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Two oleanane triterpenoids from *Gordonia ceylanica* and their conversions to taraxarane triterpenoids

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Abstract

Chemical investigation of the hot hexane extract of the stem bark of *Gordonia ceylanica* afforded two new oleanane triterpenoids, 3β-acetoxy-11α,13β-dihydroxyolean-12-one (**1**) and 3β,11α-diacetoxy-13β-hydroxyolean-12-one (**2**). The attempted acid hydrolysis of these two compounds resulted the dehydration and subsequent methyl group migration to afford the taraxarane triterpenoids 3β,11α-dihydroxytaraxer-14-en-12-one (**4**) and 3β-hydroxy-11α-acetoxytaraxer-14-en-12-one (**5**), respectively. These taraxaranes have not been previously reported.

Keywords: *Gordonia ceylanica*; Theaceae; Triterpenoids; Oleanane; Taraxarane

1. Introduction

Gordonia ceylanica belongs to the family Theaceae, which consists of approximately 520 species categorized under 25 different genera. Theaceae species are widely distributed in the tropical and warm temperate areas of the world. Twelve Theaceae species, under five different genera, are found in Sri Lanka. Of the genera *Gordonia*, all four species, *G. ceylanica*, *G. dassanayakei*, *G. speciosa* and *G. elliptica* are endemic to the country. ''Mihiriya'' is the local name for all *Gordonia* species and the colour of the flower is used as an adjective to differentiate each species (Dassanayake and Clayton, 1996).

Although the chemistry and bioactivity of the genus *Gordonia* has not been previously reported, the other species of the family Theaceae have been extensively studied. Special attention has been given to the volatiles of the genus *Camellia*, due to its commercial importance as flavoring agents of drinking tea. Bioactivity studies of some members of the Theaceae family have shown a wide range of activity, including antitumor, anti-HIV, antibacterial and antifungal (Hamaya et al., 1986; Hatano et al., 1992; Jin et al., 1993). In addition, various plants of this family are used as remedies for rheumatism, swelling, traumatic bleeding, tropical ulcers and sores (Inada et al., 1989; Khan et al., 1992; Chang et al., 1994). Although all the *Gordonia* species are being used in traditional medicine in Sri Lanka, no previous chemical investigations have been reported on any of these endemic species. Therefore, the chemical and biological investigations of Sri Lankan *Gordonia* species are of great interest. In our previous work we have reported the isolation and characterization of four oleanane triterpenoids, 3β-acetoxy-28-hydroxyolean-12-ene, 3β-hydroxyolean-12-ene, 3β-acetoxy olean-12-ene and 3β-acetoxyolean-12-ene-11-one from *G. ceylanica* (Herath and Athukoralage, 1998). This was the first report of the isolation of these compounds from *G. ceylanica*.

2. Results and discussion

The chromatographic separation of the hexane

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extract of the stem bark of *G. ceylanica* afforded two new oleanane triterpenoids, compound **1** and **2** (Fig. 1). The mass spectrum of compound **1** exhibited a weak molecular ion peak at *m/z* 516, which was in agreement with the molecular formula $C_{32}H_{52}O_5$. This was supported by the presence of 32 resolved signals in the ^{13}C NMR spectrum. The ^{13}C NMR spectrum of **1** contained characteristic peaks at δ 201.2 and 171.5, for the keto carbonyl and the acetoxy carbonyl, respectively. Further signals at δ 81.5, 80.8 and 71.9 in the DEPT spectrum of **1** indicated the presence of three oxygen bearing carbon atoms in the molecule. The doublet and doublet of a doublet at δ 4.86 and 4.40 in the ^1H NMR spectrum of **1** were indicative of the deshielded protons attached to the two of the oxygen bearing methine carbons C-3 (80.8) and C-11 (71.9), respectively. The other oxygenated carbon, which appeared at δ 81.5 as a quaternary carbon in the DEPT spectrum of **1**, was attributed to C-13. A sharp 3H singlet appeared at δ 1.98 in the ^1H NMR spectrum of compound **1**, consistent with the protons of the single acetoxyl group attached to C-3. The *trans* diaxial coupling constants J = 12.1 and 10.2 Hz for doublet and a double doublet at δ 4.86 and 4.40, respectively, suggested that both the 3-OAc and 11-OH groups should be equatorial and the 13-OH automatically should be axial to minimize the ring strain. The presence of eight angular methyl groups and other characteristic signals in the ^1H and ^{13}C NMR spectra and the mass fragmentation pattern supported the structure of compound **1** being, 3β-acetoxy-11α,13β-dihydroxyolean-12-one.

