The Piscicidal Plants in Southeast Asia and Their Active Constituents

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There are many kinds of plants which have been employed for hundred of years as a medicine, insecticide, insect repellent, antiseptic, arrow poison or fish poison. A number of such useful plants has been noted among thousands of higher plants growing in Southeast Asia. For example, *Strophantus gratus*, *Rauwolfia serpentina*, *Digitalis pur purea* and *Cinchona succirubra* were known as medicinal plants; *Derris* species were used as a fish poison and insecticide; *Albizzia procera* was said to repel ants; and *Melia azadirachta* was noted as keeping away insects.

Extensive chemical investigations to reveal the active principles of these useful plants were carried out. From medicinal plants a variety of cardiac glycosides and various alkaloids were isolated and their structures were established.

The isolation of active principles from medicinal plants is sometimes not easy since an appropriate bioassay to search the active principles is not available because of the complex remedial effects of the medicinal plants. The chemical investigation on medicinal plants can, therefore, find out some chemical constituents of the plants, but hardly reveal the active principles.

It is necessary to set up an appropriate bioassay for examining the specified biological activity in order to isolate the active principle from the plant. If the bioassay method is standardized, it is scarecely impossible to isolate the active principles even though they are contained in very small quantities.

Recently more than 10,000 plant extracts were screened for antitumor activity against the Leukemia L-12120 in mice and the Walker 256 carcinosarcoma etc. by two groups of scientists in the U.S.A.¹⁾ Among effective plant species are *Stephania hernandiifolia*, *Elephanto pus elatus*, *Acnistus arborscens*, *Catharanthus roseus* and *Acronychia baueri*, from which (\pm) -tetrandrine, elephantopin and elephantin, withaferin A, vincaleukoblastine, and acronychin were isolated as the active constituents, respectively.

Regarding plant species employed as pesticides, it is considerably easy to isolate and elucidate the active constituents of the plants because the bioassay method is readily set up.

A typical classical investigation on such a natural pesticide was that on rotenone isolated from *Derris* species. Subsequently a lot of plants was examined for insecticidal property and some of them were found to have the property to some extent. Among these effective species, are *Mammea americana*, *Quassia amara* and *Tripterygium wilfordii*, from which mammeins, quassin and ryanodine were isolated as the active constituents, respectively. More recently, *Melia azedarach* that repels insects was chemically studied, and meliantriol was isolated and characterized as the active constituent.

It should be emphasized that all the plants cited above are also known as fish poisons. It is interesting and important to investigate chemical constituents of the piscicidal plants in view of finding out novel compounds having any biological activity. In Southeast Asia about 100 species of plants are reported to have been used as fish poisons²⁾. Some of these plants, together with organs employed are listed in Table I.

A few of them were investigated chemically, and the active constituents were isolated, the Table 1. Piscicidal Plants in Southeast Asia

Araceae Stemonaceae Urticaceae Polygonaceae

Menispermaceae

Cabparidaceae Pittosporaceae Leguminosae

Linaceae Rutaceae

Buxaceae Euphorbiaceae

Guttiferae

Thymelaeaceae Lecythidiaceae Myrsinaceae

Ebenaceae

Styracaceae Verbenaceae

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Acorus calamus L., Stemona burkillii Prain, Ficus diversifolia Blume, Polygonum barbatum L., P. orientale L., Cissampelos pareira L., Stephania hernandiifolia Walp., Anamirta paniculata Coleb. (=A. cocculus Wight et Arm.) Gynandropsis gynandra Briquet, Pittosporum ferrugineum Ait., Albizzia acle Merr., A. procera Benth., Derris elliptica Benth., D. malaccensis Prain, Milletia sericea Benth., Pachyrrhizus erosus Urban, P. tuberosus Spreng., Pithecellobium ellipticum Hassk., Tephrosia candida DC., Tephrosia vogelii Hook, T. purpurea Pers., Whitfordiodendron pubescens Burkill, Erythroxylon cuneatum Kurz, Acronychia resinosa Forst., A. laurifolia Blume, Buxus rolfei Vidal, Cleistanthus collinus Benth., Euphorbia antiquorium L., E. neriifolia L., E. tirucalli L., E. trigona Haw., Jatropha curcus L., Mallotus apelta Muell.-Arg., M. philippinensis Muell.-Arg., Calophyllm inophyllum L., C. muscigerum Boerl. et Koord., C. soulattri Burm., Wickstroemia ridleyi Gamble, Barringtonia acutangula Gaertn., Aegiceras corniculatum Blanco (=A. majus Gaertn.) Diospyros ebenaster Retz., D. lucida Wall., D. wallichii King et Gamble, Styrax benzoin Dryander, Callicarpa candicans (Burm. f.) Hochr., (=C. cana L.)C. maingayi King et Gamble, Vitex trifolia L.,

