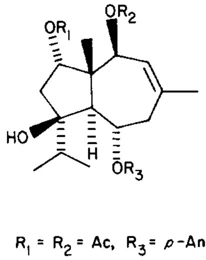
9 R_1 = Ac, R_2 = *p*-Anisate

10 R_1 = Ang, R_2 = Benzoate

11 R_1 = Ang, R_2 = *p*-Anisate

12 R_1 = Ang, R_2 = Veratrate

13 R_1 = Ang, R_2 = H



14 R_1 = R_2 = Ac, R_3 = *p*-Anisate

15 R_1 = Ac, R_2 = H, R_3 = *p*-Anisate

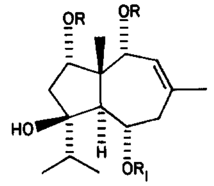
16 R_1 = R_2 = Ac, R_3 = H

The ^{1}H NMR of **14** and **15** exhibited the same doublet at *ca* δ5.1 (1H, *J* = 5 Hz), similar to the doublets observed for H-2 in the spectra of **4** and **5**. This assignment indicated that both **14** and **15** had C-2α acyl groups. Also, the observation that the H-6 acyl geminal proton signal patterns for **14** and **15** were similar to those of **4** and **5** and **8**–**12**, combined with the spectral differences between **14** and its partial hydrolysis product **16**, and other characteristic ^{1}H NMR and mass spectral data indicated that **14** and **15** are C-6α anisates.

The mass and ^{1}H NMR spectra of **15** indicated that it had an acetyl moiety at C-2. Whilst the ^{1}H NMR spectrum of **14** clearly indicated two acetyl moieties at C-2 and C-10, the mass spectrum of **14** also supported two acetyl groups in addition to the C-6-α-*p*-anisoyl moiety These assignments were confirmed when acetylation of **15** gave **14**.

Compounds **17** ($[M]^+$ at *m/z* 488, $C_{27}H_{36}O_8$) and **18** ($[M]^+$ at *m/z* 518, $C_{28}H_{38}O_9$) exhibited similar ^{1}H NMR spectra different in only a few aspects to the one recorded for **14**; these differences included a doublet at δ5.58 (1H, *J* = 6 Hz, H-9) instead of a broad singlet at δ5.4 (1H, H-9 in the spectrum of **14**) and a doublet at δ5.21 (1H, *J* = 6 Hz, H-10) instead of broad singlet at δ5.23 (1H, H-10 in the spectrum of **14**). The ^{1}H NMR data further indicated that the C-10 acyl group should be α as in compounds **9**–**12**. Other differences between the ^{1}H NMR spectra of **17** and **14** included the chemical shifts and coupling constants of the signals for the H-6 acyl geminal proton as well as the chemical shift of the signal for the H-5 proton In the ^{1}H NMR spectrum of **17**, the H-6β proton signal appeared as a *ddd* at δ5.55 (1H, *J* = 4.4, 7.6 and 10.8 Hz) and H-5 at δ3.06 as a doublet (*J* = 10.8 Hz), while the signal for H-6 of **14** appeared at δ5.32 as a *dt* (1H, *J* = 2.5, 9.5 and 10.5 Hz). Indeed, the spectra of **17** and **18** exhibited elements of the spectra of both series **4**–**7** as well as **9**–**12** suggesting that **17** and **18** combined substitution patterns of both series. The ^{1}H NMR of **19**, the partial hydrolysis product of **17**, supported these assignments: the H-6 proton signal had shifted to δ4.16 and the coupling changed to a *dt* (1H, *J* = 2.3, 10.4 and 10 5 Hz); also the H-5 signal shifted to δ2.95 (1H, *d*, *J* = 10.5 Hz). In addition to these changes, the aromatic ring signals disappeared and the isopropyl methyl doublets collapsed to two close doublets (Δ0.02 ppm). Characteristic spectral properties established that **17** and **18** were *p*-anisate and veratrate, respectively, in addition to having acetyl groups at C-2 and C-10. Stereochemistry at the C-4 assymetric centre in **8**–**18** was confirmed by ^{13}C NMR data (Table 1), which when correlated with the ^{13}C NMR data for **1** showed a β-OH and an α-isopropyl group at C-4 in **8**–**18**.

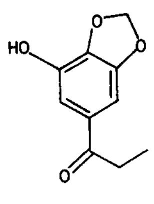
The structure and stereochemistry of **17**, which were determined by spectral studies, has just been confirmed by X-ray crystallography [W. H. Watson *et al.*, personal communication]. This confirmation of structure, including stereochemistry for **17**, adds substantial support for the structures deduced for all the related daucane esters reported here.



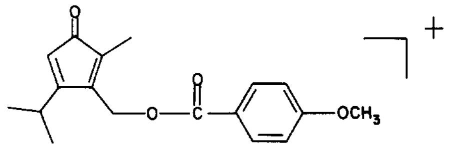
17 R = Ac, R$_1$ = *p*-Anisate

18 R = Ac, R$_1$ = Veratrate

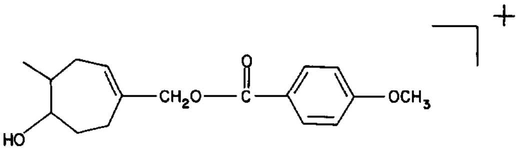
19 R = Ac, R$_1$ = H

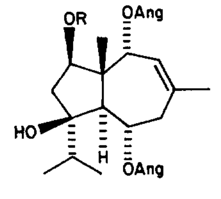


20



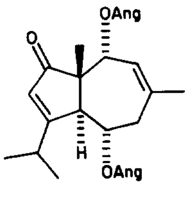
[F]$^+$





21 R = H

21a R = Ac



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EXPERIMENTAL

General. Mps are uncorr. UV spectra were taken in CHCl$_3$ and ^{1}H NMR spectra in CDCl$_3$ (unless otherwise stated) at 200 MHz. ^{13}C NMR spectra were taken in CDCl$_3$ at 22.6 MHz. MS were obtained with a direct inlet system at 70 eV.

