

Table 1. ^1H NMR spectral data of **2**, **3** and **4** (400 MHz, CDCl_3 , δ -values)

H	2	3	4
2,6	7.58 <i>m</i>	7.58 <i>m</i>	
3,4,5	7.39 <i>m</i>	7.38 <i>m</i>	
7	7.88 <i>d</i>	7.88 <i>d</i>	
8	7.79 <i>d</i>	7.79 <i>d</i>	
5'	6.07 <i>s</i>	6.07 <i>s</i>	
OH	14.44 <i>s</i>	14.36 <i>s</i>	14.41 <i>s</i>
OMe	3.91 <i>s</i>	3.90 <i>s</i>	
OCOR	6.36 <i>qq</i>	2.75 <i>tq</i>	2.53 <i>d</i>
	2.11 <i>dq</i>	1.35 <i>d</i>	2.30 <i>tqq</i>
	2.13 <i>dq</i>	1.68 <i>ddq</i>	1.09 <i>d</i>
		1.90 <i>ddq</i>	
		1.06 <i>t</i>	

J [Hz]: 7.8 = 15; OAng: 3,4 = 7; 3,5 = 4,5 = 1.3; OMeBu: 2,3 = 2,5 = 3,4 = 7; 3',1 = 3',2 = 14; OiVal: 2,3 = 3,4 = 3,5 = 7.

Acknowledgements—We thank Dr J. Jakupovic and Mr M. Grenz (Institute of Organic Chemistry, Technical University of Berlin) for active co-operation during this work and DAAD for financial support. We also thank Mr Abul Hasan (Department of Botany; University of Dhaka) for his kind help during plant collection and identification.

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Phytochemistry, Vol. 27, No. 7, pp. 2360–2361, 1988.
Printed in Great Britain.

0031 9422/88 \$3.00 + 0.00
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NEOCORYMBOSIDE, A DI-C-GLYCOSYLFLOVONE FROM *ATRACTYLIS GUMMIFERA*

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(Received 12 January 1988)

Key Word Index—*Atractylis gummifera*; Compositae; di-C-glycosylflavone, neocorymboside; 6-C- β -L-arabinopyranosyl-8-C- β -D-galactopyranosylapigenin.

Abstract—Neocorymboside, a new glycosylflavone from *Atractylis gummifera* roots was shown to be 6-C- β -L-arabinopyranosyl-8-C- β -D-galactopyranosylapigenin

INTRODUCTION

Atractylis gummifera L. grows on Mediterranean shores except on the French littoral. Its roots contain atractyloside which is very toxic to hepatic cells. Orientin, homoorientin and isoschaftoside were found in *Atractylis gummifera* leaves [1]. In this paper, we discuss the identification of a new di-C-glycosylflavone in the roots. Corymboside, its α -L-arabinopyranosyl isomer was found in *Carlina corymbosa* roots [2] and it is known that *Carlina* and *Atractylis* are closely related systematically.

RESULTS AND DISCUSSION

The compound was isolated from the butanol-soluble fraction of an methanolic extract of dry powdered roots collected in Algeria. The UV spectrum and diagnostic shifts suggested apigenin with free 4',7 and 5-hydroxyl groups [3]. Its chromatographic and hydrolytic properties were those of C-glycosides: no sugar was obtained on acid hydrolysis. Negative-ion FAB mass spectrum of the free compound and electron impact mass spectrometry of its PM ether showed the product to be a 6-C-

arabinosyl-8-C-hexosylapigenin (M^- 704; $M-131 > M-175$; $M-131 > M-119$) [4]. From chromatography (TLC and HPLC) of free and permethylated di-C-glycosylflavones, this product was found to be different from isoschaftoside (6-C- α -L-arabinopyranosyl-8-C- β -D-glucopyranosylapigenin) neoisoschaftoside (6-C- β -L-arabinopyranosyl-8-C- β -D-glucopyranosylapigenin) and corymboside (6-C- α -L-arabinopyranosyl-8-C- β -D-galactopyranosylapigenin). On TLC the new compound was different from corymboside, but similar to neoisoschaftoside and isoschaftoside. On HPLC, the free compound showed an R_f different from those of corymboside and isocorymboside. After acid hydrolysis, in the butanol fraction were two compounds which had the same R_f (TLC) and R_t (HPLC) as corymboside and isocorymboside. Thus the compound on acid treatment gives corymboside [5, 6] and the Wessely-Moser isomer isocorymboside. The original compound is thus 6-C- β -L-arabinopyranosyl-8-C- β -D-galactopyranosylapigenin, or neocorymboside.