The ^1H and ^{13}C NMR spectral data of compound **2** illustrated similar features to compound **1**, with few variations. The extra 3H singlet at δ 2.14 was attributed to an additional acetoxyl group and the downfield shift of the 11-H doublet from δ 4.86 to 6.08 in the ^1H NMR spectrum of **2** indicated that the 11-OH of compound **1** was acetylated. This was further confirmed by comparison of the spectral data of compound **2** with the acetylated product of **1** with Ac_2O in pyridine. Interestingly, although compound **1** contains two hydroxyl groups, the ^1H NMR spectrum of the acetylated product of **1** showed that only one hydroxyl group had been acetylated. Furthermore, the methylation of **1** with MeI/KOH in DMSO to give compound **3** (Fig. 1) gave only monomethylation, with the 11-OH methylated, while the second hydroxyl group had not been affected. These findings confirmed that the tertiary hydroxyl group, attached to the ring junction (C-13), does not acetylate or methylate under normal conditions, as previously reported (Itokawa et al., 1989). Similar to that of compound **1**, the *trans* diaxial coupling constants of H-11 (J = 12.3 Hz) and H-3 (J = 9.9 Hz) suggested that the α and β configurations of acetoxyl groups at H-11 and H-3, respectively and the configuration of 13-OH should be β to minimize the ring strain of the triterpene skeleton. Accordingly, the structure 3β,11α-diacetoxy-13β-hydroxyolean-12-one was suggested for compound **2**.

The correlation of eight angular methyl groups with their respective carbons in the HMBC studies of compound **2** (Fig. 2(a)) and the additional information provided by the DEPT, HMQC and HMBC spectra

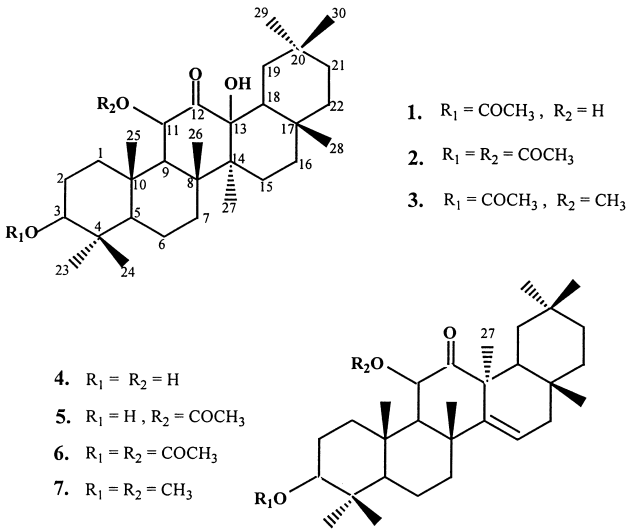

Fig. 1. Structures of compounds **1**–**7**.

