Phytochemistry, Vol. 25, No 1, pp. 264–266, 1986.
Printed in Great Britain

0031-9422/86 $3.00 + 0.00

NEO-CLERODANE DITERPENOIDS FROM *BACCHARIS INCARUM*

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(*Received* 9 *May* 1985)

Key Word Index—*Baccharis incarum*; Compositae; diterpenoids; neo-furanoclerodanes; bicyclic clerodanes; ^{13}C NMR.

Abstract—A new neo-clerodane diterpenoid was isolated from the aerial parts of *Baccharis incarum* together with the previously known diterpenoids bacchalineol and barticulidiol.

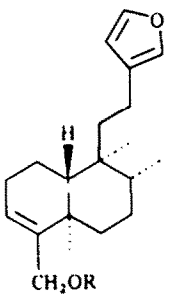
INTRODUCTION

In continuation of our investigations on the genus *Baccharis* [1], we have studied the constituents of *B. incarum* Wedd from the northern Andes region of Chile. The hexane extract of this plant yielded the triterpenes oleanolic acid and β-amyrin and spatulenol while the ethanolic extract gave three neo-clerodane diterpenoids. Two neo-clerodanes were identified as bacchalineol (**1**) [2] and barticulidiol (**2**) [3]. The third, **3**, proved to be novel and was designated bincatriol.

RESULTS AND DISCUSSION

The ^{1}H NMR spectra of **1** and **2** clearly indicated β-substituted furan derivatives as shown by sets of signals at δ7.3, 7.1 and 6.2. This was corroborated by mass spectral fragments at *m/z* 95, 94 and 81. The remaining signals in the ^{1}H NMR spectra of these compounds (Table 1) were in agreement with a clerodane-type carbon skeleton bearing oxygenated substituents at C-18 and/or C-19. Compounds **1** and **2** were identified as bacchalineol and barticulidiol diacetate, which were first described from *B. tricuneata* [2] and *B. articulata* [3] respectively. Table 2 shows the ^{13}C NMR data of these compounds (in the published spectrum of **1** [4] the assignments at C-12 and C-2 should be reversed).

The third compound, bincatriol, was shown to correspond to a clerodane-type diterpene possessing three primary hydroxyl groups (by formation of a triacetate), two trisubstituted double bonds, two tertiary and one secondary methyl group (Table 1). Decoupling experiments showed that the narrow doublet at δ4.05 in the ^{1}H NMR spectrum was coupled to the olefinic proton at δ5.33, whereas the olefinic triplet centred at δ5.57 was coupled to the doublet at δ4.16; the remaining oxymethylene protons were also of an allylic nature on the basis of their absorbance at δ4.13. The ^{13}C NMR spectrum of this compound was in agreement with these assignments and showed that the three hydroxyl substituents were at C-18, C-15 and C-16 by application of the usual shift parameters and comparison with data from the literature [5, 6]. It also defined the relative stereochemistry at C-5 and C-10 on account of the absorption of the C-19 angular methyl carbon at δ21.2, which demonstrated a trans-AB ring junction [7]. The relative configurations of carbons 8 and 9 were determinated by comparison of the δ values of the C-17 and C-20 methyl groups with those of model compounds and other closely related clerodane diterpenes [4, 5]. The values are in agreement with an equatorial methyl group at C-8 as depicted in **3** (the same values as in **1** and **2** of known relative stereochemistry). The *Z*-configuration of the 13,14-



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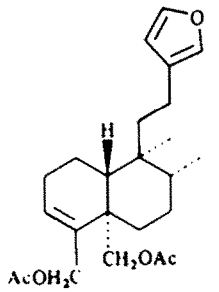

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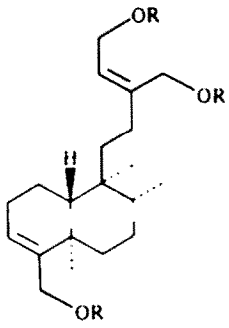

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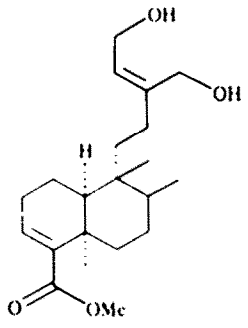

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Table 1. ^{1}H NMR data of compounds 1–3 (60 MHz (1a and 3b), 80 MHz (1b and 2) or 250 MHz (3a), $CDCl_3$, TMS as int. standard)

