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SHORT COMMUNICATION

**Phytochemical investigation from wood residues of
Dalbergia spruceana Benth**

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Abstract: *Dalbergia spruceana* Benth (Fabaceae: Papilionoideae), known in the Brazilian Amazon as “jacarandá-do-pará” recognized for the natural resistance of its wood has little scientific information about its secondary metabolism. In this paper, we report a phytochemical study of the wood residues of *D. spruceana* using classical chromatographic techniques. Thus, the chromatographic fractionation of methanolic extract resulted in the isolation of phenylpropanoid, isoflavonoids of different types (pterocarpan, isoflavonol, isoflavan, isoflavone) in addition to a neoflavonoid. A new isoflavonoid with an oxygenation pattern not previously reported was elucidated as 8,4,2'-trihydroxy-7,4'-dimethoxyisoflavonol. The structures of all the isolated compounds were determined by using 1D- and 2D-NMR techniques, mass spectrometry ESI-MS and by comparison with literature data. Most of the compounds that were identified are isoflavonoids, which are types of flavonoids that are especially recognized for their contribution to the natural resistance of the wood.

Keywords: Fabaceae; flavonoid; pterocarpan; neoflavonoid; natural resistance.

INTRODUCTION

Dalbergia spruceana Benth (*Miscobolium spruceanum* Benth, Fabaceae: Papilionoideae) is a species that is native to northern South America, and is known in the Brazilian Amazon as “jacarandá-do-pará”. It has registered occurrence in the states of Amazonas, Amapá, Rondônia and Pará^{1,2} and has great economic potential because its wood can be used for special purposes such as the manufacture of luxury furniture, decorative objects and musical instruments. It

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has medium to fast growth and easy propagation and is therefore recommended for reforestation and forest restoration programs.³

There is little scientific information about the secondary metabolism of *D. spruceana*. The chemical composition of the genus *Dalbergia* is represented mainly by phenolic compounds, which are found in different vegetative parts.⁴ The planting of this species is very promising because it has propagation potential, economic potential because the wood has natural resistance, and it is also sought after for making string instruments, among other purposes. Woods with natural strength often have interesting secondary metabolites that have promising bioactive compounds.^{5–10} In this paper, we evaluated the secondary metabolites extracted from the heartwood of *D. spruceana* using classical chromatographic techniques.

EXPERIMENTAL

General experimental procedures

NMR spectra were recorded on a Bruker Fourier 300 UltraShield (300 MHz for ¹H- and 75 MHz for ¹³C-NMR) and Bruker Avance III 400 (400 MHz for ¹H- and 100 MHz for ¹³C-NMR) spectrometers, at a temperature of 25 °C. The spectra were referenced to the residual solvent signal. HRESIMS data were obtained on a MicroTOF-Q-II, Bruker Daltonics, the ESI was operated in the positive and negative mode, and nitrogen was used as the drying gas (4.0 L/min) and nebulizing gas at 0.4–0.6 bar. Mass-to-charge ratio was scanned in the *m/z* 50–980 range. For column chromatography (CC), silica gel (particle size 70–230 and 230–300 mesh, Sigma–Aldrich), hexane, ethyl acetate, acetone and methylene chloride were used. Analytical and preparative TLC was carried out on silica gel 60 GF254 20 cm×20 cm plates, with a layer thickness of 0.25 mm (Merck).

Acquisition and identification of wood residues

D. spruceana from wood residues was supplied to the Wood Technology Laboratory of the National Institute for Amazonian Research (INPA) by a luthier. The largest residues had been previously evaluated for their technological properties and the smaller residues resulting from these procedures became available for phytochemical studies. The identification of the wood samples was done via macroscopic comparisons with standard samples from the xylotheque at INPA (INPA-Xil N0 4329).

