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CAROTANE SESQUITERPENES FROM *FERULA LANCEROTTENSIS*

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Key Word Index—*Ferula lancerottensis*; Umbelliferae; sesquiterpenes; carotane; epoxyjaeschkeanadiol; lancerodiol; lancerotriol; linkitriol.

Abstract—Six new carotane sesquiterpenes, the *p*-hydroxybenzoate of epoxyjaeschkeanadiol, the *p*-methoxybenzoate and *p*-hydroxybenzoate of lancerodiol, lancerodiol, the *p*-hydroxybenzoate of lancerotriol and the *p*-methoxybenzoate of linkitriol, and the already known *p*-hydroxybenzoate of jaeschkeanadiol have been isolated from *Ferula lancerottensis*.

INTRODUCTION

Phytochemically, the genus *Ferula* is characterized by the fact that it contains coumarins and sesquiterpenoids. From the latter series, compounds with carotane, himachalane, guaiane, germacrene and humulane skeletons have been isolated [1].

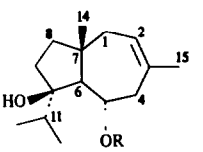
We have continued our studies on the components of the genus *Ferula*, endemic to the Canary Islands [2, 3], and we now describe the isolation and structural determination of six new carotane sesquiterpenes isolated from *Ferula lancerottensis* Parl. The new compounds are lancerodiol *p*-methoxybenzoate (**5**), lancerodiol *p*-hydroxybenzoate (**6**), lancerodiol (**7**), epoxyjaeschkeanadiol *p*-hydroxybenzoate (**8**), lancerotriol *p*-hydroxybenzoate (**10**) and linkitriol *p*-methoxybenzoate (**18**).

RESULTS AND DISCUSSION

Compound **5** was found to have a molecular formula of $C_{23}H_{30}O_5$ (high-resolution MS). Its IR spectrum showed absorptions of an aromatic ester and a conjugated ketone. Its ^1H NMR spectrum presented signals characteristic of an angular methyl group, an isopropyl group, a methyl group over a double bond, a vinylic hydrogen β to a ketone and a proton geminal to an esterified alcohol group. The spectrum also contained a pair of doublets (each 2H), typical of *ortho* hydrogens in an aromatic ring.

In addition to the molecular ion, the mass spectrum contained peaks attributable to fragmentation ions formed by the loss of water, an isopropyl group and *p*-methoxybenzoic acid.

The structure of **5** was also chemically confirmed. Thus, on treatment of **5** with thionyl chloride in pyridine, two dehydrated compounds, **12** and **13**, were obtained. The former compound was also synthesized from jaeschkeanadiol *p*-hydroxybenzoate (ferutinin) (**4**) [4, 5], also obtained from this species, in the following way: **4** was epoxidized with *m*-chloroperbenzoic acid to give the oxirane **8**. The α-configuration of this ring system was given because it is known that in this type of compound epoxidation occurs on this face [6]. The product **8** was identical with another natural compound reported here from this species, epoxyjaeschkeanadiol *p*-hydroxybenzoate. Treatment of **8** with diazomethane afforded the corresponding *p*-methoxybenzoate **9**, identical with a natural compound isolated from *F. linkii* [3]. By reaction of **9** with dilute perchloric acid, the triol **14** was obtained. The structure **14** was assigned because it is known that in this type of oxiranic cleavage the *trans*-diol is formed [2]. The structure **22** was assigned to a minor



1 R = H
2 R = Ang
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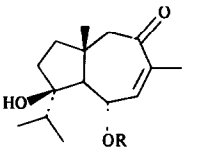
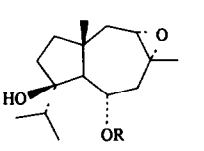
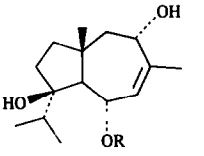
4 R = —CO—C_6H_4OH



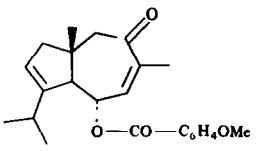
5 R = —CO—C_6H_4OMe
6 R = —CO—C_6H_4OH
7 R = H