Plant material. Roots of *F. communis* were collected from the Atakoy area, near Istanbul in June 1983. A voucher specimen, identified by Dr. E. Tuzlaci (Istanbul), is deposited in the Herbarium of Faculty of Pharmacy, University of Istanbul (ISTE 50856).

Isolation of compounds. Dried and coarsely powdered roots (1.5 kg) were extracted with C$_6$H$_6$ in a Soxhlet. Concentrating the C$_6$H$_6$ extract *in vacuo* provided 70 g crude viscous oil. This oil (15 g) was chromatographed on a silica gel column (5 × 50 cm) packed in CH$_2$Cl$_2$ and eluted with a CH$_2$Cl$_2$–EtOAc gradient. Sephadex LH-20 columns packed in cyclohexane–CH$_2$Cl$_2$–EtOH (7:4:1 or 7:2:1) and/or prep. TLC (1.5 mm thickness, silica gel developed with cyclohexane–EtOAc mixtures, 4:1, 7:3 or 3:2) were used for further purification of the compounds.

Compound **2**. Gum (4 mg); UV λ_{max} nm (ε): 314 (sh) (310), 261 (12 840); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2990, 2940, 2895, 1720 (sh), 1710, 1660, 1610, 1585, 1518, 1260, 1175, 1120, 1100, 1040, 938 and 853. ^{1}H NMR: δ8.05 (2H, *d*, *J* = 8 Hz, H-3′ and H-7′), 6.96 (2H, *d*, *J* = 8 Hz, H-4′ and 6′), 5.89 (1H, *q*, *J* = 1 and 2.1 Hz, H-3), 5.59 (1H *br t*, H-9), 5.52 (1H, *ddd*, *J* = 3.2, 4.6 and 10.5 Hz, H-6), 3.89 (3H, *s*, H-8′), 3.35 (1H, *dd*, *J* = 2 and 10.5 Hz, H-5), 2.92 (1H, *br dd*, *J* = 4.6 and 15 Hz, H-7α), 2.57 (1H, *septet*, H-11), 2.29 (1H, *dd*, *J* = 3.2 and 15 Hz, H-7β), 1.78 (3H, *d*, *J* = 2 Hz, H-14), 1.26 (3H, *s*, H-15), 1.1 (3H, *d*, *J* = 6.5 Hz, H-12)* and 1.06 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 368 [M]$^+$ (1.7), 340 [M − CO]$^+$ (1.75), 300 [F]$^+$ (5.9), 290 (8.3), 234 [M − *p*-anisate + H]$^+$ (2.9), 216 [M − *p*-anisic acid]$^+$ (25.3, 201 (9.3), 191 [M − *p*-anisate − *iso*-Pr + H]$^+$ (8.3), 173 [M − *p*-anisic acid − *iso*-Pr]$^+$ (20.9), 159 (9.2), 152 [*p*-anisic acid]$^+$ (11.5), 135 [*p*-anisate]$^+$ (100), 83 (60.5).

Compound **3**. Gum (10 mg); UV λ_{max} nm (ε): 259 (15 550); IR ν_{max}^{KBr} cm^{-1}: 2960, 2940, 2880, 1710, 1648, 1608, 1580, 1512, 1455, 1372, 1319, 1260, 1170, 1104, 1036, 850 and 772. ^{1}H NMR: δ8.1 (2H, *d*, *J* = 8 Hz, H-3′ and H-7′), 6.93 (2H, *d*, *J* = 8 Hz, H-4′ and H-6′), 5.87 (1H, *br t*, H-9), 4.73 (2H, *br s*, H-14), 3.87 (3H, *s*, H-8′), 1.07 (3H, *d*, *J* = 6.5 Hz, H-12)*, 0.94 (3H, *d*, *J* = 6.5 Hz, H-13)* and 0.91 (3H, *s*, H-15). MS *m/z* (rel. int.): 370 [M]$^+$ (49.8), 355 [M − Me]$^+$ (10.1), 327 [M − *iso*-Pr]$^+$ (6.4), 289 [FA]$^+$ (11.4), 271 [FA − H$_2$O]$^+$ (14.3), 218 [M − *p*-anisic acid]$^+$ (78.3), 203 [M − *p*-anisic acid − Me − H$_2$O]$^+$ (53.5), 175 [M − *p*-anisic acid − *iso*-Pr]$^+$ (67.4), 152 [*p*-anisic acid]$^+$ (86.4), 135 [*p*-anisate]$^+$ (100), 121 (59), 107 (64.4), 92 (60.7).

Compound **4**. Gum (5 mg); UV λ_{max} nm (ε): 285 (sh) (1230), 273 (1730) and 246 (6250); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 2980, 2940, 2882, 1720, 1710, 1608, 1582, 1510, 1450, 1380, 1320, 1300, 1260, 1120, 1075, 1032 and 732. ^{1}H NMR: δ8.04 (2H, *dd*, *J* = 1 and 8.5 Hz, H-3′ and 7′), 7.59, (1H, *td*, *J* = 1 and 8.5 Hz, H-5′), 7.48 (2H, *dt*, *J* = 1 and 8.5 Hz, H-4′ and H-6′), 5.55 (1H, *br t*, H-9), 5.47 (1H, *dt*, *J* = 2.1, 9.5 and 10.5 Hz, H-6), 4.89 (1H, *d*, *J* = 5.1 Hz, H-2), 2.53 (1H, *d*, *J* = 10.5 Hz, H-5), 2.28 (1H, *dd*, *J* = 2.1 and 15 Hz, H-7β), 2.07 (3H, *s*, H-2″), 1.84 (3H, *br s*, H-14), 1.13 (3H, *s*, H-15), 0.96 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.81 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 357 [M − *iso*-Pr]$^+$ (20.4), 297 [M − *iso*-Pr − HOAc]$^+$ (29.1), 218 [M − C$_6$H$_5$CO$_2$H − HOAc]$^+$ (46.2), 175 [M − C$_6$H$_5$CO$_2$H − HOAc − *iso*-Pr]$^+$ (46.2), 157 [M − C$_6$H$_5$CO$_2$H − HOAc − H$_2$O]$^+$ (29.5), 147 (67.8), 122 [C$_6$H$_5$CO$_2$H]$^+$ (20.9), 105 [benzoate]$^+$ (95), 43 (64.6).

