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$_2$R), MS *m/z* (rel int) 276 110 [M − H$_2$O, TiglOH]$^+$ (1) (C$_{15}$H$_{16}$O$_5$), 258 [276 − H$_2$O]$^+$ (2), 83 [C$_4$H$_7$CO]$^+$ (100), 55 [83 − CO]$^+$ (61)

Acknowledgements—We thank Drs Scott A Mori and P Alvim, Herbario Centro de Pesquisas do Cacau at Itabanu, Bahia, Brazil, for their help during plant collection and the Deutsche Forschungsgemeinschaft for financial support

REFERENCES

1 King, R M and Robinson, H (1977) *Phytologia* **23**, 307
2 Bohlmann, F, Zdero, C, King, R M and Robinson, H (1980) *Phytochemistry* **19**, 1547
3 Bohlmann, F, Abraham, W-R, Robinson, H and King, R M (1981) *Phytochemistry* **20**, 1639
4 King, R M and Robinson, H (1978) *Phytologia* **40**, 5
5 Bohlmann, F, Zitzkowski, P, Suwita, A and Fiedler, L (1978) *Phytochemistry* **17**, 2101
6 Bohlmann, F, Zdero, C, Gerke, T, Jakupovic, J, King, R M and Robinson, H (1984) *Liebigs Ann Chem* 162
7 King, R M and Robinson, H (1980) *Phytologia* **46**, 446

Phytochemistry, Vol 23, No 7, pp 1511–1512, 1984
Printed in Great Britain

0031-9422/84 $3 00 + 0 00

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

(*Revised received* 31 *August* 1983)

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$_2$O and Et$_2$O–MeOH, 10 1) gave a crude mixture of

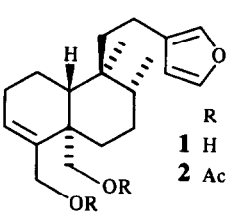

Table 1 ^{1}H NMR spectral data of compounds **1**, **2** and *Solidago* glycol (400 MHz, $CDCl_3$, TMS as internal standard)

	1	2	*Solidago* glycol
H-2	2 27 *m**	2 25 *m**	2 12 *m*
H-3	5 77 *br t*	5 79 *br t*	5 92 *br t*
H-8	1 60 *m*	1 60 *m**	1 75 *m*
H-11	1 66 *ddd*†		1 76 *ddd*
H-12	2 31 *ddd**	2 33 *ddd**	2 56 *ddd*
H-12′	2 16 *ddd**	2 20 *ddd**	2 33 *ddd*
H-14	6 24 *br s*	6 25 *br s*	6 30 *br s*
H-15	7 34 *dd*	7 34 *dd*	7 34 *dd*
H-16	7 19 *br s*	7 20 *br s*	7 24 *br s*
H-17	0 85 *d*	0 88 *d*	0 94 *d*
H-18	4 23 *br d*	4 68 *dt*	4 24 *br d*
H-18′	3 67 *d*	4 58 *dt*	3 96 *d*
H-19	3 98 *d*	4 49 *d*	3 83 *d*
H-19′	3 85 *d*	4 14 *d*	3 50 *d*
H-20	0 78 *s*	0 81 *s*	1 09 *s*
OAc	—	2 07 *s*	—
		2 05 *s*	

*Overlapped signals

†Partly overlapped

J (Hz) 2, 3 = 3 5, 2, 18 = 3, 18 = 1 3, 8, 17 = 7, 11, 12 = 11′, 12′ = 12, 12′ = 13, 11, 12′ = 11′, 12 = 4, 14, 15 = 14, 16 = 1 5, 18, 18′ = 11 5, 19, 19′ = 10 5

