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# HELIANGOLIDES AND BEJARANOLIDES FROM *CONOCLINIOPSIS PRASIIFOLIA*

FERDINAND BOHLMANN, CHRISTA ZDERO, ROBERT M KING* and HAROLD ROBINSON*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany, *Smithsonian Institution, Department of Botany, Washington, DC 20560, U S A

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**Key Word Index**—*Conocliniopsis prasiifolia*, Compositae, sesquiterpene lactones, furoheliangolides, bejaranolides

**Abstract**—A reinvestigation of the aerial parts of *Conocliniopsis prasiifolia* afforded two furoheliangolides, conoprasiolide-9-*O*,5′-*O*-diacetate and 5′-desoxyconoprasiolide, as well as two bejaranolides, 9β-hydroxy-4*E*-bejaranolide and 3α,9β-dihydroxy-4*E*-bejaranolide The structures were elucidated by $^1$H NMR spectroscopy The chemistry of *Conocliniopsis* supports the proposed close relationship to *Bejaranoa*

## INTRODUCTION

The investigation of the new monotypic Brazilian genus *Conocliniopsis* (tribe Eupatorieae, subtribe Gyptidinae) [1] afforded furoheliangolides similar to those present in the closely related genus *Bejaranoa* [2, 3] The reinvestigation of the polar fractions of the aerial parts of *Conocliniopsis prasiifolia* (DC) K et R gave two further furoheliangolides and two bejaranolides which strongly supported the close relationship of this genus to *Bejaranoa* [4] The results will be discussed in this paper

## RESULTS AND DISCUSSION

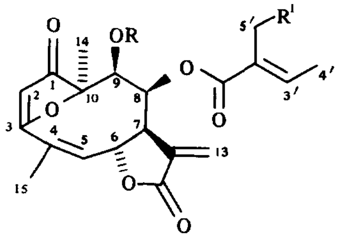
The aerial parts of *Conocliniopsis prasiifolia* afforded in addition to conoprasiolide (**1**) [2] and its 5′-*O*-acetate **2** [2] two further derivatives, the tiglate **3** and conoprasiolide-9-*O*,5′-*O*-diacetate (**4**) The structure of **3** followed from the molecular formula and the $^1$H NMR spectral data (Table 1) which were close to those of **1** [2] and **2** [2] The difference in the nature of the ester groups in **1** and **3** at C-8 caused some small variations of chemical shifts, especially of H-6 and H-8, while the nature of the ester residue at C-8 clearly followed from the typical signals of a tiglate The diacetate **4** already was prepared by acetylation of **1** and **2** [2] Accordingly, the observed $^1$H NMR spectral data (Table 1) were identical with those reported previously [2]

Furthermore, minute amounts of two additional sesquiterpene lactones were isolated The less polar lactone showed no molecular ion in the mass spectrum But as the $^1$H NMR spectrum (Table 1) clearly displayed the characteristic signals of a tiglate, the observed peak at $m/z$ 278 (corresponding to $C_{15}H_{18}O_5$) most likely was formed by elimination of tiglic acid Spin decoupling of the $^1$H NMR spectrum allowed the assignment of all signals which showed a marked similarity to the spectrum of 4*E*-bejaranolide [3] However, the H-9 signals were replaced by a double doublet at δ4 36 Irradiation of this signal collapsed the doublet at 2 29 to a singlet and the signal at 5 86 to a doublet The latter was further coupled with the fourfold doublet at 2 85 Its irradiation caused the expected changes of the H-13 signals as well as that of H-6, and therefore was due to H-7 Addition of deuterium oxide collapsed the double doublet at 4 36 to a doublet while the doublet at 2 29 disappeared, thus indicating a hydrogen bonded hydroxy group at C-9, similar to the situation in **1** and **3** Accordingly, the stereochemistry at C-9 also was the same and all data agreed with the proposed structure **5**

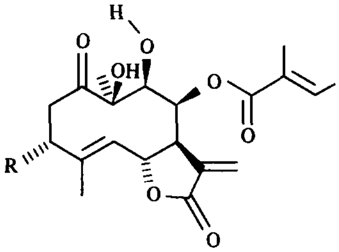
Table 1 $^1$H NMR spectral data of compounds 3–6 (400 MHz, $CDCl_3$, TMS as internal standard)