Extraction and isolation

The residues were chopped and ground (1.117 g) and submitted to maceration at room temperature with *n*-hexane and then methanol (seven days in each solvent), which provided yields of 0.05 and 3.67 %, respectively. The methanol extract (19 g) was purified on silica gel CC using gradient elution with Hexane/EtOAc (98:2 to 60:40) to obtain 90 fractions. The fraction 46 (20 mg) was purified with preparative TLC using mixture of CH₂Cl₂/acetone (98:2) for isolation of compound **1** (10 mg). The additional purification of the fraction 61 (70 mg) with silica gel column chromatography (230–400 mesh; 46 cm×2.6 cm) and CH₂Cl₂ as eluent lead to further purification of subfractions 15 and 17 and final isolation of compounds **3** (3.5 mg) and **4** (5.5 mg). The fractions 71 (52.0 mg) and 73 (80.0 mg) were subjected to additional silica gel CC with mixture of CH₂Cl₂/acetone (98:2) as eluent for obtaining compounds **5**

(10.0 mg) and **6** (3.5 mg). Fractions 50 (970 mg) and 83 (18.1 mg) represent the solid compounds **2** (805 mg) and **7** (5.8 mg), respectively.

RESULTS AND DISCUSSION

From the methanol extracts of *Dalbergia spruceana* Benth wood residues five known compounds as phenylpropanoid elemycin (**1**),¹¹ flavonoids maackiain (**2**),¹² 8-hydroxy-7-methoxy-3',4' methylenedioxypterocarpane (**3**),^{13,14} dalbergine (**5**),¹⁵ 3',4'-dihydroxy-7,8,2'-trimethoxy-isoflavan (**6**), pseudobaptigenin (**7**)¹⁶ and one (**4**) previously undescribed isoflavonoid were isolated. The isolated compounds were identified using 1D (¹H and ¹³C) and 2D NMR (HSQC and HMBC), HRESIMS spectra and by comparison with the literature data (Fig. 1). HMBC correlations provide identification of flavonoids and reveal the oxygenation patterns, Fig. 1 (for additional data see Supplementary material to this paper).

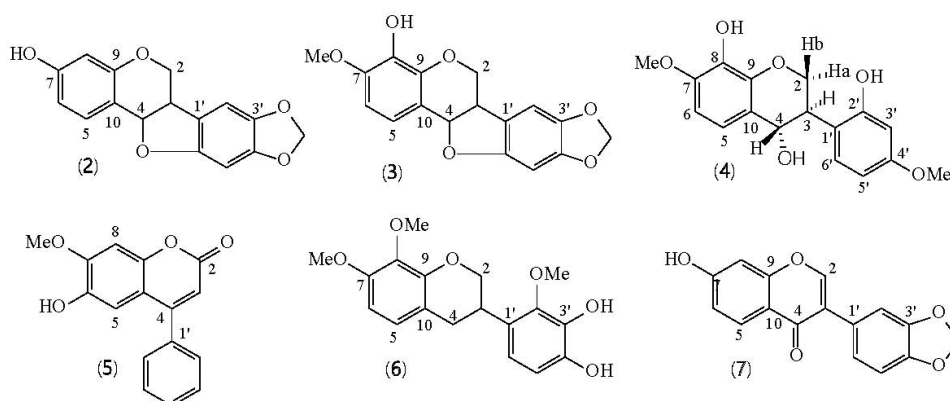


Fig. 1. Structures of the flavonoids from the wood residues of *Dalbergia spruceana*.

The molecular formula of compound **4**, C₁₇H₁₈O₇, was determined based on the HRESIMS ion [M+Na]⁺ at *m/z* 341.0994. The ¹H-NMR spectrum revealed an aromatic system of ABX-type spins observed by the set of hydrogen signals in the δ region 7.26–6.38 ppm, in addition to the *ortho*-coupled signals at δ 6.97 and 6.69 ppm (Table I). The signals of oxymethylene at δ 4.34 and 3.63 ppm, methine at δ 3.65 ppm and oxymethine at δ 5.58 ppm were indicative of 4-hydroxyisoflavanol. The ¹H- and ¹³C-NMR data with significant NOESY and HMBC correlations are presented in Table I. The HMBC correlations H-5/C-4, C-7 and C-9 and H-6'/C-3, C-1' and C-2' revealed oxygenation patterns for A and B rings. The NOESY correlations H-2a/H-3 and H2b/H-4 indicated *trans* orientation of H-3 and H-4. Based on 1D and 2D NMR data, the structure of new isoflavonoid was labelled as 8,4,2' trihydroxy-7,4'-dimethoxyisoflavanol.

