Acetylenic Fatty Acids, Triglyceride and Triterpenes from the Leaves of *Hymenodictyon excelsum*

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Received January 30, 2009; accepted March 14, 2009; published online May 22, 2009

Two new acetylenic fatty acids (1, 2), a new triglyceride (3), along with eleven known compounds including 3-oxo-11α,12α-epoxyurs-13β,28-olide (4) previously reported as a synthetic compound, have been isolated from the leaves of *Hymenodictyon excelsum*. The structural identification was established from spectroscopic data.

Key words *Hymenodictyon excelsum*; Rubiaceae; acetylenic fatty acid

Hymenodictyon excelsum (syn. *H. orixense*) of the Rubiaceae family, known in Thailand as "U Lok and Som Kop," is a deciduous tree which grows to about 9—12 m in height.[1)] Its bark is used as an astringent and febrifuge, while its leaves are used to treat ulcer, sialitis, sore throat, tonsillitis, and as an anti-inflammatory.[2)] The chemical constituents previously reported to be found in this plant were coumarins,[3)] and anthraquinones.[4)] Chromatographic separation of the hexane and CH_2Cl_2 extracts led to the isolation of two new acetylenic fatty acids (**1**, **2**), a new triglyceride (**3**), as well as, 11 known compounds, including 3β-hydroxy-11-oxours-12-en-28-oic acid[5)] (isolated as its acetate derivative), 3β-hydroxy-27-*p*-(*Z*)-coumaroyloxyolean-12-en-28-oic acid,[6,7)] 3-oxo-11α,12α-epoxyurs-13β,28-olide (**4**),[8)] 3β-hydroxy-11α,12α-epoxyurs-13β,28-olide (**5**),[8,9)] 3β-hydroxyurs-11-en-13(28)-lactone (**6**),[8,10—12)] oleanolic acid (**7**),[13,14)] β-sitosterol,[15)] uncarinic acid E (3β-hydroxy-27-(*E*)-*p*-coumaroyloxyolean-12-en-28-oic acid, **8**),[6,7)] ursolic acid (**9**),[13,14)] ursonic acid (**10**), and 3β-(formyloxy)-urs-12-en-28-oic acid (**11**).[16)] Compound **5** was reported to be isolated from *Thevetia neriifolia*,[9)] but the reported NMR chemical shifts were not consistent with the proposed structure. Our finding revealed that the ^{1}H- and ^{13}C-NMR data of **5** were similar to those reported for the corresponding synthetic product.[8)] Compound **4**, documented as a synthetic product by oxidation of **5** using CrO_3,[8)] was obtained for the first time from a natural source in this study. We herein report the structural elucidation of compounds **1**—**3**.

Results and Discussion

Compound **1** was isolated as a colourless oil, and assigned a molecular formula of $C_{21}H_{36}O_2$ based on its HR-MS spectrum. The infrared absorption bands at 2913, 1706 cm^{-1}, a carboxyl carbon signal at δ 179.5 in ^{13}C-NMR spectrum, and the presence of broad methylene protons signal at *ca.* δ 1.23 indicated compound **1** to be a fatty acid. The monomethyl ester (**1a**), prepared from **1** by treatment with diazomethane, was used for additional ^{1}H- and ^{13}C-NMR spectroscopic studies. Characteristic vinyl ABX ^{1}H-NMR signals at δ 5.79 (1H, dddd), 4.96 (1H, ddd), 4.90 (1H, ddd) and ^{13}C-NMR signals at δ 139.2 (d), 114.1 (t) in addition to the infrared absorption bands at 1458 and 908 cm^{-1} indicated a terminal double bond. The ^{13}C-NMR signals of two quaternary carbons at δ 80.8 and 79.3 required the presence of an acetylenic group. The ^{1}H-NMR spectra of both **1** and **1a** showed signals at δ *ca.* 2.31—2.33 assignable to methylene protons adjacent to a carbonyl group (H_2-2). The ^{1}H–^{1}H correlation spectroscopy (COSY) cross-peaks were observed for H-2/H-3, H-3/H-4, H-4/H-5 and H-5/H-8. The relatively high-field shifts of C-5 (δ 18.4) and C-8 (δ 18.7) of **1** which are diagnostic evidence for the bonding of these carbons to an acetylenic group,[17)] in conjunction with the long-range ^{1}H–^{13}C correlations of H-4 (δ 1.51)/C-5 (δ 18.4), C-6 (δ 79.3); H-5 (δ 2.15)/C-6, C-7 (δ 80.8); H-8 (δ 2.10)/C-6, C-7 and H-9 (δ 1.43)/C-7, C-8 (δ 18.7) help support the placement of a triple bond at C-6. The ^{1}H- and ^{13}C-NMR chemical shifts of **1** and **1a** were assigned as shown in Tables 1 and 2. Base fragment ions in the mass spectra of **1** at *m*/*z* 140 and of **1a** at *m*/*z* 154 were proposed to arise from McLafferty fragmentation with cleavage of C-8/C-9 bond resulting in the loss of trideca-1,12-diene. Compound **1** was therefore identified as henicosa-6-yn-20-en-1-oic acid.

