

POLAR CONSTITUENTS OF *Euterpe precatoria* ROOTS AND THEIR PLANT GROWTH ACTIVITY

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Euterpe precatoria Mart. (Arecaceae), known popularly as “acai or acai-de-terra-firme,” occurs in Central and Western Amazonia in areas without permanent flooding. Besides other popular medicinal uses, the decoction or syrup of roots of *E. precatoria* are used by people of the Brazilian and Peruvian Amazonian region to heal skin ulceration problems [1, 2]. To our knowledge, there are only two reports on the chemical composition of *E. precatoria* [3, 4]. Previous phytochemical investigations of the genus were reported only for *E. oleaceae* and were focused on the phytochemical composition of the fruit pulp [5].

Dried roots and leaf stalks of *E. precatoria* were collected in the Mini Campus of Amazonas Federal University, Manaus, Brazil in September, 2000. A voucher specimen (No. 7297) is kept in the Herbarium of Amazonas Federal University (Brazil).

The powdered roots (2.3 kg) of *E. precatoria* were extracted with C₂H₅OH at room temperature. To the C₂H₅OH root extract ERE (199.0 g), 350.0 mL of *n*-butanol was added, and the soluble *n*-BuOH fraction (150.5 g after concentration under vacuum) was then chromatographed over a polyamide column (62.0 g), and eluted with H₂O, C₂H₅OH, and EtOAc, with decreasing polarities. Eleven groups of fractions were obtained. G-1 (46.8 g) was submitted to chromatography over silica gel column (202.0 g), employing gradient elution of CH₂Cl₂/C₂H₅OH (9:1, 8:2, 7:3), CH₂Cl₂/C₂H₅OH/H₂O (7:3:0.1 and 7:3:0.3), and C₂H₅OH / H₂O 9:1. The fractions were combined into twelve subgroups. Final purification of G1-2 (1.23 g) on Sephadex LH-20 (eluent CHCl₃/CH₃OH 6:4) was carried out in order to obtain 157.6 mg of pure 1-ethyl- β -D-glucopyranoside (**1**) [6]; G1-3 (3.40 g) also gave, by gel filtration over Sephadex LH-20 (eluent CHCl₃/CH₃OH 6:4), 142.8 mg of 1-methyl- β -D-glucopyranoside (**2**) [7a, b], 12.1 mg of α -and β -L-rhamnose (**3**), and 20.9 mg of α - and β -D-glucose (**4**); the white insoluble solid (8.7 mg) that precipitated after EtOAc addition over G1-6 (1.42 g) was identified as α - and β -L-arabinose (**5**). To confirm whether compound **1** is an artifact formed during the extraction by C₂H₅OH, a small amount of root powder of *E. precatoria* was extracted by CH₃OH at room temperature. Also pure glucose was extracted by 70% C₂H₅OH under the same conditions. The CH₃OH extract and C₂H₅OH solution were examined by TLC with compound **1** as reference. The latter could only be found in the CH₃OH extract. The identification of the compounds was achieved by ¹H and ¹³C NMR and 2D NMR methods and co-TLC with authentic samples. The structures were confirmed by comparing with the previous reported spectral data.

This is the first report on the occurrence of 1-ethyl- or 1-methyl- β -D-glucopyranoside (**1** and **2**) in the Arecaceae family, and the first time that compounds **1–5** have been isolated from *E. precatoria* Mart. Compound **1** was already isolated from Umbelliferae species such as fennel [6], and from *Manihot esculenta* roots, Euphorbiaceae [7]. The α -isomer, one of the four major components of Japanese sake, enhance the formation of differentiated type keratin, which suppresses murine skin barrier disruption caused by ultraviolet B irradiation [8]. This activity is not described for the β -isomer; however, its presence in the root extract of *E. precatoria* can explain the popular use of the plant to heal skin ulceration problems.

The detection of 1-methyl- β -D-glucopyranoside (**2**) in higher plants since the first isolation report from ethanol extracts of white clover foliage [9a] is very rare. There are reports of isolation of **2** from stems of rose species and as a major component of leaves of an alpine herb *Geum montanum* L., Rosaceae [9b, 10]. According to Aubert et al. [10], the physiological significance of 1-methyl- β -D-glucopyranoside in higher plants can be associated with osmotic stress tolerance: considering that *E. precatoria* Mart. is found in Amazonian areas without permanent flooding, it can be hypothesized that the occurrence

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of **2** can be associated with water-stress conditions. There is no report of the presence of **2** in *E. olearaceae*, also known as “acai,” which occurs in areas with permanent flooding.

The effect of alkylglucosides as plant growth promoters (in juvenile and mature plants, as well in seeds) is described in two patents [11a, b]. The phytotoxic activity of compounds **1** and **2** was then evaluated on the growth of radicals and shoots of lettuce (*L. sativa* L.) at the concentrations 10^{-4} , 10^{-6} , and 10^{-8} M, according to the method described by Vieira et al. [12]. The results showed medium radical and shoot growth stimulation compared to the control (~ 32% on radicals at 10^{-8} M) for 1-ethyl- β -D-glucopyranoside (**1**) in all three concentrations. In contrast, the effect of 1-methyl- β -D-glucopyranoside (**2**) on radical and shoot growth was predominantly inhibitory in all tested concentrations.

1-Ethyl- β -D-glucopyranoside (1) [6]: $[\alpha]_D^{25} -17.0^\circ$ (*c* 1.87, CH_3OH); lit. [6]: $[\alpha]_D -26.4^\circ$ (*c* 0.8, CH_3OH). ^1H NMR (400 MHz, CD_3OD , δ , ppm, J/Hz): 4.27 (d, $J = 7.8$, H-1), 3.18 (t, $J = 8.6$, H-2), 3.38 (t, $J = 8.6$, H-3), 3.30 (t, $J = 8.6$, H-4), 3.26 (dd, $J = 9.5, 1.9$, H-5), 3.68 (dd, $J = 11.9, 5.1$, H-6a), 3.86 (dd, $J = 11.8, 1.9$, H-6b), 3.60 (qd, $J = 9.5, 7.1$, H-7a), 3.96 (qd, $J = 9.5, 7.1$, H-7b), 1.24 (t, $J = 7.1$, H-8). ^{13}C NMR (100 MHz, CD_3OD , δ , ppm): 104.2 (C-1), 75.2 (C-2), 78.2 (C-3), 72.0 (C-4), 78.0 (C-5), 62.9 (C-6), 66.3 (C-7), 15.5 (C-8).

1-Methyl- β -D-glucopyranoside (2) [7]: $[\alpha]_D^{25} -136.0^\circ$ (*c* 1.87, CH_3OH). ^1H NMR (400 MHz, CD_3OD , δ , ppm, J/Hz): 4.67 (d, $J = 3.7$, H-1), 3.38 (m, H-2), 3.61 (t, $J = 9.3$, H-3), 3.28 (t, $J = 9.3$, H-4), 3.51 (m, H-5), 3.80 (dd, $J = 11.8, 2.2$, H-6a), 3.67 (dd, $J = 11.8, 5.7$, H-6b), 3.40 (s, 3H-7). ^{13}C NMR (100 MHz, CD_3OD , δ , ppm): 101.1 (C-1), 73.4 (C-2), 75.0 (C-3), 71.5 (C-4), 73.4 (C-5), 62.4 (C-6), 55.4 (C-7).

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