| | **3** | **4** | **5** | **6** |
|---|---|---|---|---|
| H-2<br>H-2′ | 5 65 *s* | 5 67 *s* | 2 27 *ddd* | 2 52 *dd* |
| | | | 3 55 *ddd* | 3 68 *dd* |
| H-3<br>H-3′ | — | — | 2 17 *ddd* | 5 03 *br dd* |
| | — | — | 2 96 *br ddd* | |
| H-5 | 5 98 *dq* | 5 99 *dq* | 4 97 *br d* | 4 98 *br d* |
| H-6 | 4 95 *ddq* | 5 39 *ddq* | 5 13 *dd* | 5 15 *dd* |
| H-7 | 3 64 *dddd* | 3 63 *dddd* | 2 85 *dddd* | 2 77 *dddd* |
| H-8 | 5 09 *dd* | 5 51 *dd* | 5 86 *dd* | 5 83 *dd* |
| H-9 | 4 18 *dd* | 5 32 *d* | 4 36 *dd* | 4 33 *dd* |
| H-13 | 6 35 *d* | 6 40 *d* | 6 26 *d* | 6 26 *d* |
| H-13′ | 5 69 *d* | 5 84 *d* | 5 56 *d* | 5 53 *d* |
| H-14 | 1 70 *s* | 1 52 *s* | 1 51 *s* | 1 50 *s* |
| H-15 | 2 07 *dd* | 2 08 *dq* | 1 87 *d* | 1 85 *d* |
| OH | 3 38 *d* | | 2 29 *d* | 2 30 *d*<br>4 24 *s* |
| OCOR | 6 83 *qq* | 7 11 *q* | 6 80 *qq* | 6 79 *qq* |
| | 1 83 *dq* | 1 98 *d* | 1 83 *br d* | 1 80 *br d* |
| | 1 78 *dq* | 4 91 *d* | 1 82 *br s* | 1 79 *br s* |
| | | 4 66 *d* | | |
| OAc | | 2 04 *s* | | |
| | | 2 12 *s* | | |

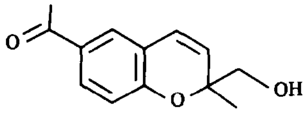
*J* (Hz) Compounds **3** and **4** 5, 6 = 4, 5, 15 = 1 7, 6, 7 = 4, 6, 15 = 1 7, 7, 8 ~ 1 5, 7, 13 = 2 8, 7, 13′ = 2 6, 8, 9 = 3, 3′, 4′ = 7 5, $5'_1, 5'_2$ = 12, compounds **5** and **6** 2, 2′ = 13, 5, 6 = 10; 5, 15 = 1, 6, 7 = 8, 7, 8 = 2 5, 7, 13 = 3 5, 7, 13′ = 3, 8, 9 = 4, 9, OH = 4, 3′, 4′ = 6, 3′, 5′ = 1, compound **5** 2, 3′ = 2′, 3 = 3, 3′ = 13, compound **6** 2, 3 = 11 5, 2′, 3 = 4



**1** R = H, R¹ = OH
**2** R = H, R¹ = OAc
**3** R = R¹ = H
**4** R = Ac, R¹ = OAc



R
**5** H
**6** OH



**7**

The $^1$H NMR spectrum of the more polar lactone was again similar to that of **5** and other bejaranolides [3], especially to that of 3α-hydroxy-4*E*-bejaranolide [3] Spin decoupling allowed the assignment of all signals clearly indicating that we were dealing with 3α,9β-dihydroxy-4*E*-bejaranolide (**6**)

Finally small amounts of the chromene derivative **7** [5] were isolated The additional chemical results on *Conoclinopsis* nicely agree with the close taxonomic relationship of this genus to *Bejaranoa* [4] and also to *Trichogonia* [6] which all are placed in the subtribe Gyptidinae [7] The co-occurrence of furoheliangolides and bejaranolides is of interest as most likely the latter are closely related to precursors of furoheliangolides Oxidation of **6** at C-3 followed by double bond isomerization and enolization could lead directly to **3**

## EXPERIMENTAL

The air dried aerial parts (260 g) (voucher RMK 8588, deposited in the US National Herbarium, Washington) was worked-up in the usual fashion and the polar CC-fractions obtained with $Et_2O$ and $Et_2O$–MeOH, 10 1, were separated by TLC (silica gel, PF 254 detected by UV 255 nm), first with $Et_2O$–petrol, 3 1, affording three bands The least polar one by repeated TLC ($Et_2O$) gave 1 mg **7** ($R_f$ ~ 0 6), while the second band ($R_f$ ~ 0 5) gave by TLC (using $Et_2O$–$C_6H_6$–$CHCl_3$, 1 1 1) and then $Et_2O$ 2 mg **5** ($R_f$ ~ 0 5), 10 mg **4** ($R_f$ 0 44) and 1 mg **3** ($R_f$ ~ 0 40) The last band ($R_f$ ~ 0 4) afforded after repeated TLC ($Et_2O$, several developments) 1 5 mg **6** ($R_f$ 0 4), 60 mg **2** ($R_f$ 0 37) and 2 mg **1** ($R_f$, ~ 0 3) The 400 MHz $^1$H NMR spectra of **1**, **2** and **7** were identical with those of authentic materials Due to the very small amount of compound **3** it could not be induced to crystallize though it was homogeneous by TLC in several different solvent systems