Compound **2**, which was isolated as a colourless waxy oil, showed a molecular formula of $C_{19}H_{32}O_2$ based on the HR-MS spectrum. FT-IR showed strong CH stretching (2918, 2848 cm^{-1}) and absorption bands for a carboxyl group (3073, 1690 cm^{-1}) and terminal double bond (1461, 911 cm^{-1}). Signals for two quaternary carbons assignable to acetylenic functionality at δ 81.3, 77.9 and the vinyl ABX ^{1}H-NMR signals at δ 5.79 (1H, dddd, H-18), 4.97 (1H, ddd, H-19) and 4.91 (1H, br d, H-19) were also detected. The ^{1}H–^{1}H COSY spectrum showed a cross-peak between H-2 (δ 2.53) and a proton signal resonating at a rather less shielded position (δ

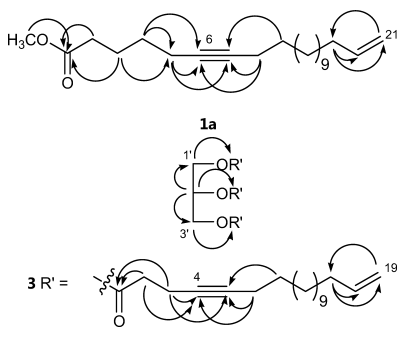

Fig. 1. Selected HMBC Correlations of **1a** and **3**

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Table 1. ^{1}H-NMR Spectroscopic Data of Compounds **1**, **1a**, **2**, **2a** and **3** (400 MHz) in $CDCl_3$ (δ ppm)

Position	**1** ^{1}H (mult., *J* in Hz)	**1a** ^{1}H (mult., *J* in Hz)	**2** ^{1}H (mult., *J* in Hz)	**2a** ^{1}H (mult., *J* in Hz)	**3** ^{1}H (mult., *J* in Hz)
1	—	—	—	—	—
2	2.33 (t, 7.5)	2.31 (t, 7.5)	2.53 (m)	2.48 (m)	2.50 (br d, 6.3)
3	1.74 (quint, 7.5)	1.71 (quint, 7.5)	2.46 (m)	2.46 (m)	2.43 (m)
4	1.51 (quint, 7.0)	1.49 (quint, 7.3)	—	—	—
5	2.15 (tt, 7.0, 2.3)	2.15 (tt, 7.0, 2.3)	—	—	—
6	—	—	2.10 (t, 6.9)	2.09 (tt, 7.1, 2.3)	2.09 (obs t, 7.1)
7	—	—	1.44 (quint, 6.7)	1.43 (quint, 7.4)	1.43 (quint, 7.0)
8	2.10 (tt, 7.1, 2.3)	2.10 (tt, 7.1, 2.4)	1.24 (m)	1.23 (m)	1.24 (m)
9	1.43 (quint, 7.4)	1.45 (obs quint, 7.2)	1.24 (m)	1.23 (m)	1.24 (m)
10—15	1.23 (m)	1.24 (m)	1.24 (m)	1.23 (m)	1.24 (m)
16	1.23 (m)	1.24 (m)	1.33 (quint, 6.9)	1.33 (br q, 6.8)	1.33 (m)
17	1.23 (m)	1.24 (m)	2.02 (q, 6.9)	2.02 (q, 6.8)	2.03 (q, 6.7)
18	1.33 (br q, 6.7)	1.34 (br q, 6.2)	5.79 (dddd, 17.0, 10.2, 6.7, 6.7)	5.79 (dddd, 16.9, 10.1, 6.8, 6.8)	5.79 (dddd, 16.9, 10.2, 6.7, 6.7)
19	2.03 (q, 6.7)	2.02 (q, 6.7)	4.97 (dq, 17.1, 1.6), 4.91 (br d, 10.2)	4.97 (ddd, 17.1, 3.6, 1.6), 4.90 (ddd, 10.2, 2.1, 1.1)	4.97 (ddd, 17.2, 3.7, 1.6) 4.90 (dt, 10.1, 1.1)
20	5.79 (dddd, 16.9, 10.2, 6.7, 6.7)	5.80 (dddd, 16.9, 10.1, 6.7, 6.7)	—	—	—
21	4.96 (ddd, 17.0, 3.4, 1.7), 4.90 (ddd, 10.1, 2.3, 1.3)	4.97 (ddd, 17.0, 3.7, 1.7), 4.90 (ddd, 10.2, 2.3, 1.3)	—	—	—
OCH_3		3.65 (s)	—	3.67 (s)	—
1′, 3′			—	—	4.30 (dd, 11.9, 4.4) 4.16 (dd, 11.9, 5.9)
2′			—	—	5.25 (quint, 5.0)