Compound **5**. Gum (105 mg); UV λ_{max} nm (ε): 261 (16 200); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3480, 2980, 2960, 2890, 1725, 1710, 1610, 1585, 1515, 1382, 1308, 1260, 1175, 1108, 1038, 952, 938 and 855. ^{1}H NMR: δ7.99 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.95 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 5.53 (1H, *br t*, H-9), 5.33 (1H, *dt*, *J* = 2.5, 9.5 and 10 5 Hz, H-6), 4.89 (1H, *d*, *J* = 4.8 Hz, H-2), 3.88 (3H, *s*, H-8′), 2.51 (1H, *d*, *J* = 10.5 Hz, H-5), 2.27 (1H, *dd*, *J* = 2.5 and 14.5 Hz, H-7), 2.07 (3H, *s*, H-2″), 1.82 (3H, *br s*, H-14), 1.13 (3H, *s*, H-15), 0.94 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.81 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 387 [M − *iso*-Pr]$^+$ (13.9), 327 [M − HOAc-*iso*-Pr]$^+$ (7 4), 218 [M − *p*-anisic acid − HOAc]$^+$ (32.2), 203 [M − *p*-anisic acid − HOAc − Me]$^+$ (8), 175 [M − *p*-anisic acid − HOAc − *iso*-Pr]$^+$ (91.5), 157 [M − *p*-anisic acid − HOAc − *iso*-Pr − H$_2$O]$^+$ (16.3), 152 [*p*-anisic acid]$^+$ (45.2), 147 (53.1), 135 [*p*-anisate]$^+$ (100), 132, (75.2), 121 (38.1), 105 (61.3), 92 (43.4).

Partial hydrolysis of **5**. Compound **5** (30 mg) was treated with 1% NaOH in EtOH at room temp. After 2 hr, the reaction mixture was worked up in the usual manner. In addition to *p*-anisic acid, two hydrolysis products, **6** and **7**, were obtained after purification by Sephadex LH-20 column.

Compound **6**. Gum (11 mg). ^{1}H NMR: δ5.42 (1H, *br t*, H-9), 4 85 (1H, *dd*, *J* = 2 and 4.2 Hz, H-2), 3.96 (1H, *dt*, *J* = 2.5, 10

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*Interchangeable.

and 10.5 Hz, H-6), 2.15 (1H, *d*, *J* = 10.5 Hz, H-5), 2.03 (3H, *s*, H-2″), 1.81 (3H, *br s*, H-14), 1.07 (3H, *s*, H-15), 0.93 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.91 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 253 [M − *iso*-Pr]$^+$ (1.42), 236 [M − HOAc]$^+$ (2.7), 218 [M − HOAc − $\mathrm{H_2O}$]$^+$ (35), 203 [M − HOAc − $\mathrm{H_2O}$ − Me]$^+$ (11.9), 193 [M − HOAc − *iso*-Pr]$^+$ (74.6), 175 [M − HOAc − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (88.8), 157 [M − HOAc − *iso*-Pr − 2 × $\mathrm{H_2O}$]$^+$ (30.8), 147 (57.9), 133 (70.5), 121 (64.4), 105 (57), 71 (57.1).

Compound **7**. Amorphous solid (3 mg). ^{1}H NMR: δ5.72 (1H, *br t*, H-9), 4.05 (1H, *dt*, *J* = 2.5, 10 and 10.5 Hz, H-6), 3.79 (1H, *d*, *J* = 7.3 Hz, H-2), 2.52 (1H, *d*, *J* = 10.5 Hz, H-5), 1.82 (3H, *br s*, H-14), 1.03 (3H, *s*, H-15), 0.98 (6H, *d*, *J* = 6.5 Hz, H-12 and H-13). MS *m/z* (rel. int.): 254 [M]$^+$ (0.12), 236 [M − $\mathrm{H_2O}$]$^+$ (3.7), 218 [M − 2 × $\mathrm{H_2O}$]$^+$ (17.9), 211 [M − *iso*-Pr]$^+$ (4.2), 200 [M − 3 × $\mathrm{H_2O}$]$^+$ (48.3), 185 [M − 3 × $\mathrm{H_2O}$ − Me]$^+$ (52.1), 175 (M − 2 × $\mathrm{H_2O}$ − *iso*-Pr]$^+$ (37.4), 157 [M − 3 × $\mathrm{H_2O}$ − *iso*-Pr]$^+$ (100), 143 (55.3), 129 (73.9), 119 (52.8), 105 (59.8), 91 (60.4), 71 (48.8).