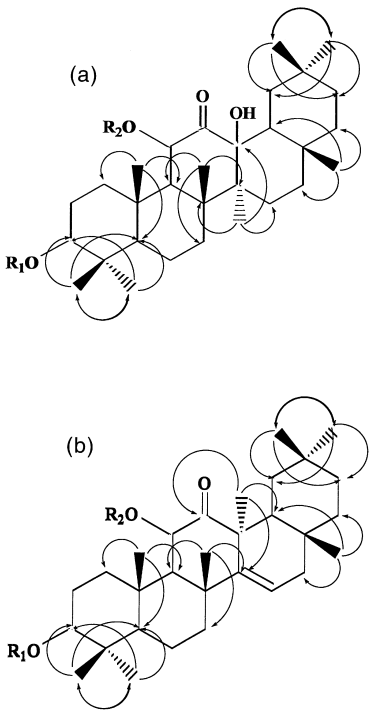

Fig. 2. HMBC of the angular methyl groups of compounds **2** (2a) and **4** (2b).

confirmed the proposed structure for compound **2**. The structure of compound **1** was similarly confirmed as 3β-acetoxy-11α,13β-dihydroxyolean-12-one. The MS, ^{1}H and ^{13}C spectral data of the methylated product of **1** (compound **3**) also gave extra evidence for the confirmation of the proposed structures for compound **1** and **2** (see Section 3).

Attempted acid hydrolysis of compound **2** with few drops of 4N HCl at 70°C gave two products, with the higher polarity compound **4** as the major product and compound **5** as the second product (Fig. 5). Spectral data of compounds **4** and **5** exhibited characteristic features of the taraxarane type of triterpenoid structures. The acid treatment of compound **2** has resulted the dehydration at C-13 and the subsequent methyl group migration from C-14 to C-13. The mass spectrum of compound **4** exhibited a molecular ion peak at m/z 456, consistent with the molecular formula $C_{30}H_{48}O_3$. The ^{13}C NMR spectrum of **4** contained 30 resolved signals, further supporting the molecular formula. An olefinic proton appeared at δ 5.57 as a doublet of doublets in the ^{1}H NMR spectrum and two olefinic carbon signals appeared at δ 151.8 and 121.9 in the ^{13}C NMR spectrum of **4**, indicative of the presence of an olefinic bond in the molecule. The strong correlation of the methyl protons of the 27-CH_3 group with the carbonyl carbon at δ 215.6 (C-12) and the olefinic carbon at δ 151.8 (C-14) and the 26-CH_3 with the same olefinic carbon (C-14) in the HMBC studies of **4** (Fig. 2(b)), not only accentuated that the position of the double bond should be at C-14, but also confirmed the migration of the methyl group at C-14 to the C-13 position. Since there were no signals that corresponded to the acetoxy group in the ^{1}H and ^{13}C-NMR spectra of **4**, both acetoxy groups of compound **2** appeared to have been hydrolyzed. This was further supported by the upfield shift of protons attached to C-3 and C-11 to δ 3.22 and 4.29, respectively, in the ^{1}H NMR spectrum of compound **4**. The proton of the 11-OH group, which is chelated with the C-12 carbonyl, appeared as a sharp doublet at δ 3.10 due to its coupling with the proton directly attached to C-11. Furthermore, this C-11 proton appeared as a doublet of doublets at δ 4.29 in the ^{1}H NMR spectrum of **4** due to its coupling with the proton of the 11-OH group and H-9. The addition of few drops of D_2O to the NMR probe indicated that the double doublet due to 11-H became doublet at δ 4.27 and the 11-OH signal at 3.10 has disappeared. In addition to the above mentioned data and other HMBC correlations of the angular methyl groups with their respective carbons (Fig. 2(b)), all the spectral data (^{1}H, ^{13}C, DEPT, HMQC and MS), were consistent with the structure of compound **4** being 3β,11α-dihydroxytaraxer-14-en-12-one. The spectral data of the acetylated product (**6**) and the methylated product (**7**) of compound **4** (Fig. 1) also strongly supported the above proposed structure for compound **4**.

