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Guaianolides from *Calycocorsus stipitatus* and *Crepis tingitana*[1]

Christian Zidorn[a], Ernst P. Ellmerer-Müller[b], Hermann Stuppner[a,*]

[a]*Institut für Pharmakognosie der Universität Innsbruck, Josef-Möller-Haus, Innrain 52, A-6020 Innsbruck, Austria*
[b]*Institut für Organische Chemie der Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

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Abstract

The dichloromethane extract of subaerial parts of *Crepis tingitana* L. afforded two sesquiterpene lactones, 8-epidesacylcynaropicrin-3-*O*-*β*-D-glucoside and ixerisoside A, already known from other members from the Lactuceae tribe of the Asteraceae family. The dichloromethane extract of subaerial parts of *Calycocorsus stipitatus* (Jacq.) Rauschert revealed a closely related new substance. The structure of the new compound has been established by MS, ^{1}H and ^{13}C NMR experiments as 3*β*-(*β*-D-glucopyranosyloxy)-8*β*-(4″-methoxyphenylacetoxy)-guaia-4(15), 10(14), 11(13)-trien-1*α*, 5*α*, 6*β*, 7*α*H-12,6-olide.

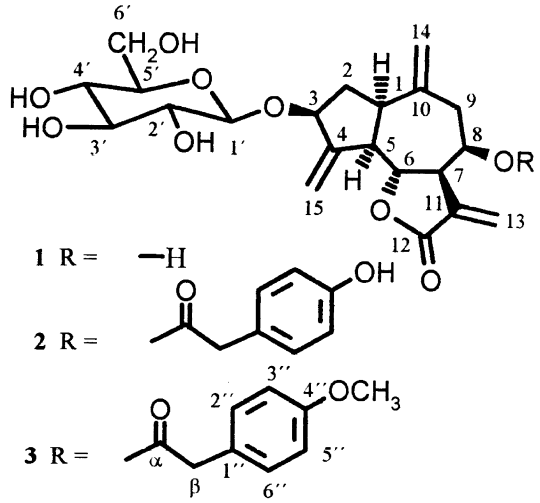
Keywords: *Calycocorsus stipitatus* (Jacq.) Rauschert; *Crepis tingitana* Ball; Asteraceae; Lactuceae; Sesquiterpene lactones; Guaianolides

1. Introduction

Phytochemical analysis of some of the 70 species of *Crepis* in Europe (Sell, 1976) led so far to the isolation and identification of several guaianolide type sesquiterpene lactones (Kisiel, 1983, 1984, 1993; Kisiel & Kohlmünzer, 1987, 1989; Kisiel, Jakupovic, & Huneck, 1994; Kisiel & Barszcz, 1996). *Crepis tingitana*, an endemic of southern Spain and Morocco, has not been investigated yet. The genus *Calycocorsus* is closely related to *Crepis* and represented by one European species, *Calycocorsus stipitatus*, which grows in southern Central Europe, Crna Gora, Albania and the eastern Pyreneés (Sell, 1976). So far nothing is known about secondary metabolites of *Calycocorsus*.

2. Results and discussion

The dichloromethane extract of the air dried subaerial parts of *C. tingitana* was repeatedly chromatographed on silica gel to give two guaianolides, 8-epidesacylcynaropicrin-3-*O*-*β*-D-glucoside (**1**) and ixerisoside A (**2**).



Identification of compounds **1** and **2** was based on comparison of mass spectra (positive ESI *m*/*z*: 447 $[M+Na]^+$ and 581 $[M+Na]^+$, respectively) and ^{1}H and ^{13}C NMR data with those given in literature (Kisiel, 1983; Warashina, Ishino, Miyase, & Ueno, 1990).

Substance **3** was isolated from the dichloromethane extract of subaerial parts of *C. stipitatus*. The mass spectrum revealed a molecular mass of 572 (positive ESI *m*/*z* 595 $[M+Na]^+$).

The ^{1}H and ^{13}C NMR spectra of **3** are almost identical with the corresponding spectra of **2** and differ only in an additional signal of a methoxy group at δ_H 3.85 and δ_C 55.7, respectively. The *β*-linkage of the glucose moiety was deduced from the coupling constant of H-1′ (7.3 Hz).

[1] Dedicated to Professor Dr. G. Heinisch (Institut für Pharmazeutische Chemie der Universität Innsbruck) on the occasion of his 60th birthday.

* Corresponding author. Tel.: +43-512-507-5307; fax: +43-512-507-2939.