Compound **8**. Gum (7 mg); UV $\lambda_{\max}$ nm (ε); 260 (12340); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3480, 2978, 2935, 2875, 1700, 1605, 1580, 1505, 1450, 1378, 1260, 1150, 1100, 1030, 950, 840, 765, 690. ^{1}H NMR; δ7.98 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.94 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 5.76 (1H, *d*, *J* = 7 Hz, H-9), 5.44 (1H, *dt*, *J* = 3.8; 10.7 and 10.8 Hz, H-6), 3.88 (3H, *s*, H-8′), 3.86 (1H, *d*, *J* = 7 Hz, H-10), 2.83 (1H, *d*, *J* = 10.7 Hz, H-5), 2.27 (1H, *dd*, *J* = 3.8 and 14.5 Hz, H-7β), 1.84 (3H, *br s*, H-14), 1.14 (3H, *s*, H-15), 0.99 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.86 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 388 [M]$^+$ (0.2), 371 [M − $\mathrm{H_2O}$ + H]$^+$ (0.9), 345 [M − *iso*-Pr]$^+$ (14.1), 327 [M − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (23.1), 236 [M − *p*-anisic acid]$^+$ (16.5), 218 [M − *p*-anisic acid − $\mathrm{H_2O}$]$^+$ (47), 203 [M − *p*-anisic acid − $\mathrm{H_2O}$ − Me]$^+$ (15.2), 201 [M − *p*-anisic acid − 2 × $\mathrm{H_2O}$ + H]$^+$ (15.6), 193 [M − *p*-anisic acid − *iso*-Pr]$^+$ (51.3), 175 [M − *p*-anisic acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (83.4), 157 [M − *p*-anisic acid − *iso*-Pr − 2 × $\mathrm{H_2O}$) (47.7), 152 [*p*-anisic acid]$^+$ (71.5), 135 [*p*-anisate]$^+$ (100), 119 (61.1), 107 (64.9), 92 (55.1).

Compound **9** Gum (7 mg); UV $\lambda_{\max}$ nm (ε): 262 (10 840); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3480, 2960, 2930, 2880, 1720 (sh), 1710, 1608, 1585, 1510, 1458, 1375, 1258, 1170, 1120, 1103, 1030, 960, 850, 772 and 718. ^{1}H NMR; δ8.0 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.94 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 5.72 (1H, *br d*, *J* = 6.5 Hz, H-9), 5.42 (1H, *dt*, *J* = 2.5, 9.5 and 10.5 Hz, H-6), 4.9 (1H, *d*, *J* = 6.5 Hz, H-10), 3.88 (3H, *s*, H-8′), 2.76 (1H, *d*, *J* = 10.5 Hz, H-5), 2.26 (1H, *dd*, *J* = 2.5 and 14.5 Hz, H-7β), 2.09 (3H, *s*, H-2″), 1.82 (3H, *br s*, H-14), 1.19 (3H, *s*, H-15), 0.99 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.86 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS: *m/z* (rel. int.) 430 [M]$^+$ (0.17), 387 [M − *iso*-Pr]$^+$ (3.4), 327 [M − HOAc − *iso*-Pr]$^+$ (15.9), 218 [M − HOAc − *p*-anisic acid]$^+$ (32.6), 175 [M − HOAc − *p*-anisic acid − *iso*-Pr]$^+$ (90.3), 157 [M − HOAc − *p*-anisic − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (38.1), 152 [p-anisic acid]$^+$ (64.4), 147 (58.4), 135 [*p*-anisate]$^+$ (100), 43 (94).

Compound **10**. Gum (82 mg); UV $\lambda_{\max}$ nm (ε): 282 (sh) (950), 274 (1190) and 246 (5990); IR $\nu_{\mathrm{nax}}^{\mathrm{KBr}}$ cm^{-1}: 3510, 2962, 2940 (sh), 2880, 1710, 1650, 1605, 1588, 1455, 1388, 1320, 1278, 1238, 1162, 1120, 1045, 989, 960, 850 and 714. ^{1}H NMR: δ8.03 (2H, *dd*, *J* = 1 and 8.5 Hz, H-3′ and H-7′), 7.58 (1H, *td*, *J* = 1 and 8.5 Hz, H-5′), 7.46 (2H, *dt*, *J* = 1 and 8.5 Hz, H-4′ and H-6′), 6.12 (1H, *dq*, H-3″), 5.8 (1H, *br d*, *J* = 6.5 Hz, H-9), 5.48 (1H, *dt*, *J* = 2.5, 9.5 and 10.5 Hz, H-6), 4.95 (1H, *d*, *J* = 6.5 Hz, H-10), 2.81 (1H, *d*, *J* = 10.5 Hz, H-5), 2.25 (1H, *dd*, *J* = 2.5 and 15 Hz, H-7β), 2.05 (3H, *dd*, *J* = 1 and 6.5 Hz, H-4″), 1.98 (3H, *t*, H-5″), 1.83 (3H, *br s*, H-14), 1.23 (3H, *s*, H-15) 0.99 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.84 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 440 [M]$^+$ (0.3), 423 [M − $\mathrm{H_2O}$ + H]$^+$ (9.4), 341 [M − angelic acid + H]$^+$ (5.8), 323 [M − angelic acid − $\mathrm{H_2O}$ + H]$^+$ (17.5), 319 [M − $\mathrm{C_6H_5CO_2H}$ + H]$^+$ (12.7), 301 [M − $\mathrm{C_6H_5CO_2H}$ − $\mathrm{H_2O}$ + H]$^+$ (7.63), 297 [M − angelic acid − *iso*-Pr]$^+$ (14.4), 279 [M − angelic acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (4.6), 275 [M − $\mathrm{C_6H_5CO_2H}$ − *iso*-Pr]$^+$ (28.1), 257 [M − $\mathrm{C_6H_5CO_2H}$ − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (15.4), 235 [M − $\mathrm{C_6H_5CO_2H}$ − angelate]$^+$ (29.2), 219 [M − $\mathrm{C_6H_5CO_2H}$ − angelic acid + H]$^+$ (53.1), 201 [M − $\mathrm{C_6H_5CO_2H}$ − angelic acid − $\mathrm{H_2O}$ + H]$^+$ (90.1), 175 [M − $\mathrm{C_6H_5CO_2H}$ − angelic acid − *iso*-Pr]$^+$ (100), 132 (32.8), 122 [$\mathrm{C_6H_5CO_2H}$]$^+$ (32.3), 105 [benzoate]$^+$ (29.2), 83 [angelate]$^+$ (70.5).