A sharp 3H singlet at δ 2.05 in the ^{1}H NMR spectrum of compound **5** (the less polar product of the acid hydrolysis of **2**) and the downfield acetoxy carbonyl signal at δ 169.6 in the ^{13}C NMR spectrum indicated the presence of one acetoxy group that had not been hydrolyzed. The absence of the corresponding doublet of the 11-OH proton and the downfield shift of the 11-H proton signal to δ 5.55 (as a doublet) in the ^{1}H NMR spectrum of **5**, confirmed the presence of an acetoxyl group at C-11. All the other signals in the ^{1}H and ^{13}C NMR spectra of compound **5** were almost identical with that of the spectra of compound **4**. Therefore, the structure of compound **5** was deduced as 11α-acetoxy-3β-hydroxytaraxer-14-en-12-one.

3. Experimental

3.1. General

Melting points were determined on a Gallenkamp apparatus and are uncorrected. ^{1}H and ^{13}C NMR (1D) spectra were recorded on either a Varian Unity 300 spectrometer at the Department of Chemistry, University of Wollongong, Australia or a Bruker AC-F 200 MHz spectrometer at the Department of Chemistry, University of Colombo, Sri Lanka. HMQC and HMBC spectra were recorded on a Varian Unity 400 spectrometer at the Department of Chemistry, University of Wollongong, Australia. IR spectra were recorded on a Shimadzu IR-460 instrument in KBr discs and mass spectra were recorded on a Shimadzu QP-1000A spectrometer at the Institute of Fundamental Studies, Kandy, Sri Lanka. Prep. TLC was carried out on Merck Kieselgel 60 F_{254}. Flash and medium pressure column chromatography were carried out on Merck Kieselgel 60 (230–400 mesh ASTM).

3.2. Plant material

The stem bark of *G. ceylanica* was collected from Nuwara Eliya district in the Central Province of Sri Lanka and the voucher specimen was authenticated by comparison with the herbarium specimen 8291, Jayasuriya (17.10.92) at the National herbarium Royal Botanic Gardens, Peradeniya, Sri Lanka.

3.3. Extraction and isolation

Air dried and powdered stem bark (1.0 kg) of *G. ceylanica* was extracted with hot hexane using a soxhlet apparatus. The concentrated hexane extract (4.8 g) was chromatographed on a medium pressure silica gel column and eluted with hexane, dichloromethane and

methanol by gradually increasing the polarity gradient. Further purification of the column fraction (577.4 mg), by eluting with hexane/dichloromethane (1:1), using small scale column chromatography followed by prep. TLC afforded compound **1** (172.9 mg) and compound **2** (30.62 mg).

3.4. 3β-Acetoxy-11α,13β-dihydroxyolean-12-one (*1*)

Colourless needles, mp 286–287°; IR ν_{max} (KBr) cm^{-1}: 3498.0, 2925.0, 1710.0, 1230.0; ^1H NMR (200 MHz, $CDCl_3/CD_3OD$) δ 4.86 (1H, *d*, *J* = 12.1 Hz, H-11), 4.40 (1H, *dd*, *J* = 10.2 and 7.4 Hz, H-3), 3.05 (1H, *s*, –OH), 2.46 (1H, *ddd*, *J* = 14.0, 3.6 and 3.6 Hz, H-18), 1.98 (3H, *s*, $-OCOCH_3$), 1.31, 1.15, 1.07, 0.87, 0.84 (each 3H, *s*, 5 × CH_3), 0.82 (6H, *br. s*, 2 × CH_3), 0.79 (3H, *s*, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$/CD_3OD) δ 201.2 (C-12), 171.5 ($O\underline{C}OCH_3$), 81.5 (C-13), 80.8 (C-3), 71.9 (C-11), 56.7 (C-9), 55.2 (C-5), 44.9 (C-18), 44.9 (C-14), 43.1 (C-8), 39.6 (C-10), 39.1 (C-16), 38.4 (C-4), 38.1 (C-1), 37.9 (C-19), 33.7 (C-21), 33.2 (C-7), 31.4 (C-17), 31.0 (C-30), 30.4 (C-22), 29.3 (C-28), 29.3 (C-29), 27.7 (C-20), 27.7 (C-23), 24.7 (C-2), 23.4 (C-27), 22.3 ($OCO\underline{C}H_3$), 20.7 (C-15), 20.2 (C-26), 17.9 (C-6), 17.2 (C-25), 15.9 (C-24); EIMS (70 eV) *m*/*z* = 516 (M^+, 0.5), 498 (1), 483 (5), 219 (20), 208 (22), 109 (18), 95 (38), 43 (100).

