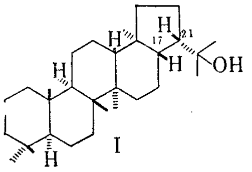
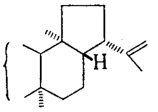
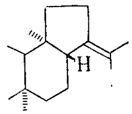
$[\alpha]_D^{16}$ +56.3, and hopene-a (III)4) m.p. 179.0～181.0°, $[\alpha]_D^{16}$ +25.0°; 2) boiling with benzoyl chloride, hopene-I (IV),5,6) m.p. 183.5～185.0°, $[\alpha]_D^{26}$ +49.0°; and 3) boiling diploptene with formic acid, hopene-II (V),6) m.p. 197.0～198.5°, $[\alpha]_D^{20}$ +2.0°. The formation of hopene-II from diploptene seems to support the 17,21 *cis* system of diplopterol, comparing with the formation of heterolupene and olean-18-ene from α-lupene in the same condition.7)



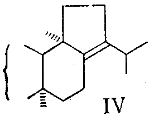
I



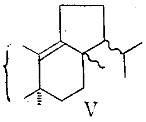
II



III



IV



V

Diplopterol is a rare example of the isolation of naturally occurring pentacyclic triterpenoid with no oxygen function on nucleus.

The authors are grateful to Dr. Kariyone, National Institute of Hygienic Sciences, for his kind encouragement, and also to Dr. Halsall, University of Oxford, for the donation of the authentic sample of hopene-I.

Shôwa College of Pharmacy,
3-577, Tsurumaki-chô,
Setagaya-ku, Tokyo

Hiroyuki Ageta (上田博之)
Kenji Iwata (岩田憲治)
Yoshiyuki Ôtake (大竹良幸)

December 25, 1962

---

5) K. Schaffner, L. Cagliotti, D. Arigoni, O. Jeger: Helv. Chim. Acta, **41**, 152 (1958).
6) H. Fazakerley, T.G. Halsall, E.R.H. Jones: J. Chem. Soc., **1959**, 1877.
7) T.G. Halsall, E.R.H. Jones, R.E.H. Swayne: *Ibid.*, **1954**, 1902.

UDC 547.91:582.394

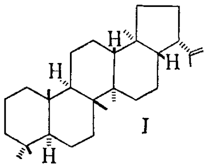
Fern Constituents: Fernene and Diploptene, Triterpenoid Hydrocarbons Isolated from *Dryopteris crassirhizoma* NAKAI

Two triterpenoid hydrocarbons were separated by chromatography from the methanol extract of the leaflets of *Dryopteris crassirhizoma* NAKAI (Aspidiaceae), distributed at Mt. Nyûgasa, Nagano. The less polar hydrocarbon (0.02% of the dried material), named fernene, $C_{30}H_{50}$, m.p. 170.0～171.0°,[*1] $[\alpha]_D^{16}$ −16.5° (c=0.79, $CHCl_3$), (*Anal.* Calcd.: C, 87.73; H, 12.27. Found: C, 87.58; H, 12.39. M.W. 410 in mass analysis), shows a pink Liebermann reaction and a positive tetranitromethane test. Treatment of fernene with 6 v/v % or 15 v/v % H_2SO_4 in benzene-acetic acid afforded an isomer, isofernene, m.p. 184.0～185.0°, $[\alpha]_D^{16}$ +15.2° (c=1.05, $CHCl_3$), infrared and nuclear magnetic resonance spectra of which showed that an original tri-substituted double bond had migrated to a tetra-substituted type.

[*1] *All melting points are corrected.*

On the other hand, more polar hydrocarbon (0.005% of the dried material), $C_{30}H_{50}$, m.p. 211.0~212.0°, $[\alpha]_D^{16}$ +61.1° (c=0.77, $CHCl_3$), (*Anal.* Calcd. : C, 87.73; H, 12.27. Found : C, 87.71; H, 12.21), having an end methylene (IR ν cm^{-1} : 3070, 1642, 886), has been identified as diploptene (hopene-b) (I).[1] Diploptene, derived from diplopterol, showed somewhat lower melting point and specific rotation. Although the infrared spectra of both compounds were quite similar, some difference in the intensity of 886 cm^{-1} band was observed. In order to clarify this point, gas chromatography, using a column packed with 1.5% SE 30 on Gas Chrom P, of these compounds was carried out.

While the naturally occuring diploptene, m.p. 211.0~212.0°, showed a single peak (retention time, 8.45 min., column temperature, 235°), the sample prepared from diplopterol, m.p. 197.0~198.5°, showed the same peak accompanied with a minor peak (ca. 4%) (retention time, 5.28 min., colum temperature, 235°) of hopene-I.[1]



I

Pure diploptene, on catalytic reduction, afforded hopane, m.p. 206.0~207.0°, $[\alpha]_D^{16}$ +42.0° (c=1.02, $CHCl_3$), and on acidic isomerisation, hopene-I and hopene-II.

Fernene and diploptene are rare example of pentacyclic triterpenoid hydrocarbons distributed in plan kingdom. Meanwhile, diplopterol[1] and diploptene are the examples of the naturally occurring pentacyclic squalenoids, next to zeorin, leucotylin and hydroxyhopanone.

The authors are grateful to Dr. T. Kariyone, National Institute of Hygienic Sciences, for his kind encouragement, and also to Prof. K. Nakanishi, Tokyo Kyoiku University, for his kind interest to this work. Thanks are due to Dr. N. Ikekawa, Institute for Physical and Chemical Research, for gas chromatography and to Miss K. Iwata, Kyoto University, for elemental analysis.

Shôwa College of Pharmacy
3-577, Tsurumaki-chô,
Setagaya-ku, Tokyo

Hiroyuki Ageta (上田博之)
Kenji Iwata (岩田憲治)
Kazuko Yonezawa (米沢和子)

December 25, 1962

---

[1] H. Ageta, K. Iwata, Y. Otake : Preceding Communication.

UDC 547.91 : 582.394

Isolation of Diploptene from *Pyrrosia lingua* Farwell

From the herbs of *Pyrrosia lingua* (Thunb.) Farwell (Polypodiaceae) which has long been employed as a diuretic in the Far East, a triterpenoid hydrocarbon (I) was separated together with β-sitosterol, $C_{29}H_{50}O$ (*Anal.* Calcd. : C, 83.99; H, 12.15. Found : C, 84.04; H, 12.19), m.p. 134~135°,*[1] $[\alpha]_D$ -41.0° (c=2.0°, $CHCl_3$), (benzoate : $C_{36}H_{54}O_2$, *Anal.* Calcd. : C, 83.34; H, 10.49. Found : C, 83.60; H, 10.50, m.p. 144.5~145°).

The hydrocarbon (I), colorless needles (from benzene-EtOH), $C_{30}H_{50}$ (*Anal.* Calcd. : C, 87.73; H, 12.27. Found : C, 87.99; H, 12.51), m.p. 207~208°, $[\alpha]_D$ +65.7° (c=1.5, $CHCl_3$), exhibited a negative Liebermann-Burchard reaction and a positive tetranitromethane test. I had the infrared spectrum which showed bands (in KBr) at 3067, 1770, 1639, and 886 ($CH_2=C\langle$) cm^{-1} and the nuclear magnetic resonance spectrum (60 Mc. in

---

*[1] All melting points are uncorrected.