H	1a	1b	2	3a	3b
3	5.56 *m*	5.58 *m*	5.76 *m*	5.53 *m*	5.53 *m*
14	6.20 *s* (*br*)	6.24 *s* (*br*)	6.24 *s* (*br*)	5.57 *t* (7)	5.55 *t* (7)
15	7.31 *m*	7.33 *m*	7.34 *m*	4.16 *d* (7)	4.60 *d* (7)
16	7.17 *s* (*br*)	7.19 *s* (*br*)	7.19 *s* (*br*)	4.13 *s*	4.56 *s*
17	0.83 *d* (6)*	0.86 *d* (6)	0.84 *d* (6)	0.79 *d* (5.9)	0.80 *d* (6)
18	4.00 *s* (*br*)	4.52 *s* (*br*)	4.62 *s* (*br*)	4.05 *d* (1.5)	4.50 *s* (*br*)
19	1.03 *s*	1.08 *s*	4.11 *d* (12) 4.49 *d* (12)	1.04 *s*	1.10 *s*
20	0.70 *s*	0.75 *s*	0.78 *s*	0.71 *s*	0.73 *s*
Ac		2.06 *s*	2.05 *s* 2.06 *s*		2.05 *s* 2.06 *s*

*Values in parentheses are coupling constants in Hz.

double bond was determined by comparison of the δ_c of C-15 and C-16 with the corresponding signals in compound 4 (δ60.0 and 58.3), whose structure was determinated by X-ray analysis [8]. The absolute configuratiom of bincatriol was not determinated in this work but it probably corresponds to that shown in 3 since all the clerodane terpenoids isolated from *Baccharis* so far have the neo-clerodane configuration [9].

EXPERIMENTAL

Plant materials. Leaves and top parts of *Baccharis incarum* Wedd were collected in November at Toconce, Antofagasta, Chile. The material was identified by Professor C. Marticorena, Facultad de Biología, Universidad de Concepción and voucher specimens are kept at U.C. herbarium.

Isolation procedure. Dried and ground plant material (1.5 kg) was successively extracted in a Soxhlet with petrol (60–80°) and EtOH during 72 hr. The concd EtOH extract (80 g) was partitioned between $CHCl_3$ and aq. Na_2CO_3 (5%). The $CHCl_3$ extract (60 g) was fractionated by CC on silica gel eluted with mixtures of increasing polarity of petrol and EtOAc. Compounds 1–3 were isolated after repeated chromatography (silica gel) of suitable fractions and further purified by preparation of the acetylated derivatives.

Bacchalineol (1a). Oil (84 mg). $[\alpha]_D^{25} = -38.7$ ($CHCl_3$, *c* 0.10); IR ν_{max}^{film} cm^{-1}: 3350, 1490, 860; MS *m/z* (rel. int.): 302 $[M]^+$ (50), 287 $[M-Me]^+$ (15), 284 $[M-H_2O]^+$ (13), 272 $[M-CH_2O]^+$ (34), 271 $[M-CH_2OH]^+$ (45), 269 $[284-Me]^+$ (30), 189 $[284-C_6H_7O]^+$ (85), 95 $[C_6H_7O]^+$ (12), 94 $[C_6H_6O]^+$ (10), 81 $[C_5H_5O]^+$ (100); ^{1}H NMR: Table 1.

Bacchalineol-18-acetate (1b). Oil (46 mg). $[\alpha]_D^{25} = -21.1$ ($CHCl_3$, *c* 1.28); IR ν_{max}^{film} cm^{-1}: 1720, 1220; ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Barticulidiol-18,19-diacetate (2). Oil (31 mg). $[\alpha]_D^{25} = -42.1$ ($CHCl_3$, *c* 0.23); IR ν_{max}^{film} cm^{-1}: 1720, 1220, 860. MS *m/z* (rel. int.): 343 $[M-OAc]^+$ (7), 329 $[M-CH_2OAc]^+$ (2), 283 $[343-HOAc]^+$ (8), 270 $[329-OAc]^+$ (100), 188 $[283-C_6H_7O]^+$ (45), 95 $[C_6H_7O]^+$ (22), 94 $[C_6H_6O]^+$ (3), 81 $[C_5H_5O]^+$ (40); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Bincatriol (3a). Oil (250 mg). $[\alpha]_D^{25} = +202.1$ ($CHCl_3$, *c* 0.29); IR ν_{max}^{film} cm^{-1}: 3350, 1650. MS *m/z* (rel. int.): 302 $[M-H_2O-2H]^+$ (1), 287 $[302-Me]^+$ (3), 284 $[302-H_2O]^+$ (1), 272 $[302-CH_2O]^+$ (2), 271 $[302-CH_2OH]^+$ (8), 269 $[284-Me]^+$ (2), 189 $[284-C_6H_7O]^+$ (80), 81 $[C_5H_5O]^+$ (100); ^{1}H NMR: Table 1; ^{13}C NMR: Table 2.

Bincatriol-15,16,18-triacetate (3b). Oil (32 mg). IR ν_{max}^{film} cm^{-1}: 1720, 1240; ^{1}H NMR: Table 1.

