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ISOLATION OF THREE NEW ALKALOIDS FROM DAPHNIPHYLLUM MACROPODUM MIQUEL

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In 1909, S.Yagi reported the isolation of an alkaloid from the Daphniphyllum macropodum Miquel. He named it daphnimacrin (1), which was white amorphous powder, m.p. 75-84°C, and gave it a molecular formula $C_{27}H_{41}O_4N$.

We have examined alkaloidal components of the above plant and could isolate three new alkaloids which were named daphniphylline, (m.p. 238-240°C), neodaphniphylline (m.p. 242-244°C) and yuzurimine (m.p. 194-200°C).

Wet, chopped bark or leaves were extracted with cold methanol and the extracts were concentrated in vacuo and filtered. The filtrate was acidified with hydrochloric acid and shaken with ether. The aqueous layer was made basic by addition of ammonia and extracted with ether. The ethereal layer was shaken with dilute hydrochloric acid and the aqueous layer was made basic with ammonia and again extracted with ether. The ethereal layer was concentrated in vacuo and the resulting resinous substance was fractionated by column chromatography on silica gel using n-hexane-ether-diethylamine (25:25:1) as a solvent. Each fraction was concentrated in vacuo to remove diethylamine completely and the residue was disolved in a mixture of chloroform and ether containing hydrogen chloride. Some fractions gave crystals, which were identified by m.p., IR and thin layer chromatography as one of the new alkaloids. Three alkaloids were not always obtained from each extraction.

Daphniphylline, when crystallized from ether containing a small amount of chloroform, forms colorless crystals, m.p. 238-240°C (in a sealed tube), having a molecular formula $C_{32}H_{49}O_5N \cdot HCl$ (Found: C, 68.14; H, 8.81; N, 2.29; Calcd. for $C_{32}H_{49}O_5N \cdot HCl$: C, 68.12; H, 8.93; N, 2.48 %). Spectral data are as follows: $\varepsilon_{210\ m.\mu.}^{EtOH}$ 527; $\nu_{max.}^{KBr}$ 3400, 2500 (broad), 1742, 1714, 1239, 1052, 898, 826, 698, 683 cm^{-1}; m/e 527 (M^+), 512 (M^+-15), 484 (M^+-43), 442 (M^+-85), 286 (M^+-241), 272 (M^+-255). NMR spectrum is shown in Fig. 1. It is optical active, $[\alpha]_D^{CHCl_3}$ +108°; and contains one acetoxyl group (Found for CH_3CO: 7.12; Calcd. for CH_3CO: 7.63 %).

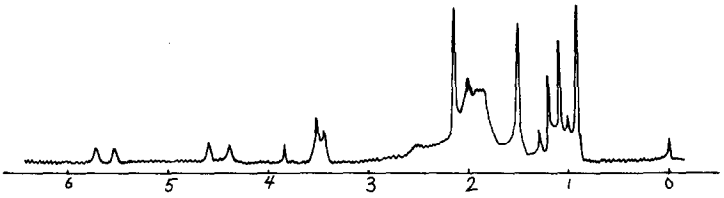

Fig. 1. NMR spectra of daphniphylline at 60 Mc., p.p.m. from internal TMS.

Molecular formula and other data of neodaphniphylline and yuzurimine will be reported soon.

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Reference

1. S.Yagi, Kyoto Igaku Zasshi (Japan) 6, 208 (1909).