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SITOSTEROL SUCROSIDE FROM THE SUCKERS OF *MENTHA ARVENSIS**

RIAZ A. KHAN, ANIL K. SINGH and PAWAN K. AGRAWAL†

Central Institute of Medicinal and Aromatic Plants, Lucknow-226 015, India

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Key Word Index—*Mentha arvensis*; Labiatae; suckers; sucrose; sitosterol sucroside.

Abstract—Two constituents, isolated from the suckers of *Mentha arvensis*, were identified as 3-*O*-β-sitosteryl-glucopyranosyl-(1α → 2)-fructofuranoside and sucrose. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Mentha arvensis var. piperascen's is one of the major sources for *l*-menthol and it has been intensively investigated [2, 3]. Four non-volatile constituents, sitosterol-β-D-glucoside [4], *l*-menthyl-β-D-glucoside, *l*-menthyl-6′-*O*-acetyl-β-D-glucoside [5] and lambda-menthyl-β-D-glucoside [6] have been isolated from leaves. The present investigation describes the isolation and characterization of two constituents from the ethanolic extracts of the suckers of *M. arvensis*.

RESULTS AND DISCUSSION

Column chromatography of the chloroform extract of the suckers of *M. arvensis* led to the isolation of compound **1** as an amorphous powder, mp 182°. The ^{1}H NMR spectrum displayed six methyl signals, distinguishable into two singlets (δ 0.71 and 1.02), three doublets (δ 0.84, 0.86 and 0.94), and a triplet (δ 0.89) in addition to a broad doublet at δ 5.36 (2H). The ^{13}C NMR spectrum showed two olefinic carbons at δ 142.0 (C) and 122.75 (CH) characteristic of Δ^5 steroidal skeleton [7, 8] and other resonances in the aliphatic region (12–55 ppm) showing significant resemblance with the literature values for sitosterol [9, 10]. The existence of two anomeric carbon resonances at δ 102.5 (C) and 94.8 (CH), together with 3 methylene resonances at δ 58.8, 62.8 and 63.7 and 7 oxymethine resonances in the 67–80 ppm region, reflected its diglycosidic nature [11]. A comparative study of the ^{13}C NMR shielding data for **1** with those observed for sucrose (**2**) (also isolated in the present studies) [12] showed appreciable similarities. A comparative study of ^{13}C NMR shielding data for **1** and **2** revealed that the C-3 resonance of the α-D-glucopyranose was at 5.8 ppm lowerfield position and the C-2 and C-4 resonances were 1.1 ppm upfield in **1** compared with **2**. These glycosylation induced ^{13}C NMR shifts [13] were consistent with the sitosterol substitution at the C-3 position of the α-D-glucopyranose. Consequently, the structure of **1** was deduced as 3-*O*-β-sitosteryl-glucopyranosyl-(1α → 2)-fructofuranoside. To the best of our knowledge, this is the first report of occurrence of any sitosterol sucroside in nature, although the rhamnoglucoside and the rhamnoarabinofuranoside of sitosterol have been reported from *Lindenbergia indica* [14]. The occurrence of sucrose esters has been recently reported from *Nicotiana caviocola* [15].

EXPERIMENTAL

General. All mps were determined in open capillaries and uncorr. The NMR measurements were carried out on Bruker WM-400 NMR spectrometer in CD_3OD for **1** and in D_2O for **2** [16].

Plant material and isolation. The suckers of *Mentha arvensis* were collected from CIMAP field station, Pantnagar (U.P.) and air dried. The ground and defatted suckers (270 g) were extracted with EtOH (3 × 500 ml) and the combined extract was concd to 1/3 its original vol. which was then held at 5° for 48 hr. This led to the deposition of white amorphous material which was filtered and repeatedly washed with MeOH to afford **2**, ^{13}C NMR (D_2O): glucopyranose: 91.9 (C-1), 72.1 (C-2), 72.3 (C-3), 68.9 (C-4), 72.8 (C-5), 59.85 (C-6), fructofuranose: 62.06 (C-1), 103.4 (C-2), 81.06 (C-3), 76.2 (C-4), 73.7 (C-5), 61.09 (C-6) identified as sucrose [12].

The filtrate was concd to viscous mass (7.5 g) and extracted with $CHCl_3$ (3 × 50 ml). The $CHCl_3$ con-

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† Author to whom correspondence should be addressed.

centrate (3.2 g) was chromatographed over silica gel with $CHCl_3$ and increasing polarities of MeOH as eluent to yield **1** (130 mg) R_f 0.6, Solvent system: $CHCl_3$–MeOH–H_2O, 3:4:1; in frs eluted with $CHCl_3$–MeOH (3:7). ^{13}C NMR (CD_3OD): sitosterol: 38.55 (C-1), 27.2 (C-2), 77.8 (C-3), 41.2 (C-4), 142.0 (C-5), 122.75 (C-6), 33.05 (C-7), 33.7 (C-8), 51.7 (C-9), 37.4 (C-10), 22.7 (C-11), 39.26 (C-12), 41.1 (C-13), 57.4 (C-14), 25.3 (C-15), 30.2 (C-16), 54.69 (C-17), 12.24 (C-18), 19.4 (C-19), 34.9 (C-20), 19.1 (C-21), 35.1 (C-22), 29.3 (C-23), 49.5 (C-24), 25.98 (C-25), 19.8 (C-26), 20.1 (C-27), 23.7 (C-28), 12.3 (C-29). Glucopyranose: 94.89 (C-1), 71.0 (C-2), 78.1 (C-3), 67.8 (C-4), 72.9 (C-5), 58.8 (C-6), fructofuranose: 63.7 (C-1), 102.5 (C-2), 80.0 (C-3), 76.4 (C-4), 74.1 (C-5), 62.8 (C-6). FAB-MS: 644, 599 $[(M+Na)\text{-Glc})]^+$, 574, 555, 518, 496, 413, 411, 397, 329, 307, 289, 184, 176, 165.

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