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11β,13-DIHYDROGUAIANOLIDES FROM *ARTEMISIA DOUGLASIANA* AND A THIOPHENE ACETYLENE FROM *A. SCHMIDTIANA*

J. JAKUPOVIC, T. V. CHAU-THI, U. WARNING, F. BOHLMANN and H. GREGER*

Institute of Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany; *Institute of Botany, University of Vienna, A-1030 Vienna, Austria

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Key Word Index—*Artemisia douglasiana*; *A. schmidtiana*; Compositae; sesquiterpene lactones; 11β,13-dihydroguaianolides; thiophene acetylene.

Abstract—The aerial parts of *Artemisia douglasiana* afforded, in addition to some known sesquiterpene lactones, 22 new closely related guaianolides. A new thiophene acetylene was isolated from the aerial parts of *A. schmidtiana* together with some known sesquiterpene lactones. The structures were elucidated by high field ^{1}H NMR spectroscopy.

INTRODUCTION

Artemisia douglasiana Bess. belongs to the North American allies of the *A. vulgaris* group which is placed in the section *Artemisia* of the subgenus *Artemisia* [1]. The North American representatives of this group form a polyploid complex of great morphological diversity [2]. This factor, together with seasonal variations, might have led to the striking chemical differences reported so far for *A. douglasiana*. Different eudesmane-6,12-olides [3, 4] or guaianolides [5] were isolated in earlier examinations, whereas a more recent analysis mainly afforded sesquiterpenes of the longipinene series together with a new type of sesquiterpene lactone [6]. The East Asiatic *A. schmidtiana* Maxim. is a member of the section *Absinthium* and has not been investigated chemically.

In this paper we describe the results of our study of a hexaploid provenance of *A. douglasiana* which originated near Corvallis (Oregon, U.S.A.) together with those of *A. schmidtiana* from Sapporo (Japan).

RESULTS AND DISCUSSION

The petrol–ether extract of the aerial parts of *A. douglasiana* afforded after a very lengthy and time consuming separation 22 new closely related guaianolides: the dihydrocumambrin B derivatives **1** and **2a–2d**, the dihydroludartin derivatives **3a–3f**, the viscidulin C esters **4a–4d**, the endoperoxides **5a–5e**, **6e** and 8α-acetoxydihydrokauniolide (**7**). Furthermore, the hydroperoxide **9**, costunolide, novanin [7], balchanolide acetate [8] and dihydrokauniolide [9] were isolated.

The structures of **2a–2d** followed from the ^{1}H NMR spectra (Table 1) which were close to that of the corresponding 8-*O*-acetate from *Chrysanthemum coronarium* [10]. The nature of the ester groups was deduced from the typical signals and the relative position followed from the chemical shift of H-8. Compounds **2a–2d** were 8-*O*-acyl derivatives of dihydrocumambrin B. The structure of **1** also was deduced from its ^{1}H NMR spectrum (Table 1). The missing oxygen function at C-8 caused the expected changes. Thus the H-7 and H-11 signals were shifted upfield.

The structures of **3a–3f** also followed from the ^{1}H NMR spectra (Table 1) which were close to that of dihydroludartin [11]. As in the case of **2a–2d** and all the other lactones the configurations at C-11 were deduced from the observed large coupling $J_{7,11}$ and the chemical shift of H-13. The stereochemistry at C-4 followed from the chemical shift of H-15 and the typical very small couplings of H-3. The presence of a 10(14)-double bond caused the expected downfield shift of H-5, H-2, H-9 and H-14. While the nature of the ester groups again followed from the typical ^{1}H NMR signals. The lactone epoxides **3a–3f** were 8α-acyloxy derivatives of dihydroludartin.

The ^{1}H NMR spectra of **4a–4d** (Table 1) differed characteristically from those of **3a–3d** though many signals were similar. The presence of a 10(14)-double bond followed from the signals of the exomethylene protons and from the result of spin decoupling which established that the broadened three-fold doublet at δ2.96 was the H-1 signal while the double doublets at δ2.47 and 2.23 were due to H-9. As the chemical shifts of these signals obviously required allylic protons the structures were settled. The common stereochemistry of these compounds was identical with that of dihydroestafiatin [12] and viscidulin D [13] as followed from comparison of the ^{1}H NMR spectra. Thus **4a–4d** were 8-*O*-acyl derivatives of viscidulin C.

