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FERN CONSTITUENTS: POLYPODATETRAENES, NOVEL BICYCLIC TRITERPENOIDS, ISOLATED FROM POLYPODIACEOUS AND ASPIDIACEOUS PLANTS

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Abstract. Two new oily triterpenoid hydrocarbons having a novel bicyclic carbon skeleton, named α- and γ-polypodatetraenes (**1** and **2**, respectively), were isolated from the fresh leaves of Polypodium fauriei and Lemmaphyllum microphyllum (**1**), and Polystichum ovato-paleaceum and P. polyblephalum (**2**). Their structures were established to be polypoda-8(26),13,17,21-tetraene (**1**) and polypoda-7,13,17,21-tetraene (**2**) by physico-chemical methods.

Recently we reported several kinds of triterpenoid hydrocarbons having rather unstable character in the air, such as eupha-7,21-diene, (18R)-dammara-13(17),21-diene,[1] baccharа-12,21-diene, lemmaphylla-7,21-diene, shiona-3,21-diene, dammara-18(28),21-diene and tirucalla-7,21-diene,[2] obtained from the Polypodiaceous ferns. Further investigations in the similar type of unstable compounds resulted in the isolation and characterization of oily triterpenoid hydrocarbons of a novel class, to which we propose the name α- and γ-polypodatetraenes.[3] This communication concerns the structural elucidation of these compounds, which are considered to be the first example of natural bicyclic triterpenoids produced from squalene by simple one end cyclization.

