

Communications to the Editor

[Chem. Pharm. Bull.]
30(6)2272-2274(1982)FERN CONSTITUENTS; ONOCEROID,¹⁾ α -ONOCERADIENE, SERRATENE AND ONOCERANOXIDE, ISOLATED FROM LEMMAPHYLLUM MICROPHYLLUM VARIETIES

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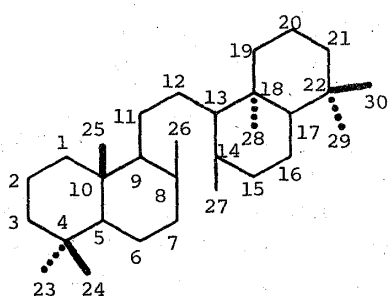
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α -Onoceradiene (I) and serratene (IV) were isolated and identified from a Polypodiaceous fern, *Lemmaphyllum microphyllum* var. *microphyllum*, while a new compound, onoceranoxide (VII), was obtained from var. *obovatum* as a main triterpenoid and its structure was established.

KEYWORDS—triterpenoid; onoceroid; α -onoceradiene; serratene; onoceranoxide; fern constituent; *Lemmaphyllum microphyllum*; *Lemmaphyllum microphyllum* var. *obovatum*

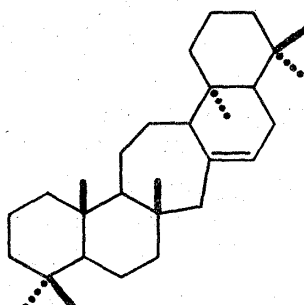
From the dried whole plants of a common Japanese fern, *Lemmaphyllum microphyllum* PRESL var. *microphyllum* ("Mamezuta", Polypodiaceae), α -onoceradiene (I)²⁾ was isolated as a main hydrocarbon, together with hop-22(29)-ene (II),³⁾ fern-9(11)-ene (III),⁴⁾ serratene (IV),⁵⁾ neohop-13(18)-ene,⁶⁾ filic-3-ene,⁷⁾ lup-20(29)-ene,⁸⁾ hydroxyhopane (V),⁶⁾ zeorin,⁹⁾ tetrahymanol (VI)¹⁰⁾ and some of the cycloartane derivatives. On the other hand, the dried whole plants of *L. microphyllum* PRESL var. *obovatum* C. CHR. ("Ryukyu-mamezuta") of Okinawa Island gave a new compound, onoceranoxide (VII), as a main triterpenoid along with I, II, III, IV, V, VI, fern-7-ene,⁷⁾ taraxer-14-ene¹¹⁾ and tetracyclics. The compounds listed above except I and VII were identified by comparison of physical data, including mp, $[\alpha]_D$, TLC, GLC, MS and ¹H-NMR spectra, with those of authentic samples from our laboratory.

The first derivation of α -onoceradiene from a natural source has been achieved by the isolation of crystalline (I), mp 209–210°C, $[\alpha]_D +22.4^\circ$, which was yielded in 0.0031% from the material of the former variety collected in the Izu district on December (only a trace from the latter variety). Compound I had very fast R_{T_R} (1.28)¹²⁾ among triterpenoids, and IR spectrum of I showed the presence of exomethylene

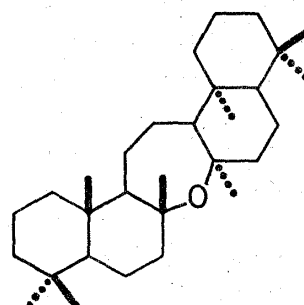


I 8(26),14(27)-diene

VIII 8,13-diene



IV



VII

($\nu_{\text{cm}^{-1}}^{\text{KBr}}$, 3070, 1644, 884) in the molecule. MS spectrum of I gave M^+ m/z 410.3893 (53), suggesting the molecular formula of I to be $C_{30}H_{50}$, 395 (M^+-CH_3 , 98), 231 (28), 206 (52), 205 (48) and 191 (100). The 1H - and ^{13}C -NMR spectra (TABLE) were very characteristic because only three singlets of singlet methyls and two proton signals of exocyclic methylenes were observed in the former, and fifteen signals including three singlets, two doublets, seven triplets and three quartets (OFR) were observed in the latter. These findings suggested that compound I must be a duplicate structure such as α -onoceradiene, with which I was identified by comparison of mp, $[\alpha]_D$, GLC, IR and 1H -NMR spectra with those of a sample derived from α -onocerin.¹³⁾

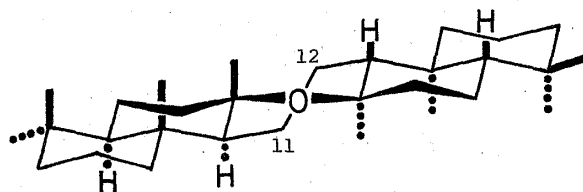
The presence of serratene (IV), mp 240-241°C, $[\alpha]_D -19.9^\circ$, $R_{T_R} 2.35$ —0.0007% in the former variety, 0.0022% in the latter—was the second example in fern plants next to *Polypodium vulgare* LINN.¹⁴⁾ The identity was proved by comparison of mp, $[\alpha]_D$, GLC, IR and 1H -NMR spectra with those of an authentic sample.⁵⁾