The tiglate **5d** showed a clear molecular ion at *m/z* 378 corresponding to $C_{20}H_{26}O_7$. Loss of oxygen (*m/z* 346) was an indication of the presence of an endoperoxide (RDA fragmentation) as has been observed in similar endoperoxides [14]. The ^{1}H NMR spectrum (Table 1) was in part close to that of one of the tanaparthinperoxides [14]. However, the presence of a 11β,13-dihydro derivative with an ester group at C-8 clearly followed from the corresponding ^{1}H NMR signals, all of which were assigned by spin decoupling. Again the stereochemistry at C-11 and C-8 was deduced from the couplings. The configuration at C-1 and C-4 was determined by comparison of the chemical shifts of H-2, H-3, H-5, H-6, H-14

Table 1. ^{1}H NMR spectral data of 1–7 (400 MHz, $CDCl_3$, TMS as internal standard)

H	1	2a (2b–2d)*†	3a (3b–3f)*‡	4a (4b–4d)*§	5a (5b–5e, 6e)*¶	7
1	2.54 *ddd*	2.58 *br ddd*	—	2.96 *br dd*	—	—
2	2.44 *br d*	2.27 *br dd*	2.72 *br d*	2.08 *dd*	6.25 *d*	3.01 *br d*
2°	2.33 *br dd*	2.16 *br dd*	2.47 *br d*	1.78 *br dd*		2.93 *br d*
3	5.44 *br s*	5.48 *br s*	3.40 *br s*	3.36 *br s*	6.33 *d*	5.54 *br s*
5	2.77 *br dd*	2.74 *br dd*	2.99 *br d*	2.34 *dd*	2.67 *d*	3.27 *br d*
6	4.11 *dd*	4.03 *dd*	3.71 *dd*	4.03 *dd*	3.74 *dd*	3.70 *dd*
7	2.00 *m*	2.80 *ddd*	2.23 *ddd*	2.25 *ddd*	2.90 *ddd*	2.23 *ddd*
8	2.00 *m* 1.35 *m*	5.13 *ddd*	4.67 *ddd*	4.94 *ddd*	5.03 *ddd*	4.77 *ddd*
9	2.00 *m*	2.29 *dd*	2.48 *dd*	2.47 *dd*	2.18 *dd*	2.50 *br dd*
9°	1.64 *ddd*	1.72 *ddd*	2.07 *dd*	2.23 *dd*	1.96 *dd*	2.20 *dd*
11	2.19 *dq*	2.42 *dq*	2.44 *dq*	2.48 *dq*	2.32 *dq*	2.45 *dq*
13	1.22 *d*	1.26 *d*	1.32 *d*	1.27 *d*	1.27 *d*	1.31 *d*
14	1.13 *s*	1.21 *s*	1.72 *br s*	5.05 *br s* 4.85 *br s*	1.36 *s*	1.75 *ddd*
15	1.81 *br s*	1.87 *br s*	1.65 *s*	1.58 *s*	1.70 *s*	1.92 *ddd*

*Signals nearly identical, ±0.02 ppm.

†Compound **2d**: H-7 2.87 *ddd*, H-8 5.19 *ddd*, H-9′ 1.80 *ddd*.

‡Compound **3d**: H-7 2.27 *ddd*, H-8 4.79 *ddd*, H-9′ 2.13 *dd*.

§Compound **4d**: H-7 2.30 *ddd*, H-8 5.03 *ddd*, H-9′ 2.29 *dd*.

