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(−)-ARISTOTETRALONE: A 4-ARYLTETRALONE FROM *ARISTOLOCHIA CHILENSIS*

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Key Word Index—*Aristolochia chilensis*; Aristolochiaceae; 4-aryltetralones; (−)-aristotetralone; lignans.

Abstract—*Aristolochia chilensis* has yielded the new 4-aryltetralone (−)-aristotetralone. The relative configuration was elucidated using NMR NOE measurements.

INTRODUCTION

The 4-aryltetralones are a small group of lignans found in *Virola sebifera* (Myristicaceae) [1, 2], and in *Schisandra henryi* and *S. sphenanthera* (Schisandraceae) [3, 4].

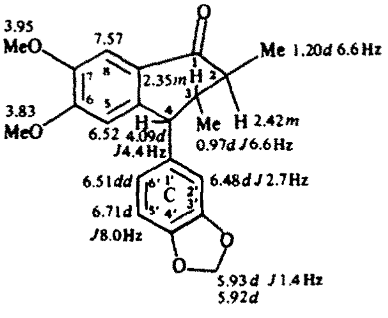
Lately, an investigation of the roots of *Aristolochia chilensis* Miers resulted in the isolation of four 2,5-diphenyltetrahydrofuranoid lignans [5]. We have now studied some of the minor components of this plant, from which we have obtained the new 4-aryltetralone, (−)-aristotetralone (1).

RESULTS AND DISCUSSION

(−)-Aristotetralone (1), $C_{21}H_{22}O_5$, was obtained as an optically active, amorphous solid, $[\alpha]_D - 164.3°$ (*c* 1.54, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1665 cm^{-1} (C=O); λ_{max}^{MeOH} 233, 280 nm (log ε 4.33, 4.00). Its mass spectrum, contained a significant fragment at *m/z* 298 $[M - 56]^+$, typical of tetralin lignans [6].

The 360 MHz ($CDCl_3$) NMR spectrum is quoted around structure 1. The relative positions of the methylenedioxy and the two methoxyl substituents, as well as the relative configurations at C-2, C-3 and C-4, were settled through decoupling experiments and a complete NMR NOE study.

Reciprocating NMR NOE's were observed between the C-7 methoxyl (δ3.95) and H-8 (δ7.57); and between the C-6 methoxyl (δ3.83) and H-5 (δ6.52). Additionally, irradiation of H-5 caused a 16% increase of the H-4 aliphatic doublet (δ4.09). Very significantly, reciprocating NOE's were also noted between the aromatic H-2′ (δ6.48) and the aliphatic H-2 (δ2.42) and Me-3 (δ0.97) signals, thus establishing the stereochemical relationships between C-2, C-3 and C-4.



1

It should be noted in conclusion that structure 1 represents only the relative configuration of (−)-aristotetralone.

EXPERIMENTAL

Extraction and isolation. A. chilensis (1.9 kg, dry roots) was collected in Lo Prado Pass, 10 km from Santiago, in November 1984. Voucher specimens were deposited in the herbarium of the Natural History Museum in Santiago. The plant was dried, powdered, and extracted with petrol at room temp. The extracts were concentrated to give a residue of 93 g, a part (5 g) of which was fractionated by CC over silica gel, using hexane gradually enriched with EtOAc. The fractions were monitored by TLC on silica gel using as solvent systems hexane–EtOAc (4:1) and $CHCl_3$, and spraying with 33% H_2SO_4. Final purification was on silica gel TLC glass plates, using $CHCl_3$.

(−)-*Aristotetralone* (1). Amorphous solid, 16 mg; IR $\nu_{max}^{CHCl_3}$: 1662, 1595 cm^{-1}; MS *m/z* (rel. int.): 354 $[M]^+$ (100), 339 (14), 299 (17), 298 (83), 267 (11), 255 (15), 165 (5), 149 (16); ^{1}H NMR NOE: H-8 to MeO-7, 16%; MeO-7 to H-8, 35%; MeO-6 to H-5, 25%; H-5 to MeO-6, 8%; H-4 to H-5, 25%; H-5 to H-4, 16%; H-4 to H-6′, 10%; H-6′ to H-4, 16%; H-2 to H-2′, 14%; H-2′ to H-2, 12%; H-2 to Me-3, 5%; Me-3 to H-2, 11%; Me-3 to H-2′, 12%; H-2′ to Me-3, 2%; Me-3 to H-4, 8.5%; H-4 to Me-3, 2%; Me-2 to H-3, 10%; H-3 to Me-2, 5%; Me-2 to H-2, 10%; H-2 to Me-2, 6%; H-3 to H-4, 7.5%; H-4 to H-3, 8%; Me-3 to H-3, 11%; H-3 to Me-3, 5%.