2.46, H-3) disclosed an electron withdrawing group adjacent to C-3. The heteronuclear multiple bond coherence (HMBC) correlations of H-2/C-1 (δ 177.8), C-3 (δ 14.9), C-4 (δ 77.9) and H-3/C-1, C-2 (δ 33.8), C-4, C-5 (δ 81.3) led to the placement of carbon–carbon triple bond between C-4 and C-5. Treatment of **2** with CH_2N_2 gave a methyl ester **2a**. The ^{1}H- and ^{13}C-NMR data for **2** and **2a** are shown in Tables 1 and 2. Intense fragment ion with *m/z* 112 in the mass spectrum of **2** and with *m/z* 126 in the mass spectrum of **2a** arising from McLafferty cleavage supported an acetylenic group at C-4. Compound **2** could therefore be assigned as nonadeca-4-yn-18-en-1-oic acid.

Compound **3** was isolated as a colourless wax and the HR-MS spectrum revealed a molecular formula of $C_{60}H_{98}O_6$. FT-IR spectrum revealed an ester group at 1730 cm^{-1} and a terminal double bond at 1469, 908 cm^{-1}. Most of the ^{1}H-NMR signals resembled those found in compound **2**, except for the presence of extra oxymethylene group signals at δ 4.30 (2H, dd, H-1′, H-3′) and 4.16 (2H, dd, H-1′, H-3′), δ 62.2 (2×t, C-1′, C-3′), as well as, an oxymethine group signal at δ 5.25 (1H, quint, H-2′), and δ 69.3 (d, C-2′) all of which exhibited cross-peaks to one another in the ^{1}H–^{1}H COSY spectrum thus indicated a glyceryl portion of the molecule. The long range ^{1}H–^{13}C correlations of H-1′, H-3′/C-1 (δ 171.6), C-2′ and H-2′/C-1 (δ 171.2), C-1′, C-3′ indicated the connectivities between fatty acid chains and the glycerol moiety. Other important long range ^{1}H–^{13}C correlations between H-2/C-1, C-3, C-4 and H-3/C-1, C-2, C-4, C-5 placed a triple bond between C-4 and C-5, as found in compound **2**. Further methanolysis of **3** in HCl[18] gave a methyl ester which showed identical ^{1}H- and ^{13}C-NMR spectroscopic chemical shifts as those of **2a** (Tables 1, 2). Compound **3** was thus identified as a triglyceride of nonadeca-4-yn-18-en-1-oic acid.

