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KOLAVANE AND KAURANE DITERPENES FROM THE STEM BARK OF *XYLOPIA AETHIOPICA**

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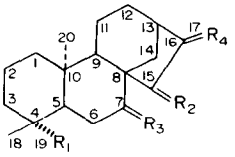
Key Word Index—*Xylopia aethiopica*; Annonaceae; diterpenes; 2-oxokolavenic acid; (−)-kaur-16-en-19-oic acid; 7-oxo-(−)-kaur-16-en-19-oic acid; 7β-hydroxy-(−)-kaur-16-en-19-oic acid.

Abstract—The stem bark of *Xylopia aethiopica* has yielded four diterpenes, two of them novel. Three of the diterpenes were identified as (−)-kaur-16-en-19-oic acid and its 7-oxo and 7β-hydroxy derivatives. The fourth was the novel kolavane derivative 2-oxo-kolav-3,13-dien-15-oic acid, a type of compound not previously recorded in the Annonaceae.

INTRODUCTION

Xylopia aethiopica (Dunal) A. Rich (Annonaceae) is a tree widely distributed in forest areas of West Africa [1]. The fruits, which are a common ingredient of African traditional cough medicines [2] and are also used as a spice and flavouring agent [3], have yielded a volatile oil [4] and the diterpenes **1–6** [2, 5]. A decoction of the bark is also reported to be employed to treat bronchitis, dysentery and biliousness [3].

In this paper we report the isolation of four diterpenes, two of which appear to be novel, from the stem bark of samples of *X. aethiopica* collected in the Korup and Douala–Edea Forest Reserves of West Cameroun.



	R_1	R_2	R_3	R_4
1	COOH	β-OAc	H_2	CH_2
2	Me	H_2	H_2	α-OH;β-Me
3	COOH	H_2	H_2	CH_2
4	COOH	OH	H_2	CH_2
5	CH_2OH	H_2	H_2	α-OH;β-Me
6	COOH	=O	H_2	CH_2
7	COOMe	H_2	H_2	CH_2
8	CH_2OH	H_2	H_2	CH_2
9	COOH	H_2	α-OH	CH_2
10	COOH	H_2	β-OH	CH_2
11	COOMe	H_2	α-OH	CH_2
12	COOH	H_2	=O	CH_2

*Part 8 in the series "Chemical Studies in the Annonaceae". For part 7 see ref. [27].

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RESULTS AND DISCUSSION

The concentrated petrol extract of the stem bark sample from Korup was subjected to CC on Si gel. Elution with petrol and then petrol containing increasing quantities of EtOAc gave sitosterol and four diterpenes.

The first three diterpenes isolated showed a number of spectral features in common. The IR spectra exhibited weak bands at *ca* 3060 and *ca* 1650 cm^{-1} for an exocyclic double bond and at *ca* 1695 cm^{-1} typical of a carboxylic acid. The ^1H NMR spectra showed the presence of two tertiary methyl substituents, and a broad singlet (2H) at *ca* δ 4.80 confirmed the presence of an exocyclic double bond. Methylation of two of the diterpenes caused shielding in the resonance positions of the two methyl substituents by *ca* δ 0.12 and 0.08 and gave rise to IR bands for the carboxy-methyl ester at *ca* 1710 and 1150 cm^{-1}. These data are typical of the changes that occur on methylation of a C-4 axial (α) carboxylic acid (i.e. C-19 COOH) in kaurane diterpenes [6, 7].

On the basis of these observations and by comparison of physico-chemical data with that published [2, 6–9] the major compound, eluted first from the column in a yield of 0.15%, was identified as (−)-kaur-16-en-19-oic acid (**3**). This was confirmed by synthesis of the methyl ester (**7**) and its reduction to **8**, both compounds giving spectral data in agreement with that anticipated.