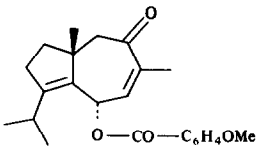
8 R = —CO—C_6H_4OH
9 R = —CO—C_6H_4OMe



10 R = —CO—C_6H_4OH
11 R = —CO—C_6H_4OMe



12



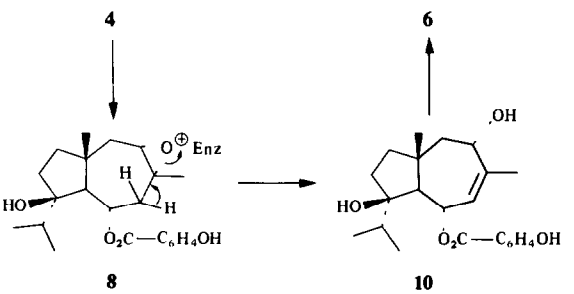
13

product formed in this reaction. Its ^{1}H NMR spectrum showed a pair of singlets at δ5.12 and 5.35 of the exocyclic double bond, a broad signal at δ4.32 assignable to the proton geminal to the alcoholic group, and a broad singlet at δ5.50 of the hydrogen geminal to the ester group. Oxidation of **14** with pyridinium dichromate [7] afforded the ketone **15**. When this substance was treated with thionyl chloride in pyridine for 5 min a mixture of two dehydrated products, **16** and **17**, was obtained and separated by dry column chromatography. Compound **16** reacted again for a longer time affording **12**, identical in all respects with one of the products obtained in the dehydration of **5**.

The new substance isolated in greatest quantity from *F. lancerottensis* was identified as lancerodiol *p*-hydroxybenzoate (**6**). Its ^{1}H NMR spectrum was similar to that of **5** except that there were no signals corresponding to the methoxyl group. Treatment of **6** with diazomethane gave **5**. Alkaline hydrolysis of **5** afforded the alcohol **7**, identical with a natural diol also isolated from this species, named lancerodiol, and reported here.

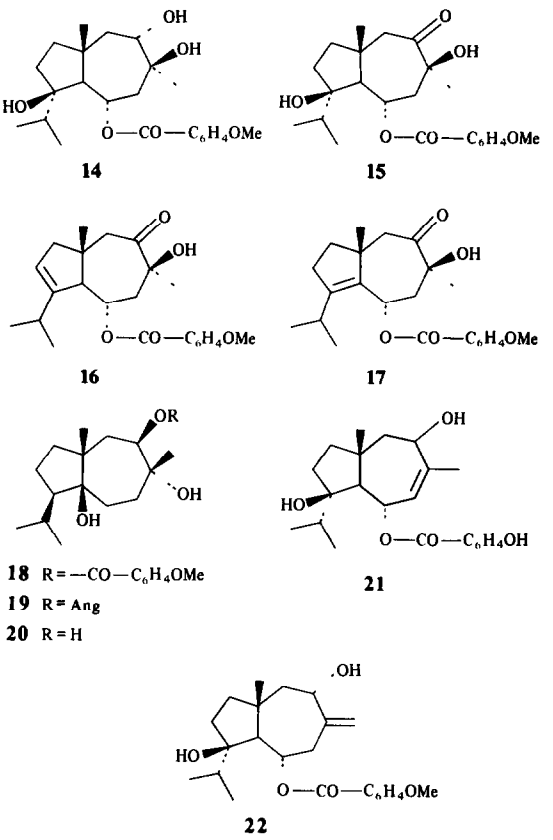
The *p*-hydroxybenzoate of lancerotriol (**10**) was the most polar compound isolated from this species. The structure of this new product was determined on the basis of the following considerations. A fragment produced by the loss of two water molecules was observed in the mass spectrum, but there was no molecular ion. Its ^{1}H NMR spectrum contained signals corresponding to the ester group, the hydrogen geminal to this ester, a vinylic proton, a methyl over a double bond and a hydrogen geminal to a hydroxyl group.