Table 2. ^{13}C-NMR Spectroscopic Data of Compounds **1**, **1a**, **2**, **2a** and **3** (100 MHz) in $CDCl_3$ (δ ppm)

Carbon	**1**	**1a**	**2**	**2a**	**3**
1	179.2	173.9	177.8	172.6	171.6,[a] 171.2[b]
2	33.5	33.7	33.8	34.0	33.9
3	23.8	24.2	14.9	14.8	14.7
4	28.4	28.6	77.9	78.0	77.7
5	18.4	18.5	81.3	81.2	81.4
6	79.3	79.4	18.7	18.7	18.7
7	80.8	80.8	28.9[e]	28.8[f]	28.9[g]
8	18.7	18.8	29.2[e]	29.2[f]	28.2[g]
9	28.9	29.2[d]	29.5[e]	29.3[f]	28.9[g]
10	29.1[c]	28.9[d]	29.6[e]	29.4[f]	29.3[g]
11	29.3[c]	29.5[d]	29.6[e]	29.5[f]	29.5[g]
12—15	29.6[c]	29.6[d]	29.6[e]	29.6[f]	29.6[g]
16	29.6[c]	29.6[d]	29.1[e]	29.0[f]	28.9[g]
17	29.6[c]	29.6[d]	33.8	33.8	33.8
18	28.9[c]	29.0[d]	139.5	139.5	139.3
19	33.8	33.8	114.1	114.1	114.1
20	139.2	139.2	—	—	—
21	114.1	114.1	—	—	—
OCH_3		51.4	—	51.7	—
1′, 3′			—	—	62.2
2′			—	—	69.3

a) C-1 of acids attached to C-1′ and C-3′. *b*) C-1 of acid attached to C-2. *c*—*g*) Interchangeable.

This work is an example of the isolation of acetylenic fatty acids, and triglyceride of acetylenic fatty acid from plant of the Rubiaceae family and may be of taxonomic importance.

Experimental

General Experimental Procedures Melting points were measured using an Electrothermal melting point apparatus and were uncorrected. Optical rotations were recorded on a JASCO DIP1020 polarimeter. The IR spectra were obtained on a Perkin-Elmer 1760x FT-IR spectrophotometer. The ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AVANCE 400 MHz spectrometer. Chemical shifts were referenced to the residual solvent signals ($CDCl_3$: ^{1}H δ 7.24 and ^{13}C δ 77.0 ppm). HR-ESI-MS and HR-APCI-MS spectra were recorded on a Bruker Daltonics microTOF instrument.

Plant Material The stems and leaves of *H. excelsum* Wall were collected from Ubonratchathani Province in 2002. The botanic identification was kindly made by Assoc. Professor Dr. Nijsiri Ruangrangsi, Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University. A voucher specimen SSHEx/2002 was deposited at the Department of Chemistry, Faculty of Science, Ramkhamhaeng University, Bangkok.

