Pergamon

PII: S0031-9422(97)00556-6

Phytochemistry, Vol. 47, No. 2, pp. 227–229, 1998

Printed in Great Britain
0031–9422/98 $19.00+0.00

EUDESMANE SESQUITERPENOIDS FROM *PLUCHEA QUITOC**

GISELLE M. S. P. GUILHON and ADOLFO H. MÜLLER†

Departamento de Química, Centro de Ciências Exatas e Naturais, Universidade Federal do Pará, Campus Universitário, 66075-970 Belém, PA, Brazil

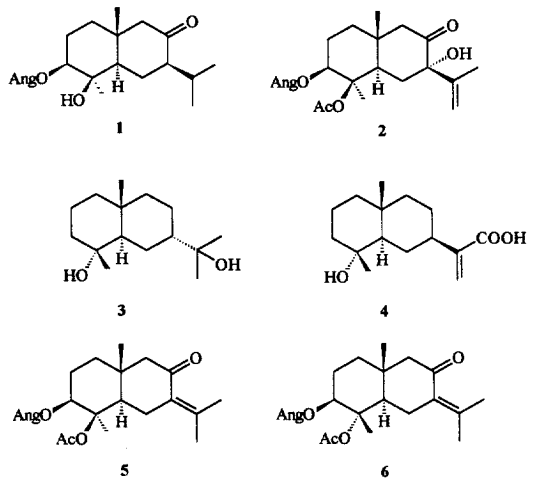
(*Received in revised form* 17 *May* 1997)

Key Word Index—*Pluchea quitoc*; Compositae; eudesmane sesquiterpenoids.

Abstract—Two new sesquiterpenoids with an eudesmane carbon skeleton, 3β-angeloyloxy-4β-hydroxy-7α-H-eudesman-8-one and 3β-angeloyloxy-4β-acetoxy-7α-hydroxy-eudesm-11-en-8-one, were isolated from the hexane extract of the aerial parts of *Pluchea quitoc* and characterized mainly by 1D and 2D NMR spectroscopy. 7β-H-eudesman-4α,11-diol was also obtained from the same extract and ilicic acid was isolated from the chloroform-soluble fraction of the ethanolic extract. © 1997 Elsevier Science Ltd

INTRODUCTION

The aerial parts of *Pluchea quitoc* DC (tribe Inulae) are a rich source of eudesmane-type sesquiterpenoids [1] like other species of this genus [2–4]. The present work deals with the isolation and structural determination of two further new sesquiterpenoids, 3β-angeloyloxy-4β-hydroxy-7α-H-eudesman-8-one (**1**) and 3β-angeloyloxy-4β-acetoxy-7α-hydroxy-eudesm-11-en-8-one (**2**). Their structures were established on the basis of 1D and 2D NMR spectral data. We also report the occurrence of 7β-H-eudesman-4α-11-diol (**3**), first isolated from *P. arguta* [5] and whose structure was later revised to **3** [6], together with ilicic acid (**4**), first obtained from *Ambrosia ilicifolia* [7].



RESULTS AND DISCUSSION

The hexane extract of the aerial parts of *P. quitoc* when chromatographed on silica gel columns afforded the sesquiterpenoids **1–3**. Compound **4** was obtained from the chloroform-soluble fraction of the ethanolic extract, using similar techniques. The structure of these compounds were deduced mainly from their ^1H and ^{13}C NMR spectral data (Tables 1 and 2), with the aid of ^1H-^1H and ^{13}C-^1H COSY spectra. The multiplicities of the carbons were determined by DEPT NMR experiments.