In the Fabaceae family, the isoflavonoids are restricted almost entirely to Papilionoideae¹⁷ and are especially recognized for their contribution to the natural resistance of the wood containing them, such as is the case of *D. spruceana*.

TABLE I. ¹H- and ¹³C-NMR spectroscopic data (δ / ppm) for compound **4** in (CD₃)₂CO; ¹H-NMR (300 MHz, *J* / Hz); ¹³C-NMR (75 MHz)

H/C	δ H (<i>J</i> in Hz)	NOESY	δ C	HMBC
2	4.33 <i>m</i> (2a) 3.63 <i>m</i> (2b)	H-3, H4	66.5	C-3, C-4, C-9, C-1'
3	3.65 <i>m</i>	H-2a	39.6	C-2, C-4, C-1'
4	5.58 <i>d</i> (6.7)	H-2b	78.6	C-2, C-3, C-10, C-1'
5	6.97 <i>d</i> (8.5)		120.5	C-4, C-7, C-9
6	6.74 <i>d</i> (8.5)	H ₃ -7	105.8	C-5, C-7, C-8, C-9, C-10
7			148.1	
8			135.1	
9			144.2	
10			114.5	
1'			119.4	
2'			160.8	
3'	6.38 <i>d</i> (2.2)		96.2	C-1', C-4', C-5'
4'			161.2	
5'	6.47 <i>dd</i> (8.1 and 2.2)	H ₃ -4'	106.0	C-1, C-3'
6'	7.26 <i>d</i> (8.1)		125.0	C-3, C-1', C-2'
OMe-7	3.84 <i>s</i>		55.7	C-7
OMe-4'	3.74 <i>s</i>		54.8	C-4'

CONCLUSION

A phytochemical analysis of woody residues of *Dalbergia spruceana* was conducted and resulted in the identification of mainly isoflavonoids of different types (pterocarpan, isoflavonol, isoflavan, isoflavone) in addition to a neoflavonoid. Among these, the compound **4** was previously undescribed. The woody residues of this species of Fabaceae gave us an opportunity to gain further knowledge regarding its secondary metabolism and therefore increase the value of solid residues from *D. spruceana* discarded by the wood processing sector.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/12948>, or from the corresponding author on request.

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ИЗВОД

ФИТОХЕМИЈСКО ИСПИТИВАЊЕ ДРВНИХ ОСТАКАКА *Dalbergia spruceana* BENTH

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Биљка *Dalbergia spruceana* Benth (Fabaceae: Papilionoideae) позната у бразилском Амазону као „jacarandá-do-pará”, иако је препозната по природној отпорности има мало научних информација о њеном секундарном метаболизму. У овом раду описано је фитохемијско испитивање дрвних остатака *D. spruceana* применом класичних хроматографских техника. Хроматографским фракционисањем метанолног екстракта изоловани су фенилпропаноиди, изофлавоноиди различитих типова (птерокарпан, изофлавонол, изофлаван, изофлавонол), као и неофлавоноиди. Нови изофлавоноид, са јединственом структуром која је настала оксидацијом која раније није пријављена, дефинисан је као 8,4,2'-трихидрокси-7,4'-диметоксиизофлавонол. Структуре свих изолованих једињења одређене су коришћењем 1D и 2D NMR техника, масене спектрометрије ESI-MS и поређењем са литературним подацима. Већина идентификованих једињења су изофлавоноиди, типови флавоноида за које је веома познато да доприносе природној отпорности дрвета.

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