Pergamon

0031-9422(95)00088-7

Phytochemistry, Vol. 39, No. 6, pp. 1483–1484, 1995

0031-9422/95 $9.50 + 0.00

HAROUNOSIDE A PENTALONGIN HYDROQUINONE DIGLYCOSIDE FROM *MITRACARPUS SCABER*

HAMIDOU HAROUNA, ROBERT FAURE,* RIAD ELIAS,† LAURENT DEBRAUWER,† MAHAMANE SAADOU,‡ GUY BALANSARD|| and GILBERT BOUDON§

Department de Biologie Végétale, Université de Sciences B.P. 10662 Niamey, Niger; *URA 1411, Université d'Aix-Marseille III, Avenue Escadrille Normandie Niemen, 13397 Marseille cedex 3, France; †Laboratoire de Pharmacognosie, Faculté de Pharmacie, 27 Boulevard Jean Moulin, 13385 Marseille cedex 5, France; ‡INRA Centre de Recherche de Toulouse, Laboratoire des Xénobiotiques, 180 Chemin du Tournefeuille, BP 3, 31931 Toulouse, France

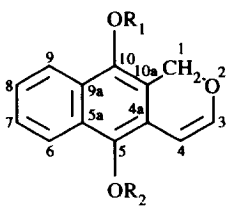
(*Received in revised form* 28 *November* 1994)

Key Word Index—*Mitracarpus scaber*; Rubiaceae; harounoside; pentalongin hydroquinone diglycoside; 2D NMR.

Abstract—The structure of a new pentalongin hydroquinone diglycoside, harounoside, from *Mitracarpus scaber* has been established as 5,10-dihydroxy-2H-naphtho[2,3-b]-pyran-5,10-β-D-bisglucopyranoside, using 1D and 2D NMR spectral data.

INTRODUCTION

Mitracarpus scaber Zucc. is an annual plant used in African traditional medicine for its antifungal and antiparasitical activities [1]. No information about the chemical composition of this plant was found in the literature. In the present paper we report the isolation and structural elucidation of a new pentalongin hydroquinone diglycoside, which we have named harounoside. Pentalongin has been isolated from other plants [2, 3].



$R_1 = R_2$ = Glucose

Harounoside (1)

RESULTS AND DISCUSSION

The molecular formula $C_{25}H_{30}O_{13}$ for harounoside (**1**) was deduced from the FAB-mass spectrum which displayed a molecular ion-associated peak at *m/z* 539 $[M - H]^+$. A *cis* olefinic bond was indicated by an AB quartet at δ 6.68 and 6.64 (^3J = 5.8 Hz) in the ^{1}H NMR spectrum. Further analysis of the remaining ^{1}H NMR signals revealed the presence of an isolated oxygen-bearing methylene resonance [an AB quartet (J = 13.9 Hz) at δ5.39 and 5.30] and four deshielded protons with multiplet patterns characteristic for an *ortho* disubstituted aromatic ring. Moreover, ^{1}H and ^{13}C NMR data suggested the occurrence of two sugar moieties which were identified as β-D-glucopyranosyl. Finally from the multiplicities of individual carbon atoms determined using DEPT pulse sequence [4], in conjunction with above data, it can be concluded that **1** is a tricyclic compound with two glucose rings.

The structure and, therefore, the ^{1}H and ^{13}C NMR spectral parameters for **1** were deduced from the concerted application of both direct and long-range heteronuclear chemical shift correlation experiments. One-bond ^{1}H-^{13}C intercoupling network was established using the protondetected C,H-correlation (HMQC) diagram [5]. Multibond connectivities were determined from the analysis of long-range correlation responses over two or three bonds (^2J and ^3J couplings) using HMBC spectroscopy [6]. All these connectivities are shown in Fig. 1. By utilizing the HMBC contour plot, it should be noted that the anomeric protons of the sugars, H-1′ (R^1) and H-1′ (R^2) indicated long-range correlation signals with quaternary carbons C-10 and C-5, respectively. In turn, these later resonances were long-range coupled with other protons: H-9 and H-1 for C-10, and H-6 and H-4 for C-5. Thus considerations of these results permit structural fragments to be assembled to give harounoside (**1**).

||Author to whom correspondence should be addressed.
§Technical collaboration.