Extraction and Isolation Dried leaves (8.6 kg) of *H. excelsum* were extracted successively with hexane, CH_2Cl_2 and methanol using a Soxhlet extractor to yield hexane (232.4 g), CH_2Cl_2 (215.1 g) and MeOH (1636.0 g) extracts, respectively. The hexane extract of the leaves was fractionated by silica gel column chromatography using a gradient of hexane→CH_2Cl_2–MeOH (50 : 50) to give eight fractions. Fraction 6 was purified by silica gel column chromatography using hexane–CH_2Cl_2 (95 : 5)→CH_2Cl_2–MeOH (60 : 40) to obtain 8 subfractions (6.1—6.8). Subfraction 6.3 after successive silica gel column chromatography using hexane–CH_2Cl_2 (40 : 60) and then hexane–EtOAc (92 : 8) gave **1** (21 mg). Purification of subfraction 6.6 by silica gel column chromatography using a gradient of hexane–CH_2Cl_2 (50 : 50)→CH_2Cl_2–MeOH (90 : 10) gave **2** (67 mg) and **3** (29.3 mg). Fraction 7 was chromatographed over a silica gel column using hexane–CH_2Cl_2 (50 : 50) to give β-sitosterol (52 mg). The CH_2Cl_2 extract of the leaves (66.5 g) was subjected to silica gel column chromatography with a gradient of hexane–CH_2Cl_2 (50 : 50)→CH_2Cl_2–MeOH (50 : 50) to afford eight major fractions. Fraction 2 was chromatographed over a silica gel column using hexane–CH_2Cl_2 (60 : 40)→CH_2Cl_2–MeOH (90 : 10) to yield **3** (18 mg). Fraction 4 was purified by silica gel column chromatography using a stepwise gradient of CH_2Cl_2→CH_2Cl_2–MeOH (50 : 50) to give eight subfractions (4.1—4.8). Subfraction 4.8 after silica gel column chromatography eluting with a gradient of CH_2Cl_2–MeOH (99.5 : 0.5→80 : 20) gave **8** (20.3 mg) and **9** (132 mg). Fraction 5 (1.54 g) was purified by reversed-phase C_{18} column chromatography using MeOH–H_2O (80 : 20→100 : 0) followed by silica gel column chromatography using hexane–EtOAc (80 : 20→75 : 25) as the mobile phase to yield 3β-hydroxy-27-*p*-(*Z*)-coumaroyloxyolean-12-en-28-oic acid (16.7 mg), **7** (30.3 mg) and an additional quantity of **9** (46.7 mg). Part of fraction 6 (680 mg) was allowed to react with acetic anhydride in pyridine, and after purification by silica gel column chromatography using a gradient of hexane–CH_2Cl_2 (20 : 80)→CH_2Cl_2–MeOH (40 : 60), pure 3β-*O*-acetyl-urs-12-en-28-oic acid (160.9 mg) and 3β-*O*-acetyl-11-oxours-12-en-28-oic acid (6.8 mg) were obtained. Further purification of fraction 6 using silica gel column chromatography with CH_2Cl_2–MeOH (100 : 0→40 : 60) as the mobile phase gave **5** (25.9 mg) and **6** (28.1 mg). Silica gel column chromatography eluting with a gradient of CH_2Cl_2→CH_2Cl_2–MeOH (50 : 50) of fraction 7 gave **4** (5 mg), **5** (234 mg), **6** (198 mg), **9** (493 mg), **10** (25 mg), and **11** (52 mg).

Henicosa-6-yn-20-en-1-oic Acid (**1**): Colourless wax; $[\alpha]_D^{23}$ 3.81 (c=0.78, $CHCl_3$); IR (KBr) cm^{-1}: 3434, 2907, 2841, 1690, 1458, 1410, 1306, 1247, 1192, 986, 908; EI-MS *m/z*: 320 $[M]^+$ (1.3), 260 $[M-CH_2=C(OH)OH]^+$ (0.6), 232 (1.9), 219 (3), 193 (2), 181 (2), 149 (6), 140 $[CH_2=C=CH-(CH_2)_4CO_2H]^+$ (100), 135 (8), 122 $[140-H_2O]^+$ (19), 108 (14), 95 $[140-HCO_2H]^+$ (32), 80 $[140-CH_2=C(OH)OH]^+$ (82), 68 (42), 55 $[CH_2CH=CH_2CH_2]^+$ (55), 41 $[CH_2CH=CH_2]^+$ (59), 29 (18); HR-APCI-MS (positive ionization mode) *m/z*: 321.2790 $[M+1]^+$ (Calcd for $C_{21}H_{37}O_2$: 321.2788); for ^{1}H-NMR ($CDCl_3$) data, see Table 1, ^{13}C-NMR ($CDCl_3$) data, see Table 2.

Henicosa-6-yn-20-en-1-oic Acid Methyl Ester (**1a**): Colourless liquid; IR (KBr) cm^{-1}: 3078, 2913, 2847, 1706, 1689, 1642, 1469, 1431, 1315, 1263, 1244, 1206, 1138, 1076, 989, 910, 717, 678; EI-MS *m/z*: 334 $[M]^+$ (3), 303 $[M-OMe]^+$ (5), 291 (1), 260 (2), 233 $[M-CH_2=C(OMe)OH]^+$ (2), 219 (3), 195 (2), 163 (5), 154 $[CH_2=C=CH(CH_2)_4CO_2Me]^+$ (87), 134 (14), 122 $[154-HOMe]^+$ (32), 108 (17), 94 $[122-HCO_2Me]^+$ (62), 80 $[154-CH_2=C(OMe)OH]^+$ (100), 74 (18), 68 (45), 55 $[CH_2CH_2CH=CH_2]^+$ (56), 41 $[CH_2CH=CH_2]^+$ (54), 29 (19). HR-ESI-MS (positive ionization mode) *m/z*: 357.2702 $[M+Na]^+$ (Calcd for $C_{22}H_{38}O_2Na$: 357.2769); for ^{1}H-NMR ($CDCl_3$) data, see Table 1, ^{13}C-NMR ($CDCl_3$) data, see Table 2.