The second diterpene (yield 0.01%) analysed for $C_{20}H_{28}O_3$ and showed the previously described characters of a (−)-kaur-16-en-19-oic acid. A band at 1725 cm^{-1} in the IR spectrum indicated an additional carbonyl function. Reduction with $NaBH_4$ gave a mixture of two hydroxy epimers (**9** and **10**), the major product being in excess of 90% of the total yield. In the ^1H NMR spectrum of the major alcohol (**9**) the oxymethine proton appeared as a poorly resolved multiplet at δ 3.38 ($W_{1/2}$ = 16 Hz). In the correspond-

ing ester alcohol (**11**) this was resolved into a double doublet (J = 11.5 Hz) for an axial proton coupled to two other protons. Coupling with two other protons restricts the oxymethine to C-1, C-3 or C-7. A 3-keto acid can be discounted because of the heat stability of the compound [10] whilst in 1-keto diterpenes the C-10 methyl signal is highly deshielded (*ca* δ 1.37) in the ^{1}H NMR spectrum[11]. In this case the C-10 methyl group is only slightly deshielded (δ 1.16) and its shift on formation of **9** is typical of a 7-keto diterpene[12, 13].

The above data strongly suggest that the isolated diterpene is 7-oxo-(−)-kaur-16-en-19-oic acid (**12**) which has been synthesized [11, 14] but not previously reported as a natural product. The proposed structure is further supported by: (1) a clear ABX system for the isolated H-6 and H-5 protons in the ^{1}H NMR spectrum; (2) a base peak m/z 147 $[C_{10}H_{11}O]^+$ in the EIMS typical of C-5/C-6 and C-9/C-10 cleavage of a 7-oxo kaurane[8]; and (3) strong deshielding (~14 ppm) in the resonance positions of C-6 and C-9 in the ^{13}C NMR spectrum when compared to **3**. In addition, the ^{13}C NMR spectrum shows shielding of C-15, due to the anisotropy of the carbonyl and C-6 occurs as a double doublet due to the striking non-equivalence of the H-6 protons.

The third diterpene was obtained in a yield of less than 0.01%. It analysed for $C_{20}H_{30}O_3$ and gave spectral characteristics for a hydroxy substituted (−)-kaur-16-en-19-oic acid. The ^{1}H NMR spectrum revealed the oxymethine proton as a triplet ($W_{1/2}$ = 6 Hz) with an equatorial configuration. A TLC comparison with the two 7-hydroxy epimers produced on reduction of **12** showed it to be identical to the minor product (**10**) and identified the diterpene as 7β-hydroxy-(−)-kaur-16-en-19-oic acid (**10**), previously reported [15] from *Didymocarpus oblonga* (Gesneriaceae). Identity was further confirmed by comparison with literature data [15] and by oxidation to **12**.

The final diterpene isolated (yield 0.064%) analysed for $C_{20}H_{30}O_3$ but lacked the characteristics of a kaurane derivative. The UV spectrum showed a maximum at 227 nm which on addition of NaOH changed to maxima at 217 nm, indicative of α, β-unsaturated acids [16], and at 233 nm, indicative of α, β-unsaturated ketones [17]. Bands in the IR spectrum at 1710 and 1640 cm^{-1} could also be attributed to conjugated carbonyl [16] and carbonyl [18], respectively.

The ^{1}H NMR spectrum revealed the presence of five methyl resonances at δ 0.83, 1.12 and 0.85 (J = 6 Hz) for two tertiary and one secondary methyl on saturated carbons, and at 1.89 and 2.13 for tertiary methyl groups on unsaturated carbons. The latter both exhibited long-range allylic coupling (*ca* 1 Hz) to olefinic protons at 5.69 and 5.75. The ^{13}C NMR spectrum showed six downfield resonances at δ 200.5, 172.8, 171.8, 162.9, 125.3 and 115.8, the first four due to quaternary carbons, the latter two to tertiary carbons. The signal at 200.5 must be assigned to the carbonyl function and either the 172.8 or 171.8 signal to the carboxyl group. The remaining four signals can be attributed to positions α (shielded) and β (deshielded) to the carbonyl and carboxyl functions. As it is the β carbons that are quaternary they must be substituted by the two methyl groups [i.e. –CO–CH=C(Me)–].

On the basis of the above data the diterpene must be bicyclic and can be assigned to the kolavane (**13**) series [16, 18, 19]. Methylation gave the ester **14** which on reduction with $LiAlH_4$ yielded the diol **15**. In the ^{1}H NMR spectrum of **15** the methylene protons of the secondary alcohol occurred as a doublet at δ 4.14 coupled to an olefinic proton at 5.41. This, and the shielding of the related methyl resonance by δ 0.45, are all compatible with a –C(Me)=CH–CH_2OH system and confirm the occurrence of –C(Me)=CH–COOH as the terminal portion of the C-9 side-chain. Both ^{1}H NMR [16, 17, 20] and ^{13}C NMR [21] resonances agree closely with published data for side-chains of this type in kolavane and labdane diterpene. The strong deshielding of the methyl group resonance in the original compound is typical of a *cis* configuration for methyl and carboxyl groups [22, 23].