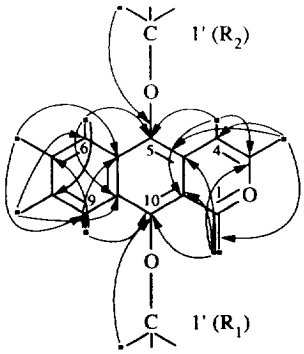


Fig. 1. HMBC connectivities used to make ^1H and ^{13}C assignments of harounoside (**1**).

Table 1. ^1H and ^{13}C NMR spectral data for compound **1**

Assignment*	δ_C	Group†	δ_H‡
3	147.8	CH	6.68
10	145.0	C	—
5	143.4	C	—
5a	131.0	C	—
9a	129.1	C	—
7	127.0	CH	7.43
8	126.3	CH	7.39
6	124.7	CH	8.42
9	123.7	CH	8.44
10a	122.7	C	—
4a	121.7	C	—
1' (R^2)	107.0	CH	4.76
1' (R^1)	106.5	CH	4.68
4	102.2	CH	6.64
1	65.4	CH_2	5.39; 5.30

In ppm with respect to TMS; other resonances: δ78.1; 78.0; 78.0; 77.8; 75.8; 75.7; 71.5; 71.5; 62.7; 62.6.

*Information obtained from concerted use of HMQC and HMBC experiments.

†Determined from DEPT spectra.

‡In ppm with respect to TMS; J_{3-4}: 5.8 Hz; J_{1A-1B}: 13.9 Hz; $J_{1'2'}$: 7.8 Hz.

EXPERIMENTAL

Mitracarpus scaber plants were collected in Niger. A voucher specimen is deposited in the Department of Pharmacognosy, Faculty of Pharmacy, Marseille.

Extraction and isolation. The dried whole plant (100 g) was extracted with MeOH–H_2O (4:1) concd *in vacuo* to a H_2O layer which was shaken successively with Et_2O and n-BuOH. Then n-BuOH extract (2 g), chromatographed over a polyamide (SC6 polycaprolactam < 0.07 Macherey Nagel) column with a gradient of MeOH in H_2O, furnished pure harounoside (25 mg).

Analytical TLC was performed on precoated silica gel plates (Kieselgel 60 F254, 0,25 mm Merck) using the following solvent system $CHCl_3$–MeOH–H_2O (11:7:1). All NMR spectra were recorded on a Bruker AMX-400 spectrometer in CD_3OD solution; TMS was used as standard in ^1H and ^{13}C measurements. Standard Bruker pulse was used for DEPT and inverse-detected heteronuclear correlation experiments. For other NMR experimental details see ref. [7]

Harounoside: 5,10-*dihydroxy*-2H-*naphtho*[2,3-b]-*pyran*-5,10-*β*-D-*bisglucopyranoside* (**1**). Amorphous powder; ^1H and ^{13}C NMR (CD_3OD): Table 1.

REFERENCES

1. Adjanohoun, E. J., Ahyi, A. M. R., Dan Dicko, L., Daouda, H., Delmas, M., de Souza, S., Garba, M., Guinko, S., Kayonga, A., N'Golo, D., Raynal, J. L. and Saadou, M. (1985) Contribution aux études ethnobotaniques et floristiques au Niger, A.C.C.T., France.
2. Hari, L., De Buyck, L. F. and De Pooter, H. L. (1991) *Phytochemistry* **30**, 1726.
3. Hayashi, T., Smith, F. T. and Lee, K. H. (1987) *J. Med. Chem.* **30**, 2005.
4. Doddrell, D., Pegg, D. T. and Bendall, M. R. (1982) *J. Magn Reson.* **48**, 323.
5. Bax, A. and Subramanian, S. (1986) *J. Magn. Reson.* **67**, 565.
6. Bax, A. and Summers, M. F. (1986) *J. Am. Chem. Soc.* **108**, 2093.
7. Faure, R., Gaydou, E. M. and Wollenweber, E. (1991) *J. Nat. Prod.* **54**, 1564.