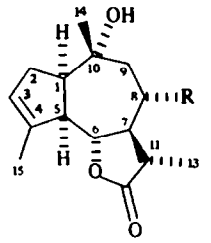
¶Compound **5d**: H-7 2.95 *ddd*, H-8 5.10 *ddd*, H-9′ 2.04 *dd*; compound **6e**: H-7 3.60 *m*, H-13 6.15 and 5.42 *d*, H-14 1.40 *s*; OiBu (±0.02): 2.57 *qq*, 1.20 *d*, 1.19 *d* ($J_{2,3} = J_{2,4} = 7$); OiVal: 2.20 *m*, 2.11 *m*, 0.98 *d* ($J_{3,4} = J_{3,5} = 7$); OMebu (0.02): 2.34 *tq q*, 1.70 *m*, 1.47 *m*, 1.18 *d*, 0.92 *t* ($J_{2,3} = J_{2,5} = J_{3,4} = 7$); OTigl: 6.90 *br q*, 1.83 *br d*, 1.85 *br s* ($J_{3,4} = 7$); OProp: 2.37 (±0.02) *q*, 1.17 *q* ($J_{2,3} = 7$); OAc: 2.08 *s*; *J*(Hz): 5,6 = 6,7 = 7,8 = 10; 7,11 = 12; 11,13 = 7; 9,9′ = 16; compounds **2a–2d**: 1,2 = 5; 1,2′ = 1,5 = 9; 1,9′ = 1; 2,2′ = 17; 2,3 = 2′,3 = 2,15 = 2′,15 = 3,15 ~ 1.5; 8,9 = 5; 8,9′ = 4; compounds **3a–3f**: 2,2′ = 18; 2,3 = 2′,3 ~ 1; 8,9 = 10; 8,9′ = 2; compounds **4a–4d**: 1,2 = 8; 1,2′ = 7.5; 1,5 = 8; 2,2′ = 14; 2,3 = 2′,3 ~ 1; 8,9 = 5; 8,9′ = 3.5; compounds **5a–6e**: 2,3 = 5; 8,9 = 6; 8,9′ = 2.5; compound **6e**: 7,13 = 3; 9,9′ = 16.5; compound **7**: 2,2′ = 21; 2,3 = 2′,3 = 2,15 = 2′,15 = 3,15 ~ 1.5; 8,9 = 11; 8,9′ = 2; 9,9′ = 13.5.

and H-15 with those of the epimeric endoperoxides [14] where the stereochemistry was established by chemical transformation to canin and artecanin. However, the configurations of these bisepoxides were erroneously assigned in the literature [15] and later corrected by X-ray [16]. Therefore the assignment for the tanaparthinperoxides have to be changed (**34** to **35** and vice versa in ref. [14]). Furthermore, a clear NOE between H-15 and H-6 was observed. The presence of a tiglate followed from the typical ^{1}H NMR signals. The nature of the corresponding esters **5a–5c** and **5e** were deduced from the spectra. Compounds **5a–5e** therefore were 8α-acyloxy derivatives of 11β,13-dihydrotanaparthin-α-peroxide (Table 1). The only lactone of this type with an exomethylene group at C-11 was **6e**, the ^{1}H NMR spectrum of which (Table 1) showed the expected differences when compared with that of **5e**. Thus compound **6e** was 8α-propionyloxytanaparthin-α-peroxide. The structure of **7** followed from the ^{1}H NMR spectrum (Table 1) which was close to that of **8** [9]. The presence of an 8α-acetoxy derivative was deduced from the results of spin decoupling. Starting with the double quartet at δ2.45 (H-11) H-7 could be assigned. Irradiation of the latter showed that the lowfield threefold doublet at δ4.77 was due to H-8. The stereochemistry followed from the couplings. Lactone **7** therefore was 8α-acetoxy-11β,13-dihydrokauniolide.

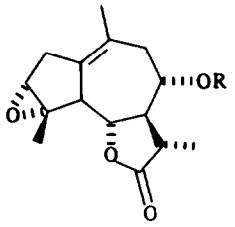
The structure of **9** followed from the mass spectrum which gave no molecular ion, but clear fragments for $[M - H_2O]^+$ and $[M - OOH]^+$. The ^{1}H NMR spectrum (see Experimental) was close to that of β-eudesmol. The position of the peroxy group, which showed a broad signal at δ7.6, followed from the absence of the H-5 signal. Thus **9** was 5α-peroxy-β-eudesmol.

All the lactones from *A. douglasiana* are most likely related to 11β,13-dihydrocumambrin B which by esterification would lead to **2a–2d** and by epoxidation and elimination of water to **3a–3f** and **4a–4d**. Probably **5a–5e** are formed by addition of oxygen to the dehydrogenation products of **2a–2d** while lactone **7** would be the direct precursor of **3f**. The presence of 8-deacyloxy derivatives **1** and **8** is of general interest as this may be an indication that enzymatic introduction of an oxygen function at C-8 is possible. The co-occurrence of **1–8** with costunolide and the corresponding 11β,13-dihydro derivative balchanolide acetate, however, may indicate that the introduction of the oxygen function is already achieved before the germacranolides are transformed to the guaianolides.

