Phytochemistry, Vol. 26, No. 4, pp. 1223–1224, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00

SESQUITERPENE ACIDS FROM *INULA VISCOSA*

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(*Received* 8 *July* 1986)

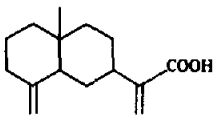
Key Word Index—*Inula viscosa*; Compositae; terpenoids; viscic acid; viscosic acid; flavonoids.

Abstract—In addition to known terpenoids and flavonoids two new sesquiterpene acids, viscic acid and viscosic acid, were obtained from the aerial parts of *Inula viscosa*.

INTRODUCTION

Inula viscosa (L.) Ait. is a well known medicinal plant grown in the western and southern parts of Turkey, the fresh leaves of which are used in folk medicine for the treatment of wounds [1].

In addition to the known sesquiterpene acids costic A (**1**), isocostic A (**2**) [2, 3] and ilicic A (**3**) [4], we have isolated two new acids, viscic A (**4**) and viscosic A (**5**). We have also obtained inuviscolide [5, 6], ψ-taraxasterol acetate [7], and the flavonoids sakuranetin, 7-*O*-methyl aromadendrin, 3-*O*-acetyl taxifolin and 3-*O*-acetyl padmatin [8] which were all isolated from *I. viscosa* in previous studies. In addition to the above compounds, we have also isolated four triterpenoid esters two of which, 3,16-dihydroxylupeol 3-palmitate and 3,16-dihydroxylupeol 3-myristate, were obtained from *I. britannica* for the first time, the other two were α-amyrin esters known to occur in *I. britannica* [S. Öksüz and G. Topçu, unpublished work]. The structures of known and new compounds were mainly established by spectral data.



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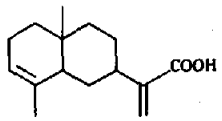

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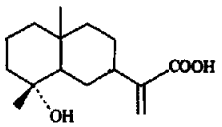

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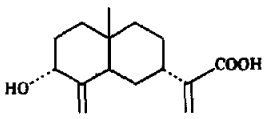

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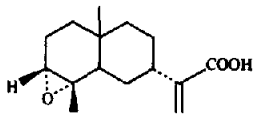

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RESULTS AND DISCUSSION

Viscic acid [3α-hydroxy-eudesma-4(15),11(13)-dien-12-oic acid] had the molecular formula $C_{15}H_{22}O_3$ (M^+, m/z 250. Its ^{1}H NMR spectrum showed signals at δ6.31 1H, *s* (*br*), H-13], 5.68 [1H, *s* (*br*), H-13′], 4.94 [1H, *s* (*br*), H-15] and 4.56 [1H, *s* (*br*), H-15′). Signals for hydrogen next to an α-hydroxyl group were observed at δ4.37 (1H, *t*, J = 2.5 Hz, H-3β), 2.57 (1H, *tt*, J = 3, 13.5 and 12 Hz, H-7β), 2.44 [1H, *d* (*br*), J = 12 Hz, H-5] and 0.73 (3H, *s*, H-14). The stereochemistry at C-3 and C-7 was established by measuring the J values of H-3 ($J_{3e,2e}$ = 2.5 Hz, $J_{3e,2a}$ = 2.5 Hz) and H-7 ($J_{7a,8a}$ = 12 Hz, $J_{7a,8e}$ = 3 Hz, $J_{7a,6a}$ = 3 Hz, $J_{7a,6e}$ = 3.5 Hz) and studying a Dreiding model.

The mass peak at m/z 264 in the mass spectrum of the methyl ester of viscosic acid (3α,4α-eudesma-11(13)-en-12-oic acid (**5**)) indicated the molecular formula $C_{15}H_{22}O_3$. The structure of **5** was established by epoxidation of the methyl ester of costic acid **1** and by the ^{1}H NMR spectrum which showed the following signals: δ6.32 [1H, *s* (*br*), H-13], 5.69 [1H, *s* (*br*), H-13′], 2.95 1H, *d*, J = 2 Hz, H-3β), 2.48 (1H, *tt*, J = 12, 13.5 and 3 Hz, H-7β), 2.02 [1H, *d* (*br*), J = 12 Hz, H-5], 1.22 (3H, *s*, H-14) and 0.82 (3H, *s*, H-15). The stereochemistry at C-3 and C-7 were established by measuring the J values of H-3 ($J_{3e,2a}$ = 2 Hz, $J_{3e,2e}$ = 2 Hz) and H-7 ($J_{7a,8a}$ = 12 Hz, $J_{7a,8e}$ = 3 Hz, $J_{7a,6a}$ = 3 Hz and $J_{7a,6e}$ = 13.5 Hz) and by using a Dreiding model.

