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Some recent isolation studies from potential insecticidal *Piper* species

Per M. Boll,* Virinder S. Parmar,[+] Om Dutt Tyagi,*
Ashok Prasad,* Jesper Wengel* and Carl Erik Olsen[§]

*Department of Chemistry, Odense University, 5230 Odense M, Denmark
[+]Department of Chemistry, University of Delhi, Delhi 110 007, India,
[§]Department of Chemistry, Royal Veterinary and Agricultural University, 1871 Frederiksberg C, Denmark

Abstract: A joint research programme between University of Delhi, India, and Odense University, Denmark, is currently investigating *ca.* 40 Indian *Piper* species. So far, long-chain amides, aristolactams, cepharadiones, wax esters, and especially a large number of lignans and neolignans have been isolated.

INTRODUCTION

Three and a half years ago the Danish International Development Agency agreed to finance a joint research programme between the Chemistry Departments of University of Delhi, India, and Odense University, Denmark. The grant was given as a result of a new policy after which the Agency would finance scientific education projects of potential benefit to a third world country and to a minor extent to Denmark. The title of the project is: "Isolation, structure elucidation and biological activity of potential insecticides from *Piper* species of importance in agriculture and rural development." The Danish producer of pesticides, Cheminova, Inc., generously agreed to carry out biological testing of plant extracts.

Naturally occurring long-chain *N*-isobutylamides have long been recognized as a class in which insecticidal activity is common. As a specific example one can refer to the investigation of Miyakado *et al.* (15) for which an amide, pipercide, from black pepper, *Piper nigrum*, was more toxic against adzuki bean weevils than pellitorine and just as active as the pyrethroids.

RESULTS AND DISCUSSION

60 plants of which *ca.* 40 are *Piper* species are being examined and so far *ca.* 500 compounds in different stages of purity have been analyzed.

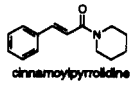
Table 1 gives the structures of 7 long-chain amides and one ester isolated from 8 different *Piper* species. It is somewhat surprising that so few have been isolated and that they are all known. In a few cases, Piperaceae has given rise to aristolactams first known from Aristolachiaceae. We have isolated such an alkaloid from *P. acutislegium* and corrected the structures of earlier isolated alkaloids (Table 2). Recently, we have isolated three other aristolactams from *P. wightii* (not given in Table 2). Five species have yielded cepharadiones and recently cepharadione B is isolated from *P. wightii* (not mentioned in Table 2).

Flavonoids have only been isolated from 4 species and all are trivial: 5-hydroxy-7,4'-dimethoxyflavone from *P. falconeri* (3), *P. peepuloides* and *P. manii*, techtochrysin from *P. falconeri* (3) and velutin from *P. clarkii* (9).

P. species are often climbing plants with wax-coated stems. Table 3 gives structures of different waxes from two species compared with similar esters from *Agave* and *Taxus*. From *A. americana* we have isolated an unusual chromone with a side-chain derived from a C_{34}-acid and four malonyl-CoA. The free C_{34}-acid and an ester containing a C_{34}-alcoholic moiety was also isolated. *P. clarkii* revealed an ester, of which the alcohol moiety was reduced p-coumaric acid, the first example of a wax ester possessing an alcoholic moiety originating from shikimic acid. Therefore, it was somewhat surprising to find structurally similar esters in two *Taxus* species.

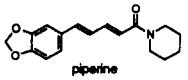
In Tables 4, 5, 6 and 7 the isolated lignans and neolignans of different structural types are presented. Only three species have been examined thoroughly with the result that a total of 25, 13 and 8 lignans/neolignans have been isolated from *P. wightii*, *P. schmidtii* and *P. clarkii*, respectively. Of those, 14 are novel compounds.

