(H-7, $J = 8\ 5$ Hz), 6 06 *t* (H-8, $J = 6\ 5$ Hz), 4 32 *d* (H-9, $J = 6\ 5$ Hz), 1 63 *s* (H-11, H-12), 2 10, 1 94 *s* (OAc)

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A FURTHER GERANYLNEROL DERIVATIVE FROM *HELIANTHOPSIS* SPECIES

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—*Helianthopsis bishopii, H utcubambensis, H microphylla*, Compositae, diterpenes, geranylnerol derivative, sesquiterpenes, furoheliangolides

Abstract—The investigation of three species of the new genus *Helianthopsis* gave in all cases furoheliangolides, as well as kaurenic, tricholobanic and beyerenic acids Furthermore, a new geranylnerol derivative was isolated from *H bishopii* The chemotaxonomy is discussed briefly

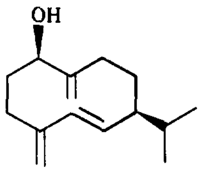
The new genus *Helianthopsis* (Compositae, tribe Heliantheae, subtribe Helianthinae) has been segregated from the North American genus *Helianthus* [1] to contain the disjunct group of the Andean Heliantheae but has maintained the traditional separation from *Viguiera*, obviously its closest relative So far, *Helianthopsis lehmannii* (Hieron) H Robins has been studied chemically [2] In addition to C_{17}-acetylenes, a furoheliangolide was isolated [2] We have now studied three further species from Peru

The aerial parts of *Helianthopsis bishopii* H Robins gave germacrene D, its oxidation product **1**, *ent*-kaurenic acid, trachylobanic acid, beyerenic acid, the furoheliangolides **6** [2] and **9** [3], as well as a very polar diterpene, the tetrol **3**, which was isolated as its tetraacetate In the mass spectrum the highest ion obviously was formed by loss of acetoxyl since the ^{1}H NMR spectrum clearly indicated that a tetraacetate was formed Thus the molecular formula of the tetrol most likely was $C_{20}H_{34}O_4$ Inspection of the ^{1}H NMR spectrum (Table 1) further showed that only two olefinic methyl groups were present However, the signals (each 2H) at δ4 59 *s*, 4 58 *s*, 4 54 *br d* and 4 44 *br s* indicated four methylol groups at double bonds Furthermore, partly overlapped signals of four olefinic protons could be seen Thus an alicyclic diterpene was present As the doublet at δ4 54 showed homoallylic coupling with the methyl signal at δ1 76, a geranylnerol

Table 1 ^{1}H NMR spectral data of **4** (400 MHz, TMS as internal standard)

	4 (CDCl$_3$)	**4** (CDCl$_3$–C$_6$D$_6$, 2 1)
H-1	5 40 *m*	5 30 *br t*
H-2	4 54 *br d*	4 48 *br d*
H-4	2 12 *m*	2 05 *m*
H-5	2 18 *m*	2 15 *m*
H-6	5 38 *m*	5 30 *br t*
H-8	2 12 *m*	2 05 *m*
H-9	2 18 *m*	2 15 *m*
H-10	5 38 *m*	5 30 *br t*
H-12	2 12 *m*	2 05 *m*
H-13	2 18 *m*	2 15 *m*
H-14	5 38 *m*	5 35 *br t*
H-16	4 44 *br s*	4 37 *br s*
H-17	1 65 *br s*	1 55 *br s*
H-18	} 4 58 *s*	} 4 51 *s*
H-19	} 4 59 *s*	} 4 53 *s*
H-20	1 76 *br s*	1 63 *br s*
OAc	2 07 *s*	1 88 *s*
	2 06 *s* (6H)	1 86 *s* (6H)
	2 04 *s*	1 85 *s*

J (Hz) 1, 2 = 5, 6 = 9, 10 = 13, 14 = 7



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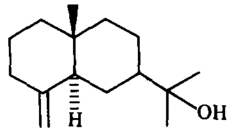

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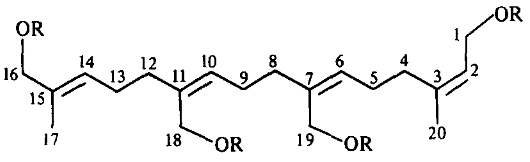
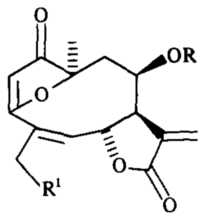
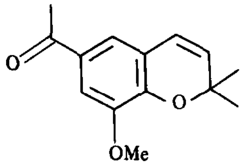


3 R=H **4** R=Ac



	5	**6**	**7**	**8**	**9**
R	iBu	Mebu	iBu	Mebu	Ang
R^1	H	H	OH	OH	H



10

derivative with no function at C-20 had to be assumed The 2*Z*-configuration followed from the characteristic chemical shifts of H-1, H-2 and H-20 After addition of deuteriobenzene, the H-14 signal was shifted downfield Irradiation of this signal sharpened the broadened singlet at δ4 37 (4 44 in $CDCl_3$) and that of the olefinic methyl at δ1 55 (1 65 in $CDCl_3$) Accordingly, the second free methyl group was at C-15 NOE difference spectroscopy established this assumption and further confirmed the configurations of the double bond since NOEs between H-16 and H-14, H-18 and H-9, H-19 and H-5, and H-20 and H-2 were visible

The aerial parts of *Helianthopsis microphylla* (HBK) H Robins gave δ-cadinene, the carbinol **2**, *ent*-kaurenic acid, trachylobanic acid, beyerenic acid, the chromene **10** [4] and the furoheliangolides **7** [5] and **8** [6] The roots contain tridecapentaynene, germacrene D, δ-cadinene, the same acids as the aerial parts, and also the chromene **10**

