Phytochemistry, Vol. 26, No. 9, pp. 2635–2636, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00

TWO FARNESOL DERIVATIVES FROM *COUSINIA ADENOSTICA*

ABDOLHOSSEIN RUSTAIYAN, ZAHRA SHARIF and ABULFAZL S. SADJADI*

Department of Chemistry, Shahid Beheshty University, Eveen, Tehran, Iran; *Department of Chemistry, University of Technology and Engineering, Tehran, Iran

(*Received* 28 *August* 1986)

Key Word Index—*Cousinia adenostica*; Compositae; Sesquiterrene lactones; cynaropicrin; chlorojanerin; janerin; farnesol derivatives.

Abstract—The aerial parts of *Cousinia adenostica* afforded, in addition to widespread compounds, cynaropicrin, chlorojanerin and janerin as well as two new farnesol derivatives, 5,8,12-trihydroxyfarnesol and 12-acetoxy-5,8-dihydroxyfarnesyl acetate.

From members of the genus *Cousinia* (Compositae, Cynareae) so far only acetylenic compounds have been reported [1]. We now have studied the constituents of *Cousinia adenostica* Bronm. In addition to lupeol and taraxasterol, the three guaianolides cynaropicrin [2], chlorojanerin [3] and janerin [3] were isolated. The polar fractions further afforded two farnesol derivatives, the tetrol **1** and the corresponding diacetate **2**, both gave the tetraacetate **3** on acetylation. The structures could be elucidated from the ^{1}H NMR data (Table 1), by spin decoupling and from the fragmentation pattern in the mass spectrum of **3**.

The ^{1}H NMR spectrum of **3** clearly showed that acetoxy groups were at C-1 and C-12 [4.56 *br d* (2H) and 4.44 *br s* (2H)] while the position of the remaining two oxygen functions could not be assigned directly. However, the corresponding signals of the protons at the acetoxy group bearing carbon indicated that one of the ester groups were α- and the other one β to the olefinic proton. Thus these two acetoxy groups could be placed at C-4 and C-9 or at C-5 and C-8.

Inspection of the mass spectrum showed that many fragments were visible which could only be explained by loss of $CH_2X(CH_2)$=$CHCH_2OAc$. This excluded a structure with an acetoxy group at C-4 and the tetraacetate therefore was **3**. The position of the free hydroxyls in **2** was thus also settled. The stereochemistry of the double bond was assigned by comparing the chemical shifts with those of similar compounds. The occurrence of guaianolides such as cynaropicrin agrees with the proposed close relationship of *Cousinia* with *Jurinea*, *Onopordon* and *Saussurea*, where these lactones are frequent [4].

EXPERIMENTAL

General. Plant material was collected in July 1982, north of Tehran (Disin) and authenticated at the Research Institute of Plant Pests and Diseases herbarium, where a specimen has been deposited.

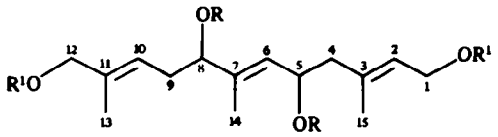
Isolation. The air-dried aerial parts of *Cousinia adenostica* (250 g) were extracted with Et_2O–petrol (2:1). The resulting extract, after removal saturated hydrocarbons by treatment with MeOH, was first separated by CC (silica gel). Repeated TLC (silica gel, PF 254) ether–petrol (4:1) gave 120 mg **2** (R_f 0.65) and ether–MeOH (98:2) of the polar fractions gave 145 mg **1** (R_f 0.50).

5,8,12-*Trihydroxyfarnesol.* Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), which was heated with Ac_2O for 1 hr at 70°. TLC (SiO_2, PF 254, Et_2O–petrol, 1:1) gave **3** (R_f 0.65); colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1745, 1240 (OAc); MS *m/z* (rel. int. %): 438.225 (0.15) $[M]^+$ (calc. for $C_{23}H_{34}O_8$: 438.225), 378 (0.3) $[M-AcOH]^+$, 318 (0.3) $[378-AcOH]^+$, 311 (6) $[M-CH_2C(Me)=CHCH_2OAc\ (A)]^+$, 258 (1) $[318-AcOH]^+$, 251 (2.3) $[311-AcOH]^+$, 209 (11) $[251-ketene]^+$, 191 (8) $[251-AcOH]^+$,

Table 1. ^{1}H NMR spectral data of **1**–**3** (400 MHz, $CDCl_3$, TMS as internal standard)

	1	2	3
H-1	4.16 *br d*	4.61 *dd* 4.58 *d*	4.56 *br d*
H-2	5.48 *br t*	5.42 *m*	5.38 *m*
H-4	2.28 *dd* 2.19 *dd*	2.29 *dd* 2.18 *dd*	2.40 *dd* 2.22 *dd*
H-5	4.56 *ddd*	4.53 *ddd*	5.63 *ddd*
H-6	5.41 *br d*	5.38 *br d*	5.37 *br d*
H-8	4.07 *br t*	4.06 *br t*	5.15 *br t*
H-9	2.33 *br t*	2.32 *br t*	2.44 *ddd* 2.35 *ddd*
H-10	5.38 *br t*	5.42 *m*	5.34 *ttq*
H-12	4.00 *br s*	4.46 *br s*	4.44 *br s*
H-13	1.67 *br s*	1.67 *br s*	1.68 *br s*
H-14	1.69 *d*	1.67 *d*	1.73 *d*
H-15	1.73 *br s*	1.76 *br s*	1.76 *br s*
OAC	—	2.07 *s*	2.09 *s*
		2.05 *s*	2.07 *s*
			2.07 *s*
			2.03 *s*

J[Hz]: 1,2 = 4,5 = 8,9 = 8,9′ = 9′,10 = 7; 4,4′ = 13.5; 4′,5 = 5.5; 5,6 = 8; 9,9′ = 14.



1 R = R¹ = H
2 R = H, R¹ = Ac
3 R = R¹ = Ac

149 (100) [209 – AcOH]⁺, 131 (21) [191 – AcOH]⁺. $[\alpha]_D^{24}$ +2.6° (589 nm), +2.6° (578 nm), +3.2° (546 nm), +4.2° (436 nm) ($CHCl_3$; *c* 0.3)

12-*Acetoxy*-5,8-*dihydroxy farnesyl acetate* (**2**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3610 (OH), 1750, 1245 (OAc), which on acetylation (Ac_2O, 1 hr, 70°) gave **3**, identical with the tetraacetate obtained from **1** (^1H NMR, IR and TLC in Et_2O–petrol, 1:1 and $CHCl_3$–petrol, 1:1).

Acknowledgements—A. Rustaiyan thanks The Ministry of Culture and Higher Education of Iran for financial support and Dr F. Termeh for identification of the plant material.

REFERENCES

1. F. Bohlmann, T. Burkhardt and C. Zdero (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
2. M. Suchy, V. Herout and F. Sorm (1960) *Coll. Czech. Chem. Commun.* **25**, 2777.
3. A. G. Gonazales, J. Bermejo, I. Cabrera, A. Galindo and G. M. Massanet (1977) *An. Quim.* **73**, 86.
4. F. C. Seaman (1982) *Bot. Rev.* **48**, 121.