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FLAVONOL GLYCOSIDES OF *EUPHORBIA RETUSA* AND *E. SANCTAE-CATHARINAE*

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Key Word Index—*Euphorbia retusa*; *E. sanctae-catharinae*; Euphorbiaceae; flavonol glycosides; kaempferol and quercetin 3-glucuronide-7-glucosides.

Abstract—The flavonoid glycosides of *Euphorbia retusa* and *E. sanctae-catharinae* are reported. Besides a number of common flavonol glycosides, kaempferol and quercetin 3-glucuronide-7-glucosides are reported for the first time.

Euphorbia is represented in Egypt by some 35 species [1]. A number of these species have been studied previously, thus quercetin 3-rhamnoside has been isolated from *Euphorbia hypericifolia* [2] and *E. geniculata* [3]. Quercetin 3-galactoside and 3-arabinoside were identified in *E. paralias* [4], while rhamnetin 3-galactoside was detected in *E. hypericifolia* [2] and *E. prostrata* [3]. *E. granulata* proved to contain apigenin 7-glucoside [5], which was also found in *E. prostrata* [3]. Four other *Euphorbia* species have also been investigated. Thus from *E. esula* kaempferol 3-glucuronide was isolated [6] and quercetin 3-galactoside-2″-gallate was identified in both *E. verrucosa* [7] and *E. sequieriana* [8], while its isomer quercetin 3-galactoside-6″-gallate was detected in *E. platiphyllos* [7].

In the present report, two more *Euphorbia* species were investigated, namely *E. retusa* Forssk. (= *E. kahirensis* Raeusch.) and *E. sanctae-catharinae* A. Fayed. The latter is a newly reported species [9]. Both plants proved to contain kaempferol and quercetin glycosides with their 3-glucuronides forming the major glycosides in *E. retusa* and quercetin 3-rhamnoside forming the major glycoside in *E. sanctae-catharinae*. The results are outlined in Table 1. Kaempferol and quercetin 3-glucuronide-7-glucosides are reported here for the first time.

EXPERIMENTAL

Material. A fresh sample of *Euphorbia sanctae-catharinae* A. Fayed was collected from Mt. Catherine, Sinai. A sample of *E. retusa* Forssk. was collected from Wadi Firan, Sinai. Both were

Table 1. The flavonoids of *Euphorbia retusa* and *E. sanctae-catharinae*

Flavonol glycosides	*E. retusa**	*E. sanctae-catharinae**
Kaempferol 3-glucuronide	−	+++
Kaempferol 3-glucuronide-7-glucoside	−	++
Quercetin 3-glucoside	+	−
Quercetin 3-glucuronide	++	+++
Quercetin 3-rhamnoside	+++	−
Quercetin 3-rutinoside	+	−
Quercetin 3-glucuronide-7-glucoside	+	++

* +++ = major, ++ = strong, + = weak, − = absent.

collected in late April, and voucher specimens have been deposited at the Herbarium, Cairo University.

Methods. The plant material was extracted with 70% EtOH and concd under red. pres. The extract was fractionated using elution techniques on PC. Fractions were subjected to detailed studies according to standard methods [10, 11].

Kaempferol and quercetin 3-glucuronide-7-glucosides. The glycosides gave kaempferol and quercetin respectively on acid hydrolysis as well as glucose and glucuronic acid in both cases. Mild acid hydrolysis gave rise to the corresponding 7-glucosides for both glycosides and enzymatic hydrolysis with β-glucosidase gave rise to the corresponding 3-glucuronides of both flavonols. The UV data confirmed that positions 3 and 7 were occupied in both glycosides. R_f values for kaempferol and quercetin 3-glucuronide-7-glucosides and quercetin 3-glucuronide (as reference), respectively, are as follows: BAW = 20, 16, 39; PhOH = 20, 13, 16; H_2O = 63, 48, 23; 15% HOAc = 54, 48, 28.

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ALKALOIDS FROM *HAPLOPHYLLUM BUXBAUMII*

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Key Word Index—*Haplophyllum buxbaumii*; Rutaceae; alkaloids; kokusaginine; skimmianine; γ-fagarine; 4,5,6-trimethoxyfuroquinoline; 4,5,7-trimethoxyfuroquinoline; *N*-hydroxymethylflindersine; justicin B.

Abstract—In addition to the known alkaloids kokusaginine, skimmianine, γ-fagarine and a lignan, justicin B, the aerial parts of *Haplophyllum buxbaumii* afforded three new alkaloids: 4,5,6-trimethoxyfuroquinoline, 4,5,7-trimethoxyfuroquinoline and *N*-hydroxymethylflindersine. The structures of the known and the new compounds were assigned by spectral methods.

INTRODUCTION

In previous studies, quinoline alkaloids [1–5], coumarins [6–8] and lignans [9–11] have been isolated from *Haplophyllum* species. In continuation of the investigation of the genus *Haplophyllum* [12], in addition to the known compounds kokusaginine [1], skimmianine [2], γ-fagarine [5] and justicin B [13, 14], we report here the isolation of three new alkaloids, two of which are furoquinolines and one is an angular pyranoquinoline type. The structures of the known and the new compounds were established by spectral methods.

RESULTS AND DISCUSSION

Benzene–chloroform extracts of the aerial parts of *Haplophyllum buxbaumii* subsp. *buxbaumii* yielded the known alkaloids kokusaginine (**1**), skimmianine (**2**), γ-fagarine (**3**), a lignan, justicin B (**4**), as well as the new alkaloids 4,5,6-trimethoxyfuroquinoline (**5**), 4,5,7-trimethoxyfuroquinoline (**6**) and *N*-hydroxymethylflindersine (**7**). The known compounds were identified by comparing their spectra to those in the literature and TLC comparison with standard samples in the case of **1** and **3**.

In the mass spectrum of **5**, the $[M]^+$ at *m/z* 259 indicated the molecular formula $C_{14}H_{13}O_4N$. The UV and IR spectra were similar to known furoquinoline alkaloids (**1–3**) indicating the same type of compound (see Experimental). In the ^1H NMR spectrum of **5**, three methoxyl singlets were present at δ4.43 (C_4-OMe), 4.10 (C_5-OMe) and 4.05 (C_6-OMe) as well as four proton doublets in the aromatic region. Since two of these protons at δ7.05 (1H, *d*, *J* = 2.5 Hz, H-1′) and 7.57 (1H, *d*,