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A DIYNOIC ACID FROM *POLYALTHIA EVECTA*

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Key Word Index—*Polyalthia evecta*; Annonaceae; roots; evectic acid; diynoic acid; 21-furan-heneicosa-5,7-diynoic acid.

Abstract—A novel diynoic acid, evectic acid (21-furan-heneicosa-5,7-diynoic acid), has been isolated from the roots of *Polyalthia evecta*. Its structure was elucidated by spectroscopic methods. The ^1H and ^{13}C NMR spectra were assigned by combined application of COSY, HMQC, DEPT, HMBC and NOESY experiments. © 1997 Elsevier Science Ltd

INTRODUCTION

The Thai herbal, *Polyalthia evecta*, is called Nam-toulang in Thai. A water decoction of the roots of this plant has been used by north-eastern natives as a galactagogue [1]. Chemical constituents in *Polyalthia* species have been investigated by many groups; indolsesquiterpenes, clerodan diterpenes, aporphine alkaloids and steroids have been isolated [2–13]. During our search for bioactive constituents from thai plants, the hexane extract of air-dried roots of *P. evecta* was shown to be active against the fungal plant pathogen, *Phytophthora palmivora*. We report herein on the isolation and characterization of a novel diynoic acid, named evectic acid (**1**). The structure of **1** was established by means of 1D and 2D NMR experiments.

RESULTS AND DISCUSSION

Evectic acid (**1**) was isolated from crude hexane as colourless plates. Elemental analysis and EI mass spectrometry gave a molecular formula of $C_{25}H_{36}O_3$ [*m/z* 384 $[M]^+$]. The IR and NMR (Table 1) showed the presence of carboxylic acid [ν_{max} 3000–3500 (OH), 1689 (C=O) cm^{-1}; δ_H 10.3; δ_C 177.8] and acetylene [$\nu_{max} \approx 2200$ cm^{-1}; δ_C 66.4, 65.0, 75.6, 78.1] groups. Methylation of **1** with thionyl chloride and methanol yielded a monomethyl ester (**2**) [δ_H 3.70; δ_C 173.3, 51.5 (CO_2Me)] to support the presence of a carboxylic acid. A broad singlet signal observed at δ_H 1.27 (14H), which correlated to overlapping signals at δ_C 28.8–29.6 in HMQC spectrum, was assigned as a long methylene chain; this was also confirmed by the DEPT spectrum. The COSY spectrum indicated the partial structures of 2-substituted furan and three —$CH_2CH_2CH_2$— units (Fig. 1). The small coupling constant ($J = 1.0$ Hz) observed between δ 2.36 (H-4) and δ 2.24 (H-9) suggested that these methylenes were connected through acetylenes, which was supported by HMBC correlations [H-4 to C-5 (δ 75.6), C-6 (δ 66.4), C-7 (δ 65.0); H-3 to C-5; H-10 to C-8 (δ 78.1); H-9 to C-6, C-7, C-8] (Fig. 1). The HMBC correlations of H-2 and H-3 to C-1 connected the carboxylic acid to C-2–C-11 unit to yield a partial structure of C-1–C-11. The ^1H and ^{13}C chemical shifts at C-1–C-8 for **1** were comparable to those reported for compound **3**, supporting this partial structure [14]. Another partial structure (C-19–C-25) was deduced from the HMBC correlations (H-20, H-21 to C-22), which were supported by NOESY data (H-20 ↔ H-21, 23; H-21 ↔ H-19, 23). The resulting two partial structures (C-1–C-11 and C-19–C-25) were connected through the methylene chain (C-12–C-18) to complete the structure of **1** as 21-furan-heneicosa-5,7-diynoic acid (Fig. 1).

EXPERIMENTAL

General. CC was carried out on silica gel 60, 63–200 mesh, TLC on silica gel 60 PF_{254}. NMR were recorded on a Bruker AMX600 spectrometer for **1** and a DPX300 spectrometer for **2**, in $CDCl_3$ using residual $CHCl_3$ (δ 7.26) and $CDCl_3$ (δ 77.0) as int. standard. IR spectra were carried out on a Bio-Rad model FTS-7 spectrometer. MS were obtained at 70 eV. UV measured in MeOH. Mps are uncorr.

