Pergamon

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Fern Constituent: Preoleanatetraene, A Novel Bicyclic Triterpenoid Hydrocarbon from *Polypodiodes formosana*

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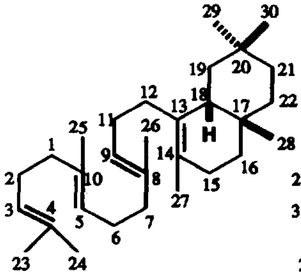
Abstract: A novel bicyclic triterpenoid hydrocarbon, preoleanatetraene (1) was isolated from the fresh rhizomes of *Polypodiodes formosana* and the structure of 1 was established by spectral data. A new biogenetic pathway for the oleanane triterpenoids in this fern is proposed. Copyright © 1996 Elsevier Science Ltd

We earlier reported the isolation and structure determination of several new triterpenoid hydrocarbons belonging to mono-, bi- and tricyclic skeleta[1,2] together with tetra-[3] and pentacyclic[4] derivatives from *Polypodiodes* ferns. Continued investigation of these studies resulted in the isolation of a novel bicyclic triterpenoid hydrocarbon, designated as preoleanatetraene (1), from the fresh rhizomes of *Polypodiodes formosana* CHING (=*Polypodium formosanum* BAKER, "Taiwan-Aone-kadzura"). We report herein the isolation and structure determination of 1. Also we propose a new biogenetic pathway for the formation of oleanane triterpenoid in *Polypodiodes* ferns.

Compound 1 was isolated as a minor component from the *n*-hexane extract (26.5 g) of the fresh rhizomes (1.70 kg) collected in Wulai, Taiwan. The TLC of the extract showed the presence of triterpenoid hydrocarbons and esters as the main components. Purification of the crude hydrocarbon mixture was done by repeated CC over $AgNO_3$-SiO_2 followed by HPLC [ODS, 5μ, 8 x 250 mm column, MeOH–$CHCl_3$ (8:2)] to give 1 (yield 0.0006 % based on dried plant materials) as an oil, $[\alpha]^{18}_{D}$ +13.9° (*c*=0.1, $CHCl_3$). HR-MS showed the molecular



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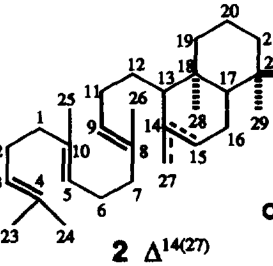
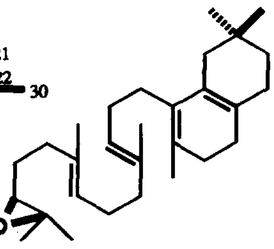


2 $\Delta^{14(27)}$
3 Δ^{14}



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formula to be $C_{30}H_{50}$ (*m/z* 410.3931) and EI-MS exhibited fragment ions at *m/z* 341, 273, 205, 191 and 69 (Fig. 1). The base peak (*m/z* 205) is the same as that observed in α- and γ-polypodatetraenes (**2**, **3**).[5] The other peaks could easily be derived by the elimination of one or two isoprene units (*m/z* 341, 273), and a side chain (*m/z* 191) from the molecular ion. ^{1}H-NMR spectrum (Table 1) of **1** showed signals due to three tertiary methyl groups (δ 0.820, 0.872, 0.893), five vinylic methyl groups [δ 1.576, 1.601 (2 x CH_3), 1.611, 1.681] and three olefinic protons [δ 5.110 (2H), 5.158 (1H)]. These observations demonstrated that the structure of **1** must be similar to those of **2** and **3**.

