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NEOLIGNANS FROM *LICARIA RIGIDA**

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Key Word Index—*Licaria rigida*; Lauraceae; benzodioxane neolignans; eusiderins.

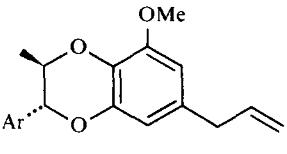
Abstract—Trunk wood of *Licaria rigida* contains the neolignans eusiderin, eusiderin-B, canellin-A and canellin-C.

Trunk wood of *Licaria rigida* Kosterm. (Lauraceae), collected at the Ducke Forest Reserve, near Manaus, Amazonas State, contains besides sitosterol, the neolignans (for nomenclature see [2]) eusiderin (**1a**), eusiderin-B (**1b**), canellin-A (**2a**) and canellin-C (**2b**). Eusiderin-B has not yet been found in any other plant, while **1a** is known to occur in species of the genera *Aniba*, *Eusideroxylon*, *Licaria* (Lauraceae) [2] and *Virola* (Myristicaceae) [3]. The canellins were isolated originally from another *Licaria* species [4].

The structural relationship between **1a** [$C_{18}H_{14}O_2(OMe)_4$] and **1b** [$C_{18}H_{15}O_2 \cdot OMe \cdot O_2CH_2$] was easily established by ^1H and ^{13}C NMR (Table 1) as well as mass spectral comparisons. A report on the sole question which is not trivial, namely the choice between the natural benzodioxane types **1** and the unnatural analogue **3**, has appeared previously [5].

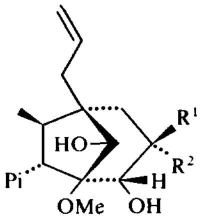
EXPERIMENTAL

Isolation of constituents. A specimen of *L. rigida* from the Ducke Forest Reserve, near Manaus, AM, was identified by Prof. K. Kubitzki, Hamburg University. Voucher: Herbarium INPA, Manaus, 43576. A trunk wood sample, reduced to powder (8.5 kg), was percolated with C_6H_6 at room temp. A powdery mixture of extract (100 g) and Si gel (150 g) was washed successively with C_6H_6 and $CHCl_3$. Evaporation of the C_6H_6 soln gave a product (16 g) which was chromatographed on Si gel (500 g). Elution was performed initially with C_6H_6 and then with solvent mixtures of gradually increasing polarity. Evaporation of the eluates (150 ml each) gave 344 fractions. Fractions 1–12 were composed of aliphatic material. Fractions 13–33 were purified by re-chromatography and crystallization from petrol to give **1b** (1.5 g). TLC (Si gel) of fractions 34–72 gave a mixture of **1b** and sitosterol (0.1 g). Fractions 73–110 were purified by re-chromatography and crystallization from MeOH to yield sitosterol (2.5 g). TLC (Si gel) of fractions 111–192 gave **1a** (0.4 g). No pure compounds were isolated from later fractions. Evaporation of the $CHCl_3$ soln gave a product (34 g) which was chromatographed on Si gel (330 g). Elution, initially with $CHCl_3$

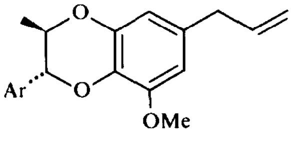


1a Ar = Tp
1b Ar = Pi

Tp, Tri-*O*-methylpyrogallyl; Pi, Piperonyl.



2a R¹ = OMe, R² = H
2b R¹ = R² = O



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* Part LXIII in the series "The Chemistry of Brazilian Lauraceae". For Part LXII—see ref. [1]. Based on part of the M.S. thesis submitted by M.G. de C. to Universidade Federal Rural do Rio de Janeiro (1980).

Table 1. ^{1}H (60 MHz) and ^{13}C (25.2 MHz) NMR spectral data for eusiderin (**1a**) and eusiderin-B (**1b**)*

	^{1}H			^{13}C	
Position	**1a** [6] δ	**1b** δ	Multiplicity, J(Hz)	**1a** [7] δ	**1b** δ
1				132.4†	130.7
2	6.62	6.90	*s*	104.4	107.1
3		6.90	*s*	153.4	147.9
4				138.3	147.9
5				153.4	108.2
6	6.62	6.90	*s*	104.4	121.3
7	4.58	4.58	*d*, 8	81.0	80.6
8	3.9–4.0	3.9–4.0	*m*	74.0	74.1
9	1.30	1.30	*d*, 6	17.3	17.2
1′				132.2†	132.2
2′	6.40†	6.50†	*d*, 2	109.4	109.4
3′				143.8	144.2
4′				131.1	131.1
5′				148.4	148.4
6′	6.52†	6.51†	*d*, 2	104.5	104.5
7′	3.32	3.30	*d*, 7	39.9	40.0
8′	5.6–6.3	5.6–6.3	*m*	137.1	137.2
9′	4.9–5.3	4.9–5.3	*m*	115.6	115.6
OMe-3			*s*	56.1	
OMe-4	3.90		*s*	60.7	
OMe-5	3.90		*s*	56.1	
OMe-5′	3.90	3.90	*s*	56.1	56.1
O_2CH_2		6.00	*s*		101.1

* In $CDCl_3$; TMS as internal standard.

† Signals may be interchanged.

and then with solvent mixtures of gradually increasing polarity, gave mixtures of **2a** and **2b** (1 g) from which small quantities of the pure compounds were separated by TLC.

Identification of known compounds **1a** [8], **2a** and **2b** [4] were performed by direct comparison with authentic samples.

rel-(7S,8R)-$\Delta^{8'}$-3,4-*Methylenedioxy-5′-methoxy*-7.O.3′,8.O.4′-*neolignan* (**1b**). Colourless crystals, mp 82–84° (petrol) (Found: C, 70.81; H, 6.02. $C_{20}H_{20}O_5$ requires: C, 70.60; H, 5.88 %). $\lambda_{\max}^{\mathrm{EtOH}}$ nm: 240, 283 (ε 7250, 4300). $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1600, 1500, 1450, 1350, 1320, 1250, 1200, 1150, 1120, 950, 930, 740. MS m/z (rel. int.): 340 (28) M^+, 298 (2), 205 (5), 191 (9), 178 (5), 162 (100), 150 (5), 135 (7), 121 (7).

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