Communications to the Editor

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# FERN CONSTITUENTS: EUPHA-7,24-DIENE AND (20*R*)-DAMMARA-13(17),24-DIENE, TETRACYCLIC TRITERPENOID HYDROCARBONS ISOLATED FROM POLYPODIUM SPECIES

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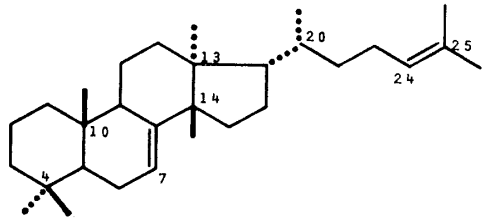
From the fresh leaves of *Polypodium someyae* eupha-7,24-diene and from the fresh rhizomes of *P. fauriei* (20*R*)-dammara-13(17),24-diene were obtained and characterized. These hydrocarbons are the first derivation from a natural source. They are rather unstable in the air.

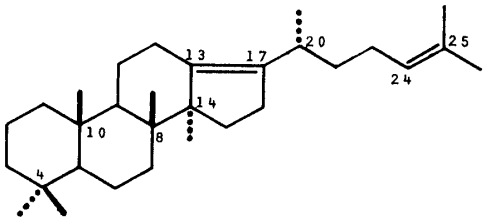
KEYWORDS——tetracyclic triterpenoid; hydrocarbon; eupha-7,24-diene; dammara-13(17),24-diene; fern constituent; *Polypodium someyae*; *Polypodium fauriei*

During the course of studies on triterpenoid hydrocarbons of Polypodiaceous ferns, some peaks having $M^+$ 410 on GC-MS were observed in the extracts of some fresh materials. These peaks weekened or disappeared in the stored extracts or the extracts of dried materials. This paper concerns these unstable oily hydrocarbons of two Polypodium ferns, and is the first report of the isolation and characterization of triterpenoid hydrocarbons of the tetracyclic class.

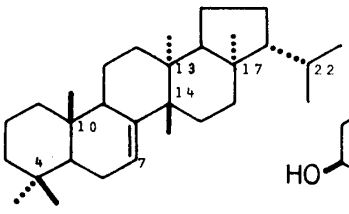
The hexane extracts of the fresh leaves of Polypodium someyae Yatabe ("Myogishida") collected both in Gumma and Shizuoka Prefectures showed by GC-MS the pre-



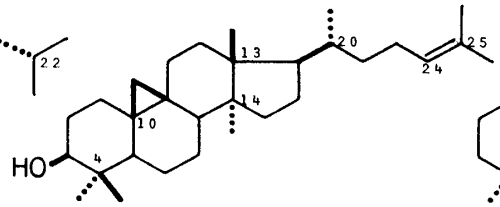

(I)




(IV)




(II)

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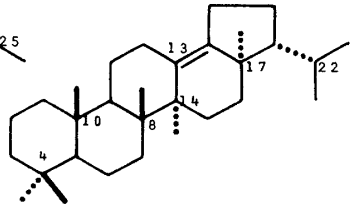


(V)

Chart 1

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

| | Methyl or methylene signals attached to C( ) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 4α | 4β | 10β | 8β | 14β | 14α | 13α | 17α | 20*R* | 22 | 25 |
| I | 0.845 | 0.882 | 0.745 | --- | 0.978 | --- | 0.818 | --- | 0.850 | --- | 1.684<br>1.603 |
| II | 0.843 | 0.877 | 0.742 | --- | 0.995 | --- | 0.906 | 0.742 | --- | 0.829*d*<br>0.897*d* | --- |
| III | 0.965 | 0.808 | 0.327*d*<br>0.558*d* | --- | 0.892 | --- | 0.965 | --- | 0.881 | --- | 1.688<br>1.600 |
| IV | 0.848 | 0.801 | 0.848 | 0.848 | --- | 1.071 | --- | --- | 0.919 | --- | 1.686<br>1.590 |
| V | 0.857 | 0.794 | 0.823 | 0.857 | --- | 1.100 | --- | 0.794 | --- | 0.888*d*<br>0.953*d* | --- |

Assignments of methyl signals were confirmed by $CDCl_3$-$C_6D_6$ solvent shifts. Olefinic proton signals attached to C-7 were observed at 5.239*ddd*(3.0,3.0,3.7 Hz)(I), 5.354*ddd* (3.2,3.2,3.7 Hz)(II), and those to C-24 at 5.100*bt*(7.0 Hz)(I), 5.100*bt*(7.0 Hz)(III), 5.127*bt*(7.0 Hz).