3.5. 3β,11α-Diacetoxy-13β-hydroxyolean-12-one (*2*)

Colourless needles, mp 340°; IR ν_{max} (KBr) cm^{-1}: 3456.0, 2960.0, 1737.8, 1708.8, 1628.0, 1456.0, 1366.4, 1267.2, 1241.6, 1024.0; ^1H NMR (300 MHz, $CDCl_3$) δ 6.11 (1H, *d*, *J* = 12.3 Hz, H-11), 4.45 (1H, *dd*, *J* = 9.9 and 7.5 Hz, H-3), 2.14 (3H, *s*, $OCOCH_3$), 2.04 (3H, *s*, $OCOCH_3$), 1.41, 1.20, 1.02, 0.96, 0.91, 0.87, 0.87, 0.86 (each 3H, *s*, 8 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.4 (C-12), 170.9 ($O\underline{C}OCH_3$), 170.1 ($O\underline{C}OCH_3$), 82.8 (C-13), 80.0 (C-3), 74.2 (C-11), 55.0 (C-5), 53.8 (C-9), 48.8 (C-18), 44.6 (C-14), 43.8 (C-8), 39.7 (C-10), 39.2 (C-16), 39.0 (C-19), 38.4 (C-1), 38.3 (C-4), 34.3 (C-21), 33.9 (C-7), 33.5 (C-17), 33.4 (C-20), 32.0 (C-29), 31.3 (C-28), 30.3 (C-22), 28.1 (C-23), 24.7 (C-30), 23.8 (C-2), 22.7 (C-15), 21.4 ($OCO\underline{C}H_3$), 21.3 ($OCO\underline{C}H_3$), 20.7 (C-26), 18.6 (C-27), 17.6 (C-6), 16.4 (C-24), 16.2 (C-25); EIMS (70 eV) *m*/*z* = 558 (M^+, 1), 541 (95), 499 (20), 481 (100), 439 (80), 421 (35), 263 (20), 203 (22).

3.6. 3β-Acetoxy-11α-methoxy-13β-hydroxyolean-12-one (*3*)

Crystalline needles, mp 276–277°; IR ν_{max} (KBr) cm^{-1}: 3440.0, 1715.2, 1254.4, 1212.8, 755.2; ^1H NMR (200 MHz, $CDCl_3$) δ 4.49 (1H, *dd*, *J* = 8.5 and 7.0 Hz, H-3), 4.05 (1H, *d*, *J* = 12.2 Hz, H-11), 3.38 (3H, *s*, OCH_3), 2.43 (1H, *ddd*, *J* = 13.5, 3.6 and 3.6 Hz, H-18), 2.04 (3H, *s*, $OCOCH_3$), 1.32, 1.15, 1.03, 0.98, 0.93, 0.88, 0.86, 0.85 (each 3H, *s*, 8 × CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 208.8 (C-12), 170.9 ($O\underline{C}OCH_3$), 85.0 (C-13), 80.7 (C-3), 74.5 (C-11), 58.8 (C-9), 55.8 ($O\underline{C}H_3$), 55.3 (C-5), 49.2 (C-18), 45.2 (C-14), 43.6 (C-8), 39.9 (C-16), 39.4 (C-10), 39.0 (C-20), 38.6 (C-19), 38.4 (C-4), 38.1 (C-1), 34.3 (C-21), 33.9 (C-7), 33.6 (C-17), 31.2 (C-28), 31.2 (C-29), 30.7 (C-22), 28.9 (C-23), 25.6 (C-30), 23.9 (C-2), 22.9 (C-15), 21.3 ($OCO\underline{C}H_3$), 20.9 (C-26), 18.6 (C-27), 17.5 (C-6), 16.5 (C-24), 16.0 (C-25); EIMS (70 eV) *m*/*z* = 530 (M^+, 8), 513 (60), 499 (3), 481 (25), 471 (75), 453 (100), 439 (70), 421 (50), 369 (20), 293 (50), 235 (45), 221 (42), 191 (50).