Plant material. Roots of *P. evecta* Finet and Gagnep were collected in Ban Sri-Than, Amphoe Muang, KhonKaen, Thailand, and identified by Pranom Chantaranothai, Department of Biology, KhonKaen

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Table 1. ^{13}C and ^{1}H NMR spectral data of compounds **1*** and **2*** (ppm, $CDCl_3$)

	δ_H		δ_C	
No.	**1**	**2**	**1**	**2**
	10.3 (1H) *br*	3.70 (3H) *s*	—	51.5
1	—	—	177.8	173.3
2	2.50 (2H) *t* (7.4)	2.45 (2H) *t* (7.4)	32.4	32.6
3	1.85 (2H) *tt* (7.4, 6.9)	1.85 (2H) *tt* (7.4, 6.9)	23.3	23.5
4	2.36 (2H) *td* (6.9, 1.0)	2.33 (2H) *td* (6.9, 1.0)	18.6	18.6
5	—	—	75.6	75.8
6	—	—	66.4	66.2
7	—	—	65.0	65.0
8	—	—	78.1	77.9
9	2.24 (2H) *td* (7.1, 1.0)	2.24 (2H) *td* (7.0, 1.0)	19.2	19.1
10	1.51 (2H) *quint* (7.1)	1.50 (2H) *quint* (7.0)	28.3	28.3
11	1.37 (2H) *m*	1.37 (2H) *m*	c	28.7
12	a	b	c	d
13	a	b	c	d
14	a	b	c	d
15	a	b	c	d
16	a	b	c	d
17	a	b	c	d
18	a	b	c	d
19	1.31 (2H) *m*	1.31 (2H) *m*	c	29.0
20	1.63 (2H) *quint* (7.6)	1.62 (2H) *quint* (7.4)	28.1	28.0
21	2.61 (2H) *t* (7.6)	2.61 (2H) *t* (7.4)	28.0	27.9
22	—	—	156.6	156.5
23	5.96 (1H) *d* (3.2)	5.96 (1H) *d* (3.1)	104.4	104.4
24	6.27 (1H) *dd* (3.2, 1.9)	6.26 (1H) *dd* (3.1, 1.9)	110.0	109.9
25	7.29 (1H) *d* (1.9)	7.28 (1H) *d* (1.9)	140.6	140.5

[a,b] 1.27 (14H *br s*). [c] 28.8, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6. [d] 29.1, 29.3, 29.4, 29.5.
* ^{13}C (150 MHz) and ^{1}H (600 MHz) NMR for **1**; ^{13}C (75 MHz) and ^{1}H (300 MHz) NMR for **2**.

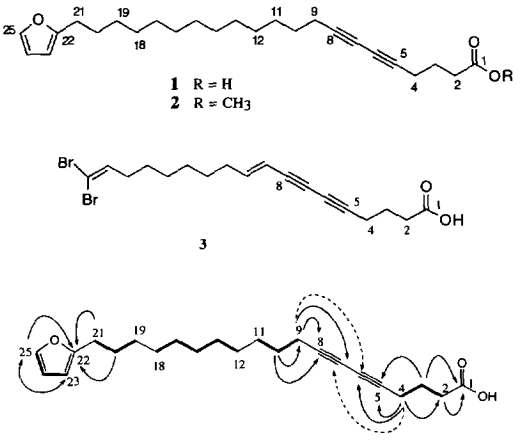

Fig. 1. COSY (bold line) and HMBC (arrow, $^{1}H \rightarrow {}^{13}C$) correlations obtained for compound **1**.

University. A plant specimen (voucher number SK94001) is deposited in the Herbarium of the Department of Biology, KhonKaen University.