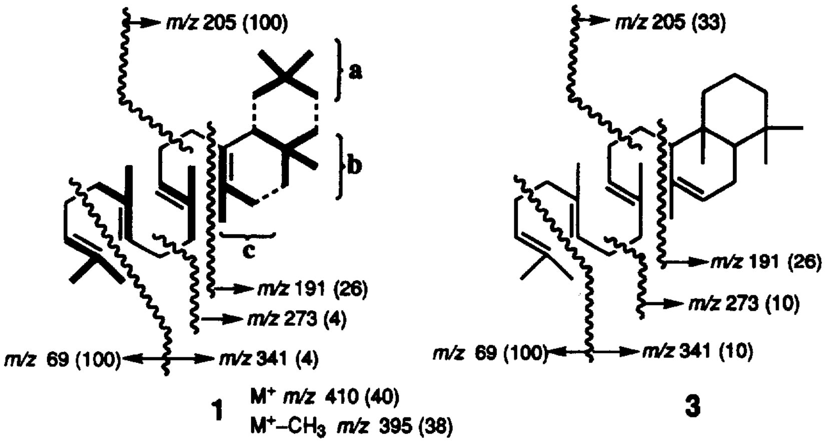

Fig. 1. MS fragment patterns of **1** and **3**, and partial structures solved by HMBC and H-H COSY.

^{13}C-NMR spectrum of **1** (Table 2) exhibited the presence of 30 skeletal carbons of which eight were CH_3, eleven CH_2, four CH and seven quaternary carbons. A comparison of ^{13}C-NMR data (Table 2) of **1** with those of **3**[5] revealed that both the compounds showed very close chemical shifts for C-1 to C-10 and C-23 to C-25 carbons clearly supporting the similarity in skeletal structures of **1** and **3** in this part of the molecules.

Table 1. ^{1}H Chemical Shifts (δ ppm, $CDCl_3$) of **1**– **3**

	1	**2**	**3**		**1**	
H_3-23	1.681	1.684	1.684	H_2-15	1.25	1.86
H_3-24	1.601	1.604	1.604	H_2-16	1.94	2.02
H_3-25	1.601	1.604	1.604	H-18	1.64	
H_3-26	1.611	1.604	1.604	H_2-19	0.96	1.38
H_3-27	1.576	1.568	1.604	H_2-21	1.11	1.34
H_2-27	—	4.540s 4.822s				
H_3-28	0.820	0.664	0.740	H_2-22	1.22	1.49
H_3-29	0.872	0.798	0.870			
H_3-30	0.893	0.868	0.850			

Table 2. ^{13}C Chemical Shifts (δ ppm, $CDCl_3$) of 1 and 3[7]

	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
1	39.75	26.77	124.29	131.27	124.41	27.16	39.74	134.93	124.29	134.81
3	39.75	26.79	124.41	131.26	124.27	26.69	39.75	134.95	124.83	134.95

	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
1	26.63	29.50	123.87	133.62	31.69	26.51	31.41	42.26	42.95	31.03
3	30.25	27.33	54.25	135.62	122.06	23.85	50.18	36.73	39.22	18.85

	C-21	C-22	C-23	C-24	C-25	C-26	C-27	C-28	C-29	C-30
1	34.61	36.56	25.71	17.69	16.00	15.97	18.64	26.98	33.18	24.21
3	42.37	32.99	25.71	17.69	16.00	16.17	22.21	13.47	21.90	33.19

Table 3 HMBC Data of 1

δ_H ppm	δ_C ppm	Two and three-bond ^1H-^{13}C correlation, δ_C ppm			
1.576 (H_3-27)	18.64 (C-27)	123.87 (C-13)	133.62 (C-14)	31.69 (C-15)	
0.826 (H_3-28)	26.98 (C-28)	26.51 (C-16)	31.41 (C-17)	42.26 (C-18)	36.56 (C-22)
0.872 (H_3-29)	33.18 (C-29)	42.95 (C-19)	31.03 (C-20)	34.61 (C-21)	