3.7. 3β,11α-Dihydroxytaraxer-14-en-12-one (*4*)

Colourless needles, mp 234–235°; IR ν_{max} (KBr) cm^{-1}: 3440.0, 2400.0, 1648.0, 1212.8, 755.2; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75 (1H, *dd*, *J* = 8.1 and 3.2 Hz, H-15), 4.29 (1H, *dd*, *J* = 11.5 and 4.1 Hz, H-11), 3.22 (1H, *dd*, *J* = 8.8 and 7.4 Hz, H-3), 3.10 (1H, *d*, *J* = 4.1 Hz, 11-OH), 2.40 (1H, *ddd*, *J* = 13.5, 3.7 and 3.7 Hz, H-18), 2.17 (1H, *s*, H-9), 1.27, 1.17, 1.11, 1.01, 0.97, 0.95, 0.82, 0.74 (each 3H, *s*, 8 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.5 (C-12), 151.8 (C-14), 121.9 (C-15), 78.5 (C-3), 74.2 (C-11), 55.7 (C-5), 54.9 (C-9), 49.4 (C-13), 42.0 (C-7), 41.7 (C-18), 40.2 (C-8), 39.8 (C-1), 39.2 (C-4), 38.7 (C-10), 37.0 (C-19), 35.9 (C-22), 35.4 (C-17), 35.1 (C-16), 33.1 (C-21), 32.7 (C-29), 29.4 (C-20), 28.9 (C-28), 28.7 (C-23), 28.1 (C-30), 27.3 (C-2), 25.7 (C-26), 23.5 (C-27), 18.8 (C-6), 17.3 (C-25), 15.4 (C-24); EIMS (70 eV) *m*/*z* = 456 (M^+, 55), 439 (50), 364 (10), 279 (20), 195 (80), 159 (40), 127 (65), 109 (100).

3.8. 3β-Hydroxy-11α-acetoxytaraxer-14-en-12-one (*5*)

Crystalline needles, mp 303–304°; IR ν_{max} (KBr) cm^{-1}: 3441.0, 2400.0, 1728.0, 1648.0, 1210.8, 756.2; ^1H NMR (300 MHz, $CDCl_3$) δ 5.7 (1H, *dd*, *J* = 7.6 and 3.0 Hz, H-15), 5.55 (1H, *d*, *J* = 12.0 Hz, H-11), 3.20 (1H, *dd*, *J* = 10.2 and 6.0 Hz, H-3), 2.05 (3H, *s*, $OCOCH_3$), 1.26, 1.04, 1.03, 1.02, 0.96, 0.93, 0.81, 0.76 (each 3H, *s*, 8 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.4 (C-12), 169.6 ($O\underline{C}OCH_3$) 152.9 (C-14), 119.7 (C-15), 78.3 (C-3), 72.8 (C-11), 54.9 (C-5), 54.3 (C-9), 50.7 (C-13), 40.2 (C-7), 40.2 (C-18), 39.0 (C-8), 39.0 (C-1), 38.9 (C-4), 38.5 (C-10), 38.1 (C-19), 37.5 (C-22), 36.7 (C-17), 35.1 (C-16), 33.1 (C-21), 32.9 (C-29), 29.4 (C-20), 29.3 (C-28), 29.2 (C-23), 28.1 (C-30), 27.2 (C-2), 24.5 (C-26), 21.7 (C-27), 21.3 ($OCO\underline{C}H_3$), 18.6 (C-6), 17.1 (C-25), 15.5 (C-24).