Table 1. Long-chain Amides



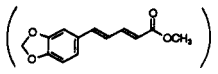
cinnamoylpyrrolidine

P. schmidtii (14)
P. wightii



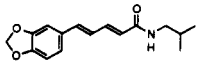
piperine

P. acutisileginum (10)
P. betle (10)



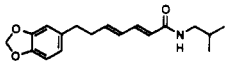
methyl piperate

P. schmidtii (14)



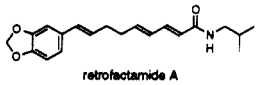
piperlonguminine

P. acutisileginum (10)
P. pedicellosum
P. betle (10)
P. khasiana



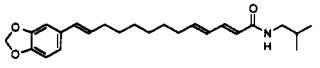
(2*E*, 4*E*)*N*-isobutyl-7-(3, 4-methylene-dioxyphenyl)-hepta-2, 4-dienamide

P. falconeri



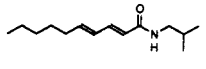
retrofactamide A

P. manii
P. longum



guineensine

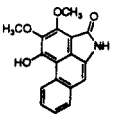
P. longum



pellitorine

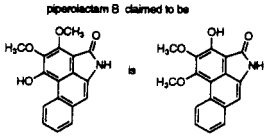
P. pedicellosum

Table 2. Heterocyclic Amides



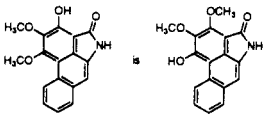
10-amino-4-hydroxy-2, 3-dimethoxy-phenanthrene-1-carboxylic acid lactam

P. acutisileginum (5)



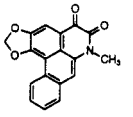
piperolactam B claimed to be is

P. acutisileginum (5)



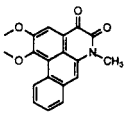
piperolactam D claimed to be is

P. acutisileginum (5)



cepharadione A

P. acutisileginum (10)
P. auritum
P. sanctum
P. pedicellosum
P. betle



cepharadione B

P. schmidtii (10)

Table 3. **Waxes**

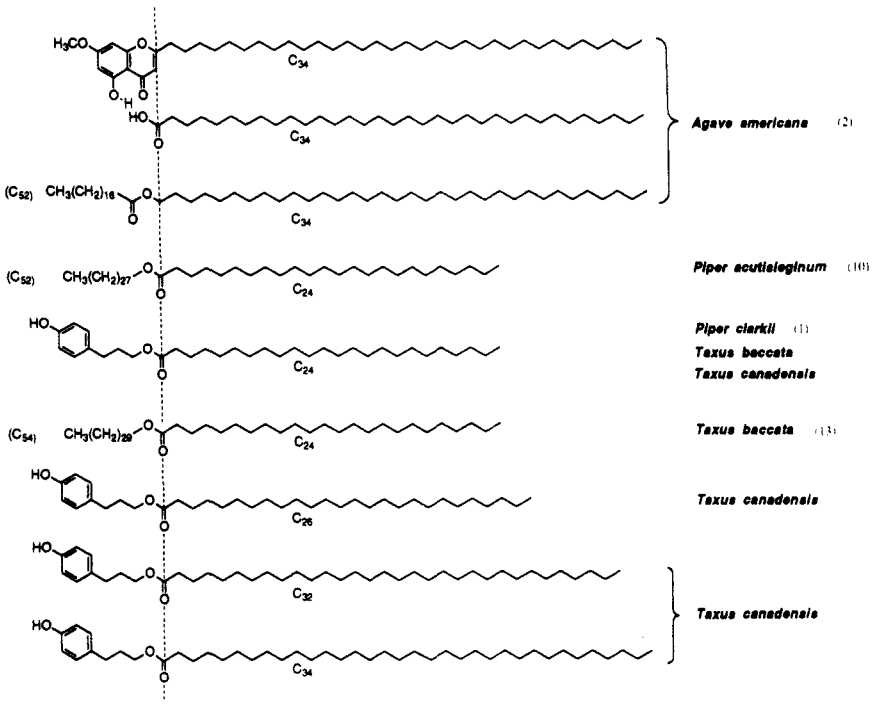


Table 4. 2.5 - Bisaryl - 3.4 - dimethyl tetrahydrofuranoid lignans

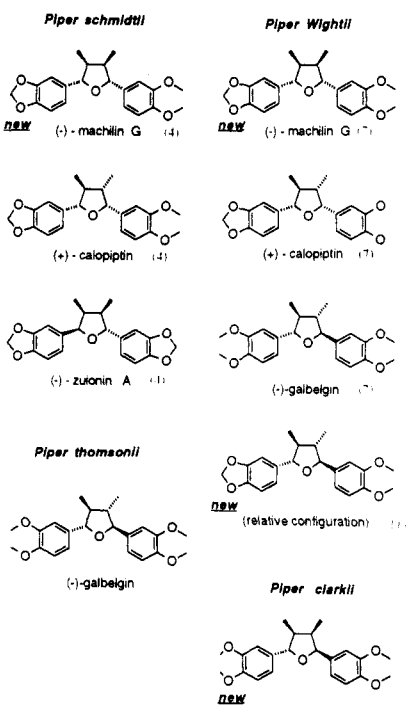


Table 5.