However, information regarding the carbon skeleton, particularly of the other part of the molecule could be obtained from HMBC spectrum of **1**. Thus, the long-range ^1H-^{13}C correlation data summarized in Table 3 clearly demonstrated the presence of six part structures as shown by heavy lines in the structure of **1** in Fig. 1. The connectivities between part structures **a**, **b** and **b**, **c** could be established by ^1H-^1H COSY and HSQC spectra. Having elucidated the skeletal structure of D/E ring system and joining the other three part structures as in **3**, the structure of the triterpene could be represented as shown in **1**. The relative stereochemistry at C-17 and C-18 were finally deduced by the NOE interactions observed between H-18β and H_3-30, H_3-30 and H-22β and, H-22β and H_3-28 in the NOESY spectrum of **1**, thereby establishing the presence of *cis* D/E ring juncture in the molecule.

It may be mentioned here that compound **1** has the same D/E ring system as in oleanane triterpenoids. A recent report by Corey *et al*[6] on the synthesis of β-amyrin from the bicyclic starting material (**6**), having a structure very close to that of **1**, as well as the co-occurrence of **1** with oleanane and migrated oleanane hydrocarbons in *P. formosana* prompted us to postulate an alternative biogenetic pathway for the formation of oleanane and migrated oleanane hydrocarbons in Polypodiaceous ferns *via* the preoleanane as shown in Chart 1. This was strongly supported by the fact that the occurrence of **1** was also detected in *Polypodiodes niponica* CHING (= *Polypodium niponicum* METT., "Aone-Kadzura") and *P. amoena* (= *Polypodium amoenum* WALL., "Alisan-Denda"), from which various oleanane and migrated oleanane derivatives have been isolated.[4,7] Compound **1**, therefore, seems to be a potential precursor in the biosynthesis of oleanane and migrated oleanane triterpenoids in Polypodiaceous ferns.

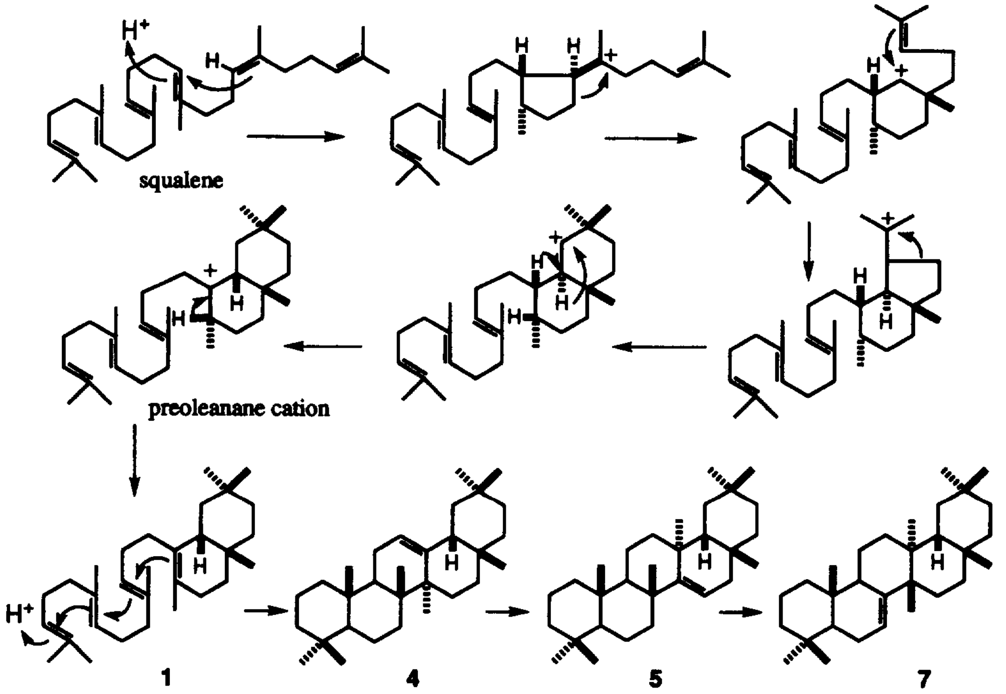

Chart 1

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