Compound **11**. Gum (134 mg); UV $\lambda_{\max}$ nm (ε): 261 (17 750); IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3510, 2980, 2940, 2882, 1710, 1660, 1610, 1583, 1516, 1464, 1445, 1428, 1380, 1320, 1305, 1263, 1172, 1120, 1108, 1040, 960, 936 and 853. ^{1}H NMR: δ7.98 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.95 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 6.11 (1H, *dq*, H-3″), 5.79 (1H, *br d*, *J* = 7.5 Hz, H-9), 5.44 (1H, *dt*, *J* = 2.5, 9.5 and 10.5 Hz, H-6), 4.94 (1H, *d*, *J* = 7.5 Hz, H-10), 3.88 (3H, *s*, H-8′), 2.79 (1H, *d*, *J* = 10.5 Hz, H-5), 2.24 (1H, *dd*, *J* = 2.5 and 14.5 Hz, H-7β), 2.05 (3H, *dd*, *J* = 1 and 6.5 Hz, H-4″), 1.98 (3H, *t*, *J* = 1 Hz, H-5″), 1.81 (3H, *br s*, H-14), 1.22 (3H, *s*, H-15), 0.97 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.85 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 470 [M]$^+$ (0.1), 427 [M − *iso*-Pr]$^+$ (0.51), 327 [M − angelic acid − *iso*-Pr]$^+$ (18.9), 275 [M − *p*-anisic acid − *iso*-Pr]$^+$ (12.5), 257 [M − *p*-anisic acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (3.93), 235 [M − *p*-anisic acid − angelate]$^+$ (28.9), 218 [M − *p*-anisic acid − angelic acid]$^+$ (57.6), 203 [M − *p*-anisic acid − angelic acid − Me]$^+$ (22.2), 201 [M − *p*-anisic acid − angelic acid − $\mathrm{H_2O}$]$^+$ (26.5), 175 [M − *p*-anisic acid − angelic acid − *iso*-Pr]$^+$ (91.5), 157 [M − *p*-anisic acid − angelic acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (51.3), 152 [*p*-anisic acid]$^+$ (66.8), 147 (53.2), 135 [*p*-anisate]$^+$ (100), 83 [angelate]$^+$ (72.3).

Partial hydrolysis of **11**. Compound **11** (35 mg) was hydrolysed as described for **5**. After hydrolysis, **11** afforded compound **13** (12 mg).

Compound **13**. ^{1}H NMR: δ6.05 (1H, *dq*, H-3″), 5.74 (1H, *br d*, *J* = 7.9 Hz, H-9), 4.93 (1H, *d*, *J* = 7.9 Hz, H-10), 4.08 (1H, *dt*, *J* = 2.5, 10.5 and 10.5 Hz, H-6), 2.47 (1H, *d*, *J* = 10.5 Hz, H-5), 2.18 (1H, *dd*, *J* = 2.5 and 14.5 Hz, H-7β), 2.01 (3H, *td*, *J* = 1 and 7 Hz, H-4″), 1.92 (3H, *t*, *J* = 1 Hz, H-5″), 1.81 (3H, *br s*, H-14), 1.13 (3H, *s*, H-15), 0.97 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.94 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 336 [M]$^+$ (0.12), 293 [M − *iso*-Pr]$^+$ (1.1), 275 [M − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (8.8), 257 [M − *iso*-Pr − 2 × $\mathrm{H_2O}$]$^+$ (6.8), 235 [M − angelate − $\mathrm{H_2O}$]$^+$ (16.3), 218 [M − angelic acid − $\mathrm{H_2O}$]$^+$ (30.9), 203 [M − angelic acid − $\mathrm{H_2O}$ − Me]$^+$ (31), 193 [M − angelic acid − *iso*-Pr]$^+$ (39.3), 175 [M − angelic acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (100), 157 [M − angelic acid − *iso*-Pr − 2 × $\mathrm{H_2O}$]$^+$ (62.6), 147 (60.5), 133 (64), 123 (76.3), 119 (74), 83 [angelate]$^+$ (81.8), 55 (86.2).

Compound **12**. Gum (15 mg); UV $\lambda_{\max}$ nm (ε): 295 (4220), 265 (11 050); IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1} 3460, 2970, 2935, 2885, 1710 (sh), 1703, 1660, 1640, 1608, 1580, 1560, 1548, 1515, 1462, 1440, 1425, 1385, 1350, 1272, 1260, 1140, 1120, 1068, 1040, 960, 935, 880 and 850. ^{1}H NMR: δ7.68 (1H, *dd*, *J* = 2 and 8.5 Hz, H-7′), 7.54 (1H, *d*, *J* = 2 Hz, H-3′), 6.91 (1H, *d*, *J* = 8.5 Hz, H-6′), 6.11 (1H, *dq*, H-3″), 5.79 (1H, *br d*, *J* = 7.5 Hz, H-9), 5.42 (1H, *dt*, *J* = 2.5, 9.5 and 10.5 Hz, H-6), 4.94 (1H, *d*, *J* = 7.5 Hz, H-10), 3.96 (3H, *s*, H-8′)*, 3.93 (3H, *s*, H-9′)*, 2.8 (1H, *d*, *J* = 10.5 Hz, H-5), 2.27 (1H, *dd*, *J* = 2.5 and 14.5 Hz, H-7β), 2.05 (3H, *td*, *J* = 1 and 7 Hz, H-4″), 1.97 (3H, *t*, *J* = 1 Hz, H-5″), 1.83 (3H, *br s*, H-14), 1.23 (3H, *s*, H-15), 0.99 (3H, *d*, *J* = 6.7 Hz, H-12)* and 0.87 (3H, *d*, *J* = 6.7 Hz, H-13)*. MS *m/z* (rel. int.): 500 [M]$^+$ (0.24), 483 [M − $\mathrm{H_2O}$ + H]$^+$ (4.1), 401 [M − angelic acid + H]$^+$ (2.7), 383 [M − angelic acid − $\mathrm{H_2O}$ + H]$^+$ (8.6), 357 [M − angelic acid − *iso*-Pr]$^+$ (32.9), 319 [M − veratric acid + H]$^+$ (3.6), 275 [M − veratic acid − *iso*-Pr]$^+$ (16.3), 257 [M − veratric acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$ (7.2), 235 [M − veratric acid − angelate]$^+$ (45.6), 218 [M − veratric acid − angelic acid]$^+$ (55.2), 201 [M − veratric acid − angelic acid − $\mathrm{H_2O}$ + H]$^+$ (59.8), 182 [veratric acid]$^+$ (90.3), 175 [M − veratric acid − angelic acid − *iso*-Pr]$^+$, (86.4), 165 [veratrate]$^+$ (100), 157 [M − veratric acid − angelic acid − *iso*-Pr − $\mathrm{H_2O}$]$^+$

(58.6), 132 (77.3), 121 (50.9), 119 (74.9), 107 (64.9), 83 [angelate]$^+$ (70.6).