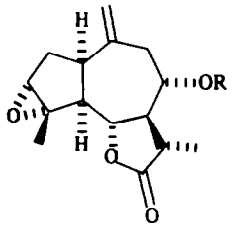
The aerial parts of *A. schmidtiana* afforded in addition to several widespread compounds (see Experimental) costunolide, reynosin [17], artemorin [18], anhydroverlotorin [18] and the thiophene derivative **10**. The molecular formula of the latter was $C_{12}H_{12}O_2S$ and the nature of the sulphur atom followed from the characteristic thiophene signals in the ^{1}H NMR spectrum (see Experimental) which further indicated a *trans*-double bond. Three further lowfield signals required an additional oxygen function. As one must be a hydroxyl (IR 3610 cm^{-1}) group, the second could only be an ether oxygen. Spin decoupling allowed the assignment of the sequence H-1 through H-6. The configuration at C-3 and C-4 followed



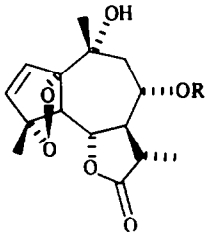
1 R = H
2a–d R = OCOR*



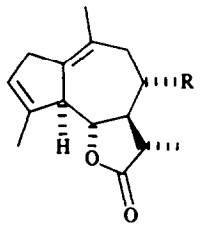
3a–f R = COR*



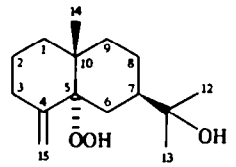
4a–d R = COR*



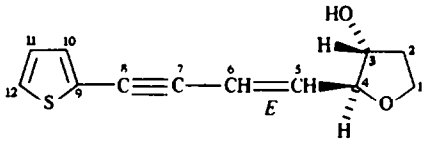
5a–e R = COR*
6e Δ 11(13)



7 R = OAc
8 R = H



9



10

* a = iBu, b = iVal, c = Mebu, d = Tigl, e = Prop, f = Ac

from the coupling $J_{3,4}$. Most likely the precursor of **10** is the corresponding 1-hydroxy-3,4-epoxide which itself is formed by epoxidation of the corresponding diene. Probably compound **10**, which we have named schmidtiol, is the precursor of the more widespread thienylbutenyne furan [19].