The compound VII, mp 226-227.5°C, $[\alpha]_D +7.9^\circ$, $R_{T_R} 2.22$, was isolated in a yield of 0.018% from the material of var. *obovatum* collected at Mt. Katsuu on August. MS spectrum of VII gave the molecular ion peak, m/z 428.4006 (14), suggesting the molecular formula to be $C_{30}H_{52}O$. MS fragments were m/z 413 (M^+-CH_3 , 2), 410 (M^+-H_2O , 8), 395 ($M^+-CH_3-H_2O$, 6), 218 ($C_{16}H_{26}^+$, 15), 204 ($C_{15}H_{24}^+$, 40) and 191 ($C_{14}H_{23}^+$, 100). As the absence of a hydroxyl or a carbonyl group (IR spectrum) and a double bond (tetranitromethane test and ^{13}C -NMR spectrum) in the molecule was shown, VII should be pentacyclic including one epoxy ring. The most characteristic feature was obtained by 1H - and ^{13}C -NMR spectra (TABLE), which gave only four tertiary methyl signals (one was remarkably shifted to a lower field like a methyl group attached to a carbon-bearing oxygen atom) and fifteen carbon signals including three singlets (one at $\delta 79.9$ to be assigned for carbons bearing a methyl group and an oxygen atom), two doublets, six triplets and four quartets (OFR). These findings coupled with biogenetic considerations suggested that VII has a quite symmetrical structure like onocerane skeleton, and the presumption was proved by BF_3 -etherate treatment of VII to give β -onoceradiene (VIII), mp 166-167°C, $[\alpha]_D +122.2^\circ$, $R_{T_R} 1.60$, as a main product. The only possible stereostructure of VII having line symmetry (VII is optically active) was concluded by Dreiding model examination to be VIIa, i.e., $8\alpha,14\beta$ -epoxy configuration and

TABLE. 1H - and ^{13}C -Chemical Shifts in $CDCl_3$ Solution (JEOL FX-100)

| | Protons attached to C() ^{a)} | | | | Carbon() ^{b)} | | | | | |
|------|--|-------|-------|--------------------|-------------------------|-------|-------|-------|-------|-------|
| | 23,30 | 24,29 | 25,28 | 26,27 | 1,19 | 2,20 | 3,21 | 4,22 | 5,17 | |
| I | 0.870 | 0.791 | 0.639 | 4.549bs 4.806bs | 39.1 | 19.5 | 42.3 | 33.6 | 55.8 | |
| VII | 0.845 | 0.735 | 0.767 | 1.259 | 40.5 | 19.0 | 42.2 | 33.5 | 56.3 | |
| VIII | 0.882 | 0.835 | 0.963 | 1.664 | 34.1 | 19.3 | 41.9 | 33.5 | 51.9 | |
| | Carbon() ^{b)} continued | | | | | | | | | |
| | 6,16 | 7,15 | 8,14 | 9,13 | 10,18 | 11,12 | 23,30 | 24,29 | 25,28 | 26,27 |
| I | 24.6 | 38.6 | 149.1 | 58.0 | 39.1 | 22.7 | 33.6 | 21.7 | 14.6 | 106.2 |
| VII | 20.8 | 45.4 | 79.9 | 60.9 | 38.9 | 25.0 | 33.5 | 21.5 | 15.8 | 25.4 |
| VIII | 19.3 | 37.7 | 126.0 | 141.7 | 39.1 | 28.8 | 33.5 | 21.8 | 20.9 | 20.6 |

a) Assignments were confirmed by $CDCl_3$ - C_6D_6 solvent shifts (I, VII, VIII) and Lanthanide shifts (VII). b) Assignments were established by comparison with those of diterpenoid,¹⁵⁾ and confirmed by solvent shifts (VIII) and Lanthanide shifts (VII) on PRFT method.



VIIa

seven membered ring conformation as shown in the figure. The compound VII was recommended to be named onoceranoxide or $8\alpha, 14\beta$ -epoxyonocerane.

It will be very interesting to compare the above-mentioned onoceroid triterpenes in Polypodiaceous fern with Physeteridous whale,¹⁶⁾ Leguminosous,²⁾ Pinaceous¹⁷⁾ and Lycopodiaceous plants,^{5,13)} and *Polypodium vulgare*.¹⁴⁾ Further studies on the onoceroid isolated from Polypodiaceous fern are still in progress from a chemotaxonomical point of view.

REFERENCES AND NOTES

- 1) The term "onoceroid" will be called a triterpenoid group, being biosynthesized from squalene by both-end cyclization, including compounds having onocerane, serratane and ambrane, but gammacerane skeletons at this time. This group can be contrasted with all the other triterpenoids derived from squalene by one-end cyclization biogenetically.
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