compounds which after TLC (Et_2O–petrol, 3 1, three developments, $R_f \sim 0$ 4) and HPLC (reversed phase, RP 8, detected by UV and refractometry, MeOH–H_2O, 4 1) afforded 10 mg quercetin-3,3′-dimethyl ether (identical with an authentic sample by UV in MeOH and in the presence of sodium methylate, ^{1}H NMR and TLC) and 60 mg **1**, colourless crystals mp 93° (petrol–Et_2O), IR $\nu_{max}^{CCl_4}$ cm^{-1} 3620, 3460, 3260 (OH), 3030, 1640 (CH=C), 1510, 880 (furan), MS *m/z* (rel int) 318 $[M]^+$ (0 2), 300 209 $[M-H_2O]^+$ (2 2) ($C_{20}H_{28}O_2$), 287 $[M-CH_2OH]^+$ (4), 270 $[300-CH_2O]^+$ (22), 269 $[287-H_2O]^+$ (17), 175 $[270-CH_2CH_2C_4H_3O]^+$ (51), 81 $[C_5H_5O$, pyrylium ion$]^+$ (100)

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436 \quad 365\,nm}{-94 \quad -98 \quad -112 \quad -192 \quad -307} \quad (CHCl_3,\ c\ 0\,2)$$

10 mg **1** were heated for 1 hr with 0 1 ml Ac_2O at 70° TLC (Et_2O–petrol, 3 1) gave 7 mg **2**, IR $\nu_{max}^{CCl_4}$ cm^{-1} 1740, 1240 (OAc), 1500, 875 (furan), MS *m/z* (rel int) 342 218 $[M-HOAc]^+$ (4) ($C_{22}H_{30}O_3$), 329 $[M-CH_2OAc]^+$ (1 5), 282 $[342-HOAc]^+$ (5), 269 $[329-HOAc]^+$ (64), 187 $[282-CH_2CH_2C_4H_3O]^+$ (38), 81 $[C_5H_5O]^+$ (100)

Reduction of hautriwaic acid 10 mg hautriwaic acid in 2 ml THF were heated for 2 h with 20 mg $LiAlH_4$ under reflux Usual work-up and TLC (Et_2O) gave 7 mg **1**, identical with the natural compound by ^{1}H NMR, TLC and optical rotation

Acknowledgements—We thank the 'Fonds der Chemischen Industrie' and the 'Deutsche Forschungsgemeinschaft' for financial support

REFERENCES

1 Wollenweber, E and Egger, K (1970) *Tetrahedron Letters* 1601
2 Henderson, M S, McCrindle, R and McMaster, D (1973) *Can J Chem* **51**, 1346
3 Guerrero, C and Romo de Vivar, A (1973) *Rev Latinoam Quim* **4**, 178
4 Herz, W, Pilotti, A M, Soderholm, A C, Shuhana, I K and Vichnewski, W (1977) *J Org Chem* **42**, 3913
5 Wagner, H, Seitz, R, Chasi, V, Lotter, H and Herz, W (1977) *Tetrahedron Letters* 3039
6 Wagner, H, Seitz, R, Lotter, H and Herz, W (1978) *J Org Chem* **43**, 3339
7 Bohlmann, F, Knauf, W, King, R M and Robinson, H (1979) *Phytochemistry* **18**, 1011
8 Bohlmann, F, Zdero, C, Robinson, H and King, R M (1979) *Phytochemistry* **18**, 1993
9 Stapel, G, Meussen, H G and Snatzke, G (1980) *Planta Med* **39**, 366
10 Bohlmann, F, Zdero, C, Grenz, M, Dhar, E K, Robinson, H and King, R M (1981) *Phytochemistry* **20**, 281
11 Bohlmann, F, Kramp, W, Grenz, M, Robinson, H and King, R M (1981) *Phytochemistry* **20**, 1907
12 Tonn, C E and Giordano, O S (1980) *An Asoc Quim Argent* **68**, 237
13 Bohlmann, F, Kramp, W, Jakupovic, J, Robinson, H and King, R M (1982) *Phytochemistry* **21**, 399