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DISTRIBUTION OF COUMARINS IN AMAZONIAN *BROSIMUM* SPECIES*

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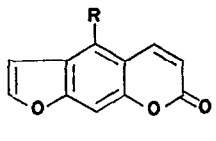
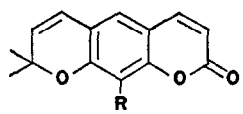
Abstract—Fourteen *Brosimum* species (Moraceae) contain either pyranocoumarins or furocoumarins, besides *O*-prenylbrosiparin which gives rise to brosiprenin by a Claisen type rearrangement.

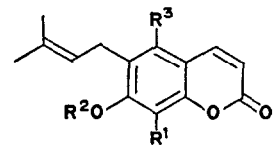
TWO BRAZILIAN *Brosimum* species have so far been examined phytochemically: *B. gaudichaudii* Trécul whose roots were reported to contain psoralen (Ia)[2] and bergapten (Ib),[2,3] and *B. rubescens* Taubert whose trunk wood contains xanthyletin (IIa), luvangetin (IIb), 7-demethylsuberosin (IIIa), brosiparin (IIIb) and brosiprenin (IIIc).[4] It was considered that the biosynthesis of IIIc might involve a Claisen type rearrangement, in spite of the fact that *O*-prenylbrosiparin (IIId) had not been detected in the extract of *B. rubescens*.[4] The hypothesis, however, seemed so attractive that a search for the putative precursor IIId was undertaken in wood samples of 13 Amazonian *Brosimum* species. As far as TLC comparisons of extracts obtained from preserved voucher specimens merit confidence, the analysis of the results (Table 1) leads to the following comments.



	R
(Ia)	H
(Ib)	OMe



	R
(IIa)	H
(IIb)	OMe



	R^1	R^2	R^3
(IIIa)	H	H	H
(IIIb)	OH	Me	H
(IIIc)	OH	Me	Pre
(IIId)	OPre	Me	H

Phytochemically, the examined *Brosimum* species fall into two sections characterized by the predominant presence either of pyranocoumarins or of furocoumarins. Prenylcoumarins are, of course, precursors to both types of compounds, as indicated by the constant quantitative ratio of xanthyletin (IIa) and 7-demethylsuberosin (IIIa) in most extracts, as well as the co-occurrence of luvangetin (IIb) and brosiparin (IIIb). *O*-Prenylbrosiparin (IIId) was detected in the particular species of the pyranocoumarin section which contains

* Part IV in the series "Plant Chemosystematics and Phylogeny". For Part III see Ref. 1.

[1] O. R. GOTTLIEB, *Phytochem.* **11**, 1537 (1972).
[2] G. L. POZETTI, *Rev. Fac. Farm. Odont. Araraquara Brasil* **3**, 215 (1969).
[3] O. ARAÚJO LIMA and O. RIBEIRO, *Anais Assoc. Brasil. Quím.* **26**, 67 (1967).
[4] R. BRAZ FILHO, A. FARIAS MAGALHÃES and O. R. GOTTLIEB, *Phytochem.* **11**, 3307 (1972).

exceptional amounts of brosiparin (IIIb) and brosiprenin (IIIc), and is ubiquitous in the furocoumarin section where its transformation into brosiparin (IIIb) and brosiprenin (IIIc) seems to be blocked. The biosynthetic association of IIIb and IIIc with *O*-prenylbrosiparin is thus a reasonable postulate. Indeed, both in nature and in the laboratory through pyrolysis of *O*-prenylbrosiparin (IIId),[4] brosiparin (IIIb) and brosiprenin (IIIc) are formed in substantially equal amounts.

TABLE 1. $CHCl_3$-EXTRACTS OF THE WOOD OF AMAZONIAN *Brosimum* SPECIES: RELATIVE AREA OF TLC (SiO_2, BENZENE-ACETONE, 8:2) SPOTS

Species	Collection site	1	2 IIIa	3	4 IIIb IIIc	5 Ia Ib	6 IIa IIb	7 IIId	8
B. parinarioides Ducke INPA 3876/21178	Ducke Reserve, Manaus	5	50	0	300	0	100	10	10
B. guianense Ducke INPA 1311/10350	Navio Mt., Amapá	10	10	0	80	0	100	0	50
B. potabile Ducke INPA 1200/-	Cachoeira Alta, Manaus	10	20	0	80	0	100	0	50
B. rubescens Taubert INPA 2020/-	Ducke Reserve, Manaus	15	15	0	20	0	100	0	10
B. paraense Ducke INPA 3869/21171	Ducke Reserve, Manaus	15	15	0	20	0	100	0	10
B. brevipedunculatum Ducke INPA 551/5086	Ducke Reserve, Manaus	10	10	0	0	0	100	0	50
B. lanciferum Ducke INPA 3886/-	Ducke Reserve, Manaus	10	20	0	0	0	100	0	50
B. lecointei Ducke INPA 2057/14252	Ducke Reserve, Manaus	10	0	0	0	0	100	0	10
B. utile (H.B.K.) Pittier INPA 1386/10728	Rio Preto, Manaus	10	0	0	0	0	100	0	10
B. melanopotamicum Berg IPEAN E-002682/115165	Rio Negro, Amazonas	0	0	0	0	100	0	2	0
B. acutifolium Huber INPA 3619/-	Manaus-Itacoatiara Road, km 109	50	0	0	0	100	0	10	0
B. amplicoma Ducke IPEAN F-34936/106008	Belém-Brasilia Road, km 145	20	15	50	0	100	0	5	0
B. krukovii Standl. IPEAN 6656/39012	Humaitá Rio Madeira	20	15	50	0	100	0	5	0

Visualization of spots Nos. 1 (R_f 0·24): blue fluorescence in UV, 2 (R_f 0·30): blue fl. in UV, 3 (R_f 0·42): green fl. in UV, 4 (R_f 0·48): brown colour with I_2-vapour, 5 (R_f 0·49): green fl. in UV, 6 (R_f 0·50): blue fl. in UV, 7 (R_f 0·58): green fl. in UV, 8 (R_f 0·90): brown col. with I_2-vapour. Spots Nos. 4, 5 and 6 were formed by mixtures of two compounds each. The approximate relative proportion of the constituents were determined for spot No. 4 (IIIb–IIIc, 1:1) with all samples using $CHCl_3$ for their separation by TLC (the R_f value for IIIc is slightly higher than for IIIb); and for spots Nos. 5 (Ia–Ib, 8:1) and 6 (IIa–IIb, 20:1) only for *B. gaudichaudii*[3] and for *B. rubescens*[4] through their isolation by column chromatography. INPA—Instituto Nacional de Pesquisas da Amazônia, Manaus, IPEAN—Instituto de Pesquisas Agropecuárias do Norte, Belém. Nos. of voucher specimens: wood collection/herbarium.

We were not able to locate a wood sample of *B. uleanum* Kruk. Results on all other recognized Amazonian *Brosimum* species, however, are listed in Table 1. This records identical chromatograms for 5 pairs of extracts, a fact which suggests that a revision of the genus, already announced by Berg,[5] is necessary.

[5] C. C. BERG, *Acta Bot. Neerl.* **19**, 326 (1970).