*5′-Desoxyconoprasiolide* (**3**) Colourless oil, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$ 3610 (OH), 1775 (γ-lactone), 1720 (C=$CCO_2R$), 1655, 1600 (C=C), MS *m/z* (rel int ) 374 137 $[M]^+$ (3) ($C_{20}H_{22}O_7$), 274 $[M - \text{TiglOH}]^+$ (2 5), 246 $[274 - CO]^+$ (9), 232 $[274 - C_2H_2O]^+$ (12), 83 $[C_4H_7CO]^+$ (91), 55 $[83 - CO]^+$ (100)

*Conoprasiolide-9-O,5′-O-diacetate* (**4**) Colourless crystals, mp 137° ($Et_2O$–petrol), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$ 1780 (γ-lactone), 1740 (OAc), 1720, 1660, 1610 (C=$CCO_2R$, C=CC=O), MS *m/z* (rel int ) 474 153 $[M]^+$ (20) ($C_{24}H_{26}O_{10}$)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\ \text{nm}}{-62 \quad -67 \quad -74 \quad -135 \quad -307} (CHCl_3, c\ 0\ 07)$$

*9β-Hydroxy-4E-bejaranolide* (**5**) Colourless crystals, mp 211° ($Et_2O$), IR $\nu_{max}^{CCl_4}$ cm$^{-1}$ 3600 (OH), 1780 (γ-lactone), 1715 (C=$CCO_2R$), MS *m/z* (rel int ) 278 115 $[M - \text{TiglOH}]^+$ (1 3) ($C_{15}H_{18}O_5$), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (77)

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\ \text{nm}}{+105 \quad +115 \quad +147 \quad +241} (CHCl_3, c\ 0\ 02)$$

*3α,9β-Dihydroxy-4E-bejaranolide* (**6**) Colourless crystals, mp, ~ 203°, IR $\nu_{max}^{CCl_4}$ cm$^{-1}$ 3600 (OH), 1780 (γ-lactone), 1715 ($C{=}CCO_2R$), MS m/z (rel int) 276 110 $[M - H_2O, \text{TiglOH}]^+$ (1) ($C_{15}H_{16}O_5$), 258 $[276 - H_2O]^+$ (2), 83 $[C_4H_7CO]^+$ (100), 55 $[83 - CO]^+$ (61)

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# KINGIDIOL, A KOLAVANE DERIVATIVE FROM *BACCHARIS KINGII*

Ferdinand Bohlmann, Christa Zdero, Robert M King* and Harold Robinson*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany, *Smithsonian Institution, Department of Botany, Washington, DC 20560, U S A

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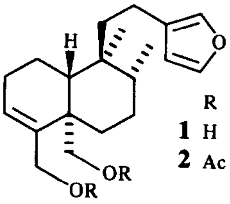
**Key Word Index**—*Baccharis kingii*, Compositae, diterpene, kolavane derivative

**Abstract**—The aerial parts of *Baccharis kingii* afforded quercetin 3,3′-dimethyl ether and a new diterpene closely related to hautriwaic acid Structure and absolute configuration was established by partial synthesis

Diterpenes, especially kolavane derivatives, are widespread in the large genus *Baccharis* with about 400 species The aerial parts of a new species collected in Peru, named *Baccharis kingii* Cuatr , afforded, in addition to germacrene D and quercetin-3,3′-dimethyl ether [1], a diterpene, molecular formula $C_{20}H_{30}O_3$, which could be separated from the flavone by HPLC The $^1$H NMR spectrum (Table 1) indicated the presence of a β-substituted furan [δ7 34 *dd* ($J$ = 1 5 Hz), 7 19 *br s* and 6 24 *br s*] and two hydroxy methylene groups (pairs of doublets at δ4 22 and 3 67 as well as 3 98 and 3 85) This assignment was supported by acetylation of the natural compound which afforded a diacetate The $^1$H NMR spectral data of the latter showed the expected down field shift of the signals of the methylene groups Furthermore a characteristic olefinic broadened triplet showed allylic coupling with one of these doublets as followed by spin découpling The signals of the allylic protons were overlapped with those of the methylene group next to the furan ring All data were close to those of a diol obtained by reduction of Solidago acid B [2] However, several chemical shift differences indicated at least a different stereochemistry, the chemical shifts of the signals of H-12 and H-2 as well as those of H-17–H-20 were markedly different (Table 1) As the configuration of Solidago acid B was different from that of hautriwaic acid, which was isolated from other *Baccharis* species [3–13], it was likely that we were dealing with the diol related to that acid Reduction of hautriwaic acid with lithium aluminium hydride afforded a diol which was identical with the natural product The optical rotation was the same and the absolute configuration was therefore established as **1**, and we have named compound **1**, kingidiol

## EXPERIMENTAL

The air dried aerial parts (350 g) collected in January 1982 in Peru (voucher RMK 9028) were worked-up in the usual fashion The CC-fraction (100 ml) with petrol afforded by TLC (silica gel, petrol) 10 mg germacrene D ($R_f$ 0 7) and the polar CC-fractions ($Et_2O$ and $Et_2O$–MeOH, 10 1) gave a crude mixture of



R
**1** H
**2** Ac