Oleanolic acid, β-amyrin and spathulenol were isolated from the hexane extract and their identity was confirmed by direct comparison with authentic samples.

Table 2. ^{13}C NMR spectra of compounds 1–3 (20 MHz, $CDCl_3$, TMS as int. standard)*

Carbon	1b	2	3a
1	17.8	17.1	18.0
2	26.4†	25.9	26.4
3	125.6	128.4	121.8
4	142.4	139.0	147.6
5	37.5	40.4	37.6
6	35.9	31.7	36.9
7	26.9†	26.8	27.2
8	36.0	36.2	36.2
9	38.4	38.4	38.5
10	45.9	46.1	46.2
11	38.3	38.5	38.5
12	17.9	18.1	28.8
13	125.3	125.2	144.2
14	110.7	110.8	125.8
15	138.1	138.2	60.4
16	142.4	142.6	58.1
17	15.8	15.7	15.8
18	64.6	65.4	62.5
19	20.9	67.9	21.2
20	17.9	18.3	18.2
MeCO	170.5	170.8	—
MeCO	20.9	21.1	—

*Multiplicities were obtained with proton-flip method (APT).

†Interchangeable.

Acknowledgements—We are indebted to Dr. M. González of Universidad de Rosario, Argentina for NMR measurements. This work was supported by DIB (Universidad de Chile), Fondo Nacional de Ciencias (Grant 1060-84) and the Organization of American States.

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Phytochemistry, Vol 25, No. 1, pp 266–268, 1986
Printed in Great Britain

0031 9422 86 $3.00 + 0.00

ABIETANE DITERPENOIDS FROM THE ROOT OF *SALVIA LAVANDULAEFOLIA*

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(*Received* 27 *March* 1985)

Key Word Index—*Salvia lavandulaefolia*; Labiatae; diterpenoids; abietane derivatives; 7α-ethoxyroyleanone; 7α-ethoxy-12-*O*-methyl-royleanone.

Abstract—Two new derivatives of royleanone, 7α-ethoxyroyleanone and 7α-ethoxy-12-*O*-methyl-royleanone, besides the previously known diterpenes royleanone, 6,7-dehydroroyleanone, 7α-acetoxyroyleanone and inuroyleanol, have been isolated from the root of *Salvia lavandulaefolia*. The triterpenoid *O*-acetyloleanolic aldehyde has also been obtained from the same source.

INTRODUCTION

In a continuation of our studies on the diterpenoid compounds from *Salvia* spp. [1–3], we have now investigated the root of *S. lavandulaefolia* Vahl., a species from the aerial part of which ursolic acid and the known abietane diterpenoid galdosol have been isolated [4]. The presence in the root of this plant of unidentified derivatives of the abietane diterpenoid royleanone has also been reported [5]. Now, from the root of *S. lavandulaefolia*, six diterpenoid compounds have been isolated, four of which are the previously known royleanone (1) [6, 7], its 6,7-dehydroderivative [6, 8], inuroyleanol (11,14-dihydroxy-12-methoxy-abieta-8,11,13-trien-7-one) [9] and 7α-acetoxyroyleanone (2) [6]. The other two diterpenoids are new substances, whose structures were established as 7α-ethoxy-12-hydroxy-abieta-8,12-diene-11,14-dione (3, 7α-ethoxyroyleanone) and 7α-ethoxy-12-methoxy-abieta-8,12-diene-11,14-dione (4, 7α-ethoxy-12-*O*-methyl-royleanone). In addition, the rare triterpenoid *O*-acetyloleanolic aldehyde [10, 11] was also isolated from the same source.

RESULTS AND DISCUSSION

Compound 3, molecular formula $C_{22}H_{32}O_4$, had very similar UV properties (Table 1) to those of royleanone (1), thus establishing the presence of an identical chromophore in both substances (1 and 3). Moreover, the ^{1}H NMR spectrum of compound 3 (Table 2) was identical with that of horminone (5) [12], except for the presence of three additional signals which were assigned to an ethoxyl group (δ1.21, 3H, *t*, J = 7.1 Hz; 3.71, 1H, and 3.68, 1H, both *dq*, J_{gem} = 8.9 Hz, J_{vic} = 7.1 Hz), instead of the hydroxyl proton of horminone (5). From the above data it was clear that compound 3 was the 7α-ethoxy derivative of royleanone, since an alternative structure with a hydroxyl function at the C-7α position and the ethoxyl group in C-12 was firmly discarded on the basis of the UV data (see Table 1).

The other new diterpenoid isolated from the root of *S. lavandulaefolia* was a $C_{23}H_{34}O_4$ substance, the ^{1}H NMR spectrum of which was identical with that of compound 3 (Table 2), except for the presence of a three-proton singlet signal at δ3.82 instead of the phenolic one-proton singlet