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Stereochemistry of the aglycone, as indicated by ^{1}H and ^{13}C NMR data, is identical with the one given in literature for **1** and **2** (Kisiel, 1983; Warashina et al., 1990). HMBC experiments localized the methoxy group in para position of the phenyl acetic acid moiety of the molecule. Therefore, **3** was determined as 3β-(β-D-glucopyranosyloxy)-8β-(4″-methoxyphenylacetoxy)-guaia-4(15), 10(14), 11(13)-trien-1α, 5α, 6β, 7αH-12,6-olide.

3. Experimental

3.1. Plant material

C. tingitana was collected in April 1997 near Majada Madrid/Andalucia/Spain. *C. stipitatus* was gathered at the Wildmoosalm near Seefeld/Tyrol/Austria. Voucher specimens are deposited at the Institute of Pharmacognosy.

3.2. Extraction and isolation of compound *1–3*

Air dried subaerial parts of *C. tingitana* (120 g) and *C. stipitatus* (90 g) were ground and extracted exhaustively at room temperature with CH_2Cl_2 yielding 1.3 and 2.1 g of residue after evaporation in vacuum, respectively. **1** (95 mg) and **2** (25 mg) were isolated by repeated silica gel chromathography of the *C. tingitana* dichloromethane extract with gradients of CH_2Cl_2 and MeOH and CH_2Cl_2 and EtOAc, respectively. **3** (4.0 mg) was isolated by silica gel CC of the dichloromethane extract of *C. stipitatus* (gradient: CH_2Cl_2 and MeOH) and following Sephadex LH20 CC (mobile phase: MeOH).

3.3. 3β-(β-D-glucopyranosyloxy)-8β-(4″-methoxyphenylacetoxy)-guaia-4(15), 10(14), 11(13)-trien-1α, 5α, 6β, 7αH-12,6-olide (**3**)

^{1}H NMR (300 MHz in MeOH-d_4): aglycone 6.08 (1 H, d, $J=3.9$ Hz, H-13a), 5.57* (H-8), 5.57* (H-15a), 5.50 (1 H, d, $J=3.9$ Hz, H-13b), 5.41 (1 H, br s, H-15b), 5.15 (1 H, s, H-14a), 4.87 (1 H, s, H-14b), 4.73 (1 H, dd, $J=8.8$, 6.9 Hz, H-3), 4.53 (1 H, dd, $J=10.2$, 9.8 Hz, H-6), 3.35* (H-3), 3.05 (1 H, ddd, $J=9.8$, 8.4, 2.5 Hz, H-1), 2.88 (1 H, dd, $J=9.8$, 9.8 Hz, H-5), 2.63 (1 H, dd, $J=12.8$, 4.5 Hz, H-9a), 2.57 (1 H, dd, $J=12.8$, 5.4 Hz), 2.45 (1 H, ddd, $J=14.3$, 8.8, 8.4 Hz, H-2a), 2.03 (1 H, ddd, $J=14.3$, 6.9, 2.5 Hz, H-2b), glucose 4.55 (1 H, d, $J=7.3$ Hz, H-1′), 3.96 (1 H, dd, $J=11.8$, 2.0 Hz, H-6a′), 3.75 (1 H, dd, $J=11.8$, 4.9 Hz, H-6b′), 3.35-3.46* (4 H, m, H-2′-5′), p-methoxyphenylacetic acid 7.17 (2 H, br d, $J=8.8$ Hz, H-2″, H-6″), 6.90 (2H, br d, $J=8.8$ Hz, H-3″, H-5″), 3.85 (3 H, s, OCH_3), 3.62 (1 H, d, $J=14.6$ Hz, βa-H), 3.56 (1 H, d, $J=14.6$ Hz, βb-H); ^{13}C NMR (75 MHz in $CDCl_3$): aglycone 171.3 (C-12), 150.8 (C-4), 144.5 (C-10), 136.7 (C-11), 122.2 (C-13), 117.7 (C-14), 112.6 (C-15), 81.6 (C-3), 80.2 (C-6), 69.3 (C-8), 51.1 (C-5), 48.0 (C-7), 45.4 (C-1), 41.2 (C-9), 38.6 (C-2), glucose 103.9 (C-1′), 78.2 (C-3′), 78.0 (C-5′), 75.4 (C-2′), 71.8 (C-4′), 62.9 (C-6′), p-methoxyphenylacetic acid 172.2 (α-C), 160.3 (C-4″), 131.4 (C2″, C-6″), 127.4 (C-1″), 115.0 (C-3″, C-5″), 55.7 (OCH_3), 41.5 (β-C), * means signals are overlapping; all assignments have been confirmed by HMBC experiments.

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