Compound **10** was related to **6** chemically. Reduction of **6** with sodium borohydride gave a mixture of epimeric alcohols which was separated by chromatography. The less polar compound was identical with the natural product **10**. The α-stereochemistry, given to the hydroxyl group at C-2 in **10**, is based on biosynthetic considerations and ^{1}H NMR data. Thus **10** can be derived from epoxyjaeschkeanadiol *p*-hydroxybenzoate (**8**) by enzymatic cleavage of the oxirane ring with formation of a carbocation at C-3 and neutralization of this with the loss of a hydrogen at C-4 and the formation of a double bond C-3 (C-4) (Fig. 1). The configuration of the alcoholic group formed must be α, as in the original oxirane ring in **8**. From the ^{1}H NMR data of **10** and its β-epimer **21**, the stereochemistry of both hydroxyl groups was also inferred. Thus, of the different conformations that molecules **10** and **21** can adopt, we have chosen the one which explains the coupling constant of zero between H-4 and H-5, observed in the ^{1}H NMR spectra of both epimers. This corresponds to a chair conformation, with an



8 10

Fig. 1.



equatorial hydroxyl (α) for **10** and an axial hydroxyl (β) for **21**. The geminal proton to the alcohol in **10** and **21** had resonances at δ4.30 (*br*, $W_{1/2}$ = 19 Hz) and 4.70 (*t*, $W_{1/2}$ = 13 Hz) respectively, in agreement with the angles formed with the H-1 hydrogens and with the generalization that an axial proton resonates at a higher field than its equatorial epimer [8]. Also the chemical shifts of the C-14 hydrogens at δ1.17 and 1.26 in **10** and **21**, respectively, were in accord with the structures given to these two epimeric compounds. When **10** and **21** were oxidized separately, the original *p*-hydroxybenzoate of lancerodiol (**6**) was obtained.

Finally, a further carotane sesquiterpene was isolated. Its high-resolution mass spectrum was in accord with the molecular formula $C_{23}H_{34}O_5$. Its ^{1}H NMR spectrum was similar to that of linkiol (**19**) [2] except for the signals due to the replacement of the angelic acid residue of **19** with *p*-methoxybenzoate. On hydrolysis it gave the alcohol **20**, identical with that obtained by hydrolysis of linkiol [2]. We have named this new natural derivative the *p*-methoxybenzoate of linkitriol (**18**).

The known compound jaeschkeanadiol *p*-hydroxybenzoate (ferutinin) (**4**) [4, 5] was identified by its ^{1}H NMR spectrum and because on treatment with diazomethane it gave the *p*-methoxybenzoate of jaeschkeanadiol (ferutidin) (**3**) [3, 9, 10].

Angelic (**2**) and other aromatic acid esters of jaeschkeanadiol have recently been isolated from *F. elaeochytris* [10].

A probable biosynthetic pathway of jaeschkeanadiol (**1**) has been described [11]. In *F. lancerottensis* the epoxidation of jaeschkeanadiol *p*-hydroxybenzoate (**4**) must

give the epoxyjaeschkeanadiol ester **8**. Enzymatic cleavage of the oxirane ring with elimination of one of the hydrogens over C-4 affords lancerotriol *p*-hydroxybenzoate (**10**). This can be oxidized to give the lancerodiol ester **6** (Fig. 1).

EXPERIMENTAL

Mps: uncorr.; NMR: $CDCl_3$, unless indicated otherwise; IR: $CHCl_3$; UV: EtOH; MS: 70 eV (probe); column and dry column chromatography: silica gel 0.063–0.2 mm.

Isolation of the products. F. lancerottensis Parl. was collected near Haria (Lanzarote, Canary Islands) and a voucher specimen deposited at the Herbarium of the Instituto Canario de Investigaciones Agrarias (ORT 28379). The freshly gathered aerial parts (10 kg) of the plant were finely cut and extracted in a Soxhlet apparatus several times with EtOH. The extracts were combined, filtered, concd *in vacuo* and extracted with $CHCl_3$. CC of the residue (70 g) using petrol–EtOAc mixtures afforded lancerodiol *p*-methoxybenzoate (**5**) (110 mg), lancerodiol (**7**) (60 mg), linkitriol *p*-methoxybenzoate (**18**) (220 mg), jaeschkeanadiol *p*-hydroxybenzoate (**4**) (180 mg), epoxyjaeschkeanadiol *p*-hydroxybenzoate (**8**) (220 mg), lancerodiol *p*-hydroxybenzoate (**6**) (2.5 g) and lancerotriol *p*-hydroxybenzoate (**10**) (650 mg).

