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SHORT COMMUNICATION

YELLOW CONSTITUENTS OF TASMANIAN SASSAFRAS HEARTWOOD

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Abstract—The yellow colour of the heartwood of *Atherosperma moschatum* Labill. (Tasmanian sassafras) is due principally to the presence of the alkaloids spermatheridine (I) and atherospermidine (II); atherosperminine (III) was the only other alkaloid isolated.

INTRODUCTION

THE wood of *A. moschatum* (Tasmanian sassafras; Monimiaceae) has some economic importance since it is used in the manufacture of pegs and in the production of paper pulp. Its value for the latter purpose, however, is limited by its yellow colour which is difficult to remove. Intensive hypochlorite treatment is effective in reducing the colour, but the cost is uneconomic, and although sassafras is an abundant rain-forest tree in Tasmania, not more than about five per cent of sassafras wood can be incorporated in pulp, which is composed chiefly of the wood of the eucalypt species *Eucalyptus regnans* F. Muell., *E. delegatensis* R. T. Baker, and *E. obliqua* L'Herit.

RESULTS AND DISCUSSION

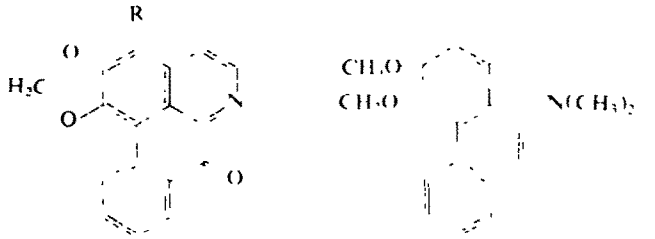
The yellow colour of the heartwood of sassafras was found to be readily extractable by cold methanol, and moreover, was associated with the basic fraction of the extract. The yellow constituents of this fraction (pink in acid) were separated on a Craig machine into two highly coloured substances which were further purified by crystallization from chloroform. They proved identical with the alkaloids spermatheridine (I; 5 mg/kg) and atherospermidine (II; 2 mg/kg), which had been previously isolated in small amounts from the bark and leaves of sassafras by a corresponding method,[1] where they are accompanied by large amounts of the bisbenzylisoquinoline alkaloids, berbamine and isotetrandrine, and lesser amounts of several other alkaloids including atherosperminine (III). No bisbenzylisoquinoline alkaloids were found in the heartwood; the only other alkaloid obtained therefrom was atherosperminine (III).

The alkaloid spermatheridine (I) has also been isolated from a number of other plants all in the Magnoliaceae, another family of the order Ranales. Under the name of liriodenine it was obtained from *Lirodendron tulipifera L.*[2] (yellow poplar, tulipwood), from *Michelia*

[1] I. R. C. BICK, P. S. CLEZY and W. D. CROW, *Australian J. Chem.* **9**, 111 (1956); I. R. C. BICK and G. K. DOUGLAS, *Tetrahedron Let.* No. 25, 1629 (1964).

[2] M. A. BUCHANAN and E. E. DICKEY, *J. Org. Chem.* **25**, 1389 (1960); M. TOMITA and H. FURUKAWA, *Yakugaku Zasshi* **82**, 1199 (1962).

champaca Linn.,[3] from *M. alba* DC.,[4] and from *Magnolia coco* (Lour) DC.[5]; when isolated from *Michelia compressa* Maxim.[6] and from *Michelia compressa* Maxim. var. *formosana* Kanehira it was called oxoushinsunine[7] or micheline B.[8] The name spermatheridine is preferred for this alkaloid since it was the original term under which it was described.[1] Its structure was proved independently by Taylor.[9] by S.-S. Yang *et al.*,[8] and by T.-H. Yang.[10] and confirmed synthetically by Taylor.[9]



I, R=H; Spermatheridine II, R=OCH_3; Atherospermidine III, Atherosperminine

In addition to its isolation from Tasmanian sassafras,[1] atherospermidine (II) has also been found in *Guatteria psilopus* (Anonaceae) Mart.[11] under the name of psilopine; its structure was proved independently by Bick and Douglas[1] and by Harris and Geissman[11] and confirmed by synthesis.[12]