In typical kolavanes the second centre of unsaturation involves C-3 and C-4 and 2-oxokolavanes have been reported [18, 19]. A high-field (360 MHz) ^{1}H NMR spectrum clearly resolved an isolated ABX system for H-1 and an axial H-10 proton agreeing closely with published data [19] for 2-oxokolavanes. As reported for other 2-oxokolavanes [18] reduction gave a 2-hydroxy function in an axial configuration.

On the basis of the above data the isolated compound was identified as 2-oxokolavenic acid (**16**). This was supported by the EIMS of **14** and **16** which exhibited preferential cleavage between C-9 and C-11 to give **17** as a major fragment [17]. The absolute configuration of the related compound **13** is established [24] and in view of the close similarity of optical rotations observed for **16** and **13** it seems probable that **16** has the same configuration. This is partly confirmed by the ^{1}H NMR spectrum which shows H-10 to be axial and, by comparison of H-1 and H-10 resonances to published data for 2-oxo C-5-Me/H-10 *trans* [18, 19] and *cis* [25] fused systems, to be *trans* to the C-5 methyl substituent.

Examination of a second sample of *X. aethiopica* stem bark from Douala–Edea gave **12** (yield 0.003%) and **16** (0.02%).

This is the first report of a kolavane diterpene from the Annonaceae, although related furano-diterpenes are reported from *Annona coriacea* [26]. As was the case with the recently reported trachylobane diterpene from the closely allied *X. quintasii* [27] the major source of the kolavanes appears to be the Compositae [18, 19].

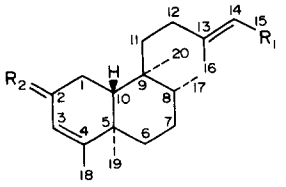
EXPERIMENTAL

UV spectra were run in EtOH and IR spectra as KCl discs. ^{1}H NMR spectra were run at 90 MHz in $CDCl_3$ using TMS as int. standard unless otherwise stated. ^{13}C NMR spectra were run in $CDCl_3$ at 25.1 MHz using FT mode and TMS as int. standard unless otherwise stated. EIMS were obtained at 70 eV and elevated temps. Mps are uncorr. Petrol refers to the bp 40–60° fraction.

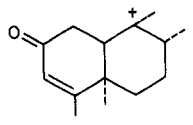
Plant material. Stem bark of *X. aethiopica* was collected in the Douala–Edea Forest Reserve in the summer of 1976 (voucher: P. G. Waterman and D. McKey 837) and in the Korup Forest Reserve in the summer of 1979 (voucher: D. W. Thomas 348). Both vouchers have been deposited at the Herbarium of the Royal Botanic Gardens, Kew.

Isolation of compounds from Korup sample. The milled stem bark (220 g) was extracted with petrol. The conc. extract was subjected to CC on Si gel eluting with petrol followed by petrol containing increasing amounts of EtOAc. Elution with petrol gave **3** (300 mg); with 5% EtOAc gave sitosterol (15 mg); with 10% EtOAc gave **12** (20 mg) followed by **10** (20 mg); and with 15% EtOAc gave **16** (140 mg).

Isolation of compounds from Douala–Edea sample. Milled stem bark (500 g) was extracted with petrol and subjected to CC on Si gel. Elution with petrol–EtOAc (4 : 1) gave **12** (17 mg) followed by impure **16**. Prep. TLC of the latter on Si gel (toluene–EtOAc–HOAc, 40 : 9 : 1) gave pure **16** (R_f = 0.31, 100 mg).