EXPERIMENTAL

Inula viscosa (L.) Ait. was collected from the outskirts of Istanbul in September 1985. It was identified by Dr. E. Tuzlaci (University of Marmara, Istanbul) and a voucher is deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul (ISTE 56112).

Isolation and characterization of compounds. Air dried and powdered aerial parts of the plant (1 kg) were extracted with petrol (bp 40–70°)–Et_2O (2:1). After filtration, the extract was concentrated *in vacuo* at room temp. A portion (30 g) of the residue (45.5 g) was subjected to CC over silica gel (5 × 70 cm). Elution was started with petrol, a gradient of ether was then added up to 100% Et_2O, followed by MeOH up to 10% MeOH. Triterpenoid esters were obtained from the first fractions. The compounds under study were further separated and/or purified by PTLC.

Viscic acid (**4**). Oil (10 mg). UV λ_{max}^{MeOH} nm: 218 (log ε 4.5); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 2960, 2840, 2600 (*br* sh), 1690, 1620, 1450, 1375, 1150, 1040, 990, 970, 950, 900 820; ^{1}H NMR (400 MHz, $CDCl_3$): see text; MS (probe) 70 eV, m/z (rel. int.): 250 $[M]^+$ (22), 232 $[M-H_2O]^+$ (64), 217 $[M-H_2O-Me]^+$ (28), 200 (80), 193 (44), 182 (38).

Viscosic acid (**5**). Oil (8 mg). UV λ_{max}^{MeOH} nm: 215 (log ε 4.3); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2950, 2840, 2600 (*br* sh), 1695, 1620, 1445, 1380, 1100, 1050, 980, 820, 750; ^{1}H NMR (400 MHz, $CDCl_3$) see text; MS (probe) 70 eV (rel. int.): 264 $[M]^+$ ($C_{16}H_{24}O_3$) (methyl ether of viscosic acid) (18), 250 $[M-CH_2]^+$ (16), 249 $[M-Me]^+$ (68), 233 (13), 203 (20), 156 (31), 117 (98).

Epoxidation of costic acid methyl ester. *p*-Chloroperbenzoic acid (10 mg) was added to costic acid methyl ester (5 mg) in 1 ml CH_2Cl_2 in the presence of $NaHCO_3$ (10 mg). The mixture was left at room temp. for 1 hr. The ^{1}H NMR spectrum of the resulting compound was identical with that of compound **5**.

Acknowledgements—This work was supported by the Health Sciences Institute of the University of Istanbul (Grant No. 114). The authors thank Dr. J. Jakupovic (Berlin) for his kind help in structure determination.

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Phytochemistry, Vol. 26, No. 4, pp. 1224–1226, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00
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A FLAVONOL GLYCOSIDE FROM *LYSIMACHIA MAURITIANA*

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(*Revised received* 29 *September* 1986)

Key Word Index—*Lysimachia mauritiana*; Primulaceae; mauritianin; kaempferol-3-*O*-(2,6-di-*O*-α-rhamnopyranosyl-β-galactopyranoside); flavonol glycoside.

Abstract—From the whole plant of *Lysimachia mauritiana*, a new flavonol glycoside (mauritianin) was isolated together with hyperin, kaempferol-3-*O*-robinobioside and kaempferol-3-*O*-α-rhamnopyranosyl-(1-2)-β-galactopyranoside. The structure of mauritianin was established as kaempferol-3-*O*-(2,6-di-*O*-α-rhamnopyranosyl-β-galactopyranoside).

INTRODUCTION

Flavonol glycosides of the kaempferol, quercetin and myricetin type have already been isolated from the genus *Lysimachia*, a member of the Primulaceae (*L. vulgaris* [1, 2], *L. punctata* [3] and *L. nummularia* [4]). Initial chemical investigations of *L. mauritiana* led to the isolation and structure elucidation of sapogenins [5, 6]. In this paper we report the isolation and characterization of four flavonol glycosides from this plant. Hyperin and kaempferol-3-*O*-rhamnosyl galactosides are reported for the first time in *Lysimachia*; mauritianin is a new compound, which an anti-tumour promoter [7].

RESULTS AND DISCUSSION

The concentrated methanol extract prepared from the air dried plant was extracted successively with ethyl acetate and *n*-butanol. One flavonol glycoside (compound **1**) was isolated on a Sephadex LH-20 column using water–methanol from the ethyl acetate fraction, and another three flavonol glycosides (compounds **2**–**4**) were isolated by the same method from the *n*-butanol fraction.

Compound **1**, yellow needles, mp 238.5–239°, gave positive ferric chloride and Mg + HCl tests and was identified as hyperin by direct comparison with an authentic sample.