EXPERIMENTAL

The air dried aerial parts of *A. douglasiana* (500 g, voucher AR 892, deposited in the Herbarium of the Institute of Botany, University of Vienna, Austria) were extracted with Et_2O–petrol (1:1), and the extract obtained was separated by CC (silica gel) affording three polar fractions (1) Et_2O–petrol (1:1); (2) Et_2O; (3) Et_2O–MeOH (9:1). TLC of fraction 1 (silica gel, PF 254, CH_2Cl_2–C_6H_6, 1:1) afforded 15 mg dihydrokauniolide, 15 mg costunolide and a mixture which gave by HPLC (MeOH–H_2O, 1:1, always RP 18, flow rate, *ca* 3 ml/min, 200 bar) 2.7 mg **7** (R_t 9.5 min). TLC of fraction 2 (Et_2O–petrol, 1:1) gave four bands (2/1–2/4). HPLC of 2/1 (MeOH–H_2O, 4:1) gave 3 mg **3a** (R_t 6.5 min), 1 mg **3b** (R_t 8.0 min) and 1 mg **3c** (R_t 8.3 min). TLC of 2/2 (CH_2Cl_2–C_6H_6–Et_2O, 4:4:1) gave two bands (2/2/1 and 2/2/2). HPLC of 2/2/1 (MeOH–H_2O, 7:3) gave 1.5 mg novanin (R_t 8.5 min), 3 mg **3a** (R_t 9.7 min), 1.5 min balchanolide acetate (R_t 10.2 min) and 2.2 mg **3d** (R_t 15.0 min). HPLC of 2/2/2 (MeOH–H_2O, 7:3) gave 2 mg **3e** (R_t 11.5 min), 2 mg **2d** (R_t 17.5 min), 1 mg **3c** (R_t 18.0 min), 2 mg **3b** (R_t 18.5 min), 1 mg **2c** (R_t 19.5 min), 2 mg **2b** and **2c** (R_t 19.8 min) and 1.5 mg **2b** (R_t 20.5 min). TLC of 2/3 (CH_2Cl_2–C_6H_6–Et_2O, 4:4:1) gave 3 mg novanin, two mixtures (2/3/2 and 2/3/3) and 3 mg **9** (R_f 0.2). HPLC of 2/3/2 (RP 8, MeOH–H_2O, 7:3) gave 0.7 mg **3f** (R_t 6.0 min), 2 mg **2a** (R_t 9.0 min), 1.5 mg **2d** (R_t 10.5 min), 2.2 mg **4a** (R_t 11.5 min), 1 mg **4c** (R_t 15.0 min) and 1 mg **4b** (R_t 15.5 min). HPLC of 2/3/3 (RP 8, MeOH–H_2O, 7:3) gave 1 mg **5a** (R_t 6.5 min), 2 mg **5d** (R_t 7.5 min), 1.5 mg **5c** (R_t 8.0 min) and 1.5 mg **5b** (R_t 8.3 min). HPLC of fraction 2/4 (MeOH–H_2O, 4:1) afforded 2.5 mg **5a** (R_t 5.2 min), 3 mg **5d** (R_t 6.0 min), 1.5 mg **4d** (R_t 14.2 min), 1.3 mg **9** (R_t 17.0 min), 1 mg **6e** (R_t 4.5 min) and 1 mg **5e** (R_t 4.8 min). TLC of fraction 3 (Et_2O–petrol, 4:1) gave 5 mg **1** (R_t 0.4) and a mixture which by HPLC (MeOH–H_2O, 3:2) gave 1 mg **5a** (R_t 9.0 min) and 2.5 mg **5d** (R_t 11.5 min). Probably due to the minute amounts compounds **1**–**7** were

Table 2. MS data of 1–7 [m/z (rel. int.)]

	[M]$^+$	Calc. for	[M − RCO$_2$H or H$_2$O]	[RCO]$^+$	Base peak
1	250.157 (2)	$C_{15}H_{22}O_3$	232 (72)	—	107
2a	336.194 (25)	$C_{19}H_{28}O_5$	248 (37)	71 (100)	71
2b	350.209 (2)	$C_{20}H_{30}O_5$	248 (20)	85 (72)	57
2c	350.209 (2)	$C_{20}H_{30}O_5$	248 (24)	85 (63)	57
2d	348.194 (0.5)	$C_{20}H_{28}O_5$	248 (11)	83 (100)	83
3a	334.178 (1)	$C_{19}H_{26}O_5$	246 (100)	71 (38)	246
3b	348.194 (1)	$C_{20}H_{28}O_5$	246 (25)	85 (38)	57
3c	348.194 (1)	$C_{20}H_{28}O_5$	246 (28)	85 (42)	57
3d	346.178 (0.5)	$C_{20}H_{26}O_5$	246 (20)	83 (59)	57
3e	320.162 (0.4)	$C_{18}H_{24}O_5$	246 (40)	57 (100)	57
3f	306.147 (0.6)	$C_{17}H_{22}O_5$	246 (48)	43 (100)	43
4a	334.178 (2)	$C_{19}H_{26}O_5$	246 (36)	71 (65)	97
4b 4c	348.194 (1.2)	$C_{20}H_{28}O_5$	246 (30)	85 (46)	57
4d	346.178 (0.5)	$C_{20}H_{26}O_5$	246 (18)	83 (100)	83
5a	366.168 (2.5)	$C_{29}H_{26}O_7$	278 (11)	71 (70)	111*
5b 5c	380.184 (2)	$C_{20}H_{28}O_7$	278 (6.5)	85 (52)	57†
5d	378.168 (1)	$C_{20}H_{26}O_7$	278 (4)	83 (100)	83‡
5e	352.152 (1.3)	$C_{18}H_{24}O_7$	278 (9)	57 (80)	111§
6e	350.136 (1)	$C_{18}H_{22}O_7$	276 (10)	57 (100)	57‖
7	290.152 (38)	$C_{17}H_{22}O_4$	230 (100)	43 (50)	230