The ^1H NMR spectrum of compound **1** in $CDCl_3$ (Table 1) contained some overlapping signals. It was possible to assign these signals when the ^1H NMR spectrum was obtained in deuteriobenzene (Table 1). The assignment of H-9α was confirmed by the presence of a cross-correlation peak due to *W*-coupling with Me-14 in the ^1H-^1H COSY spectrum. The presence of a non-conjugated ketone function was evident from the ^{13}C NMR data (Table 2). The stereochemistry at C-3 was determined from the $J_{2,3}$ values, and that at C-4 was based on the chemical shift of Me-15 at δ_H 1.15 [8]. The isopropyl group in **1** was proposed to be β (equatorial) in accordance with the coupling constants observed for H-6α.

The ^1H NMR spectrum (Table 1) of compound **2** showed characteristic signals of acetoxy and angeloyloxy moieties. There were also two lower field signals attributed to the olefinic hydrogens (H-13), both showing cross-correlation peaks with Me-12 in the ^1H-^1H COSY spectrum, and also between Me-

* Based in part on the doctoral thesis that will be presented by G.M.S.P.G. to the Universidade Federal do Pará, PA, Brazil.

† Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR spectral data of compounds **1** and **2** (300 MHz)

H	**1**	**1** (in C_6D_6)	**2**
3α	4.83 *dd* (11.5; 4.7)	4.85 *dd* (12.0; 4.5)	5.88 *dd* (11.2; 5.3)
5α	2.00†	1.80 *m*	3.09 *dd* (13.6; 2.8)
6α	2.30 *bd* (12.4)	2.17 *dt* (13.7; 1.9)	2.56 *dd* (14.1; 2.8)
6β	1.75 *m*	1.48 *m*	1.74 *dd* (14.1; 13.6)
7α	2.00†	1.68†	—
9α	2.00†	1.87 *dd* (12.7; 1.5)	2.55 *d* (12.2)
9β	2.30 *d* (12.4)	2.23 *bd* (12.7)	2.19 *d* (12.2)
11	2.00†	1.68†	—
12	0.99 *d* (5.8)	0.88 *d* (6.6)	1.66 *bs*
13	0.81 *d* (5.8)	0.82 *d* (6.6)	5.10 *q* (1.4)
13′	—	—	4.92 *bs*
14	0.90 *s*	0.60 *s*	0.93 *s*
15	1.15 *s*	0.95 *s*	1.36 *s*
3′	6.10 *qq* (7.2; 1.4)	5.73 *qq* (7.2; 1.5)	6.06 *qq* (7.2; 1.5)
4′	1.99 *dq* (7.2; 1.4)	1.97 *dq* (7.2; 1.5)	1.97 *dq* (7.2; 1.5)
5′	1.90 *dq* (1.4; 1.4)	1.84 *dq* (1.5; 1.5)	1.89 *dq* (1.5; 1.5)
4-AcO	—	—	1.97 *s*
7-OH	—	—	4.08 *bs**

Solution in $CDCl_3$ referenced to $CHCl_3$ at δ 7.26 p.p.m. Coupling constant *J*(Hz) in parentheses.

* Signal changes with D_2O.

† Overlapping signals, determined by ^{1}H-^{1}H and ^{13}C-^{1}H COSY spectral data.

Table 2. ^{13}C NMR spectral data of compounds **1**, **2** and **4** (75.4 MHz)