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A CHROMONE FROM THE ROOT-BARK OF *HARRISONIA ABYSSINICA*

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Key Word Index—*Harrisonia abyssinica*; Simaroubaceae; chromone; 2-methylalloptaeroxylin; 2-hydroxymethylalloptaeroxylin.

Abstract—In addition to the known 2-methylalloptaeroxylin, a new chromone has been isolated from a diethyl ether extract of the root-bark of *Harrisonia abyssinica*; its structure was elucidated as 2-hydroxymethylalloptaeroxylin.

INTRODUCTION

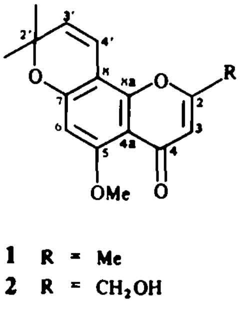
Owing to the antibacterial and antifeedant properties of *Harrisonia abyssinica* Oliv. against the African army-worm *Spodoptera exempta* and the Southern species *S. eridania*, several investigations into its chemical constituents have been reported [1–4]. Since phytochemical differences between samples of *H. abyssinica* collected from different regions have been found [4], a chemical investigation of Guinean samples was undertaken.

RESULTS AND DISCUSSION

A diethyl ether extract of the air dried root-bark of *H. abyssinica* was subjected to column chromatography and preperative thin-layer chromatography (TLC) on silica gel. Two chromones were isolated among the less polar fractions; they gave unusual positive reactions on TLC after being sprayed successively with Dragendorff and iodoplatinate reagents. Compound **1** gave a molecular ion at 272 corresponding to the molecular formula $C_{16}H_{16}O_4$ and had UV, IR and ^1H NMR spectral data in close agreement with the data reported for methylalloptaeroxylin [4, 5]. The assignments of the ^1H NMR and ^{13}C NMR signals were based on previously published data [6–8] and on the ^1H–^{13}C-2D chemical shift correlation spectrum. Therefore, **1** was identified as 2-methylalloptaeroxylin. Compound **1** was recently isolated from a Nigerian sample of *H. abyssinica* [4] but was not reported in East African specimens [2, 4]. Compound **2** gave a molecular ion at 288 corresponding to the molecular formula $C_{16}H_{16}O_5$. Its IR spectrum showed hydroxy absorption at 3360 cm^{-1} in addition to bands which can be assigned to a chromone structure as further confirmed by the electronic spectrum. The ^1H NMR spectra of **1** and **2** were similar but the 2-methyl signal at 2.28 ppm showed by **1** was replaced by a two proton singlet at 4.51 ppm suggesting a CH_2OH group; this was confirmed by a fragment at m/z 270 $[M - H_2O]^+$ and the ^{13}C NMR-Dept spectrum, which exhibited a negative signal at 61.16 ppm. Furthermore, acetylation of **2** resulted in the downfield shifts of the methylene signal from 4.51 to 4.96 ppm and in an additional three protons singlet at 2.18 ppm (OAc). The ^1H–^{13}C chemical shift correlation spectrum confirmed the assignments made for both ^1H NMR and ^{13}C NMR spectra. Thus, the structure of **2** can be formulated as 2-hydroxymethylalloptaeroxylin. The presence of this new chromone in Guinean samples of *H. abyssinica* confirmed the probable existence of chemical races of this plant.

EXPERIMENTAL

UV spectra were recorded in EtOH and IR in KBr discs. ^1H MNR (250 MHz) and ^{13}C NMR (62 MHz) were recorded in $CDCl_3$; chemical shifts are reported as δ values downfield from internal TMS. MS: direct inlet, 70 eV.



1 R = Me
2 R = CH_2OH