The aerial parts of *Helianthopsis utcubambensis* H Robins also gave the same diterpene acids, as well as verbenol and the furoheliangolides **5** [4], **6**, **7** and **8**

So far, the chemistry of the genus *Helianthopsis* is very uniform and is characterized by the co-occurrence of furoheliangolides, and diterpene acids of three different types These diterpenes, however, are also reported from several *Helianthus* species, though here only a few species gave furoheliangolides [7, 8] while other types of germacranolides are more widespread in the genus The proposed close relationship of *Helianthopsis* to *Viguiera* is supported by the chemistry as here the co-occurrence of the furoheliangolides and the above-mentioned diterpene acids is common The absence of other germacranolides in *Helianthopsis* may be of chemotaxonomic importance The proposal that *Viguiera* is the most likely ancestral genus in the complex and that the two elements of *Helianthus* are derived separately [9] may also be supported by the chemistry Further investigations are necessary to obtain a clear picture

EXPERIMENTAL

The air-dried plant material, collected in January 1983 in Peru, was extracted with Et_2O–petrol–MeOH (1 1 1) and worked up in the usual fashion [10] CC fractions of the aerial parts (600 g) of *H bishopii* (voucher RMK 9141) were as follows 1 (petrol), 2 (Et_2O–petrol, 1 10 and 1 4), 3 (Et_2O–petrol, 1 1) and 4 (Et_2O and Et_2O–MeOH, 1 10) TLC of fraction 1 gave 2 mg germacrene D and TLC of fraction 2 (Et_2O–petrol, 1 4, $AgNO_3$-coated SiO_2) gave 20 mg *ent*-kaurenic acid (R_f 0 4), 6 mg beyerenic acid (R_f 0 5) and 20 mg trachylobanic acid (R_f 0 75) TLC of fraction 3 (Et_2O–petrol, 1 1) afforded 3 mg **1** and TLC of fraction 4 (Et_2O–petrol, 3 1, 2 developments) gave 60 mg **9** (R_f 0 45), 60 mg **6** (R_f 0 40) and crude **3** (R_f 0 15), which was transformed to **4** by heating for 1 hr at 70° with Ac_2O TLC (Et_2O–petrol, 1 3) gave 8 mg **4** (R_f 0 45), colourless oil (homogeneous by TLC in different solvent mixtures), IR $\nu_{max}^{CCl_4}$ cm^{-1} 1730, 1235 (OAc), MS m/z (rel int) 447 $[M-OAc]^+$ (1), 446 267 $[M-HOAc]^+$ (1) (calc for $C_{26}H_{38}O_6$ 446 267), 406 $[M-AcOCHMe]^+$ (1 5), 388 $[406-H_2O]^+$ (2), 386 $[446-HOAc]^+$ (2 5), 346 $[388-ketene]^+$ (5 5), 344 $[386-ketene]^+$ (2), 326 $[386-HOAc]^+$ (11), 266 $[326-HOAc]^+$ (14), 133 (77), 105 (94), 91 (100)

CC fractions of *H utcubambensis* (voucher RMK 9155, 220 g aerial parts) were as follows 1 (Et_2O–petrol, 1 10), 2 (Et_2O–petrol, 1 1) and 3 (Et_2O and Et_2O–MeOH, 1 10) TLC of fraction 1 (one tenth) (Et_2O–petrol, 1 4, $AgNO_3$-coated SiO_2) gave 20 mg *ent*-kaurenic acid (R_f 0 45), 20 mg beyerenic acid (R_f 0 53) and 70 mg trachylobanic acid (R_f 0 78) TLC of fraction 2 (Et_2O–petrol, 1 1) gave 10 mg verbenol and TLC of fraction 3 (Et_2O–petrol, 3 1) gave a mixture of **5** and **6** (I) and of **7** and **8** (II) TLC of I (one tenth, Et_2O–petrol, 3 1, 3 developments) gave 20 mg **5** (R_f 0 4) and 20 mg **6** (R_f 0 5) TLC of II (C_6H_6–$CHCl_3$–Et_2O, 2 2 1, 2 developments) gave 30 mg **8** (R_f 0 4) and 30 mg **7** (R_f 0 35)

CC fractions of the aerial parts (270 g) of *H microphylla* (voucher RMK 9104) were as follows 1 (petrol), 2 (Et_2O–petrol, 1 10 and 1 4), 3 (Et_2O–petrol, 1 1) and 4 (Et_2O and Et_2O–MeOH, 1 10) TLC (petrol) of fraction 1 gave 10 mg δ-cadinene TLC of fraction 2 ($AgNO_3$-coated SiO_2, Et_2O–petrol, 1 4) gave 100 mg *ent*-kaurenic acid, 10 mg beyerenic acid and 100 mg trachylobanic acid TLC of fraction 3 (Et_2O–petrol, 1 1) gave 10 mg **2** and 5 mg **10** CC fractions of the roots (35 g) were as follows 1 (petrol), 2 (Et_2O–petrol, 1 10) and 3 (Et_2O–petrol, 1 1 and Et_2O) TLC of fraction 1 (petrol) gave 2 mg tridecapentaynene, 5 mg δ-cadinene and 1 mg germacrene D TLC of fraction 2 ($AgNO_3$-coated SiO_2, Et_2O–petrol, 1 4) gave 40 mg *ent*-kaurenic acid, 4 mg beyerenic acid and 40 mg trachylobanic acid TLC of fraction 3 gave 30 mg **10**

All known compounds were identified by comparing the 400 MHz ^1H NMR spectra with those of authentic material, by co-TLC and by comparing other physical data (IR, mp)

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