Extraction and isolation. Air-dried roots (2.4 kg) were ground and extracted with 5 l *n*-hexane at room temp. for 2 days, then filtered; the process was repeated × 3. Filtrates were combined and the solvent removed *in vacuo* to yield a dark brown crude extract 60 g (2.5%). This was dissolved in hexane to obtain a grey ppt. after standing at room temp. for 2 weeks. The ppt. was purified by silica gel flash CC using EtOAc–hexane (1:1) as eluent to give a white amorphous powder. Further recrystallisation from CH_2Cl_2–hexane gave 5 g of **1** (0.2%).

Evectic acid, 21-furan-heneicosa-5,7-diynoic acid (**1**). Colourless plates, mp 65–67°. $R_f = 0.26$ (EtOAc–hexane, 1:1). UV λ_{max}^{MeOH} 213 nm (log $\varepsilon = 3.99$). IR ν_{max}^{KBr} cm^{-1}: 3500–3200 (COOH, *br*, *m*), 2918 (*s*), 2845 (*m*), 2300, 2150 (C≡C, *vw*), 1689 (C=O, *s*), 1541 (*w*), 1508 (*w*), 1457 (*w*), 1206 (*w*), 725 (*w*). EIMS 70 eV, *m/z* (rel. int.): 384 $[M]^+$ (17.0), 339 $[M\text{-}CO_2H]^+$ (3.4), 325 $[M\text{-}CH_2CO_2H]^+$ (3.4), 311 $[M\text{-}C_2H_4CO_2H]^+$ (6.7), 297 $[M\text{-}C_3H_6CO_2H]^+$ (10.0), 109 $[M\text{-}C_{17}H_{26}CO_2H]^+$ (5.7), 95 $[M\text{-}C_{18}H_{28}CO_2H]^+$ (26.6), 81 $[C_4H_3OCH_2]^+$ (100.0). Found: C, 78.39; H, 9.36 $C_{25}H_{36}O_3$ requires: C, 78.08; H, 9.44%. ^{1}H and ^{13}C NMR: Table 1.

Methyl 21-furan-heneicosa-5,7-diynoate (**2**). Compound **1** (0.1 g) was dissolved in anhydrous MeOH (10 ml) and few drops of $SOCl_2$ added. The reaction mixt. was stirred at room temp. for 2 hr then evapd to dryness *in vacuo* to yield a yellow oil. The crude Me ester was purified by prep. TLC using EtOAc–hexane (1:4, $R_f = 0.64$) to give **2** (98 mg) as a pale yellow oil (94.6%). UV λ_{max}^{MeOH} 213 nm (log $\varepsilon = 3.92$). IR ν_{max}^{Neat} cm^{-1}: 2924 (*vs*), 2855 (*vs*), 2257 (*vw*), 2164 (C≡C, *vw*),

1742 (C=O, *vs*), 1435 (*s*), 1221 (*m*), 1061 (*s*). EIMS 70 eV, *m/z* (rel. int.): 398 $[M]^+$ (0.4), 367 $[M\text{-}OMe]^+$ (0.53), 339 $[M\text{-}CO_2Me]^+$ (3.26), 325 $[M\text{-}CH_2CO_2Me]^+$ (0.36), 311 $[M\text{-}C_2H_4CO_2Me]^+$ (0.9), 297 $[M\text{-}C_3H_6CO_2Me]^+$ (1.8), 249 $[M\text{-}C_7H_6CO_2Me]^+$ (2.4), 165 $[M\text{-}C_{13}H_{18}CO_2Me]^+$ (1.0), 151 $[M\text{-}C_{14}H_{20}CO_2Me]^+$ (0.9), 137 $[M\text{-}C_{15}H_{22}CO_2Me]^+$ (1.2), 123 $[M\text{-}C_{16}H_{24}CO_2Me]^+$ (3.17), 109 $[M\text{-}C_{17}H_{26}CO_2Me]^+$ (4.8), 95 $[M\text{-}C_{18}H_{28}CO_2Me]^+$ (19.9), 81 $[C_4H_3OCH_2]^+$ (100.0), 74 $[C_3H_6O_2]^+$ (11.4), 59 $[CO_2Me]^+$ (9.3). Found: C, 77.70; H, 9.72 $C_{26}H_{38}O_3$ requires: C, 78.35; H, 9.61%.

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