EXPERIMENTAL

EIMS were recorded on an VG 30 F spectrophotograph to 70 eV; FAB mass spectra on a ZAB-HF spectrophotograph and the matrix used was thioglycerol; HPLC was performed on a Touzart et Matignon liquid chromatograph using Lichrosorb RP 18 Merck column.

Plant material. *Atractylis gummifera* roots were collected in Algeria.

Extraction and isolation of the components. Dried powdered roots (300 g) were extracted with boiling MeOH (3×24 hr) then with boiling 50% MeOH (3×24 hr). The combined extracts were concd under red. pres., dissolved in boiling H_2O , kept 24 hr at 5°, then filtered. The solution was successively extracted with CH_2Cl_2 , Et_2O , EtOAc and *n*-BuOH. The BuOH was chromatographed on a Sephadex LH-20 column with MeOH as eluent; 16 fractions were obtained. After comparative TLC, some were collected to give four different fractions. From the second fraction, neocorymboside was obtained by PPC on Whatman 3 MM paper in BAW (4:1:5) and HOAc- H_2O (3:17).

Neocorymboside. UV λ_{max}^{MeOH} : 270, 332; + AlCl₃ 265, 280, 306, 356, 387; + AlCl₃ + HCl 262, 277, 304, 345, 382; + NaOAc 278, 307, 377; + NaOMe 278, 320, 395; CP (Whatman 1) in 15% HOAc R_f 0, 35 (schaftoside 0.60) in BAW R_f 0.18 (schaftoside 0.18); TLC (cellulose) in 15% HOAc R_f 0.21 (isoschaftoside 0.37), in BAW R_f 0.30 (isoschaftoside 0.35); HPLC (MeOH- H_2O , 3:7; 1.5 cm³/min) R_t (min): neocorymboside: 6.3; corymboside: 10.1; isocorymboside: 7.3; isoschaftoside: 9.2. Negative ion FAB mass: 563 [M-H]⁻.

Permethylation of neocorymboside. TLC (silica) in $CHCl_3$ -EtOAc-Me₂CO (5:4:1) R_f 0.21 (PM corymboside 0.17, PM isoschaftoside 0.15, PM neoisoschaftoside 0.30); in $CHCl_3$ -EtOAc-Me₂CO (5:1:4) R_f 0.67 (PM corymboside 0.62; PM isoschaftoside 0.62; PM neoisoschaftoside 0.75); in $CHCl_3$ -Me₂CO (4:1) R_f 0.33 (PM corymboside 0.27; PM isoschaftoside 0.27; PM neoisoschaftoside 0.42); MS of the PM ether: *m/z* (%) 704 M⁺ (17), 689 M-15 (13), 673 M-31 (100), 585 M-119 (13), 573 M-131 (39), 529 M-175 (15).

Acid hydrolysis of neocorymboside. Neocorymboside (1 mg) in MeOH-HCl 4 N (1:1) was heated for 60 min at 100°. The aq. layer was extracted with Et_2O and *n*-BuOH. The BuOH fraction was studied by TLC (cellulose) in 15% HOAc: R_f 0.31-0.41 (corymboside 0.35; isocorymboside 0.42; isoschaftoside 0.32; neoisoschaftoside 0.17). BuOH fraction was also studied by HPLC (MeOH- H_2O , 3:7; 1.5 cm³/min.) R_t (min): 7.3 and 9.9.

Acknowledgements—We wish to thank Professor Victoria Hammie, University of Alger for supplying plant material.

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