p-*Methoxybenzoate of lancerodiol* (**5**). Obtained as a gum. $[M]^+$ *m/z* 386.2073 ($C_{23}H_{30}O_5$ requires: 386.2093). IR ν_{max} cm^{-1}: 3540, 2990, 1720, 1670, 1610, 1520, 1470, 1395, 1180, 1105, 1040, 850; ^1H NMR (90 MHz): δ0.86 and 0.95 (each 3H, *d*, *J* = 8 Hz), 1.28 (3H, *s*, H-14), 1.80 (3H, *s* (*br*), H-15), 2.51 (1H, *d*, *J* = 11 Hz, H-6), 2.70 (2H, *s* (*br*), H-1), 3.90 (3H, *s*), 6.15 (1H, *d*, *J* = 11 Hz, H-5), 6.20 (1H, *s* (*br*), H-4), 6.98 and 8.05 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 368 $[M]^+$, 359, 343, 325, 276, 251, 248, 234, 219, 216, 205, 201, 191.

Lancerodiol (**7**). $[M-H_2O]^+$ *m/z* 244.1610 ($C_{15}H_{22}O_2$ requires: 234.1600). IR ν_{max} cm^{-1}: 3480, 3010, 2965, 2880, 1660, 1610, 1470, 1450, 1380, 1240, 1175, 1080, 1050, 1000, 980, 855; UV λ_{max} nm: 220; ^1H NMR (90 MHz): δ0.91 and 0.98 (each 3H, *d*, *J* = 8 Hz), 1.09 (each 3H, *s*, H-14), 1.87 (3H, *s* (*br*), H-15), 2.14 (1H, *d*, *J* = 11 Hz, H-6), 2.55 and 2.80 (each 1H, *d*, *J* = 8 Hz, H-1), 4.62 (1H, *d*, *J* = 11 Hz, H-5), 6.35 (1H, *s* (*br*), H-4); EIMS *m/z*: 234 $[M-H_2O]^+$, 219, 209, 194, 191, 173, 165, 163.

p-*Methoxybenzoate of linkitriol* (**18**). IR ν_{max} cm^{-1}: 3600, 3480, 2960, 2880, 1710, 1605, 1580, 1510, 1465, 1380, 1260, 1180, 1110, 1035, 950, 850; ^1H NMR (90 MHz): δ0.95 (9H, apparent *t*), 1.31 (3H, *s*), 3.86 (3H, *s*), 5.15 (1H, *d*, *J* = 8 Hz, H-2), 6.93 and 8.10 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 390 $[M]^+$, 372, 319, 307, 277, 264, 238, 220, 212, 209, 207.

p-*Hydroxybenzoate of jaeschkeanadiol* (*ferutinin*) (**4**). ^1H NMR (90 MHz): δ0.90 (6H, apparent *t*, *J* = 6 Hz), 1.10 (3H, *s*, H-14), 1.80 (3H, *s* (*br*), H-15), 5.15 (1H, *t*, *J* = 11 Hz, H-5), 5.55 (1H, *s* (*br*), H-2), 6.92 and 7.92 (each 2H, *d*, *J* = 9 Hz).

p-*Hydroxybenzoate of lancerodiol* (**6**). Mp 227–228° (Found: C, 71.73; H, 7.65. $C_{22}H_{28}O_5$ requires: C, 70.94; H, 7.58%). IR ν_{max} cm^{-1}. 3590, 2970, 1700, 1670, 1610, 1595, 1520, 1460, 1390, 1330, 1270, 1170, 1100, 1040, 940, 850; ^1H NMR (60 MHz): δ0.83 and 0.94 (each 3H, *d*, *J* = 5 Hz), 1.23 (3H, *s*, H-14), 1.88 (3H, *s* (*br*), H-1), 6.13 (1H, *d*, *J* = 11 Hz, H-5), 6.21 (1H, *s* (*br*), H-4), 6.92 and 8.00 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 372 $[M]^+$, 329, 234, 219, 191, 163, 148.

p-*Hydroxybenzoate of epoxyjaeschkeanadiol* (**8**). Mp 133–134°. IR ν_{max} cm^{-1}: 3600, 3350, 2970, 2890, 1695, 1620, 1590, 1515, 1450, 1385, 1310, 1270, 1170, 1120, 1100, 960, 920, 880, 850; ^1H NMR (90 MHz): δ0.88 (6H, *t*, *J* = 8 Hz), 1.26 (3H, *s*, H-14), 1.48 (3H, *s*, H-15), 2.93 (1H, *t*, 8 Hz), 5.48 (1H, *t*, *J* = 11 Hz, H-5), 6.90 and 7.90 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 345 $[M-C_3H_7]^+$, 234, 207, 191, 163, 151, 148.