Nonadeca-4-yn-18-en-1-oic Acid (**2**): Colourless wax; $[\alpha]_D^{23}$ 2.74 (c=0.68, $CHCl_3$); IR (KBr) cm^{-1}: 3073, 2918, 2848, 1690, 1641, 1461, 1430, 1410, 1296, 1264, 1214, 1179, 988, 911, 773, 740, 723; EI-MS *m/z*: 292 $[M]^+$ (1.1), 274 $[M-OH]^+$ (1.1), 233 $[M-CH_2CO_2H]^+$ (2.7), 219 $[M-CH_2CH_2CO_2H]^+$ (6.4), 151 (19.7), 121 (24.9), 112 $[CH_2=C=CH(CH_2)_2CO_2H]^+$ (42), 95 $[112-OH]^+$ (49), 81 (65), 67 $[112-HCO_2H]^+$ (74), 55 $[CH_2CH_2CH=CH_2]^+$ (100), 41 $[CH_2CH=CH_2]^+$ (54); HR-APCI-MS (positive ionization mode) *m/z*: 293.2473 $[M+1]^+$ (Calcd for $C_{19}H_{33}O_2$: 293.2475); for ^{1}H-NMR ($CDCl_3$) data, see Table 1, ^{13}C-NMR ($CDCl_3$) data, see Table 2.

Nonadeca-4-yn-18-en-1-oic Acid Methyl Ester (**2a**): Colourless wax; $[\alpha]_D^{24}$ 13.20 (c=0.20, $CHCl_3$); IR (KBr) cm^{-1}: 2925, 2853, 1742, 1638, 1458, 1365, 1289, 1256, 1166, 1041, 1014, 991, 909, 796; EI-MS *m/z*: 306 $[M]^+$ (6), 291 $[M-Me]^+$ (2.7), 275 $[M-OCH_3]^+$ (11), 233 $[M-CH_2CO_2Me]^+$ (4), 149 (11), 126 $[CH_2=C=CH(CH_2)_2CO_2Me]^+$ (67), 107 (41), 95 $[126-OMe]^+$ (53), 84 (86), 67 $[126-HCO_2Me]^+$ (92), 55 $[CH_2CH_2CH=CH_2]^+$ (100), 41 $[CH_2CH=CH_2]^+$ (33); HR-APCI-MS (positive ionization mode) *m/z*: 307.2622 $[M+1]^+$ (Calcd for $C_{20}H_{35}O_2$: 307.2632); for ^{1}H-NMR ($CDCl_3$) data, see Table 1, ^{13}C-NMR ($CDCl_3$) data, see Table 2.

1′,2′,3′-*O*-Trinonadeca-4-yn-18-en-1-oyl-glycerol (**3**): Colourless wax; $[\alpha]_D^{27}$ −0.51 (c=0.87, $CHCl_3$); IR (KBr) cm^{-1}: 2914, 2848, 1730, 1469, 1267, 1174, 990, 908, 773, 715; HR-APCI-MS (positive ionization mode) *m/z*: 915.7440 $[M+1]^+$ (Calcd for $C_{60}H_{99}O_6$: 915.7436); for ^{1}H-NMR ($CDCl_3$) data, see Table 1, ^{13}C-NMR ($CDCl_3$) data, see Table 2.

Acknowledgments The authors wish to thank the Thailand Research Fund, Ramkhamhaeng University and the Center for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education for financial support. P. N. acknowledges the Royal Golden Jubilee Ph. D. Program, Thailand Research Fund for a scholarship. We acknowledge Mr. N. Chimnoi, Chulabhorn Research Institute for his HR-MS measurements and Ms. C. Seeka for her valuable technical assistance.

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