Compound **14**. Gum (91 mg); UV λ_{max} nm (ε): 263 (13 150); IR ν^{KBr}_{max} cm^{-1}: 3450, 2970, 2940, 2880, 2850, 1738, 1712, 1650, 1610, 1580 (sh), 1514, 1460, 1380, 1320, 1260, 1174, 1110, 1080, 1038, 970, 950, 852 and 778. ^{1}H NMR: δ7.98 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.96 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 5 51 (1H, *br s*, H-9), 5.32 (1H, *dt*, *J* = 2.1, 9.5 and 10.5 Hz, H-6), 5.23 (1H, *br s*, H-10), 5.09 (1H, *d*, *J* = 5.5 Hz, H-2), 3.88 (3H, *s*, H-8′), 2.64 (1H, *d*, *J* = 10.5 Hz, H-5), 2.27 (1H, *dd*, *J* = 2.1 and 14.5 Hz, H-7β), 2.02 (3H, *s*, H-2″), 2 (3H, *s*, H-2‴), 1.83 (3H, *br s*, H-14), 1.25 (3H, *s*, H-15), 0.96 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.81 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.): 488 [M]$^+$ (0.5), 471 [M − H_2O + H]$^+$ (23.7), 445 [M − *iso*-Pr]$^+$ (14.7), 429 [M − HOAc + H]$^+$ (7.8), 411 [M − HOAc − H_2O + H]$^+$ (6.6), 385 [M − HOAc − *iso*-Pr]$^+$ (19.6), 368 [M − 2 × HOAc]$^+$ (0.4), 337 [M − *p*-anisic acid + H]$^+$ (0.7), 325 [M − 2 × HOAc − *iso*-Pr]$^+$ (6.1), 319 [M − *p*-anisic acid − H_2O + H]$^+$ (4.9), 293 [M − *p*-anisic acid − *iso*-Pr]$^+$ (24.5), 277 [M − *p*-anisic acid − HOAc + H]$^+$ (30.8), 259 [M − *p*-anisic acid − HOAc − H_2O + H]$^+$ (35.2), 251 [M − *p*-anisic acid − acetate − *iso*-Pr + H]$^+$ (17.3), 233 [M − *p*-anisic acid − HOAc − *iso*-Pr]$^+$ (52.7), 217 [M − *p*-anisic acid − 2 × HOAc + H]$^+$ (56.4), 201 [M − *p*-anisic acid − 2 × HOAc − Me]$^+$ (33.7), 199 [M − *p*-anisic acid − 2 × HOAc − H_2O + H]$^+$ (38.1), 191 [M − *p*-anisic acid − HOAc − acetate − *iso*-Pr + H]$^+$ (45.7), 173 [M − *p*-anisic acid − 2 × HOAc − *iso*-Pr]$^+$ (51.9), 152 [*p*-anisic acid]$^+$ (45 2), 135 [*p*-anisate]$^+$ (100), 119 (50.3), 43 (52.4).

Partial hydrolysis of **14**. Compound **14** (30 mg) was hydrolysed as described for **5**. After hydrolysis, **14** yielded **16** (9 mg).

Compound **16**. ^{1}H NMR: δ5.42 (1H, *br s*, H-9), 5.12 (1H, *br s*, H-10), 5.04 (1H, *dd*, *J* = 2 and 4.2 Hz, H-2), 4.01 (1H, *dt*, *J* = 2.5, 10 and 10.5 Hz, H-6), 2.23 (1H, *d*, *J* = 10 Hz, H-5), 2 (3H, *s*, H-2″), 1.97 (3H, *s*, H-2‴), 1.81 (3H, *br s*, H-14) 1.18 (3H, *s*, H-15), 0.93 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.9 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.). 311 [M − *iso*-Pr]$^+$ (1.2), 294 [M − HOAc]$^+$ (3.4), 276 [M − HOAc − H_2O]$^+$ (11.2), 251 [M − HOAc − *iso*-Pr]$^+$ (87.2), 234 [M − 2 × HOAc]$^+$ (57.8), 216 [M − 2 × HOAc − H_2O]$^+$ (54.6), 201 [M − 2 × HOAc − H_2O]$^+$ (54 6), 201 [M − 2 × HOAc − H_2O − Me]$^+$ (15.8), 191 [M − 2 × HOAc − *iso*-Pr]$^+$ (77 3), 173 [M − 2 × HOAc − *iso*-Pr − H_2O]$^+$ (85.4), 149 (48.5), 145 (81.3), 135 (77.7), 121 (53.4), 71 (45.4), 43 (100)