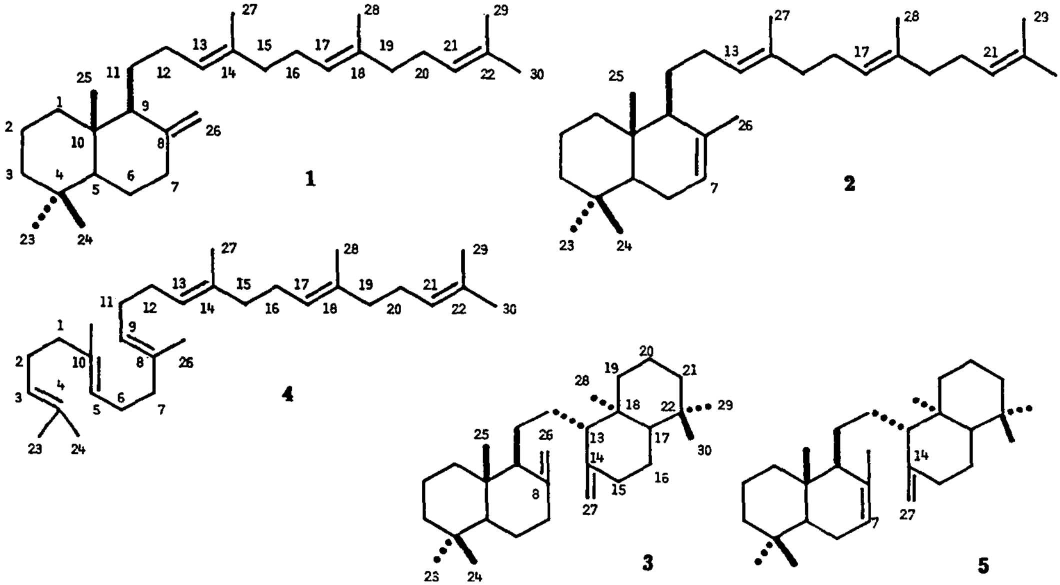

Chart 1

α-Polypodatetraene (**1**), oil, Rt$_R$ 1.12,[4] $[\alpha]_D^{23}$ +27.4° ($CHCl_3$, c=0.4) was isolated from fresh leaves of Polypodium fauriei H. Chr. ("Oshakuji-denda" in Japanese, collected in Yamanashi Prefecture in November, Polypodiaceae) and also from fresh leaves of Lemmaphyllum microphyllum Presl var. microphyllum ("Mamezuta, collected in Shizuoka Prefecture in May, Polypodiaceae) by extraction with n-hexane followed by silica gel and $AgNO_3$ impregnated silica gel chromatography in yields of 0.011% and 0.0004% of the dried materials estimated, respectively. Compound **1** was suggested to have the molecular formula $C_{30}H_{50}$ by MS (M^+ m/z 410.3919) and also to have a exocyclic methylene by IR (ν_{max}^{film} cm^{-1}: 3080, 1643, 887). The MS fragmentation pattern of **1** (Chart 2) indicated that **1** was a bicyclic triterpenoid having three isoprene units in the side chain. The structure of **1** being consisted of a half molecule of α-onoceradiene (**3**)[5] and that of squalene (**4**)[6-8] was confirmed by comparisons of ^{1}H- and ^{13}C-NMR spectra of **1** with **3** and **4** (Table I and II). Compound **3** was already isolated from the latter fern as a main hydrocarbon[5] and the presence of **4** in the both extracts was proved by GC (Rt$_R$ 0.91) and ^{1}H-NMR spectrum this time. ^{1}H-Chemical shifts of four methyl or methylene groups of **1** (C-23, 24, 25 and 26) including their $CDCl_3$-C_6D_6 solvent shifts curves were almost the same with those of the counterparts of **3**, while the ^{1}H-NMR charactor of the remaining four methyl groups (C-27, 28, 29 and 30) of **1** corresponded to those of a half part of **4**. ^{13}C-NMR spectrum of **1** gave more reliable support for the above conclusion including identity of the relative stereochemistry and the geometry of double bonds, because the chemical shifts of the thirty carbon signals of **1** exactly corresponded to those of the counterparts of **3** and **4** except the signals of C-11 and C-12, which can be effected from the other parts of the molecule. The remaining problem to elucidate the structure of **1** could be the absolute configuration of rings A and B, for which the fact that compound **1** had positive rotation like **3** ($[\alpha]_D^{23}$ +22.4°)[3] should be enough to establish the same configuration as **3** by additive character of the optical rotation.

γ-Polypodatetraene (**2**), oil, Rt$_R$ 1.24, $[\alpha]_D^{23}$ +8.7° ($CHCl_3$, c=0.9), was isolated from fresh leaves of Polystichum ovato-paleaceum (Kodama) Kurata ("Tsuyanashi-inode", collected in Shizuoka Prefecture in December, Aspidiaceae) and P. polyblepharum (Roem.) Pr. ("Inode", collected in Kanagawa Prefecture in September) in respective yields of 0.006% and 0.008% of the dried materials estimated. Compound **2** also showed M^+ m/z 410.3932 by MS suggesting its molecular formula to be $C_{30}H_{50}$. The MS fragments of **2** (Chart 2) was similar to that of **1** indicating **2** was also a bicyclic triterpenoid hydrocarbon like **1**. ^{1}H-NMR spectrum of **2** (Table I) exhibited the presence of Δ^7 double bond in **2** because a olefinic proton signal (δ 5.376 m, $W_{1/2h}$ 10 Hz) and a olefinic methyl signal (δ 1.684 bs) were observed, the former of which was similar to those of fern-7-ene (δ 5.358 ddd, J=3.2, 3.2, 3.7 Hz)[9] and eupha-7,21-diene (δ 5.240 ddd J=3.0, 3.0, 3.7 Hz).[1] The presence of the counterparts of squalene in **2** was also demonstrated like **1**. Final proof of the structure of **2** including relative stereo-