The presence of spermatheridine and another unnamed yellow alkaloid of similar structure[9, 13] in tulipwood (*Liriodendron tulipifera* L.) limits the use of this tree for papermaking in America,[2] as in the case of sassafras wood in Tasmania; a recent report, however, indicates the successful use of tulipwood for making paper pulp by the calcium bisulphite process in Russia.[14] The isolation of spermatheridine from sassafras heartwood confirms predictions made independently on the grounds of the taxonomic-relationships of the families by Dr. E. C. Bate-Smith[15] and by Dr. J. A. F. Gardner.[15] who were unaware at the time (1960) of its isolation from the bark of sassafras, its identity with liriodenine or its structure.

EXPERIMENTAL

Finely ground sassafras heartwood (5·5 kg) was exhaustively extracted by cold percolation with methanol. The volume of the extract was reduced to 4 l. *in vacuo*, the temperature being kept below 45 . The concentrate was acidified with conc. HCl (5 ml) and the remainder of the

[3] T.-H. Yang and C.-Y. Hsiao, *Yakugaku Zasshi* **83**, 216 (1963); P. L. Majumder and A. Chatterjee, *J. Indian Chem. Soc.* **40** (11), 929 (1963); S. K. Banerjee, R. N. Chakravarti and H. M. Fales, *Bull. Calcutta School Trop. Med.* **12** (1), 23 (1964).

[4] T.-H. Yang, *Yakugaku Zasshi* **82**, 811 (1962).

[5] T.-H. Yang, S.-T. Lu and C.-Y. Hsiao, *Yakugaku Zasshi* **82**, 816 (1962)

[6] M. Tomita and H. Furukawa, *Yakugaku Zasshi* **82**, 925 (1962).

[7] T.-H. Yang, *Yakugaku Zasshi* **82**, 794 (1962).

[8] S.-S. Yang, W.-Y. Huang, L. C. Linn and P.-Y. Yeh, *Chemistry (Taipei)* 144 (1961)

[9] W. I. Taylor, *Tetrahedron* **14**, 41 (1961).

[10] T.-H. Yang, *Yakugaku Zasshi* **82**, 798 and 811 (1962).

[11] W. M. Harris and T. A. Geissman, *Abstr. Pap., IUPAC Symp. Chemistry of Natural Products, Kyoto* 80 (1964).

[12] I. R. C. Bick and G. K. Douglas, *Australian J. Chem.* In press.

[13] J. Cohen, W. von Langenthal and W. I. Taylor, *J. Org. Chem.* **26**, 4143 (1961).

[14] Z. N. Chkhulatanishvili and B. S. Polskhverashvili, *Bumazhn. Prom.* **6**, 26 (1964).

[15] E. C. Bate-Smith; J. A. F. Gardner, Personal communications during their visits to Tasmania

methanol removed *in vacuo*. The acid insoluble material was filtered off, and the solution made alkaline with aqueous ammonia. The resulting yellow-brown precipitate was filtered off, extracted in chloroform, and the extract washed with aqueous alkali to remove phenolic material. Evaporation of the chloroform extract left a yellow-brown residue (4·3 g); chromatography of this residue on alumina failed to separate the yellow constituents. These were eventually separated by counter-current distribution between chloroform and dilute hydrochloric acid. The separation could be followed by the two pink bands moving progressively along the fifty tubes of the Craig machine, spermatheridine (28 mg) distributing into acid of lower strength (1%) than atherospermidine (11 mg; 5%). The yellow bases were further purified by crystallization from chloroform and proved identical (m.p. and mixed m.p., i.r. spectra) with samples of spermatheridine (I) and atherospermidine (II) previously obtained from sassafras bark. When evaporated to dryness, the chloroform layers of tubes 26–50 of the Craig machine gave a yellowish oil which was chromatographed over alumina; 15% chloroform–benzene eluted atherosperminine (III), isolated as its picrate (30 mg), m.p. 188–189° (lit. records[1] 189–190°).

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