root tuberous root latex whole plant whole plant root root seeds seeds leaves and fruits bark bark root root root leaves and seeds seeds bark root, bark and leaves whole plant whole plant seeds bark and leaves bark root fruits bark, root and leaves latex leaves latex latex latex seeds seeds bark, leaves and seeds bark bark and roots bark bark and seeds bark immature fruits fruits root, leaves and fruits bark and root leaves

leaves bark, fruits and leaves

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structures of which were established. The others remain uninvestigated or partially investigated, the active constituents of which have not yet been established.

Herewith we wish to summarize the piscicidal plants whose active constituents have been established, and to show the structures³⁾.

1) Stemona burkillii Prain (Stemonaceae) is a tuberous herb found in Southeast Asia. Its tuberous root is a fish poison and was used as an insecticide. From the root of S. tuberosa, tuberostemonine (I) was isolated and the structure established.



2) Cissampelos pareira L. (Menispermaceae) is a small woody climber distributed throughout the tropics. The pounded root is used as a fish poison. The active principles are similar to those of tubocurare in the Amazon (Chondrodendron tomentosum Ruiz et Pavon). They are alkaloids of biscoclaurine type, bebeerine (II), (\pm) -curine, hayatinine, isochondrodendrine, sepeerine, cissampareine (III) and 4"-O-methylcurine⁴).



3) Stephania hernandiifolia (Willd.) Walp. (Menispermaceae) is a climber found from India to Australia. The tuberous root is extremely poisonous and was used as a fish poison. It was said that the active principles were picrotoxin and the related compounds, but several alkaloids, isotrilobine (IV), (\pm) -tetrandrine,

fangchinoline, (+)-tetrandrine (V), isochondrodendrine have been isolated as active constituents⁵⁾. It is noteworthy that (\pm) -tetrandrine has been found to exhibit antitumor activity.



4) Anamirta paniculata Coleb. (Menispermaceae) is a small woody climber found throughout Southeast Asia. Its seeds were used as a fish poison. The piscicidal principles are picrotoxinin (VI) and picrotin (VII)⁶.



5) Albizzia procera Benth. (Leguminosae) is a woody climber found in India, Burma, Thailand and Java. The bark was used as a fish poison. The action was confirmed due to a saponin which consists of a triterpene acid as an aglycone and arabinose, rhamnose and glucose as a sugar moiety.

6) Derris elliptica Benth. and Derris malaccensis Prain (Leguminosae) are woody climbers found throughout Southeast Asia. The roots are old famous fish poisons and also insecticides. Besides rotenone (VIII) (10% of the dried root), deguelin (IX), toxicarol (X), elliptone (XI) and tephrosin are contained as active constituents⁷). Rotenone has long been used as one of the three important natural insecticides.



7) Milletia sericea Benth. (Leguminosae) is a large woody climber found throughout Malaysia. The root is used as a fish poison. The active principle seems to be rotenone since the Formosan *M. taiwaniana* Hayata was found to contain rotenone.

8) Pachyrrhizus erosus Urban (Leguminosae) is a herbaceous climber, native of tropical America. It's leaves and seeds were used as fish poisons. Rotenone, pachyrrhizone (XII), pachyrrhizin (XIII) and erosnin (XIV) were isolated from the seeds.