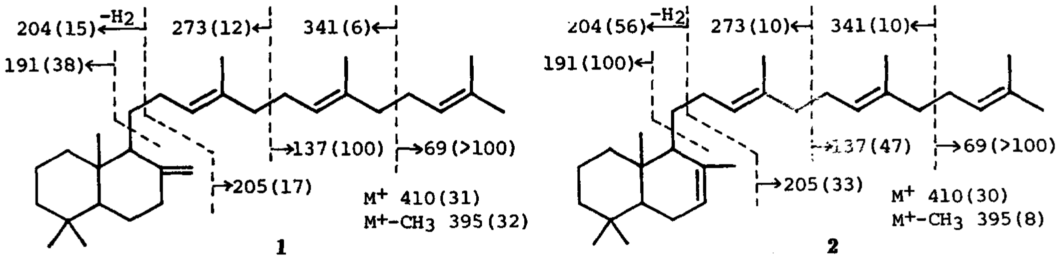

Chart 2 MS Fragmantation Patterns [m/z (rel. int.)]

Table I. ^{1}H-Chemical Shifts (δ) in $CDCl_3$ Solution (JEOL FX-100)

	Methyl or methylene signals of C-								Olefinic protons attached to C[ ]
	23	24	25	26	27	28	29	30	
3	0.868 (-0.014)	0.790 (0.006)	0.638 (0.110)	4.552 (0.262) 4.806 (0.190)	[26]	[25]	[24]	[23]	———
1	0.868 (-0.024)	0.798 (-0.002)	0.664 (0.074)	4.540 (0.168) 4.822 (0.144)	1.568 (0.054)	1.606 (-0.042)	1.606 (0.016)	1.684 (-0.008)	[13,17,21] 5.10-5.12bt(J=6.4)
4	[30]	[29]	[28]	[27]	1.606 (0.008)	1.606 (-0.028)	1.606 (0.008)	1.682 (0.002)	[3,5,9,13,17,21] 5.10-5.12bt(J=6.6)
2	0.850 (0.002)	0.870 (0.006)	0.740 (0.088)	1.684 (0.106)	1.604 (0.052)	1.604 (-0.028)	1.604 (0.026)	1.684 (0.002)	[13,17,21] 5.10-5.12bt(J=6.3) [7] 5.376($W_{1/2h}$=10)
5	0.860 (-0.002)	0.872 (-0.002)	0.705 (0.142)	1.696 (0.142)	4.534 (0.208) 4.819 (0.156)	0.670 (0.108)	0.802 (0.014)	0.872 (-0.002)	[7] 5.368($W_{1/2h}$=10)

Values in ( ) are $\Delta_{\delta(C_6D_6)-\delta(CDCl_3)}$. [26] and others mean the same values with those of C-26 and others because of the symmetric structure.

Table II. ^{13}C-Chemical Shifts (δ) in $CDCl_3$ Solution (JEOL FX-100)

	Number of carbons										
	1	2	3	4	5	6	7	8	9	10	11
3	39.1	19.5	42.3	33.6	55.8	24.6	38.6	149.1	58.0	39.6	22.7
1	39.1	19.4	42.3	33.6	55.6	24.5	38.4	148.4	56.2	39.6	23.8
4	(39.9)	(26.8)	(124.6)	(131.1)	(124.4)	(26.9)	(39.9)	(134.7)	(124.4)	(134.9)	(28.4)
2	39.3	18.9	42.4	33.0	54.4	23.9	122.1	135.6	50.3	36.8	27.3
5	39.2	19.0	42.4	33.0	55.6	23.9	121.9	135.7	50.3	36.7	26.0

	12	13	14	15	16	17	18	19	20	21	22
3	(22.7)	(58.0)	(149.1)	(38.6)	(24.6)	(55.8)	(39.6)	(39.1)	(19.6)	(42.3)	(33.6)
1	29.7	125.1	134.8	39.8	26.8	124.3	134.8	39.8	26.8	124.4	131.1
4	28.4	124.4	134.7	39.9	26.9	124.4	134.9	39.9	26.8	124.6	131.1
2	30.3	124.9	134.9	39.8	26.9	124.3	134.9	39.8	26.8	124.5	131.1
5	(25.3)	(57.5)	(148.9)	(38.4)	(24.6)	(55.7)	(39.6)	(39.2)	(19.5)	(42.3)	(33.6)