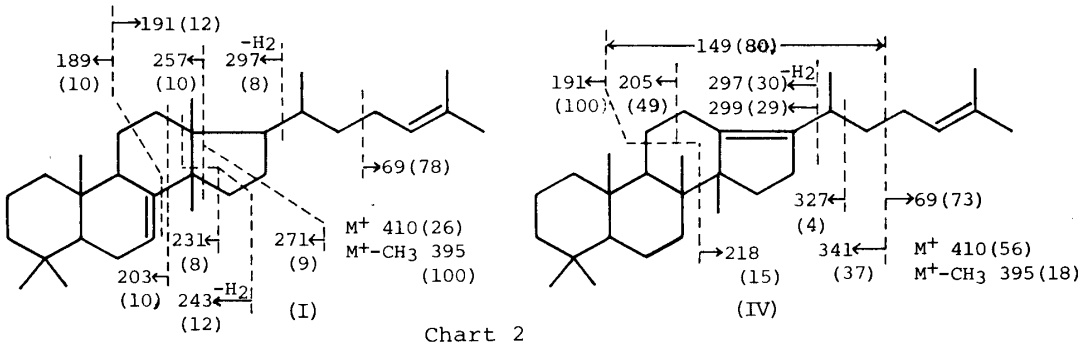


Chart 2

sence of a triterpenoid hydrocarbon of $Rt_R$ 1.62,[1] which deteriorated when exposed to air. The oily compound (I),[2] separated from the latter source by $AgNO_3$-Si gel chromatography, had the molecular formula $C_{30}H_{50}$ by MS ($M^+$ m/z 410.3915), and the fragmentation pattern of the MS spectrum of I (Chart 2, m/z (rel. int.)) indicated that I was like the 7,24- or 9(11),24-diene of the euphane or lanostane groups (m/z 231, 243 and 257 for 7- or 9(11)-ene, m/z 297 for tetracyclic triterpenoid, and m/z 69 for 24-ene). The $^1$H-chemical shifts (TABLE) of the methyl groups attached to C-4α, C-4β, C-10β and C-14β of I as well as the splitting pattern of the olefinic proton attached to C-7 of I were very similar to those of fern-7-ene (II),[3] while the signals of the methyl groups attached to C-20 and C-25, and also the signals of the olefinic proton at C-24 were superimposable to those of cycloartenol (III).[4] These facts strongly supported I to be eupha-7,24-diene. To confirm the structure of I, the compound, oil, $Rt_R$ 1.62, $[\alpha]_D^{23}$ -3.3° ($CHCl_3$, c=0.5), was prepared from butyrospermone[5] by Wolff-Kishner reduction, and the MS and $^1$H-NMR spectra of the prepared hydrocarbon proved to be identical with those of I.

The second oily hydrocarbon (IV) was obtained in a yield of 0.015% from the fresh rhizomes of Polypodium fauriei CHRIST ("Oshaguji-denda"), collected in Yamanashi Prefecture, together with I (0.003%), serratene (0.02%), fern-7-ene (II, 0.01%), fern-8-ene (0.004%) and hop-22(29)-ene (0.008%). Compound IV, $Rt_R$ 1.20, $[\alpha]_D^{23}$ -14.4 ($CHCl_3$, c=1.0) was also shown by MS ($M^+$ m/z 410.3917) to have the molecular formula

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$C_{30}H_{50}$, the fragmentation pattern of which (Chart 2) suggested IV to be like 13(17), 24-diene of dammarane skeleton (m/z 191 for A, B rings, m/z 297 and 299 for tetracyclic triterpenoid with 13(17)-ene, and m/z 69 and 341 for 24-ene). The $^1$H-NMR spectrum of IV (TABLE) also supported the presumption. The methyl signals attached to C-4α, C-4β, C-10β, C-8β and C-14β resembled those of neohop-13(18)-ene (V) and the signals of the methyl groups attached to C-20 and C-25 as well as the signal of the olefinic proton attached to C-24 were comparable to those of III. Treatment of eupha-7,24-diene (I) with 20% $BF_3$-etherate in ether at 20°C for 24 h. gave an oily hydrocarbon, $Rt_R$ 1.20, $[\alpha]_D^{23}$ -14.0° ($CHCl_3$, c=0.9), in 90% yield. As the compound proved to be identical with IV by comparison of $Rt_R$, $[\alpha]_D$ and the $^1$H-NMR spectrum, the structure of IV was established to be (20 )-dammara-13(17),24-diene.

It is interesting from the chemotaxonomical point of view that in fresh materials these unstable oily hydrocarbons were detected from the rhizomes of Polypodium vulgare LINN. ("Ooezo-denda") and P. virginianum LINN. ("Ezo-denda") by GC fo diene hydrocarbon fractions, but not from those of P. niponicum METT. ("Aone-kazura") and P. formosanum BAK. ("Taiwan-aone-kazura").

## REFERENCES AND NOTES


1) 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.
2) Because of a small quantity of the sample, an effective value for optical rotatory was not obtained.
3) H. Ageta, K. Shiojima, K. Masuda, Chem. Pharm. Bull., 30, 2272 (1982), and the references therein.
4) Cycloartenol was obtained from the leaves of *Microlepia strigosa* in our laboratory.
5) M.C. Dawson, T.G. Halsall, E.R.H. Jones, G.D. Meakins, P.C.Phillips, J.Chem.Soc., 1956, 3172. Butyrospermol was isolated from shea nut butter in our laboratory.


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