	R_1	R_2
13	COOH	H_2
14	COOMe	=O
15	CH_2OH	β-OH
16	COOH	=O



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(−)-*Kaur*-16-*en*-19-*oic acid* (**3**). Recrystallized from petrol as cubes, mp 167–171° (lit. [2], mp 169–173°). $[\alpha]_D^{19}$ −110° ($CHCl_3$, *c* 0.2) (lit. [2], −112°). Found: M^+ 302.2238; $C_{20}H_{30}O_2$ requires 302.2246. IR ν_{max} cm^{-1}: 3070, 1650 (C=CH_2), 1690 (COOH). ^1H NMR: δ 0.97 (3H, *s*, H-20), 1.25 (3H, *s*, H-18), 2.65 (1H, *m*, H-13), 4.77 (2H, *br.s*, $W_{1/2}$ = 9 Hz, H-17). ^{13}C NMR: δ 15.7 (*q*, C-20), 18.5 (*t*, C-11), 19.2 (*t*, C-2), 22.0 (*t*, C-6), 29.0 (*q*, C-18), 33.2 (*t*, C-12), 38.0 (*t*, C-3), 39.8 (*t*, C-14), 39.8 (*s*, C-10), 40.9, 41.5 (2 × *t*, C-1, C-7), 44.0 (*s*, C-4), 44.0 (*d*, C-13), 44.4 (*s*, C-8), 49.0 (*t*, C-15), 55.4 (*d*, C-9), 57.3 (*d*, C-5), 103.3 (*t*, C-17), 156.0 (*s*, C-16), 185.4 (*s*, C-19). EIMS *m/z* (rel. int.): 302 $[M]^+$ (77), 287 (35), 259 (43). **3** (20 mg) in Et_2O was treated with CH_2N_2. Normal work-up gave (−)-kaur-16-en-19-oate (**7**) as a gum. Found: M^+ 316.2400; $C_{21}H_{32}O_2$ requires 316.2402. IR ν_{max}^{film} cm^{-1}: 1725, 1155 (COOMe, *ax*). ^1H NMR: δ 0.83 (3H, *s*, H-20), 1.16 (3H, *s*, H-18), 3.64 (3H, *s*, COOMe). **7** (20 mg) in dry Et_2O was refluxed with $LiAlH_4$ for 3 hr. Normal work-up gave (−)-kaur-16-en-19-ol (**8**, 16 mg), recrystallized from petrol–Et_2O as needles, mp 132–137° (lit. [6], 140–141°). Found: M^+ 288.2427 $C_{20}H_{32}O$ requires 288.2453. IR ν_{max} cm^{-1}: 3400 (OH). ^1H NMR: δ 0.96 (3H, *s*, H-20), 1.02 (3H, *s*, H-18), 3.46, 3.76 (2H, AB_q, *J* = 11 Hz, H-19).