	23	24	25	26	27	28	29	30
3	33.6	21.7	14.6	106.2	(106.2)	(14.6)	(21.7)	(33.6)
1	33.6	21.7	14.5	106.1	16.0	16.0	17.7	25.7
4	(25.7)	(17.6)	(16.0)	(16.0)	16.0	16.0	17.6	25.7
2	33.2	21.9	13.6	22.2	16.2	16.0	17.7	25.7
5	33.2	21.9	13.6	22.5	(106.3)	(14.7)	(21.7)	(33.6)

Assignments were confirmed by OFR and PRFT methods. Values assignable to the carbons of **3**, **4** or **5** having different character to the carbons of **1** or **2** are shown in parentheses.

chemistry of the A, B rings and geometry of the side chain was achieved by comparison of ^{1}H- and ^{13}C-NMR spectra of **2** with those of onocera-7,14(27)-diene (**5**), mp. 83-85°, $[\alpha]_D^{23}$ +15.0° ($CHCl_3$, c=0.9), derived from the corresponding 3,21-diketone[10] and **4** (Table I and II). The absolute configuration of rings A, B of **2** was assumed by comparison of optical rotation between **1**, **2** and **3**, **5**,[11] and also from biogenetical standpoints.

Biogenetically, polypodatetraenes are presumed to be the bicyclic compounds derived from squalene corresponded to the labdane diterpenoids. It is very interesting to mention that the fresh leaves of Lemmaphyllum microphyllum varieties contain various kinds of triterpenoid hydrocarbons belonging to aliphatic (squalene), bicyclic (this paper), tricyclic,[12] tetracyclic,[2,5] and pentacyclic[5] classes of squalenoid (including migrated type) and onoceroid.[5]

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REFERENCES AND NOTES

1) Y. Arai, K. Masuda, H. Ageta, Chem. Pharm. Bull., **30**, 4219 (1982).
2) K. Masuda, K. Shiojima, H. Ageta, Chem. Pharm. Bull., **31**, 2530 (1983).
3) To the basic saturated hydrocarbon of polypodatetraenes the name polypodane and the numbering system of their thirty carbons are proposed as shown as in Chart 1, and the compounds, α- and γ-polypodatetraenes can be called as polypoda-8(26),13,17,21-tetraene and polypoda-7, 13,17,21-tetraene, respectively. The name β-polypodatetraene is remained unused for 8,13,17, 21-tetraene isomer like β-onocerin. In this paper the same numbering system was also used for tetracyclic triterpenoids and squalene to facilitate comparison of the compounds according to our earlier proposal.[2]
4) GC was run on Chromosorb G HP coated with SE-30 (1.4%) at 260°C in the flow of N_2. Cholestane was used as reference and its retention time was set at 3.5 min.
5) H. Ageta, K. Shiojima, K. Masuda, Chem. Pharm. Bull., **30**, 2272 (1982).
6) A pure sample of squalene was purchazed from Tokyo Kasei Co., Ltd., and comfirmed its structure and purity by ^{1}H- and ^{13}C-NMR spectra.[7,8]
7) R. B. Bates, R. H. Carnighau, R. O. Rakutis, J. H. Schauble, Chem. & Ind., **1962**, 1020.
8) J. M. Brown, D. R. M. Martens, Tetrahedron, **33**, 931 (1977).
9) H. Ageta, Y. Arai, Phytochemistry, **22**, 1801 (1983).
10) K. Habaguchi, M. Watanabe, Y. Nakadaira, K. Nakanishi, A. K. Kiang, F. Y. Lin, Tetrahedron, Lett., **1968**, 3731.
11) Between the $[\alpha]_D$s of **1**, **2**, **3** and **5** (a, b, c and e, respectively) the following correlation was observed. a : b = c/2 : e - c/2.
12) Two new compounds of malabaricane group have been isolated in our laboratory.

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