Phytochemistry, Vol. 24, No. 6, pp. 1392–1393, 1985.
Printed in Great Britain.

0031–9422/85 \$3.00 + 0.00

ONOGNAPHALIN, A FURTHER 5-METHYL COUMARIN FROM *ONOSERIS GNAPHALIOIDES*

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(*Revised received* 10 *August* 1984)

Key Word Index—*Onoseris gnaphalioides*; *O. acerifolia*; *O. lopezii*; *Gerbera ambigua*; Compositae; Mutisieae; 5-methyl coumarins; 6-methyl-2-hydroxyacetophenone.

Abstract—From the roots of *Onoseris gnaphalioides* in addition to a known 5-methyl coumarin a new type was isolated. The aerial parts contain a glucoside of 4-hydroxy-5-methyl coumarin. From *Gerbera ambigua* a compound related to the possible precursor of the 5-methyl coumarins was isolated.

From three species of the genus *Onoseris* (Compositae, tribe Mutisieae, subtribe Mutisiinae) a characteristic 5-methyl coumarin with a methyl mercapto group at C-4 was isolated [1–3]. We now have studied a further species from Peru, *Onoseris gnaphalioides* Muschler. The roots gave widespread triterpenes (see Experimental), 5-methyl-4-methylmercaptocoumarin [1], 2-methoxy-5-methyl-8-chromone [1], the lactone **1** [3] as well as a further compound, the coumarin **2**, molecular formula $C_{16}H_{14}O_3$. The ^{1}H NMR spectrum (see Experimental) indicated that most likely also a 5-methyl coumarin was present with substituents at C-3 and C-4. Spin decoupling allowed the assignment of all signals. The homoallylic couplings between H-11 and H-14 which both were coupled with the same proton (H-10) indicated the presence of a cyclopentene ring with an allylic oxygen function as the chemical shift of the broadened doublet at δ5.30 (H-11) required such a substitution. A pair of double doublets at δ2.77 and 2.59 (H-9) also were coupled with H-10. Thus the whole sequence could be assigned, while the chemical shifts of H-9 and H-9′ obviously required an benzylic position. Accordingly, the only possible structure was **2**. Also the mass spectrum supported this assumption. The base peak most likely was formed by loss of cyclopentadienyl radical. Compound **2** most likely is formed by degradation of a 5-methyl coumarin which was linked with a geranyl moiety as these side chains are often found in 5-methylcoumarins. Compound **2** we have named onognaphalin.

The aerial parts gave in addition to widespread triterpenes, the β-D-glucopyranoside of 4-hydroxy-5-methyl coumarin, so far only isolated from an *Ethulia* species [4].

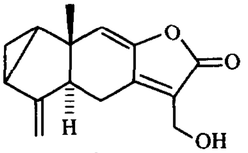
The roots of *Onoseris lopezii* Ferreyra, also collected in Peru, gave trideca-pentaynene and the typical 4-methyl mercapto-5-methyl coumarin, while the roots of *Onoseris acerifolia* H.B.K. afforded 2-hydroxy-α-curcumene [5], most likely the precursor of the perezones, which are widespread in the tribe.

From the aerial parts of *Gerbera ambigua* (Cass.) Sch. Bip. collected in Transvaal, in addition to trideca-1,11-dien-3,5,7,9-tetrayne, the acetophenone derivative **3** was isolated. The structure easily could be deduced from the ^{1}H NMR spectrum (see Experimental). Probably **3**, which itself is most likely an acetogenin, is formed by decarboxylation of the precursor of all 5-methyl coumarins. These compounds are found in several *Gerbera* species [6–8] and in some other genera of the Mutisieae like *Jungia* [9], *Trixis* [10] and *Perezia* [11]. However, these 5-methylcoumarins are present too in representatives of the tribe Vernonieae [4, 12]. The roots gave also trideca-dien-tetrayne and isocomene [13].

The chemotaxonomic importance of 4-methyl mercaptane-5-methyl coumarin for the genus *Onoseris* is established again, while the role of the 5-methyl coumarins in general still is not clear.

EXPERIMENTAL

The air dried plant material of *Onoseris gnaphalioides* (voucher RMK 9305) was worked-up in the usual fashion [13]. The CC (SiO_2) fractions of the roots (50 g) were as follows: 1 (Et_2O–petrol, 1:9), 2 (Et_2O–petrol, 1:1) and 3 (Et_2O and Et_2O–MeOH, 9:1). TLC (SiO_2, PF 254) of fraction 1 (Et_2O–petrol, 1:9) gave 5 mg lupenone, 5 mg lupeyl acetate, 5 mg



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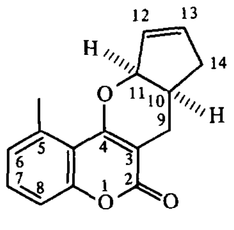

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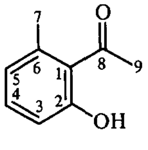

