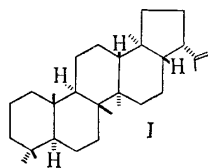


On the other hand, more polar hydrocarbon (0.005% of the dried material),  $C_{30}H_{50}$ , m.p. 211.0~212.0°,  $[\alpha]_D^{16} +61.1^\circ$  ( $c=0.77$ ,  $CHCl_3$ ), (*Anal. Calcd.* : C, 87.73; H, 12.27. Found : C, 87.71; H, 12.21), having an end methylene (IR  $\nu$   $cm^{-1}$  : 3070, 1642, 886), has been identified as diploptene (hopene-b) (I).<sup>1)</sup> 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 occurring 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., column temperature, 235°) of hopene-I.<sup>1)</sup>



Pure diploptene, on catalytic reduction, afforded hopane, m.p. 206.0~207.0°,  $[\alpha]_D^{16} +42.0^\circ$  ( $c=1.02$ ,  $CHCl_3$ ), 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<sup>1)</sup> and diploptene are the examples of the naturally occurring pentacyclic squalenoids, next to zeorin, leucotylin and hydroxyhopanone.

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### 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  $\beta$ -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°, \*<sup>1</sup>  $[\alpha]_D -41.0^\circ$  ( $c=2.0^\circ$ ,  $CHCl_3$ ), (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°,  $[\alpha]_D +65.7^\circ$  ( $c=1.5$ ,  $CHCl_3$ ), 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 ( $CH_2=C<$ )  $cm^{-1}$  and the nuclear magnetic resonance spectrum (60 Mc. in

\*<sup>1</sup> All melting points are uncorrected.

$\text{CCl}_4$  vs.  $\text{Me}_4\text{Si}$  as internal reference) which exhibited singlets ( $\text{CH}_3\text{-C}\langle$ , respectively) at  $9.28\tau$  (3H),  $9.20\tau$  (3H),  $9.19\tau$  (3H),  $9.15\tau$  (3H), and  $9.05\tau$  (6H) as well as a singlet ( $\text{CH}_3\text{-C}=\text{C}$ ) at  $8.29\tau$  (3H) with fine splitting and a singlet ( $\text{CH}_2=\text{C}\langle$ ) at  $5.29\tau$  (2H) with fine splitting. These physical constants of I was in agreement with those of diploptene.<sup>1,2)</sup> By the comparison with the authentic sample the identity of these compounds was established.

Isolation of the triterpenoid hydrocarbons from the natural sources has been the rare case. However, the same hydrocarbon (I) has also been separated independently in almost same time from the leaflets of *Dryopteris crassirhizoma* NAKAI (Polypodiaceae).<sup>1)</sup> Further, hydroxyhopane (=diplopterol), the corresponding alcohol of I, has been separated from the leaves of *Hicriopteris glauca* (HOUTT.) ST. JOHN (= *Diplopterygium glaucum* (HOUTT.) NAKAI) (Polypodiaceae).<sup>2)</sup> It is of interest that the series of these simplest pentacyclic squalenoids exist in the fern plants.

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