2.6 - Bisaryl - 3.7 - dioxa [3.3.0] bicyclooctanes

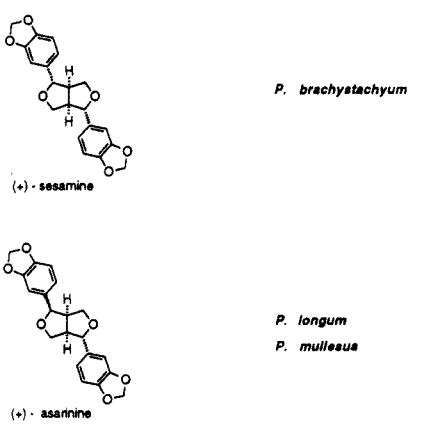


Table 6. **Benzofuran lignans**

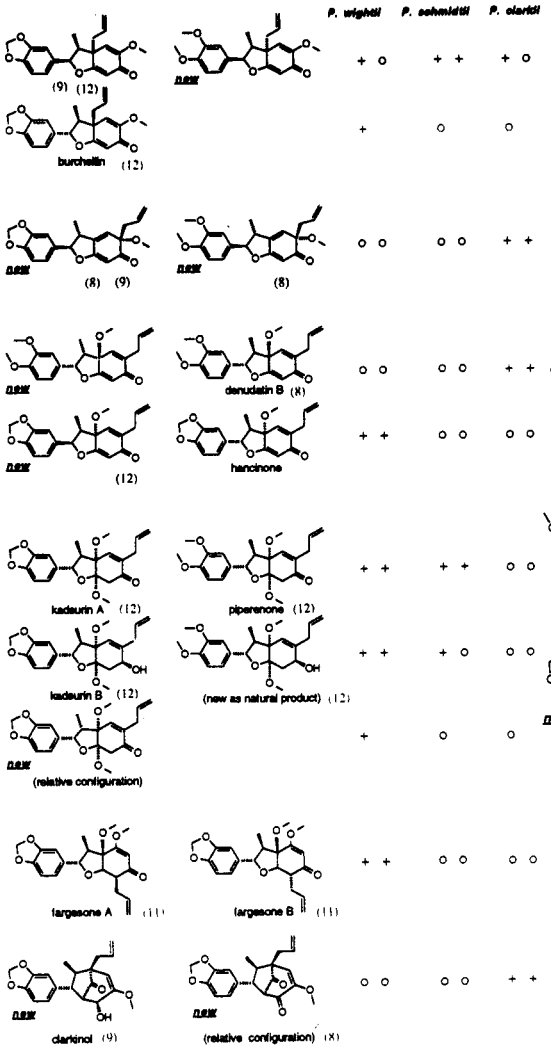
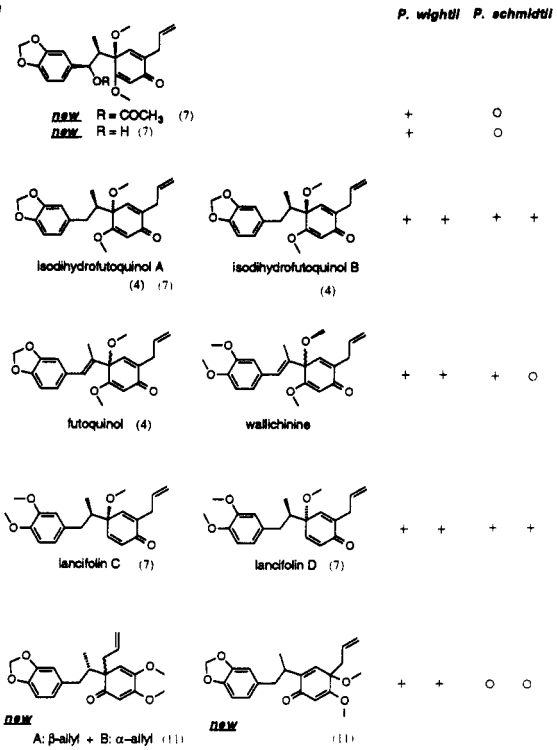


Table 7. **1.2 - Diarylpropanes**



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