

(mulled in Nujol) showed the following major bands: no bands in the OH or NH region; 6.35 (S), 6.27 (S), 6.14 (S).

*Aspidofiline picrate*. The picrate was prepared by treating an ethereal solution of aspidofiline with picric acid in ether; the crystalline picrate was separated and recrystallized several times from acetone, m.p. 146° (capillary, non-corrected).

*Anal.* Calcd. for  $C_{26}H_{25}N_5O_9$ : C, 56.62; H, 4.57; N, 12.70. Found: C, 56.83; H, 4.7; N, 12.49.

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### Extractives from the Dipterocarpaceae

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The Dipterocarpaceae are an important family of trees which grow in southeast Asia and are characterized by an abundant secretion of resins such as dammar and gurjun which possess economic importance. References to early researches on dammar are given by Glimmann<sup>1</sup> and recently a comprehensive investigation of the constituents of dammar has been carried out by Mills<sup>2,3</sup> who determined the constitution of the neutral triterpenes present. Among those triterpenes was hydroxydammarenone-II first isolated by van Itallie<sup>4</sup> from the balsams of *D. hasseltii* and *D. trinervis*. King<sup>5</sup> *et al.* isolated this compound from three Dipterocarpus woods, "gurjun," "yang," and "keruing" and established the identity of hydroxydammarenone-II with dipterocarpol isolated by Ourisson<sup>6,7</sup> from the balsams of several Dipterocarpus species—*D. Dyeri*, *D. alatus*, *D. intricatus* and *D. atroparpifolius*.

From the acidic fraction of gum dammar we have isolated asiatic acid and will report our findings in a future communication. From two woods of the *Dipterocarpus* species, *D. verrucosus* and *D. grandiflorus* we have isolated dipterocarpol in yields of 0.12% and 0.16% respectively.

### EXPERIMENTAL

*D. Verrucosus*. The wood (4 lb.) in the form of shavings was extracted continuously with light petroleum for 24 hr. The extract was concentrated to give a resin (32.7 g.) which was hydrolyzed for 6 hr. with 10% methanolic potassium hydroxide (300 ml.). The hydrolysis liquor was filtered to remove a small amount of insoluble matter, diluted with much water, and extracted with ether to give a viscous oil (17.1 g.). Chromatographic analysis of the oil on alumina (500 g.) in light petroleum solution followed by elution with petrol (b.p. 60–80°) benzene mixtures, then by benzene gave eluates (2.5 g.) which did not contain triterpenoid material. Elution with benzene-ether, ether, and finally with ether containing methanol gave gums (12.5 g.) which when dissolved in methanol slowly deposited crystalline material, m.p. 118–123°. Repeated recrystallization from light petroleum (b.p. 60–80°) gave dipterocarpol, m.p. 132–134°,  $[\alpha]_D^{20} +67^\circ$  ( $CHCl_3$ ; *c*, 1.09); infrared bands at 3500, 1695, 1440, 1370 and 815  $cm^{-1}$ . A mixed melting point with an authentic specimen of dipterocarpol kindly supplied by Dr. T. J. King of Nottingham University showed no depression and the infrared spectra of both specimens were identical.

*D. grandiflorus*. Wood shavings (4 lb.) of *D. grandiflorus* were extracted as above with light petroleum (b.p. 60–80°) and the extract (33.2 g.) when hydrolyzed with methanolic potassium hydroxide gave a non saponifiable fraction (20.2 g.) which was chromatographed as above. The eluates resulting from elution with benzene-ether and ether yielded gummy material which deposited dipterocarpol from methanol solution. Repeated recrystallization from light petroleum (b.p. 60–80°) gave dipterocarpol (2.9 g.), m.p. 132–134° identical with the material obtained above from *D. verrucosus*; *oxime*, m.p. 176–178° (Mills<sup>3</sup> gives m.p. 178–179°); *semicarbazone*, m.p. 203–205°. (Ourisson<sup>7</sup> gives m.p. 206–207°).

*Dammarendiol-II*. Reduction of dipterocarpol, isolated from *D. grandiflorus*, with lithium aluminium hydride followed by chromatography of the product on alumina gave dammarendiol-II, m.p. 130–133°,  $[\alpha]_D^{20} +33^\circ$  (*c*, 1.01). Mills<sup>3</sup> gives m.p. 131–133°,  $[\alpha]_D^{20} +34^\circ$ .

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### 9,11-Dihalosteroids

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Exploratory experiments directed to the development of a program for the systematic investigation of dihalosteroids, in particular those with fluorine at C-11, were undertaken in these laboratories in 1957. The 11 $\beta$ -fluoro-9 $\alpha$ -halosteroids were made either by the use of an *N*-haloamide in anhydrous hydrogen fluoride containing about 30% pyridine or by the reaction of an 11 $\beta$ -hydroxy-9 $\alpha$ -bromosteroid with this same solvent pair.

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