

QUINOLINE ALKALOIDS OF SKIMMIA JAPONICA THUNB.

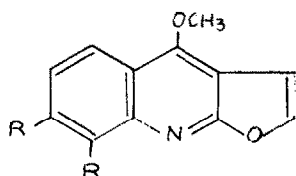
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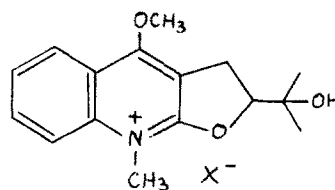
The principal alkaloid of Skimmia japonica Thunb. and other Skimmia species is the furanoquinoline, skimmianine (I) (1), although the related alkaloid, dictamnine (II) is found in Skimmia repens Nakai (2). We have now examined the alkaloids of female bushes of Skimmia japonica Thunb. (S. foremanii Knight).

Extraction of the dry leaves gathered in January with light petroleum, and chromatography of the basic fraction yielded dictamnine (II) (0.035%) identical with a synthetic sample (3). Skimmianine was not detected, but it is not yet known whether the absence of this alkaloid is characteristic of the female shrub or whether dictamnine replaces skimmianine at certain periods in the life cycle of the plant.



I R = OCH<sub>3</sub>

II R = H



III

Since quinolinium alkaloids have been obtained from certain rutaceous plants (4), we examined the quaternary alkaloids of Skimmia japonica. These were isolated as reineckates and then converted into their chlorides, which were separated by thick-layer chromatography. The principal alkaloid gave a crystalline perchlorate, m.p. 200-202<sup>o</sup>, [α]<sub>D</sub> + 33<sup>o</sup> (CH<sub>3</sub>OH) and a methiodide, m.p. 155-156<sup>o</sup>. Analysis indicated that the perchlorate had the empirical

formula,  $C_{16}H_{20}ClNO_7$ . The n.m.r. spectrum at 100 Mc./sec. in deuterated dimethylsulphoxide showed a multiplet at 1.6 - 2.3, a triplet at 4.75 (CH), singlets at 5.45 and 5.95 ( $\geq N^+-CH_3$  and  $-OCH_3$ ), a doublet at 6.65 ( $CH_2$ ) and singlets at 8.65 and 8.75  $\tau$  ( $2 CH_3$ ). A singlet at 5.0  $\tau$  (OH) disappeared on addition of deuterium oxide. These data show that the alkaloid has structure (III), and is thus (+)-platydesmine methosalt; the parent base, platydesmine, was isolated from Platydesma campanulata Mann (5) and from Geijera salicifolia Schott (6). The structure of the new alkaloid was confirmed by comparing the n.m.r. and infrared spectra of the methiodide with those of ( $\pm$ )-platydesmine methiodide, which we synthesised previously (7). This is the third recent case of synthesis of a quinoline alkaloid before its isolation from natural sources; other samples are a dimethylallylquinoline from Fagara zanthoxyloides Lam. (8) prepared earlier (7), and the dimethylpyranoquinoline alkaloid, ribalinine, synthesised in 1966 (7) and identified as a natural product in the following year (9).

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