p-*Hydroxybenzoate of lancerotriol* (**10**). $[M-2H_2O]^+$ *m/z* 338.1895 ($C_{22}H_{26}O_3$ requires: 338.1882). ^1H NMR (90 MHz): δ0.87 (6H, *t*, *J* = 6 Hz), 1.17 (3H, *s*, H-14), 1.88 (3H, *s* (*br*), H-15), 2.23 (1H, *d*, *J* = 11 Hz, H-6), 4.32 (1H, *br*, H-2), 5.40 (1H, *s* (*br*), H-4), 5.87 (1H, *d*, *J* = 11 Hz, H-5), 6.90 and 7.94 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 338 $[M-2H_2O]^+$, 236, 218, 193, 175, 157, 151.

Dehydration of **5**. The *p*-methoxybenzoate of lancerodiol (**5**) (130 mg) was treated with $SOCl_2$ (0.5 ml) in C_6H_5N (2.5 ml) at 0° for 5 min. Usual work-up and chromatography eluting with petrol–EtOAc (9:1) gave **12** (65 mg). $[M-C_6H_5(OMe)CO_2H]^+$ *m/z* 216.1534 ($C_{15}H_{20}O$ requires. 216.1514); IR ν_{max} cm^{-1}: 3040, 2980, 2940, 2850, 1710, 1660, 1610, 1580, 1520, 1470, 1450, 1425, 1385, 1360, 1330, 1265, 1240, 1180, 1110, 1040, 1015, 950, 850, 790; ^1H NMR (90 MHz): δ0.90 and 0.98 (each 3H, *d*, *J* = 4 Hz), 1 16 (3H, *s*), 1.90 (3H, *d*, *J* = 2 Hz), 2.76 and 2.99 (each 1H, *d*, *J* = 15 Hz, H-1), 3.28 (1H, *d* (*br*), *J* = 11 Hz, H-6), 5.50 (1H, *s* (*br*), H-9), 5.82 (1H, *d* (*br*), H-5), 6.20 (1H, *s* (*br*), H-4), 6.95 and 8.06 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 216 $[M-C_6H_4(OMe)CO_2H]^+$, 201, 189, 173, 159, 152, 135. Further elution gave **13** (18 mg). ^1H NMR (90 MHz): δ0.90 (3H, *s*, H-14), 0.80 and 1.03 (each 3H, *d*, *J* = 6 Hz), 1.92 (3H, *s* (*br*), H-15), 2.70 (1H, *m*, H-11), 2.60 and 2.87 (each 1H, *d*, *J* = 15 Hz, H-1), 3.86 (3H, *s*), 5.90 and 6.62 (each 1H, *d*, *J* = 8 Hz, H-5 and H-4), 6.95 and 8.02 (each 2H, *d*, *J* = 9 Hz).

Reduction of **6**. The *p*-hydroxybenzoate of lancerodiol (**6**) (50 mg) was added to a soln of $NaBH_4$ (25 mg) in MeOH (5 ml). After 2 hr the mixture was diluted with H_2O and extracted as usual. Evapn of the solvent and chromatography of the residue eluting with petrol–EtOAc (3:2) afforded **10** (24 mg) (identical with the natural compound). Further elution gave **21** (17 mg). ^1H NMR (90 MHz): δ0.87 and 0.98 (each 3H, *d*, *J* = 6 Hz), 4.63 (1H, *t*, *J* = 8 Hz, H-2), 5.50 (1H, *s* (*br*), H-4), 5.96 (1H, *d* (*br*), *J* = 11 Hz, H-5), 6.89 and 7.85 (each 1H, *d*, *J* = 9 Hz); EIMS *m/z*. 236 $[M-C_6H_5(OH)CO_2H]^+$, 218, 207, 193, 175, 165, 161.

