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5-DEHYDROORICIOPSIN, A RING-D CLEAVED TETRANORTRITERPENOID FROM *HARRISONIA ABYSSINICA*

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Key Word Index—*Harrisonia abyssinica*; Simaroubaceae; tetranortriterpenoid; furylketone limonoid; 5-dehydrooriciopsin.

Abstract—A new ring-D cleaved tetranortriterpenoid, 5-dehydrooriciopsin, has been isolated from the root-bark of Guinean samples of *Harrisonia abyssinica*. Its structure was established by spectral methods.

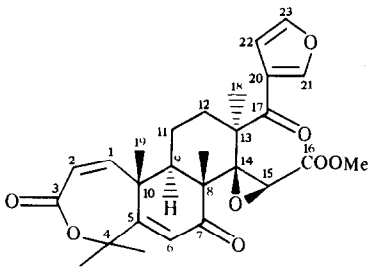
INTRODUCTION

Five limonoids have been isolated from the African shrub *Harrisonia abyssinica* Oliv. (Simaroubaceae). In addition to the common obacunone, harrisonin, acetoxyharrisonin and pedonin were isolated from Kenyan samples [1–3], whereas atalantolide was found in Nigerian samples [4]. The first four limonoids have been shown to exhibit insect antifeeding activity [2, 5, 6]. In the course of our study on the biologically active constituents of *H. abyssinica*, we report here the isolation of a new furylketone limonoid.

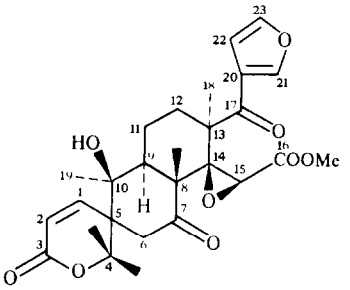
RESULT AND DISCUSSION

Isolation of the limonoids was performed by extraction of the root-bark with diethyl ether and submitting the extract to successive CC and prep. TLC on silica gel. This procedure afforded two limonoids, obacunone and **1**. Obacunone was identified by its spectral data [1, 4, 7, 8]. It was found to be the major limonoid in the samples under investigation (0.30%).

Although the purity of compound **1** was checked in several TLC systems, attempts to crystallize it were unsuccessful. Its EIMS exhibited a $[M]^+$ ion peak at *m/z* 482 corresponding to $C_{27}H_{30}O_8$ as confirmed by HRMS. Other spectral features of **1** such as a signal in the ^1H NMR spectrum for H-21 at δ 8.61 highly indicative of a 17-ketone showed clearly its relationship with obacunone [1], pedonin, **2** [3] and oriciopsin [9]. In comparison with this last limonoid, the conjugation of the C-7 carbonyl was supported in the ^{13}C NMR spectrum by the signal at δ 196.50 or δ 196.40 (C-7), by the signals attributed to C-5 and C-6 respectively at δ 166.35 and 124.62 and in the ^1H NMR by the proton singlet at δ5.73 corresponding to the vinylic proton H-6. Other ^1H NMR and ^{13}C NMR assignments of **1** were based on comparison of the spectral data of obacunone, **2** and oriciopsin [1, 3, 9] and confirmed by DEPT measurements; it was noticed that the attribution of the C-4, C-9 and C-11 signals of oriopsin [9] was not clearly defined. From the above data, **1** was identified as 5-dehydrooriciopsin. As this new limonoid was directly detectable by TLC of the crude $CHCl_3$ extract of the plant, it could not be considered as an artefact. **1** is the second ring-D cleaved tetranortriterpenoid isolated from *H. abyssinica*; the first one, **2**, exhibits a spirotetranortriterpenoid skeleton and the structure of **1** is more similar to that of oriociopsin



1



2

which was isolated from *Oriciopsis glaberrima* Eng. (Rutaceae) [9].

EXPERIMENTAL

UV spectra were recorded in MeOH with a Perkin–Elmer 402 UV-Vis spectrometer. IR spectra were measured with a Bruker IFS48 FTIR spectrometer. MS were obtained on a VG Micromass 7070F instrument by direct inlet at 70 eV. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ with a Bruker instrument at 250 and 62.8 MHz respectively; chemical shifts are reported in δ values downfield from internal TMS.

Plant material. Root bark of *H. abyssinica* was collected around Seredou (Guinea-Conakry) in December 1985 and identified by the Department of Botany of the Research Center on Medicinal Plants of Seredou; a voucher specimen has been deposited at this Center.

Extraction. The hydromethanolic extract of the powdered root-bark of *H. abyssinica* (500 g) was exhausted with Et_2O; the Et_2O extract was concd under vacuum and yielded a thick yellow oil which was homogenized with cellulose MN2100FF (Macherey Nagel) and chromatographed on a column of silica gel eluting with CCl_4 and a CCl_4–MeOH gradient; purification of the more polar fractions by repeated CC and prep. TLC on silica gel with C_6H_{12}–MeCOOEt (2:3) afforded obacunone and **1**.

Compound **1** (45 mg). EIMS *m/z* 482 $[M]^+$, 387, 371, 327, 311, 269; UV λ_{max}^{MeOH} nm: 257; IR γ_{max}^{KBr} cm^{-1}: 1760, 1662, 1560, 1511, 876; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.00, 1.05, 1.48, 1.67, 1.69 (each 3H, *s*), 3.35 (1H, *s*, H-15), 3.81 (3H, *s*, OMe), 5.75 (1H, *s*, H-6), 6.08 (1H, *d*, J = 12 Hz, H-2), 6.50 (1H, *d*, J = 12 Hz, H-1), 6.95 (1H, *d*, J = 1.6 Hz, H-22), 7.40 (1H, *dd*, J = 1.6, 1.3 Hz, H-23) and 8.61 (1H, *d*, J = 1.3 Hz, H-21); ^{13}C NMR (62.8 MHz, $CDCl_3$): δ18.6, 19.6, 23.8, 30.9 and 31.5 (Me), 20.1 (C-11), 35.2 (C-12), 44.0 (C-10), 49.3, 49.8 (C-8, C-13: these assignments may be reversed), 52.4, 52.8 (C-9, OMe: these assignments may be reversed), 57.3 (C-15), 69.2 (C-14), 84.11 (C-4), 110.3 (C-22), 123.9 (C-2), 124.6 (C-6), 125.8 (C-20), 143.1 (C-23), 149.6 (C-21), 151.6 (C-1), 166.3 (C-5), 168.3, 168.5 (C-3, C-16: these assignments may be reversed), 196.4 and 196.5 (C-7, C-17: these assignments may be reversed).

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