7-*Oxo*-(−)-*kaur*-16-*en*-19-*oic acid* (**12**). Recrystallized from petrol–$CHCl_3$ as needles, mp 210–213° (lit. [14], 208–210°). $[\alpha]_D^{23}$ −95° ($CHCl_3$, *c* 0.35). Found: M^+ 316.2002; $C_{20}H_{28}O_3$ requires 316.2038. IR ν_{max} cm^{-1}: 3070, 1660 (C=CH_2), 1725 (CO), 1695 (COOH). ^1H NMR: δ 1.16 (3H, *s*, H-20), 1.25 (3H, *s*, H-18), 2.67 (1H, ABX, J_{AB} = 16 Hz, J_{BX} = 4 Hz, H_{eq}-6), 2.75 (1H, *m*, H-13), 3.13 (1H, ABX, J_{AB} = 16 Hz, J_{AX} = 14 Hz, H_{ax}-6), 3.20 (1H, *d*, *J* = 14 Hz, H_{eq}-14), 4.87 (2H, *br. s*, $W_{1/2}$ = 6 Hz, H-17). ^{13}C NMR (90.56 MHz): δ 15.0 (*q*, C-20), 17.9 (*t*, C-11), 18.8 (*t*, C-2), 28.3 (*q*, C-18), 32.5 (*t*, C-12), 37.5 (*dd*, C-6), 38.8 (2 × *t*, C-3, C-14), 39.6 (*s*, C-10), 40.5 (2 × *t*, C-1, C-15), 42.8 (*d*, C-13), 43.8 (*s*, C-4), 54.3, 54.9 (2 × *d*, C-5, C-9), 57.8 (*s*, C-8), 104.4 (*t*, C-17), 153.4 (*s*, C-16), 182.6 (*s*, C-19), 212.7 (*s*, C-7). EIMS *m/z* (rel. int.): 316 $[M]^+$ (82), 301 (3), 271 $[M-CO_2H]^+$ (10), 270 $[M-CO_2H-H]^+$ (43), 255 (12), 147 $[C_{10}H_{11}O]^+$ (100). Treatment of **12** with CH_2N_2 gave 7-oxo-(−)-kaur-16-en-19-oate as a gum. Found: M^+ 330.2213; $C_{21}H_{30}O_3$ requires 330.2213. IR ν_{max}^{film} cm^{-1}: 1730 (CO), 1705, 1160 (COOMe, *ax*). ^1H NMR: δ 1.05 (3H, *s*, H-20), 1.19 (3H, *s*, H-18), 3.68 (3H, *s*, COOMe). 7-Hydroxy-(−)-kaur-16-en-19-oic acid (**9** + **10**). Compound **12** (10 mg) in MeOH (5 ml) was reacted with $NaBH_4$ for 3 hr. Normal work-up gave a solid which was shown by TLC (Si gel; toluene–EtOAc–HOAc, 40 : 9 : 1) to be a mixture of **9** (90%, R_f = 0.28) and **10** (R_f = 0.33). Found: M^+ 318.2208; $C_{20}H_{30}O_3$ requires 318.2195. ^1H NMR: δ 0.98 (3H, *s*, H-20), 1.24 (3H, *s*, H-18), 3.38 (1H, *m*, H_{ax}-7). EIMS *m/z* (rel. int.): 318 $[M]^+$ (85), 300 (100). Methylation of **9** + **10** with CH_2N_2 gave 7-Hydroxy-(−)-kaur-16-en-19-oate (mainly **11**). IR ν_{max}^{film} cm^{-1}: 1725, 1150 (COOMe, *ax*). ^1H NMR: δ 0.84 (3H, *s*, H-20), 1.17 (2H, *s*, H-18), 2.65 (1H, *m*, H-13), 3.36 (1H, *dd*, J_1 = 11 Hz, J_2 = 5 Hz, H_{ax}-7), 3.63 (3H, *s*, COOMe).

