Communications to the Editor

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FERN CONSTITUENTS: SIX TETRACYCLIC TRITERPENOID HYDROCARBONS HAVING DIFFERENT CARBON SKELETONS, ISOLATED FROM LEMMAPHYLLUM MICROPHYLLUM VAR. OBOVATUM

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The presence of six tetracyclic triterpenoid hydrocarbons, bacchara-12,21-diene (**1**), lemmaphylla-7,21-diene (**2**), shiona-3,21-diene (**3**), dammara-18(28),21-diene (**4**), tirucalla-7,21-diene (**5**) and eupha-7,21-diene (**6**) was proved in the fresh whole plants of Lemmaphyllum microphyllum var. obovatum.

KEYWORDS——tetracyclic triterpenoid; hydrocarbon; bacchara-12,21-diene; lemmaphylla-7,21-diene; shiona-3,21-diene; dammara-18(28),21-diene; tirucalla-7,21-diene; eupha-7,21-diene; fern constituent; Lemmaphyllum microphyllum var. obovatum

From the dried whole plants of a Japanese fern, Lemmaphyllum microphyllum Pr. var. obovatum C. Chr. ("Ryūkyū-mamezuta", Polypodiaceae) various kinds of triterpenoids including α-onoceradiene, onoceranoxide, serratene; hop-22(29)-ene, neohop-13(18)-ene, fern-7-ene, fern-9(11)-ene, filic-3-ene, hydroxyhopane, zeorin; tetrahymanol, lup-20(29)-ene and taraxer-14-ene were reported from our laboratory.[1] Further studies on fresh whole plants of the fern resulted in isolation and characterization of six tetracyclic triterpenoid hydrocarbons, namely bacchara-12,21-diene (**1**), lemmaphylla-7,21-diene (**2**), shiona-3,21-diene (**3**), dammara-18(28),21-diene (**4**), tirucalla-7,21-diene (**5**) and eupha-7,21-diene (**6**).[2] These compounds were rather unstable in the air and little were obtained from the dried materials.

n-Hexane extraction of the fresh materials of the fern collected on February at Nakagusuku, Okinawa Prefecture, followed by chromatography of the extract on Si gel gave first the mono-enes[1] and then more polar hydrocarbons. The latter fractions were further separated by chromatography on $AgNO_3$-Si gel to afford the six compounds being monitored by GC-MS.

Compound **1**, mp 103-104°C, $[\alpha]_D^{23}$+46.6° ($CHCl_3$, c=0.4), Rt_R 1.88,[3] was obtained in a yield of 0.038% (of the dried materials, estimated). **1** was shown to have the molecular formula $C_{30}H_{50}$ by high MS (M^+ m/z 410.3908), and the fragmentation pattern of low MS of **1** (Chart 2) indicated that **1** was like the 12,21-diene of baccharane group[4] (m/z 325 and 327 for tetracyclic part of the molecule; 218 and 133 for 12-ene; 69 for 21-ene). The ^{1}H-NMR

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

	Methyl or methylene signals of C-								Olefinic protons	
	23	24	25	26	27	28[a]	29	30	21[b]	Others
1	0.870	0.823	0.963	0.997	1.066	0.750	1.603	1.681	5.103bdd	5.220m(C-12)
2	0.838	0.877	0.750	1.068	0.860	0.953	1.591	1.671	5.084bdd	5.362ddd[c](C-7)
7	0.855	0.884	1.054	0.693	0.843	0.987	1.598	1.674	5.098bdd	5.301ddd[d](C-11)
3	1.566	0.978	0.884	0.884	1.076	0.906	1.590	1.676	5.110bdd	5.154m(C-3)
4	0.848	0.806	0.848	0.973	0.875	4.708 4.728	1.612	1.686	5.130bdd	
8	0.843	0.803	0.843	0.965	0.884	1.117	1.617	1.683	5.115bdd	
5	0.845	0.884	0.745	0.968	0.821	0.885d	1.598	1.676	5.100bdd	5.237ddd[e](C-7)
9	0.870	0.830	0.946	0.870	0.767	0.918d	1.603	1.683	5.100bdd	
6	0.845	0.882	0.745	0.978	0.818	0.850d	1.603	1.684	5.100bdd	5.239ddd[e](C-7)
10	0.875	0.830	0.948	0.875	0.764	0.860d	1.610	1.688	5.095bdd	

Assignments of methyl signals were confirmed by $CDCl_3$-C_6D_6 solvent shifts. Signals otherwise stated were singlet. Coupling constants were: a) 5.6 Hz; b) 7.0-7.2, 7.0-7.2 Hz; c) 2.4, 2.4, 4.2 Hz; d) 2.4, 2.4, 4.9 Hz; e) 2.7, 2.7, 3.7 Hz.

