Phytochemistry, Vol. 23, No. 3, pp. 667–669, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

STRUCTURAL CONFIRMATION OF NEOLIGNANS*

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(*Received* 8 *June* 1983)

Key Word Index—Neolignans; canellin-A; macrophyllin-B; eusiderin; X-ray analysis.

Abstract—The proposed structures of the neolignans canellin-A, macrophyllin-B and eusiderin were confirmed by X-ray crystallographic analyses.

INTRODUCTION

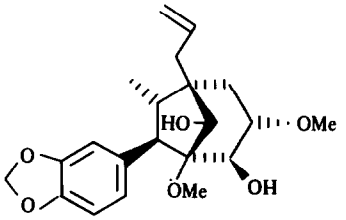
The structures of benzofuranoid neolignans have been confirmed by direct X-ray crystallographic analyses [2]. Confirmation of the constitutions and relative stereochemistries of bicyclo[3.2.1]octanoid and benzodioxane neolignans is provided in the present paper. Among the former, canellin-A (**1**) from *Licaria canella* [3] and *Ocotea aciphylla* [4] and the MnO_2 oxidation product (**2**) of macrophyllin-B from *Nectandra* sp. [5] were chosen because they are easily obtained in crystalline form. Among the latter, eusiderin (**3**) from *Eusideroxylon*, *Aniba* and *Licaria* species (Lauraceae [6], as well as *Virola* (Myristicaceae) [7] was chosen because a final decision on its structure had been deferred to X-ray analysis [8].

RESULTS AND DISCUSSION

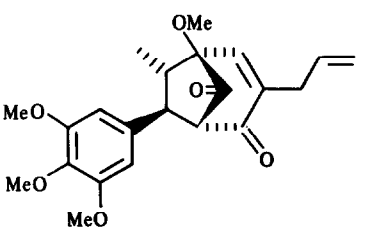
Crystals of **1** are orthorrhombic, space group $P2_12_12_1$ with $a = 12.988$ Å, $b = 10.100$ Å, $c = 14.532$ Å and $Z = 4$. Crystals of **2** are monoclinic, space group $P2_1$ with $a = 10.869$ Å, $b = 6.940$ Å, $c = 13.988$ Å, $\beta = 95.18°$ and $Z = 2$. Crystals of **3** are triclinic, space group P1, with $a = 5.388$ Å, $b = 13.263$ Å, $c = 15.143$ Å, $\alpha = 109.11°$, $\beta = 96.86°$, $\gamma = 91.87°$ and $Z = 2$. The intensities of 1738 (**1**), 2147 (**2**) and 4322 (**3**) independent reflections were measured with an automatic four-circle diffractometer using graphite monochromated CuKα radiation. The phase problem was solved by direct methods. The E-map of the best set gave the position of 25 (**1**) and 15 (**2**) atoms. Difference Fourier maps were used to locate the additional atoms. The crystals of **3** present two molecules per unit cell and a pseudo-symmetry centre. Hence the two molecules are in a near symmetric position. Through the use of a MULTAN programme 28 atoms of one molecule were located. Difference Fourier maps were used to locate all the atoms of the second molecule. Several cycles of full matrix least-squares refinement considering anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the hydrogen atoms gave the final residual *R* factors 0.069 (**1**), 0.082 (**2**) and 0.076 (**3**). The probable locations of the28 (**1**), 26 (**2**) and 26 (**3**) hydrogen atoms were determined by orbital geometric considerations. Details of the X-ray structural analyses will be published elsewhere.

The molecular structures found in the crystals of **1**, **2** and **3** are shown in Figs. 1, 2 and 3 respectively and are

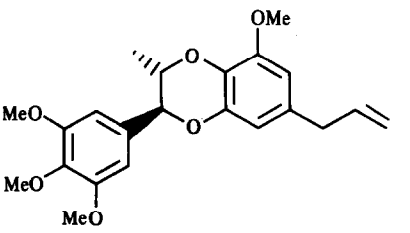
*Part LXXIII in the series "The Chemistry of Brazilian Lauraceae". For Part LXXII see ref. [1].



1



2



3

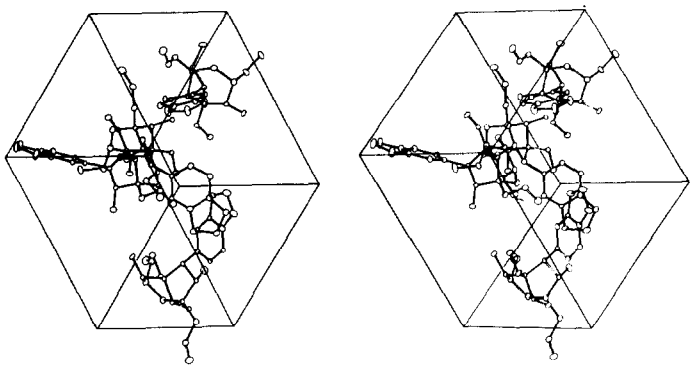


Fig. 1. Stereoscopic view of **1**.

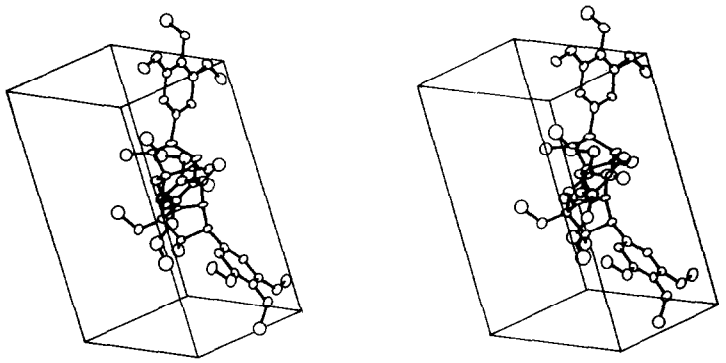


Fig. 2. Stereoscopic view of **2**.

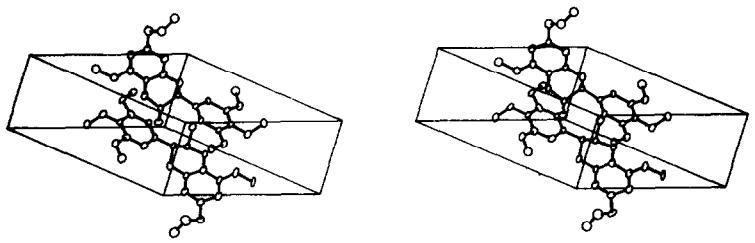


Fig. 3. Stereoscopic view of **3**.

consistent with the structures proposed by spectrometric methods.

Acknowledgements—We are indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Financiadora de Estudos e Projetos (FINEP) for fellowships and financial aid.

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