9) Cleistanthus collinus Benth. (Euphorbiaceae) is a tree common in the more open forests of the tropics. The bark and root are recorded to be used as criminal poisoning, and the leaves as fish poison. From the leaves was isolated diphyllin (XV), to which the piscicidal action was ascribed. Methyl ether of diphyllin, justicidin A was isolated with justicidin B as the active constituents of Formosan fish poison,



Justicia hayatai var. decumbens Yamamoto.

10) Calophyllum inophyllum L. (Guttiferae) is a big tree distributed throughout Southeast Asia. It was used as a medicine in India. The seeds, bark and leaves were employed as fish poisons. From the seeds calophyllolide (XVI), (\pm) -inophyllolide (XVII) and calophyllic acid (XVII) were isolated by Prof. Polonsky⁸⁾. Calophyllolide was reported to have anticoagulant activity. As the piscicidal constituents of the leaves we isolated (+)-inophyllolide and the four related compounds (XIX)⁹⁾.



These 4-phenylcoumarines are allied to mammeins, isolated from *Mammea americana* as the piscicidal and insecticidal principles. The piscicidal activities of these calopyllolides were found to be rather weak.

11) Barringtonia acutangula Gaertn. (Lecythidaceae) is a tree of moderate size found on sandy shores. Its bark and seeds are fish poisons, which are ascribed to poisonous saponins.

12) Aegiceras corniculatum Blanco (=A. majus Gaertn.) (Myrsinaceae) is a bush commonly occurring throughout Southeast Asia. The bark and seeds contain saponins and on this account are fish poison.

13) Callicar pa candicans (Burm. f.) Hochr. (=C. cana L.) (Verbenaceae) is a shrub growing from Bengal to Caroline Islands. Its leaves have been used as a fish poison in Palau and Philippine Islands. The chemical studies on the active principle were started by Prof. Mitsui. We recently established that the active principle is a tricarbocyclic diterpene carrying α -oxoene-1, 4-dione function, which was named callicarpone (XX)¹⁰). Its piscicidal activity was found to be as strong as that of rotenone, but no insecticidal activity was observed. It has been found that callicarpone has antifungal activity and herbicidal activity.

Callicar pa longifolia Lam. was said to be fish poison, but has been confirmed to have no piscicidal activity.



Callicar pa maingayi King et Gamble is a tree found throughout Southeast Asia. We isolated maingayic acid (XXI) recently as the piscicidal constituent. As summarized above, very few species have been investigated to find their active constituents. Most of them have not even been screened for the pisciccidal activity. To find novel biological active compounds, more extensive studies on chemical constituents of these species of plants should be continued.

References

- Chemical and Engineering News, Dec. 12, p. 64 1966. Plants supply promising antitumor agents.
- I. E. Burkill: A dictionary of the economic products of the Malaya Peninsula, University Press, Oxford, England 1935.
- K. Kawazu: Piscicidal plants in Southeast Asia and their active principles, The Southeast Asian Studies (Kyoto University), 5, 166 1967.
- R. M. Srivastava and M. P. Khare: On the water-soluble alkaloids from the root crust of *Cissampelos pareira* L., Ber., 97, 2732 (1964).
- S. M. Kupchan, W. L. Asbun and B. S. Thyagarajan: *Menispermaceae* Alkaloids III. Alkaloids of *Stephania hernandifolia*, J. Pharm. Sci., 50, 819 1961.
- L. A. Porter: Picrotoxinin and related substances, Chem. Revs., 67, 441 1967.
- H. L. Haller, L. D. Goodhue and H. A. Jones: The Constituents of *Derris* and other Rotenonebearing plants, Chem. Revs., 30, 33 1942.
- J. Polonsky: Structure of Calophyllolide, Inophyllolide, and Calophyllic Acid, Constituents of *Calophyllum inophyllum* Nuts, Bull. Soc. Chim. France, 1079 1957.
- 9) Kawazu, K. Ohigashi H. and Mitsui, T. The Piscicidal Constituents of *Calophyllum* inophyllum L., *Tetrahedron Letters*, 2383 1968.
- Kawazu K. and Mitsui, T. Callicarpone, fishkilling components of *Callicarpa candicans*, *Tetrahedron Letters*, 3519 1966.