C	**1**	**1** (in C_6D_6)	**2**	**4**
1	38.6 *t*	38.5 *t*	37.6 *t*	40.9 *t*
2	25.6 *t*	25.9 *t*	25.6 *t*	20.1 *t*
3	81.3 *d*	81.5 *d*	73.7 *d*	44.5 *t*
4	74.0 *s*	73.7 *s*	86.7 *s*	72.6 *s*
5	57.6 *d*	57.9 *d*	44.5 *d*	54.9 *d*
6	23.9 *t*	23.9 *t*	33.3 *t*	26.7 *t*
7	47.4 *d*	47.6 *d*	80.3 *s*	40.0 *d*
8	213.6 *s*	209.9 *s*	211.3 *s*	27.1 *t*
9	56.0 *t*	56.0 *t*	55.0 *t*	43.3 *t*
10	39.2 *s*	38.5 *s*	40.5 *s*	34.7 *s*
11	28.1 *d*	27.9 *d*	143.9 *s*	145.3 *s*
12	20.7 *q*	20.8 *q*	18.2 *q*	171.2 *s*
13	20.9 *q*	21.2 *q*	115.1 *t*	124.2 *t*
14	18.9 *q*	17.9 *q*	19.3 *q*	18.7 *q*
15	17.9 *q*	18.8 *q*	16.8 *q*	22.3 *q*
1′	168.4 *s*	167.7 *s*	167.0 *s*	—
2′	127.8 *s*	126.2 *s*	128.0 *s*	—
3′	138.6 *d*	138.3 *d*	137.9 *d*	—
4′	15.8 *q*	15.9 *q*	15.7 *q*	—
5′	20.6 *q*	20.8 *q*	20.6 *q*	—
4-CH_3CO	—	—	170.3 *s*	—
4-CH_3CO	—	—	22.7 *q*	—

Solution in $CDCl_3$ referenced to $CHCl_3$ at δ 77.23 ppm. Multiplicity of the carbons were determined by DEPT experiments. Assignments were confirmed by ^{13}C-^{1}H COSY spectral data.

14 and H-9α (*W*-coupling). The presence of a non-conjugated carbonyl (δ_C 211.3) and a hydroxy group bounded to a non-protonated carbon (δ_C 80.3) was also evident from the ^{13}C NMR spectrum (Table 2) and permitted us to locate the hydroxy group at C-7. The stereochemistry at C-3 was proposed from the $J_{2,3}$ values, and that at C-4 from the chemical shifts of C-4 and C-15 (δ_C 86.7 and 16.8) when compared with those of compounds **5** (δ_C 87.4 and 16.7) [1] and **6** (δ_C 83.4 and 19.3) [9], that suggested the β configuration of the acetoxy group as in **5**. The diaxial dishielding effect of the hydroxyl group on H-9α, led us to propose the α (axial) orientation of this group at C-7.

Compound **3**, first isolated from *Pluchea arguta* [5], whose structure was confirmed by synthetic methods [6], showed ^{1}H and ^{13}C NMR data in accordance with the literature. Compound **4**, known as ilicic acid, first isolated from *Ambrosia ilicifolia* [7] and later from many other Compositae, showed ^{1}H NMR data in accordance with the literature. The assignments of carbons C-1, C-3, C-5, C-7, C-8 and C-9 in the ^{13}C NMR spectrum (Table 2) were revised on the bases of the ^{1}H-^{1}H and ^{13}C-^{1}HCOSY spectral data, and are in agreement with those of the methyl ester of compound **4** [10]. Comparison of the chemical shifts of C-5 in compounds **3** (δ_C 49.4) and **4** (δ_C 54.9), confirms their opposite stereochemistry at C-7, since it is known that when the substituent at C-7 is axial, as in compound **3**, there is an upfield shift of the signal of C-5 [6].

EXPERIMENTAL

General. Mps: uncorr; IR: $CHCl_3$; ^{1}H and ^{13}C NMR: 300 and 75.4 MHz, respectively, on a Varian GEMINI 300 instrument; EIMS: VG.AUTO SPEC-300; TLC: Silica gel 60H (Merck 7736); CC: Silica gel (Merck 7734).

For *plant material* and *extraction* with hexane see reference [1]. The residue of the aerial parts of *P. quitoc*, after extraction with hexane, was percolated with EtOH. The soln was concd on a rotatory evaporator and the extract submitted to partition with $CHCl_3$, EtOAc and *n*-BuOH.