7β-*Hydroxy*-(−)-*kaur*-16-*en*-19-*oic acid* (**10**). Recrystallized from petrol–EtOAc as prisms, mp 240–245° (lit. [15], 239–243°). $[\alpha]_D^{23}$ −56° (MeOH, *c* 0.33). Found: M^+ 318.2192; $C_{20}H_{30}O_3$ requires 318.2195. IR ν_{max} cm^{-1}: 3500 (OH), 3050, 1640 (C=CH_2), 1700 (COOH). ^1H NMR (Me_2CO-d_6): δ 1.00 (3H, *s*, H-20), 1.15 (3H, *s*, H-18), 2.60 (1H, *m*, H-13), 3.55 (1H, *t*, $W_{1/2}$ = 6 Hz, H_{eq}-7), 4.75 (2H, *br. s*, H-17). EIMS *m/z* (rel. int.): 318 $[M]^+$ (26), 300 $[M-H_2O]^+$ (100), 285 $[M-H_2O-CH_3]^+$ (20), 255 $[M-H_2O-CO_2H]^+$ (19). Treatment of **10** in dry Me_2CO with Jones' reagent gave **12**.

2-*Oxokolavenic acid* (**16**). Recrystallized from petrol–EtOAc (4 : 1) as cubes, mp 187–189°. $[\alpha]_D^{21}$ −56.5° ($CHCl_3$, *c* 0.52). Found: M^+ 318.2221; $C_{20}H_{30}O_3$ requires 318.2195. UV λ_{max} nm: 227; (+NaOH) 217, 232. IR ν_{max} cm^{-1}: 1710 (COOH), 1640 (CO), 1220, 1160. ^1H NMR (360 MHz): δ 0.83 (3H, *s*, H-20), 0.85 (3H, *d*, *J* = 6 Hz, H-17), 1.12 (3H, *s*, H-19), 1.30–1.46 (2H, *m*, H-7), 1.40 (1H, *dt*, J_t = 12.2 Hz, J_d = 5.5 Hz, H_{ax}-6), 1.50 (3H, *m*, H-11, H-8), 1.83 (1H, *br. td*, J_d = 12.6 Hz, J_t = 3 Hz, H*cis*-12), 1.86 (1H, ABX, J_{AX} = 13.3 Hz, J_{BX} = 4.7 Hz, H_{ax}-10), 1.89 (3H, *d*, *J* = 1 Hz, H-18), 1.90 (1H, *m*, H_{eq}-6), 2.05 (1H, *dt*, J_t = 12.6 Hz, J_d = 4.6 Hz, H*trans*-12), 2.15 (3H, *d*, *J* = 1 Hz, H-16), 2.33 (1H, ABX, J_{AB} = 18 Hz, J_{BX} = 4.7 Hz, H_{eq}-1), 2.40 (1H, ABX, J_{AB} = 18 Hz, J_{AX} = 13.3 Hz, H_{ax}-1), 5.68 (1H, *br. s*, H-14), 5.74 (1H, *br. s*, H-3). ^{13}C NMR: δ 15.8 (*q*, C-17), 17.8 (*q*, C-20), 18.4 (*q*, C-18), 18.9 (*q*, C-16), 19.5 (*q*, C-19), 27.1 (*t*, C-7), 34.5, 35.1 (2 × *t*, C-11, C-6), 35.9 (2 × *t*, C-1, C-12), 36.4 (*d*, C-8), 39.0 (*d*, C-9), 40.2 (*d*, C-5), 46.1 (*d*, C-10), 115.8 (*d*, C-14), 125.3 (*d*, C-3), 162.9 (*s*, C-13), 171.8, 172.8 (2 × *s*, C-4, C-15), 200.5 (*s*, C-2). EIMS *m/z* (rel. int.): 318 $[M]^+$ (31), 303 $[M-Me]^+$ (6), 300 $[M-H_2O]^+$ (23), 285 $[M-H_2O-Me]^+$ (11), 259 $[M-Me-CO_2]^+$ (20), 205 $[C_{14}H_{21}O]^+$ (70), 203 (27), 189 (19), 177 (10), 163 (22), 161 (12), 135 $[C_9H_{10}O]^+$ (56), 123 (40), 121 (48), 109 (100). Treatment of **16** (20 mg) with CH_2N_2 under standard conditions gave 2-oxo-kolavenic acid methyl ester (**14**, 20 mg) recrystallized from Et_2O as prisms, mp 85–93°. Found: M^+ 332.2348; $C_{21}H_{32}O_3$ requires 332.2351. IR ν_{max} cm^{-1}: 1720, 1670 (COOMe and C=C), 1650 (C=C–CO). ^1H NMR: δ 0.81 (3H, *s*, H-20), 0.84 (3H, *d*, *J* = 6 Hz, H-17), 1.11 (3H, *s*, H-19), 1.87 (3H, *d*, *J* = 1 Hz, H-18), 2.13 (3H, *d*, *J* = 1 Hz, H-16), 2.40 (2H, *m*, H-1), 3.67 (3H, *s*, COOMe), 5.66 (1H, *br. s*, H-14), 5.73 (1H, *br. s*, H-3). EIMS *m/z* (rel.

int.): 332 $[M]^+$ (90), 301 $[M-OMe]^+$ (24), 300 $[M-OMe-H]^+$ (17), 285 (30), 259 (19), 205 $[C_{14}H_{21}O]^+$ (84), 189 (17), 135 (55), 123 (29), 121 (51), 109 (68). **14** (15 mg) in dry Et_2O was refluxed with $LiAlH_4$ for 1 hr and after normal work-up gave 2β-hydroxykolavenol (**15**, 14 mg) as a colourless gum. Found: M^+ 306.2543; $C_{20}H_{34}O_2$ requires 306.2559. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (OH). ^1H NMR: δ 0.74 (3H, *s*, H-20), 0.81 (3H, *d*, $J = 6$ Hz, H-17), 1.05 (3H, *s*, H-19), 1.62 (3H, *d*, $J = 1$ Hz, H-18), 1.68 (3H, *s*, H-16), 4.14 (2H, *d*, $J = 7$ Hz, H-15), 4.22 (1H, *m*, H_{eq}-2), 5.22 (1H, *br. s*, H-3), 5.41 (1H, *t*, $J = 7$ Hz, H-14). EIMS *m/z* (rel. int.): 306 $[M]^+$ (20), 289 $[M-H_2O]^+$ (14), 274 $[M-H_2O-Me]^+$ (26), 259 (17), 205 $[C_{14}H_{21}O]^+$ (100), 189 (39), 136 (33), 124 (26), 123 (98), 121 (42), 119 (21), 109 (20).

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