Epoxidation of **4**. The *p*-hydroxybenzoate of jaeschkeanadiol (**4**) (140 mg) in $CHCl_3$ (4 ml) was added to a soln of *m*-chloroperbenzoic acid (66 mg) in $CHCl_3$ (4 ml). The mixture was left at room temp. for 45 min and then washed with a saturated soln of $NaHCO_3$. Usual work-up and chromatography of the residue with petrol–EtOAc (7:3) gave **8** (110 mg), identical with the natural compound. Treatment of **8** with ethereal CH_2N_2 afforded **9**, identical with the data reported in ref. [3].

Triol **14**. The epoxide **9** (80 mg) in THF (11 ml) was stirred with aq. 3% perchloric acid (10 ml) at room temp. for 45 hr. Usual work-up and chromatography of the residue eluting with $CHCl_3$ afforded **22** (6 mg), mp 78–81°. ^1H NMR (90 Hz): δ0.86 and 0.93 (each 3H, *d*, *J* = 3 Hz), 1.32 (3H, *s*), 3.87 (3H, *s*), 4.32 (1H, *br*, H-2), 5.12 and 5.35 (each 1H, *s*, H-15), 5.50 (1H, *t*, H-5), 7.01 and 8 08 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 345 $[M-C_3H_7]^+$, 314, 312, 286, 285, 236, 203, 193, 175, 152, 147, 135. Further elution gave the triol **14** (58 mg). ^1H NMR (90 MHz): δ0.81 and 0.89 (each 3H, *d*, *J* = 3 Hz), 1.28 (6H, *s*, H-14 and H-15), 2.60 (1H, *d*, *J* = 10 Hz, H-6), 3.82 (1H, *s* (*br*), H-2), 3.86 (3H, *s*), 5.78 (1H, *oct.*, *J* = 10, 7 and 2 Hz, H-5), 6.94 and 7.98 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 363 $[M-C_3H_7]^+$, 254, 236, 218, 211, 193, 183, 175.

Oxidation of **14**. The triol **14** (55 mg) in CH_2Cl_2 (5 ml) was treated with pyridinium dichromate (85 mg) at room temp. for 3 hr. The soln was diluted with Et_2O, filtered and evapd giving **15** (46 mg). ^1H NMR (90 MHz): δ0.80 (6H, *complex*), 1.27 and 1.35 (each 3H, *s*, H-14 and H-15), 2.15 (1H, *d*, *J* = 11 Hz, H-6), 2.53 and 2.71 (each 1H, *d*, *J* = 12 Hz, H-1), 3.87 (3H, *s*), 5.63 (1H, *d* (*br*), *J* = 11 Hz), 6.94 and 8.03 (each 2H, *d*, *J* = 9 Hz); EIMS *m/z*: 361 $[M-C_3H_7]^+$, 343, 252, 224, 209, 206, 191.

Dehydration of **15**. The ketone-diol **15** (44 mg) in C_5H_5N (1 ml)

was treated at 0° with $SOCl_2$ (0.3 ml) in C_5H_5N (1 ml) for 5 min, then poured onto ice and extracted as usual, affording a mixture of products (30 mg). Chromatography of this residue eluting with petrol–EtOAc (4:1) gave **17** (11 mg). ^{1}H NMR (90 MHz): δ0.76 and 0.98 (each 3H, *d*, J = 7 Hz), 1.26 (6H, *s*, H-14 and H-15), 2.38 and 2.93 (each 1H, J = 12 Hz, H-1), 3.28 (1H, *m*, H-11), 3.88 (3H, *s*), 5.33 (1H, *c*, J = 11 and 3 Hz), 6.96 and 8.04 (each 2H, *d*, J = 9 Hz); EIMS m/z: 386 $[M]^+$, 368, 313, 299, 251, 234, 219, 193, 191. Further elution afforded **16** (13 mg). ^{1}H NMR (90 MHz): δ0.87 and 0.94 (each 3H, *d*, J = 6 Hz), 1.16 and 1.27 (each 3H, *s*, H-14 and H-15), 2.67 and 2.93 (each 1H, *d*, J = 12 Hz, H-1), 3.18 (1H, *d*, J = 11 Hz, H-6), 3.78 (3H, *s*), 5.42 (1H, *d*, J = 9 Hz); EIMS m/z: 386 $[M]^+$, 368, 313, 299, 234, 191. When **16** was treated again with $SOCl_2$ in the same way but for 5 hr, **12** (9 mg) was obtained, identical with one of the products formed in the dehydration of **5**.

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