3.9. 3β,11α-Diacetoxytaraxer-14-en-12-one (6)

Colourless needles, mp 266–267°; IR ν_{max} (KBr) cm^{-1}: 3440.0, 2928.0, 2832.0, 1744.0, 1728.0, 1632.0, 1452.8, 1363.2, 1238.4, 1219.2, 1017.6; ^1H NMR (300 MHz, $CDCl_3$) δ 5.68 (1H, *dd*, J = 7.5 and 3.0 Hz, H-15), 5.53 (1H, *d*, J = 12.0 Hz, H-11), 4.45 (1H, *dd*, J = 9.0 and 6.0 Hz, H-3), 2.15 (3H, *s*, $OCOCH_3$), 2.08 (3H, *s*, $-OCOCH_3$), 1.26, 1.08, 1.03, 0.96, 0.94, 0.90, 0.89, 0.77 (each 3H, *s*, 8 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.0 (C-12), 170.6 ($O\underline{C}OCH_3$), 169.5 ($O\underline{C}OCH_3$), 152.9 (C-14), 119.6 (C-15), 80.2 (C-3), 72.6 (C-11), 55.1 (C-5), 54.4 (C-9), 50.7 (C-13), 40.2 (C-7), 40.1 (C-18), 38.9 (C-8), 38.5 (C-1), 37.9 (C-4), 37.8 (C-10), 37.5 (C-19), 36.8 (C-22), 35.3 (C-17), 35.2 (C-16), 33.2 (C-21), 33.0 (C-29), 29.5 (C-20), 29.4 (C-28), 29.3 (C-23), 28.2 (C-30), 24.6 (C-2), 23.5 (C-26), 21.6 (C-27), 21.4 ($OCO\underline{C}H_3$), 21.2 ($OCO\underline{C}H_3$), 18.6 (C-6), 17.2 (C-25), 16.6 (C-24).

3.10. 3β,11α-Dimethoxytaraxer-14-en-12-one (7)

Crystalline needles, mp 262–263°; IR ν_{max} (KBr) cm^{-1}: 3440.0, 2928.0, 1696.0, 1632.0, 1456.0, 1376.0, 1091.2, 1068.8, 1030.4, 1004.8; ^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (1H, *dd*, J = 8.5 and 3.0 Hz, H-15), 3.37 (1H, *d*, J = 12.0 Hz, H-11), 3.28 (6H, *s*, 2 × OCH_3), 3.20 (1H, *dd*, J = 10.5 and 6.0 Hz, H-3), 1.28, 1.09, 1.03, 1.02, 0.97, 0.85, 0.83, 0.80 (each 3H, *s*, 8 × CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.8 (C-12), 154.7 (C-14), 118.4 (C-15), 82.7 (C-3), 78.6 (C-11), 56.7 ($O\underline{C}H_3$), 56.6 ($O\underline{C}H_3$), 55.0 (C-5), 50.4 (C-9), 50.3 (C-13), 39.8 (C-7), 39.7 (C-18), 39.0 (C-8), 38.9 (C-1), 38.8 (C-4), 38.5 (C-10), 38.3 (C-19), 37.8 (C-22), 37.2 (C-17), 35.2 (C-16), 33.3 (C-21), 33.2 (C-29), 29.9 (C-20), 29.7 (C-28), 29.2 (C-23), 28.2 (C-30), 27.3 (C-2), 24.6 (C-26), 20.4 (C-27), 18.8 (C-6), 17.5 (C-25), 15.6 (C-24).

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