Compound **15**. White prisms (23 mg) from hexane–EtOAc (3:1). Mp 152–4° UV λ_{max} nm (ε): 263 (11 720), IR ν^{KBr}_{max} cm^{-1}. 3460, 2965, 2930, 2875, 1703, 1672, 1603, 1580, 1510, 1468, 1440, 1420, 1380, 1315, 1275, 1258, 1170, 1128, 1100, 1085, 1033, 970, 932, 900, 850, 830, 770 and 700. ^{1}H NMR: δ7.97 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.94 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 5.39 (1H, *br s*, H-9), 5.28 (1H, *dt*, *J* = 2.5, 10.7 and 11.2 Hz, H-6), 5.08 (1H, *d*, *J* = 5 Hz, H-2), 4.34 (1H, *br s*, H-10), 3.88 (3H, *s*, H-8′), 2.52 (1H, *d*, *J* = 10 7 Hz, H-5), 2.22 (1H, *dd*, *J* = 2 5 and 14.5 Hz, H-7β), 2.12 (3H, *s*, H-2″), 1 84 (3H, *br s*, H-14), 1 17 (3H, *s*, H-15), 0.98 (3H, *d*, *J* = 6 5 Hz, H-12)* and 0.83 (3H, *d*, *J* = 6.5 Hz, H-13)*. MS *m/z* (rel. int.)· 446 [M]$^+$ (0.25), 403 [M − *iso*-Pr]$^+$ (14 5), 386 [M − HOAc]$^+$ (0.6), 343 [M − HOAc − *iso*-Pr]$^+$ (16.9), 251 [M − *p*-anisic acid − *iso*-Pr]$^+$ (14.3), 234 [M − *p*-anisic acid − HOAc]$^+$ (34.8), 216 [M − *p*-anisic acid − HOAc − H_2O]$^+$ (37.5), 201 [M − *p*-anisic acid − HOAc − H_2O − Me]$^+$ (9.2), 191 [M − *p*-anisic acid − HOAc − *iso*-Pr]$^+$ (68.7), 173 [M − *p*-anisic acid − HOAc − H_2O]$^+$ (48.3), 163 (44.5), 152 [*p*-anisic acid]$^+$ (64.5), 148 (63 2), 135 [*p*-anisate]$^+$ (100), 120 (68.5), 105 (59.7), 92 (51), 77 (50.9), 71 (53), 43 (85 7).

Acetylation of **15** (5 mg) with Ac_2O–C_5H_5N in the usual way, afforded **14**. Spectral properties of the product were found to be identical with our authentic sample

Compound **17**. Colorless tetragonal plates (90 mg) from hexane–EtOAc (3:1). Mp 155–156°. UV λ_{max} nm (ε): 263 (8200); IR ν^{KBr}_{max} cm^{-1}: 3520, 2975, 2940 (sh), 2885, 2860 (sh), 1739, 1720 (sh), 1693, 1650, 1608, 1580, 1465, 1442, 1380, 1320, 1302, 1258, 1172, 1130, 1103, 1080, 1031, 995, 850, 775 and 700. ^{1}H NMR: δ8.0 (2H, *d*, *J* = 8.5 Hz, H-3′ and H-7′), 6.96 (2H, *d*, *J* = 8.5 Hz, H-4′ and H-6′), 5.58 (1H, *br d*, *J* = 6 Hz, H-9)†, 5.55 (1H, *ddd*, *J* = 4.4, 7.6 and 10.8 Hz, H-6)†, 5.21 (1H, *br d*, *J* = 6 Hz, H-10), 5.03 (1H, *dd*, *J* = 2 and 6.5 Hz, H-2), 3.88 (3H, *s*, H-8′), 3.06 (1H, *d*, *J* = 10.8 Hz, H-5), 2.67 (1H, *dd*, *J* = 7.6 and 14.7 Hz, H-7α), 2.36 (1H, *dd*, *J* = 4.4 and 14.7 Hz, H-7β), 2.07 (3H, *s*, H-2″), 2.01 (3H, *s*, H-2‴), 1.86 (3H, *br s*, H-14), 1.22 (3H, *s*, H-15), 0.94 (3H, *d*, *J* = 6.7 Hz, H-12)* and 0.82 (3H, *d*, *J* = 6.7 Hz, H-13)*. MS *m/z* (rel. int.): 488 [M]$^+$ (0.4), 471 [M − H_2O + H]$^+$ (1.4), 445 [M − *iso*-Pr]$^+$ (3.3), 385 [M − HOAc − *iso*-Pr]$^+$ (12.5), 325 [M − 2 × HOAc − *iso*-Pr]$^+$ (5.5), 293 [M − *p*-anisic acid − *iso*-Pr]$^+$ (17.1), 276 [M − *p*-anisic acid − HOAc]$^+$ (9.3), 261 [M − *p*-anisic acid − HOAc − Me]$^+$ (4 7), 251 [M − *p*-anisic acid − acetate − *iso*-Pr + H]$^+$ (6.2), 233 [M − *p*-anisic acid − HOAc − *iso*-Pr]$^+$ (79.8), 216 [M − *p*-anisic acid − 2 × HOAc]$^+$ (60.9), 201 [M − *p*-anisic acid − 2 × HOAc − Me]$^+$ (14.2), 191 [M − *p*-anisic acid − HOAc − acetate − *iso*-Pr + H]$^+$ (66.5), 173 [M − *p*-anisic acid − 2 × HOAc − *iso*-Pr]$^+$ (85.8), 152 [*p*-anisic acid]$^+$ (70.3), 148 (63.8), 145 (76.9), 135 [*p*-anisate]$^+$ (100), 131 (48.6), 124 (54.3), 121 (69 1), 119 (73), 107 (66.7), 92 (61.7), 77 (52.9), 71 (59.2), 43 (93.6).

Partial hydrolysis of **17**. Compound **17** (34 mg) was hydrolysed as described for **5**. The product was **19** (11 mg).

