Anthocleistol, a New Secoiridoid from *Anthocleista nobilis*

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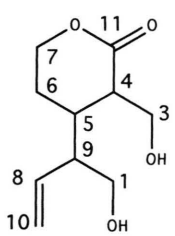
The root bark of *Anthocleista nobilis* is used in Nigeria against liver diseases, malaria and gastrointestinal worms. The secoiridoid pattern of the root bark was investigated. Sweroside and Anthocleistol a new secoiridoid have been isolated from the methanol extract. The structures were elucidated from spectroscopic data.

Introduction

Anthocleistia nobilis G. Don (Loganiaceae), a small tropical plant known as "uko nkirisi" in Igbo language has a good reputation as a herbal drug for liver protecting effects. Decoctions of the root bark are commonly used to treat diabetes mellitus, gastrointestinal worms, malaria and jaundice at Mbano in Imo State, Nigeria (Madubunyi *et al.,* 1993). Although the occurrance of secoiridoids has been reported in the genus *Anthocleistia* (Koch *et al.,* 1964; Chapelle, 1973; Weber, 1974; Chapelle, 1974; Chapelle, 1976a; Chapelle, 1976b; Cornelis and Chapelle, 1976), the secoiridoids in the species *A. nobilis* have not been investigated.

This paper reports the isolation and characterization of sweroside (**2**) and the new secoiridoid anthocleistol (**1**) from the root bark of the title species.



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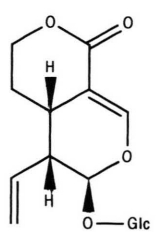

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Materials and Methods

Solvents used for spectral measurements were CD_3OD [^1H NMR (400 MHz), ^{13}C NMR (100 MHz)], MeOH ($[\alpha]_D^{20}$).

Cl^+MS: direct inlet, 120 eV.

Plant material

The plant material was collected in June 1993 from Nsukka (Enugu State, Nigeria) and identified as *Anthocleista nobilis* G. Don by J. M. Ekekwe of the Department of Botany, University of Nigeria, Nsukka. A voucher specimen is retained in the Department.

Extraction and isolation

The fresh root bark of *A. nobilis* was dried at room temperature. 2.1 kg of the powdered plant material was extracted with Et_2O and MeOH. The evaporated methanol extract (470 g) was partitioned between EtOAc and H_2O. The H_2O soluble fraction was extracted with n-BuOH. After the removal of solvents the fractions were lyophilized to afford the ethyl acetate- (43.5 g), butanol- (248.9 g) and the water fraction (151.1 g). 5.3 g of the ethyl acetate soluble fraction were separated by vacuum liquid chromatography (VLC) (Targett *et al.,* 1979) on RP-8 silica gel (MeOH/H_2O gradient) to give 3 fractions. Fraction 2 was further purified by VLC on diol-modified silica gel using a gradient of ethyl acetate/methanol to afford **2** (579 mg) and a fraction containing compound **1.** This fraction was purified by HPLC on diol silica gel (Merck, Lichrospher, 5 µm, hexane/ethyl acetate (40 + 60 volume parts)) to obtain 45 mg of compound **1.**

Anthocleistol (**1**)

IR ν_{max} cm^{-1}: 3400, 2910, 1720, 1645, 1485, 1410, 1270, 1195, 1075, 1055, 1005, 930. $[\alpha]_D^{20}$: −21.97°. ^{13}C NMR (CD_3OD) δ_C: 27.2 (t, C-6), 35.3

(d), 49.0 (d), 51.0 (d), 63.5 (t), 64.0 (t), 69.0 (t, C-7), 118.4 (t, C-10), 138.9 (d, C-8), 176.3 (s, C-11). Cl^+MS *m/z:* 201.2 $[M + H]^+$ ($C_{10}H_{16}O_4$).

Results and Discussion

Compounds **1** and **2** were isolated from the methanol extract of the root bark of *A. nobilis*. **2** was identified as sweroside according its ^1H NMR, ^{13}C NMR and MS data (van der Sluis and Labadie, 1981). Compound **1** was obtained as a brown oily substance. The IR spectrum showed the presence of hydroxyl groups (3400 cm^{-1}), aliphatic structures (2910 cm^{-1}) and a lacton ring (1720 cm^{-1}). The molecular ion peak $[M + H]^+$ at 201.2 was in agreement with the molecular formula of $C_{10}H_{16}O_4$. The ^1H NMR and ^{13}C NMR data were similar to the iridoid part of sweroside suggesting a non-glucosylated secoiridoid structure. ^{13}C NMR and DEPT data indicated the presence of a carboxyl group or lactone (δ_C 176.3 s, C-11), a partial structure consisting of a monosubstituted ethylene (δ_C 138.9 (d, C-8), 118.4 (t, C-10)) and three aliphatic methin carbons (δ_C 51.0, 49.0, 35.3). The signals at δ_C 69.0, 64.0, 63.5 and 27.2 were attributed to four methylene carbons. The former three appear with oxygene shift indicating CH_2OR groups. The structure of **1** and the assignment of the ^1H NMR signals could be finally obtained from the analysis of the H-H COSY spectrum. The signal of the olefinic proton H-8 appears at δ_H 5.77 (m) and couples with the olefinic methylene protons H-10a (δ_H 5.15, dd, $J = 1.6$, 11.7 Hz) and H-10b (δ_H 5.18, dd, $J = 1.7$, 5.5 Hz) as well as with H-9 (δ_H 2.28) which in turn couples with the hydroxymethyl protons at C-1 (2H, δ_H 3.63, m). The signals of H-9 and H-5 are partly overlapped (2H, δ_H 2.28, m). The signal of H-4 appears at δ_H 2.70 (m) and couples with H-5 and the hydroxymethyl protons H-3a (δ_H 3.73, dd, $J = 4.0$, 10.9 Hz) and H-3b (δ_H 3.96, dd, $J = 3.9$, 10.8 Hz). The signal at δ_H 4.34 (2H, m) is attributed to H-7a and H-7b. The remaining two multipletts at δ_H 1.73 (m) and δ_H 1.98 (m), both coupling with H-7a,b and H-5 respectively, correspond to the methylene protons H-6a and H-6b. Thus, the structure **1** was proposed for the new secoiridoid, named anthocleistol.

Table I. ^1H NMR spectral data of compound **1** (CD_3OD).

	1
H-1a,b	3.63 m
H-3a	3.73 dd (10.9, 4.0 Hz)
H-3b	3.96 dd (10.8, 3.9 Hz)
H-4	2.70 m
H-5, H-9	2.28 m
H-6a	1.73 m
H-6b	1.98 m
H-7a,b	4.34 m
H-8	5.77 m
H-10a	5.15 dd (11.7, 1.6 Hz)
H-10b	5.18 dd (5.6, 1.7 Hz)

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