The tertiary alkaloids of some Asian species of *Strychnos*

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In our screening program for alkaloids, the extracts from more than 200 samples mostly from herbarium collections, belonging to 34 Asian *Strychnos* species, have been examined by t.l.c. and g.l.c. methods. The results obtained with *S. nux-vomica* L. and *S. wallichiana* Steud. ex DC. (*S. colubrina* L.) are particularly interesting in that:—

1. The alkaloid composition of the leaf and seed, irrespective of age (up to 300 years old) appeared to be unchanged.

2. Both species contained alkaloids of the following types:—Normal series: strychnine, brucine, strychnine *N*-oxide, brucine *N*-oxide; pseudo series: pseudostrychnine, pseudobrucine; *N*-methyl-pseudo series: icajine, vomicine, novacine.

3. Examination of different plant parts of the two species showed that in the root bark and root wood alkaloids of the normal series tend to predominate; in the stem bark pseudo and *N*-methyl-pseudo alkaloids are the most important; in the leaves the main alkaloids belong to the *N*-methyl-pseudo series (cf. Maier & Groger, 1968; Sefcovic, Dubravkova & Torto, 1968); and in the seeds again normal seriesbases predominate. There is evidence that in *S. nux-vomica* the normal bases are formed in the roots (Schlatter, Waldner & others, 1969). Our data from *S. nux-vomica* and *S. wallichiana* suggest that as the alkaloids are transported up the plant through the wood they are gradually converted from bases of the normal series to bases of the pseudo and *N*-methyl-pseudo series, so that when they reach the leaves the *N*-methyl-pseudo alkaloids predominate. It is possible that the reverse process may be taking place if the alkaloids descend from the leaves through the bark.

Among the other species screened were:—

1. *S. ignatii* Berg., seed samples of which gave results very similar to those of *S. nux-vomica*.

2. *S. nux-blanda* A. W. Hill, leaf and seed samples of which contained small amounts of alkaloids similar in composition to those of *S. nux-vomica* except for the frequent occurrence of diaboline.

3. *S. potatorum* L.f., which contained diaboline as the major alkaloid in the leaves, seeds, and bark.

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The conversion of *pseudo* heteroyohimbine alkaloids to oxindole alkaloids

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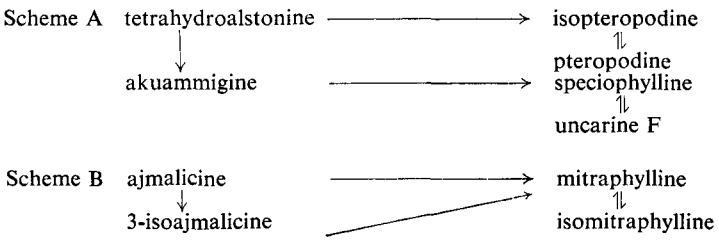
In the hypothesis put forward by Shellard, Phillipson & Gupta (1969) regarding the origin of oxindole alkaloids in the genus *Mitragyna*, the possibility that *pseudo* indole alkaloids could be involved was discounted because of the instability of the corresponding *pseudo* oxindole alkaloids. However, in some species of *Mitragyna* there is evidence that while *normal* oxindoles are present, the corresponding *normal* indoles do not occur although the corresponding *pseudo* indoles are present. This has led to a reconsideration of the hypothesis.

Employing the methods of Finch & Taylor (1962) and Shavell & Zinnes (1962) the *pseudo* mitrajavine has been converted to the *normal* javaphylline and isojavaphylline and the *pseudo* mitraciliatine has been converted to the normal rhynchociline and ciliaphylline. These *in vitro* conversions encouraged attempts to obtain similar *in vivo* conversion of *pseudo* indole alkaloids to *normal* oxindole alkaloids.

Young plants of *Mitragyna parvifolia* (Roxb.) Korth grown from seeds obtained from Ceylon

and containing the alkaloidal system shown in Scheme A were used. By means of the wick method of feeding through the xylem both ajmalicine (*normal*, closed E ring) and 3-isoajmalicine (*pseudo*, closed E ring) were introduced to the plant. In both cases after 24 h the corresponding *normal* closed E ring oxindoles, mitraphylline and isomitraphylline were present in the leaves. Since 3-isoajmalicine could not be detected when ajmalicine was fed into the plant there is some doubt about the hypothesis that this alkaloid is formed by conversion of the C(3)H-α ajmalicine to C(3)H-β. These results support the modified proposals that *normal* oxindoles may be derived from corresponding *pseudo* oxindoles (Scheme B).



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The distribution of alkaloids in *Mitragyna parvifolia* (Roxb.) Korth in young plants grown from Ceylon seed

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Initial investigations of the alkaloidal pattern in *Mitragyna parvifolia* obtained from Ceylon showed the leaves to contain the closed E ring alkaloids, tetrahydroalstonine, akuammigine, pteropodine, isopteropodine, speciophylline and uncarine F while the trunk bark contains the open E ring alkaloids isorhynchophylline and rhynchophylline in addition. The root bark contained isorhynchophylline and rhynchophylline only (Shellard & Houghton, 1971).

A more detailed examination of all parts of a young plant grown from seed and of the seeds and seedlings has revealed an interesting distribution of alkaloids throughout the plant. The root xylem and phloem both contain isorhynchophylline, rhynchophylline and corynoxeine (Δ^{18}-rhynchophylline). This latter alkaloid occurs in large quantities in the root tips and is also present in the seeds and seedlings as the main alkaloid. This group of alkaloids also occurs in the stem xylem at all positions in the stem but could not be found in the petioles, leaves or stipules. Hirsutine and hirsuteine (Δ^{18}-hirsutine) also occur in the root phloem. The alkaloids in the stem phloem vary according to the position in the stem. No indole alkaloids were detected and the oxindole alkaloids present in the leaves also occur in the stem phloem in the upper part of the stem although the amounts present decrease to zero in a zone just above the hypocotylar region. This region contains isorhynchophylline, rhynchophylline and corynoxeine but in a narrow zone just above this region there are traces of an alkaloid which appears to correspond to mitraphylline on many t.l.c. systems. The stipules contain the same oxindole alkaloids as in the leaves with speciophylline predominant.

This distribution of alkaloids can lead to an interesting speculation regarding their movement and possible role in the plant.

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