3

friedelinyl acetate and 5 mg taraxasteryl acetate. TLC of fraction 2 (Et_2O–petrol, 1:1) gave 10 mg 4-methyl mercapto-5-methyl coumarin and TLC of fraction 3 (Et_2O) gave 8 mg 2-methoxy-5-methyl-8-chromone (R_f 0.50) and a mixture (R_f 0.75), which was separated again by TLC (Et_2O–petrol, 1:1, two developments) affording 2 mg **2** (R_f 0.72), 4 mg stigmasterol (R_f 0.63) and 2 mg **1** (R_f 0.40). The polar CC fraction of the aerial parts (300 g) (Et_2O–MeOH, 9:1 and 1:1) gave 20 mg crystals, which were identical with the β-D-glucopyranoside of 4-hydroxy-5-methyl coumarin (mp 150°, lit. 150° [4]) while the less polar fraction (Et_2O–petrol, 1:9) afforded by TLC (Et_2O–petrol, 1:9) 15 mg squalene, 10 mg lupenone, 10 mg lupeyl acetate, 5 mg friedelinyl acetate and 10 mg taraxasteryl acetate.

The extract of 40 g roots of *Onoseris lopezii* (voucher RMK 9123) was separated first by CC. TLC (petrol) of the petrol fraction gave 1 mg trideca-3,5,7,9,11-pentayn-1-ene and the fraction obtained by Et_2O–petrol, 1:1, gave by TLC (Et_2O) 2 mg 4-methyl mercapto 5-methyl coumarin (R_f 0.68). The aerial parts (420 g) afforded 15 mg lupenone and 10 mg lupeol.

The air dried roots (60 g, voucher RMK 9295) of *Onoseris acerifolia* gave by CC and TLC (s.a.) 75 mg sesquicarene and 200 mg 2-hydroxy-α-curcumene (TLC: Et_2O–petrol, 1:3, R_f 0.55).

The air dried aerial parts (90 g) of *Gerbera ambigua* (voucher 81/252, collected in Transvaal) afforded by CC and TLC 0.5 mg trideca-1,11-dien-3,5,7,9-tetrayne (petrol, R_f 0.55), 2 mg squalene (petrol, R_f 0.40), 2 mg benzyl benzoate (Et_2O–petrol, 1:9, R_f 0.62) and 3 mg **3** (Et_2O–petrol, 1:1, R_f 0.46), colourless oil, IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 3500–2500, 1630, 1575 (hydrogen bonded *o*-hydroxyacetophenone); MS *m/z* (rel. int.): 150.068 $[M]^+$ (38) (calc. for $C_9H_{10}O_2$: 150.068), 135 $[M-Me]^+$ (100), 107 $[135-CO]^+$ (8); ^1H NMR ($CDCl_3$): δ6.74 *br d* (H-3), 6.86 *br d* (H-5), 7.30 *dd* (H-4), 2.62 *br s* (H-7), 2.69 *s* (H-9) (*J* [Hz]: 3,4 = 4,5 = 8). The roots (95 g) gave 2 mg trideca-1,11-dien-3,5,7,9-tetrayne and 5 mg isocomene. Known compounds were identified by comparison of the 400 MHz ^1H NMR spectra with those of authentic compounds and by co-TLC.

Onognaphalin (**2**). Colourless crystals, mp 129° (petrol); IR $\nu_{\max}^{CCl_4}$ cm^{-1}: 1695, 1625, 1605, 1570 (coumarin); UV (Et_2O): (319), 306, 289, 279, 208 nm; MS *m/z* (rel. int.): 254.094 $[M]^+$ (61) (calc. for $C_{16}H_{14}O_3$: 254.094), 189 $[M-C_5H_5]^+$ (100), 188 $[M-C_5H_6]^+$ (21), 135 $[189-CO_2]^+$ (44); ^1H NMR (400 MHz $CDCl_3$): δ7.00 *br d* (H-6), 7.32 *dd* (H-7), 7.15 *br d* (H-8), 2.77 *dd* (H-9), 2.59 *dd* (H-9′), 2.85 *ddddd* (H-10), 5.30 *br d* (H-11), 6.11 *br ddd* (H-12), 6.00 *dddd* (H-13), 2.62 *br d* (H-14), 2.26 *ddddd* (H-14′), 2.68 *s* (H-15), (*J* [Hz]: 6,7 = 7,8 = 8; 9,9′ = 16; 9,10 = 7; 9,10′ = 4.5; 10,11 = 6; 10,14 = 6; 10,14′ = 5.5; 11,12 = 11,13 = 11,14′ ~ 1.5; 12,13 = 5.5; 13,14 = 13,14′ ~ 2; 14,14′ = 17).

Acknowledgements—We thank the Deutsche Forschungsgemeinschaft for financial support and Dr. L. E. Bishop, Seattle, Washington, for his help during plant collection.

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