Isolation. The fr. of the hexane extract eluted with mixts of hexane–EtOAc (9:1) on CC, afforded compound **3** (9 mg) that was purified by CC with hexane–CH_2Cl_2–MeOH (100:100:3.8). Compounds **1** (17 mg) and **2** (8 mg) were obtained from the former column eluted with hexane–EtOAc (17:3), and both purified by CC with mixts of hexane–Me_2CO (49:1). The

$CHCl_3$-soluble fr. was submitted to chromatography on a silica gel column eluted with mixts of hexane–$CHCl_3$–EtOAc. The frs eluted with $CHCl_3$–EtOAc (1:1) afforded compound **4** (19 mg) which was purified by CC with hexane–Me_2CO (17:3).

3β-Angeloyloxy-4β-hydroxy-7α-H-eudesman-8-one (**1**). Oil, $[\alpha]_D$ +87.5° ($CHCl_3$, *c* 0.12). IR ν_{max} cm^{-1}: 3464 (OH), 1706, 1240 (CO, CO_2R); ^1H NMR: Table 1; ^{13}C NMR: Table 2; EIMS *m/z* (rel. int.): 336 $[M]^{\pm}$ (45); 294 $[M-C_3H_6]^{\pm}$ (11); 253 $[M-83]^+$ (33); 236 $[M-AngOH]^+$ (19); 221 $[236-Me]^{\pm}$ (23); 195 $[294-AngO]^+$ (41); 83 $[C_4H_7CO]^+$ (100).

4β-Acetoxy-3β-angeloyloxy-7α-hydroxy-11,12-dehydroeudesman-8-one (**2**). $[\alpha]_D$ +125.21° ($CHCl_3$, *c* 0.12). IR ν_{max} cm^{-1}: 3424 (OH), 1710, 1240 (CO, CO_2R), 1647, 825 (=CH_2); ^1H NMR: Table 1; ^{13}C NMR: Table 2; EIMS *m/z* (rel. int.): 392 $[M]^{\pm}$ (0); 332 $[M-AcOH]^{\pm}$ (3); 314 $[M-AcOH[H_2O]^{\pm}$ (10); 232 $[M-AcOH-AngOH]^{\pm}$ (10); 214 $[M-AcOH-AngOH-H_2O]^+$ (44); 199 $[214-Me]^+$ (24); 83 $[C_4H_7CO]^+$ (100).

Acknowledgements—The authors are grateful to Financiadora de Estudos e Projetos (FINEP) and Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES) for financial support. NMR studies were performed in the Universidade Federal do Pará NMR Laboratory. We also thank LEMAR-LPN-PADETEC, Universidade Federal do Ceará, for the mass spectra.

REFERENCES

1. Guilhon, G. M. S. P. and Müller, A. H., *Phytochemistry*, 1996, **43**, 417.
2. Bohlmann, F., Ziesche, J., King, R. M. and Robinson, H., *Phytochemistry*, 1980, **19**, 969.
3. Dominguez, X. A., Franco, R., Cano, G., Villarreal, R., Bapuji, M. and Bohlmann, F., *Phytochemistry*, 1981, **20**, 2297.
4. Ahmad, V. U., Fizza, K. and Sultana, A., *Phytochemistry*, 1989, **28**, 3081.
5. Ahmad, V. U., Farooqui, T. A., Fizza, K., Sultana, A. and Khatoon, R., *Journal of Natural Products*, 1992, **55**, 730.
6. Ando, M., Arai, K., Kikuchi, K. and Isogai, K., *Journal of Natural Products*, 1994, **57**, 1189.
7. Herz, W., Chikamatsu, H. and Tether, L. R., *Journal of Organic Chemistry*, 1966, **31**, 1632.
8. Ahmad, V. U. and Fizza, K., *Phytochemistry*, 1986, **25**, 949.
9. Rojatkar, S. R., Puranik, V. G., Tavale, S. S., Row, T. N. G. and Nagasampagi, B. A., *Phytochemistry*, 1987, **26**, 569.
10. Marco, J. A., Sanz, J. F. and Carda, M., *Magnetic Resonance Chemistry*, 1992, **30**, 678.