Compound **19**. ^{1}H NMR: δ5.65 (1H, *br d*, *J* = 7 Hz, H-9), 5.11 (1H, *d*, *J* = 7 Hz, H-10), 4.92 (1H, *dd*, *J* = 1.1 and 5.8 Hz, H-2), 4.16 (1H, *dt*, *J* = 2.9, 10.3 and 10.5 Hz, H-6), 2.95 (1H, *d*, *J* = 10.3 Hz, H-5), 2.74 (1H, *dd*, *J* = 10.5 and 14 Hz, H-7α), 2.28 (1H, *septet*, H-11), 2.12 (1H, *dd*, *J* = 2.9 and 14 Hz, H-7β), 2.04 (3H, *s*, H-2″), 1 95 (3H, *s*, H-2‴), 1.81 (3H, *br s*, H-14), 1.1 (3H, *s*, H-15), 0.95 (3H, *d*, *J* = 6.8 Hz, H-12)* and 0.93 (3H, *d*, *J* = 6.8 Hz, H-13)*. MS *m/z* (rel. int): 354 [M]$^+$ (0.15), 294 [M − HOAc]$^+$ (4.8), 276 [M − HOAc − H_2O]$^+$ (11.6), 251 [M − HOAc − *iso*-Pr]$^+$ (30), 233 [M − HOAc − *iso*-Pr − H_2O]$^+$ (64), 216 [M − 2 × HOAc − H_2O]$^+$ (48.2), 201 [M − 2 × HOAc − H_2O − Me]$^+$ (30.6), 191 [M − 2 × HOAc − *iso*-Pr]$^+$ (79), 173 [M − 2 × HOAc − *iso*-Pr − H_2O]$^+$ (100), 163 (43.8), 145 (86.6), 135 (65.5), 131 (49.7), 121 (73.1), 107 (59.6), 95 (61.2), 71 (65.2), 43 (82.6).

Compound **18**. Gum (6 mg), UV λ_{max} nm (ε): 297 (3210) and 268 (6150); IR ν^{KBr}_{max} cm^{-1}: 3445, 2960, 2935, 2865, 1738, 1715, 1700 (sh), 1650, 1640, 1608, 1580, 1560, 1540, 1520, 1460, 1420, 1380, 1300 (sh), 1275, 1260, 1230, 1185, 1142, 1115, 1080, 1035, 965, 880, 770 and 700 ^{1}H NMR: δ7.68 (1H, *dd*, *J* = 2 and 8.5 Hz, H-7′), 7.56 (1H, *d*, *J* = 2 Hz, H-3′), 6.93 (1H, *d*, *J* = 8.5 Hz, H-6′), 5.59 (1H, *br d*, *J* = 6 Hz, H-9)†, 5.56 (1H, *ddd*, *J* = 3.2, 6.5 and 10.7 Hz, H-6)†, 5 21 (1H, *br d*, *J* = 6 Hz, H-10), 5.04 (1H, *dd*, *J* = 2 and 6.5 Hz, H-2), 3.97 (3H, *s*, H-8′)*, 3.95 (3H, *s*, H-9′)*, 3.07 (1H, *d*, *J* = 10.7 Hz, H-5), 2.77 (1H, *dd*, *J* = 6.5 and 14 3 Hz, H-7α), 2.37 (1H, *dd*, *J* = 3.2 and 14.3 Hz, H-7β), 2.08 (3H, *s*, H-2″), 2.02 (3H, *s*, H-2‴), 1.88 (3H, *br s*, H-14), 1 23 (3H, *s*, H-15), 0.96 (3H, *d*, *J* = 6.5 Hz, H-12)* and 0.83 (3H, *d*, *J* = 6 5 Hz, H-13)*. MS *m/z* (rel. int.). 518 [M]$^+$ (0.7), 475 [M − H_2O]$^+$ (2.1), 428 [M − HOAc − 2 × Me]$^+$ (8), 415 [M − HOAc − *iso*-Pr]$^+$ (7 7), 355 [M − 2 × HOAc − *iso*-Pr]$^+$ (2.9), 293 [M − veratric acid − *iso*-Pr]$^+$ (9.8), 276 [M − veratric acid − HOAc]$^+$ (5.7), 261 [M − veratric acid − HOAc − Me]$^+$ (2.9), 251 [M − veratric acid − acetate − *iso*-Pr + H]$^+$ (3 9), 233 [M − veratric acid − HOAc − *iso*-Pr]$^+$ (63.3), 216 [M − veratric acid − 2 × HOAc]$^+$ (34.9), 201 [M − veratric acid − 2 × HOAc − Me]$^+$ (9.6), 191 [M − veratric acid − HOAc − acetate − *iso*-Pr + H]$^+$ (49.9), 182

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† Partially obscured by one another

[veratric acid]$^+$ (89.3), 173 [M − veratric acid − 2 × HOAc − *iso*-Pr]$^+$ (80.1), 165 [veratrate]$^+$ (100), 148 (54.7), 145 (68.2), 135 (61.5), 121 (67.6), 119 (62.6), 105 (48), 95 (49.4), 79 (49.3), 71 (55.3) and 43 (76.2).

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REFERENCES

1. Miski, M., Ulubelen, A. and Mabry, T. J. (1983) *Phytochemistry* **22**, 2231.
2. Miski, M., Ulubelen, A., Mabry, T. J., Watson, W H., Vickovic, I. and Holub, M. (1984) *Tetrahedron* **40**, 5197.
3. Gunther, R. T. (1959) *The Greek Herbal of Dioscorides*, p. 323. Hafner, New York.
4. French, D. H. (1971) in *The Chemistry and Biology of the Umbelliferae* (Heywood, V. H., ed.), p. 400. Academic Press, London.
5. Saidkhodzhaev, A. I. (1979) *Khim. Prir. Soedin.* 437.
6. Kadyrov, A. S. and Saidkhodzhaev, A. I. (1978) *Khim. Prir. Soedin.* 137.
7. Golovina, L A., Saidkhodzhaev, A. I. and Malikov, V. M. (1978) *Khim. Prir. Soedin.* 712.
8. Sagitdinova, G. V. and Saidkhodzhaev, A. I (1977) *Khim. Prir. Soedin.* 790.
9. Golovina, L. A. and Saidkhodzhaev, A. I. (1981) *Khim. Prir. Soedin.* 318
10. Golovina, L. A., Saidkhodzhaev, A. I. and Malikov, V. M. (1983) *Khim. Prir. Soedin.* 301.