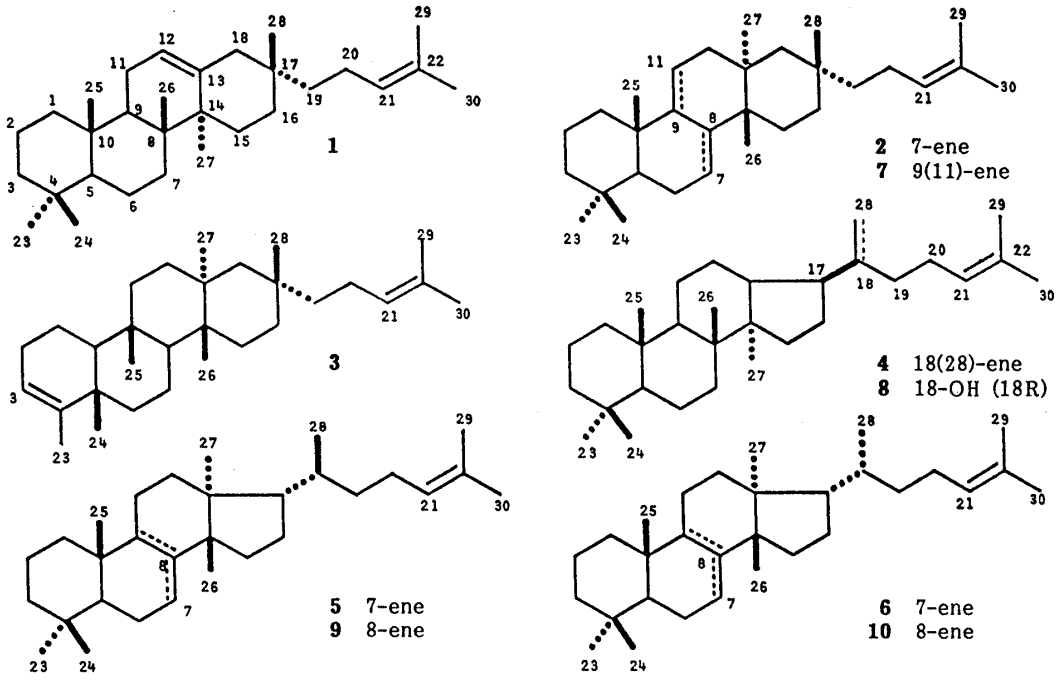

Chart 1

spectrum of **1** (Table) indicated six singlet methyl signals (C-23 - 28) and two olefinic methyl signals (C-29, 30), and five of the former were similar to those of their counterparts in olean-12-ene[5] at the chemical shifts including $CDCl_3$-C_6D_6 solvent shifts. The chemical shift of C-28 methyl being observed at higher field (Δ0.083) and the splitting pattern of 12-olefinic proton different from that of olean-12-ene can be explained as results of the different conformations of ring D. The signals of isopropylidene end of the side chain were very similar to those of eupha-7,21-diene.[5] Finally compound **1** as bacchara-12,21-diene was firmly established by identifying **1** with a synthetic sample described below.

Compound **2**, oil, $[\alpha]_D^{23}$ -39.8°, Rt_R 1.76, $C_{30}H_{50}$ (M^+ m/z 410.3931), was obtained in a yield of 0.00002% (of the dried materials, estimated). The fragmentation pattern of **2** (Chart 2) suggested **2** to be a migrated baccharane having two double bonds at 7(or 9(11)) and 21 (m/z 325 and 327 for tetracyclic part; 257, 243 and 231 for 7(or 9(11))ene; 69 for 21-ene). The ^{1}H-NMR spectrum of **2** (Table) indicated the presence of six tertiary methyls (C-23 - 28) and two olefinic methyls (C-29, 30). The chemical shifts of the four methyls (C-23 - 26) and the splitting patterns of 7-olefinic proton were similar to those of their counterparts in multiflor-7-ene.[5] Two signals attributed to C-27 and 28 methyls being observed at higher field (Δ0.238 for C-27, Δ0.105 for C-28) were assumed as effect of ring E in the latter compound. The signals of isopropylidene end were also observed. As described below, **2** itself and its double bond isomer, 9(11),21-diene (**7**), were synthesized. Comparison of ^{1}H-NMR and MS spectra of **2** and **7** with those of multiflor-7- and 9(11)-enes[5] gave good evidence to confirm the structures of **2** and **7**. For the basic saturated hydrocarbon of **2** and **7** the name lemmaphyllane is proposed, for **2** lemmaphylla-7,21-diene and for **7** lemmaphylla-9(11),21-diene.

The presence of the third migrated baccharane derivative, shiona-3,21-diene (**3**), Rt_R 2.18, in a fraction of the extract was proved by comparison of GC-MS and ^{1}H-NMR spectrum with those of a synthetic sample derived from shionone.[7] The sample, mp 93-94°, $[\alpha]_D^{23}$ +16.1° ($CHCl_3$, c=0.5), Rt_R 2.18, showed very reasonable MS and ^{1}H-NMR spectra (Chart 2 and Table) comparing with those of friedel-3-ene[5] and **2**. To confirm the basic skeletons of **1** and **2**, synthetic **3** was treated with 40% BF_3-etherate in ether at 30°C for 18 h to give **7** (main), mp 42-45°C, $[\alpha]_D^{23}$ -22.3° ($CHCl_3$, c=0.3), Rt_R 1.53, and **1**, or with 50% BF_3-etherate in ether at 20°C for 1 h **7** (main) and **2** with the starting material.[4]