*$C_6H_7O_2$ (splitting of 5.6 and 1.10 bonds), 334 [M − O$_2$]$^+$ (4).
†348 [M − O$_2$]$^+$ (8); 111 (68).
‡346 [M − O$_2$]$^+$ (6), 111 (38).
§320 [M − O$_2$]$^+$ (5).
‖111 (82).

isolated as colourless oils which were homogeneously by their ^{1}H NMR spectra, by TLC and by HPLC. The mass spectral data are summarized in Table 2. The IR spectra ($\nu_{max}^{CHCl_3}$ cm^{-1}) showed the expected bands: **1**: 3600 (OH), 1765 (γ-lactone); **2a–2c, 5a–5c, 5e, 6e**: 3600 (OH), 1770 (γ-lactone), 1730 (CO$_2$R); **2d** and **5d**: 3600 (OH), 1700 (γ-lactone), 1715 (C=CCO$_2$R); **3a–3c, 3e, 4a–4c**: 1775 (γ-lactone), 1735 (CO$_2$R); **3d** and **4d**: 1775 (γ-lactone), 1720 (C=CCO$_2$R); **3f** and **7**: 1775 (γ-lactone), 1740 (OAc).

Compound **9** showed the following typical ^{1}H NMR signals ($CDCl_3$): 7.60 (*br*, OOH), 5.05 and 4.77 (*t*, H-15, J = 1 Hz), 2.50 (*m*, H-3α), 2.18 (*d* (*br*), H-3β, H-6α, J = 13 Hz), 1.87 (*tt*, H-7, J = 13, 4 Hz), 1.37 (*t*, H-6β, J = 13 Hz), 1.01 (*d* (*br*) H-1β, J = 13 Hz), 1.25 (*s*, H-12), 1.20 (*s*, H-13), 0.90 (*s*, H-14); MS *m/z* (rel. int.): 236.178 [M − H$_2$O]$^+$ (1.7) ($C_{15}H_{24}O_3$), 203 [236 − O$_2$H]$^+$ (44), 95 [C_7H_{11}]$^+$ (100); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540 (OH), 910 (C=CH$_2$).

The extract of 170 g aerial parts of *A. schmidtiana* (voucher AR 975) was separated as above first by CC and further by TLC affording 40 mg germacrene D, 5 mg bicyclogermacrene, 5 mg γ-humulene, 5 mg γ-curcumene, 5 mg caryophyllene, 8 mg β-farnesene, 10 mg squalene, 2 mg geranyl acetate, 8 mg thujyl acetate, 10 mg phloracetophenone-2,4-*O*-dimethyl ether, 2 mg nerolidol and 2 mg of its 5-acetoxy derivative, 9 mg costunolide, 3 mg neointermediol, 2.5 mg reynosin, 3 mg artemorin, 2 mg anhydroverlotorin and 1 mg **10** (TLC: Et$_2$O–petrol, 1:1, four developments, R_f 0.5), colourless oil; UV $\lambda_{max}^{Et_2O}$ nm: 308, 292; MS *m/z* (rel. int.): 220.056 [M]$^+$ (78) ($C_{12}H_{12}O_2S$), 202 [M − H$_2$O]$^+$ (8), 192 [M − CO]$^+$ (32), 164 [192 − CO]$^+$ (31), 163 [M − HC≡CS]$^+$ (100), 135 [163 − CO]$^+$ (58), 134 [163 − CHO]$^+$ (57), 91 [C_7H_7]$^+$ (33); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1630, 950 (CH=CH *trans*); $[\alpha]_D^{24°}$ = −14 ($CHCl_3$; *c* 0.05); ^{1}H NMR ($CDCl_3$): 4.05 (*m*, H-1), 2.14 (*m*, H-2), 1.93 (*m*, H-2'), 4.23 (*ddd*, H-4), 6.18 (*dd*, H-5), 5.99 (*dd*, H-6), 7.18 (*dd*, H-10), 6.97 (*dd*, H-11), 7.25 (*dd*, H-12); [J (Hz): 2,3 = 5; 2',3 = 2.5; 3,4 = 3; 4,5 = 5; 4,6 = 1.5; 5,6 = 16; 10,11 = 3.5; 10,12 = 1; 11,12 = 5]. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

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