The chemistry of Brazilian Lauraceae. LXV.
5, 7, 8, 3', 4', 5' - Hexamethoxyflavone from an Aniba species

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Abstract

Aniba species (Lauraceae) are characterized by the presence of neolignans or of 6-aryl (or 6-styryl) 2-pyrones. Flavonoids occur either together with pyrones or, in rare cases, as predominant micromolecular type. The branch wood of an Aniba species from Marapí, Pará do Oeste River, near Tiríós (Pará State), constitutes such a case. It contains 5,7,8,3',4',5'-hexamethoxyflavone, obtained for the first time from a natural source.

INTRODUCTION

One of the chemosystematically significant results of our studies on the genus Aniba (family Lauraceae) (for the previous part of the series see Dias et al., 1981) concerns the near dichotomy between neolignan versus pyrone containing species (Gottlieb & Kubitzki, 1981). Not once both types of compounds have yet been reported for a single species. This fact is apparently associated with reduction in biosynthetic capability. Allylphenols and propenylphenols, the oxidative coupling of which leads to neolignans, are end products of the shikimate pathway (see Fig. 5 in Gottlieb, 1980). Blocking of reaction steps would imply the availability of cinnamates as biosynthetic starting materials for pyrones, benzophenones and flavonoids. Indeed, these latter groups of micromolecules do occur together, as in A. roseodora Ducke and A. duckei Kosterm. (now merged under the former binomial by Kubitzki, 1982), as well as in A. coto (Rusby) Kosterm. and A. pseudocoto (Rusby) Kosterm. (the validity of the latter binomial being questioned by Kubitzki, 1992) (Gottlieb, 1972, and references cited therein). In rare cases species which use cinnamates as starting material for

the synthesis of secondary metabolites may even accumulate flavonoids to the apparent exclusion of pyrones. This phenomenon has been noted so far only once for A. riparia (Nees) Mez which was reported to contain, besides a relatively large proportion of tri-O-methylgalangin (1a) (Franca et al., 1976), lesser quantities of isalpinin (1b), di-O-methylpinocembrin (2a), pinostrombin (2b), flavokavin-B (3) and 3-hydroxy-5,7-dimethoxy-flavanone (4) (Fernandes et al., 1978). All these flavonoids possess 5,7-dioxygenated A-rings and unsubstituted B-rings. Except for pinocembrin (2c), which was isolated from A. roseodora (Gottlieb & Morris, 1958), all are strongly O-methylated.

RESULTS

The botanical material with which the present report is concerned, registered under number 14952 in the Herbarium of EMBRAPA, Pará, was collected from a tree growing at Marapí, Pará do Oeste River, near Tiríós (Pará State). Professor Klaus Kubitzki, Hamburg University, albeit unable to identify the material conclusively on account of its sterile condition, suggested that it should either belong to Aniba burchelli Kosterm. or to a new species.

An extract of branch wood failed to yield burchellin (Lima et al., 1972) and related neolignans (Alvarenga et al., 1977). Compound 5 was isolated instead. Its structural elucidation was based on the molecular formula C_{29}H_{25}O_{12}, determined by high resolution mass spectrometry. Analysis of the proton nuclear magnetic resonance spectrum allowed this formula to be expanded to C_{29}H_{25}(OMe), which, together with the infrared and ultraviolet
spectra, suggested the existence of a basic flavone skeleton. Indeed, the typical H-3 singlet was registered at δ 6.60. The three additional yet undefined protons were represented by two singlets: one at δ 6.93, which can only stand for two symmetrical H-2’ and H-6’, and one at δ 6.36, which can only stand for H-6, δ 6.80 being typical for H-8 on a 5,6,7-trimethoxyated flavone (Henrick & Jefferies, 1964). 5,6,7,3’, 4’,5-Hexamethoxy flavone differs from the compound in question also on account of its melting point (152-154° (Braz Filho & Gottlieb, 1971) versus 120-121° for 5).

DISCUSSION

Thus still another Aniba species in which so far neither neolignans nor pyrones could be located, contains a flavonoid in its trunk wood. The compound (5), the first flavone to be described for an Aniba, has a surprisingly high oxidation level. Tri-oxygenated cinnamate derived B-rings have not been reported previously for pyrones, benzophenones or flavonoids from Aniba. In contrast, Aniba species of the neolignan group contain either di-oxyphenyl or tri-oxyphenyl substituted neolignans and the feature is thus of clear systematic importance (Fernandes et al., 1978). Furthermore, the acetate derived ring is oxygenated at C-8. Extra A-ring oxygenation of flavonoids can occur at C-6 or at C-8; the former mode characterizing compounds from the relatively advanced subclass Asteridae (sensu Cronquist, 1968) and the latter mode characterizing the relatively primitive angiosperms belonging, e.g., to the Ranunculaceae, Papaveraceae (Harborne, 1977) and, as shown in the present paper, Lauraceae. The per-methylation of the novel compound 5 is in line with the fact that most micromolecules from Aniba species are strongly O-methylated.

While 5,7,8,3’,4’,5’-hexamethoxy flavone was not reported previously as a natural product, four less fully O-methylated derivatives of 5,7,8,3’,4’,5’-hexahydroxy flavone were isolated from Gardenia (Rubiaceae) species (Wollenweber & Dietz, 1981). The structure of 5,3’-dihydroxy-7,8,4’,5’-tetramethoxy flavone, attributed in the review by Wollenweber & Dietz (1981) to a compound from Lychnophaora affinis Gardn. (Asteraceae) has recently been revised to 5,3’-dihydroxy-3,7,4’,5’-tetramethoxy flavone (Le Quesne et al., 1979). Interest in such highly oxygenated flavonoids was stimulated by observations that some of them showed activity versus the KB cell culture (Edwards et al., 1979). Our compound from Aniba should, consequently, also be submitted to pharmacological testing.

EXPERIMENTAL

Isolation of the flavone. Powdered branch wood (1.8 kg) was percolated with light petrol. The extract (350 mg) was separated by preparative TLC (Si gel, CH3OH-AcOEt 4:1) into a more polar fraction (200 mg) and a less polar fraction (100 mg). The latter was purified by repeated TLC (Si gel, CH3OH-AcOEt 6:4) to 5,7,8, 3’,4’,5’-hexamethoxy flavone (8 mg).

5,7,8,3’,4’,5’-Hexamethoxy flavone m.p. 120-
121° (C6H12) (Found: 402.1394; C71H66O16 requires: 402.1315). UV λ max MeOH 364 nm: 235, 266,
316 (9800, 6030, 12100). IR νBr cm-1: 1629.

1H NMR (60 MHz, CCl4) δ: 6.93 (s, H-6’), 6.60 (s, H-3), 6.36 (s, H-6), 3.95 (s, OCH3), 3.92 (s, OCH3, OCH2), 3.88 (s, OCH3), 3.80 (s, OCH3, OCH2). MS m/z (rel. int.): 402 (9), 388 (5), 387 (19), 343 (7), 151 (9), 145 (20), 113 (9), 69 (100), 57 (5).

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Espécies de Aniba (Lauraceae) são caracterizadas pela presença de neolignanas ou de 6-aryl-(ou 6-estiril-) 2-pironas. Flavonoïdes ocorrem seja juntos com pironas, seja, em raros casos, como tipo micromolecular predominante. A madeira dos ramos de uma espécie de Aniba colhida em Marapi, no alto rio Paru do Oeste, nas proximidades de Tiriós (Pará), constitui um caso desta índole. Contém 5,7,8,3',4',5'-hexametoxiflavona, obtida pela primeira vez de fonte natural.

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