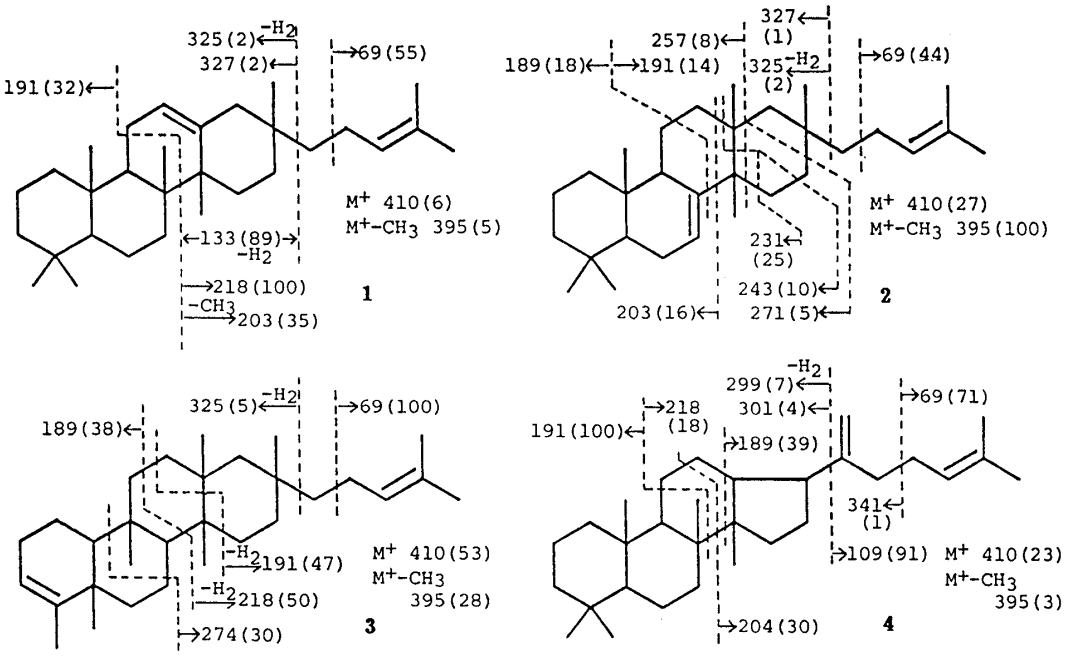

Chart 2. Low Mass Fragmantation Patterns 300e/V, m/z (rel. int.)

Compound **4**, oil, Rt_R 1.53, $C_{30}H_{50}$ (M^+ m/z 410.3861), was obtained in 0.0007% yield (of dried material, estimated). The IR spectrum of **4** showed the presence of endomethylene in the molecule (ν_{max}^{KBr} cm^{-1}: 3080, 1642, 886). The fragmentation pattern of **4** (Chart 2) suggested **4** to be a dammarane derivative having two double bonds in the side chain. The ^{1}H-NMR spectrum of **4** (Table) indicated the presence of five tertiary methyls (C-23 - 27), and their chemical shifts including $CDCl_3$-C_6D_6 solvent shifts were very similar to those of 18-hydroxydammar-21-ene (**8**) prepared from dammarenediol I.[8] Also the signals of endomethylene and isopropylidene were observed. To confirm the structure of **4** to be dammara-18(28),21-diene, **8** was dehydrated with $POCl_3$ in pyridine, and one of the products, Rt_R 1.53, $[\alpha]_D^{23}$ +57.1° ($CHCl_3$, c=0.7) was proved to be identical with **4** in all respects.

Compound **5**, oil, $[\alpha]_D^{23}$ -24.8° ($CHCl_3$, c=0.5), Rt_R 1.78, $C_{30}H_{50}$ (M^+ m/z 410.3920), was obtained in 0.005% yield (of dried material, estimated). The facts that the MS spectrum of **5** was almost the same to that of eupha-7,21-diene (**6**)[6] and the ^{1}H-NMR spectrum of **5** also very similar to that of **6** (Table), except that C-28 methyl signal was observed at slightly lower field than that of **6**, suggested **5** to be tirucalla-7,21-diene, the isomer of **6**. Although this compound or its derivative has not yet been known, additional evidence to prove the structure was obtained by comparison of C-28 signals with those of tirucalla-8,21-diene (**9**) and eupha-8,21-diene (**10**) both derived from the corresponding alcohols.[9] Presence of the last compound, eupha-7,21-diene (**6**) in the fern, was proved by GC-MS and ^{1}H-NMR spectra of a fraction. **6** was already obtained from Polypodium someyae by us.[6]

The five compounds mentioned above (**1** - **5**) could be all the first report with modern physicochemical properties and also as natural products. It is very interesting to know that all six hydrocarbons have different tetracyclic carbon skeletons, including baccharane and dammarane and their migrates.

REFERENCES AND NOTES

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