column as single compounds, crystallized from Et_2O Compounds **3**, **4** and **5** were obtained as a mixture which was separated by prep TLC A part of **5** was used to record UV and IR spectra, the rest was kept in a deep freeze to prevent oxidation before recording its ^1H NMR and mass spectra.

Compound **1** yield 3 g, spectral data including X-ray given in [1] Compound **2** yield 600 mg, spectral data including ^{13}C NMR given in refs [4, 5] Compounds **3** and **4** yield 20 mg and 25 mg, respectively, spectral data including ^{13}C NMR given in [2] Compound **5** yield 50 mg, amorphous UV λ_{max}^{MeOH} nm 220 (log ε 4 6), IR ν_{max}^{KBr} cm^{-1} 2940, 2840, 1730, 1640, 1560, 1440, 1360, 1235, 1110, 1080, 1070, 1040, 1020, 1005, 880 ^1H NMR (Bruker WM, 400 MHz) given in text MS (Varian MAT 711) (direct inlet, 70 eV), *m/z* (rel int) 274 157 ($C_{17}H_{22}O_3$) $[M]^+$ (42), 215 $[M-OAc]^+$ (24), 214 $[M-AcOH]^+$ (100), 199 $[214-Me]^+$ (68), 185 $[214-CHO]^+$ (46), 172 $[214-C_3H_6]^+$ (98), 108 [a] (54)

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A REARRANGED EUDESMANE AND FURTHER VERBESINDIOL DERIVATIVES FROM *VERBESINA EGGERSII*

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Key Word Index—*Verbesina eggersii*, Compositae, sesquiterpenes, eudesmane derivatives, rearranged eudesmane, benzofuran

Abstract—A reinvestigation of *Verbesina eggersii* gave in addition to compounds isolated previously two further verbesindiol derivatives, a rearranged eudesmane and a benzofuran related to tremetone

From most species of the large genus *Verbesina* (Compositae, tribe Heliantheae, subtribe Ecliptinae) verbesindiol derivatives like **1** and **2** [1–3] have been isolated The configuration at C-4 has been assigned differently but in one case was determined by X-ray analysis [4] We have reinvestigated *V eggersii* Hieron which is rich in these eudesmane derivatives Clear NOEs between H-14 and H-15 with **1** and **2** agreed with the configuration assigned for C-4 [1, 3] and therefore the proposed change [2] was an error Also the corresponding *p*-coumarate and ferulate [2] obviously have a 4α-hydroxy group In addition to known compounds the 15-hydroxy derivatives **3** and **4** as well as the rearranged eudesmane **6** and the triol **9** were isolated

The structures of **3** and **4**, which was isolated as its diacetate **5** followed from the spectral data which were close to those of **1** and **2** In the ^1H NMR spectrum of **3** (Table 1) the H-15 singlet in the spectrum of **1** was replaced by a pair of signals at δ 3 72 and 3 33 The latter was a narrowly split doublet, which was due to a W-coupling, usually indicating an axial orientation of the very likely hydroxy methyl group A clear NOE between H-14 and H-15 established this assumption Similarly the configuration of **5** at C-4 followed from the NOE of H-14 with H-15 The signals of H-1 and H-15 were shifted downfield Furthermore, in the mass spectra a strong fragment ion appeared for $M-CH_2OAc$

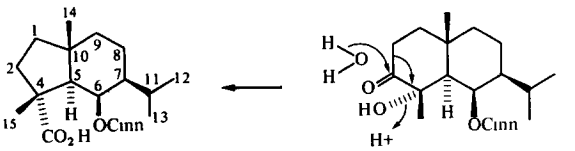
The acid **6** showed some ^1H NMR signals similar to those of **1** (Table 1) However, as followed from the IR spectrum and the mass spectrum an acid was present The H-5 signal was assigned by spin decoupling. As it only showed a coupling with H-6 the carbonyl group had to be placed at C-4 In agreement with this assignment a proton at the neighbouring carbon was seen as a downfield shifted double doublet at δ 2 36 (H-2α) Spin decoupling allowed the assignment of the signals of H-2β, H-1α and H-1β Inspection of a model showed that the couplings observed agreed well with the observed angles Most likely

Table 1 ^{1}H NMR spectral data of compounds **3**, **5** and **6** (400 MHz, $CDCl_3$, TMS as internal standard)

	3*	5*	6*
H-1α		4 69 *dd*	1 73 *m*
H-1β		—	1 30 *m*
H-2α	1 58 *m*	1 55 *m*	2 36 *br dd*
H-2β			1 40 *ddd*
H-3β			—
H-3α	2 28 *br d*	2 30 *br d*	—
H-5	1 60 *d*	1 46 *d*	2 05 *d*
H-6	5 92 *br t*	6 06 *br t*	5 85 *br t*
H-12	0 90 *d*	0 84 *d*	0 96 *d*
H-13	0 84 *d*	0 72 *d*	0 84 *d*
H-14	1 10 *s*	1 11 *s*	1 26 *s*
H-15	3 72 *d*	4 65 *d*	1 26 *s*
H-15′	3 33 *dd*	3 94 *br d*	
OAc	—	1 92 *s*	—
		1 91 *s*	

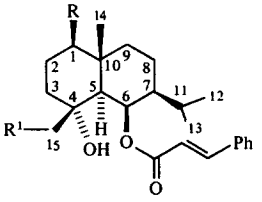
*OCinn 6 39 *d*, 7 70–7 65 *d*, 7 38 *m*, 7 53 *m*

J (Hz) 5, 6 = 6, 7 = 2, 11, 12 = 11, 13 = 7, compound **3** 3α, 3β = 13, 3, 15′ = 1 3, 15, 15′ = 12, compound **5** 1α, 2α = 4 5, 1α, 2β = 12 5, 3α, 3β = 13, 15, 15′ = 12, compound **6** 1α, 1β ~ 13, 1α, 2α = 8 5, 1α, 2β = 7, 1β, 2α ~ 1, 1β, 2β = 7, 2α, 2β = 14

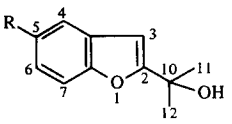


6 **7**

Scheme 1



	1	2	3	4	5
R	H	OH	H	OH	OAc
R^1	H	H	OH	OH	OAc



8 R = COMe
9 R = $CH(OH)CH_2OH$
10 R = $^8CH(OAc)^9CH_2OAc$

compound **6**, which we have named vernoeggersic acid, is formed by a rearrangement of the ketone **7** as indicated in Scheme 1

The ^{1}H NMR spectrum of **10** obtained by acetylation of the naturally occurring triol **9** clearly showed that a 2,5-disubstituted benzofuran was present The furane signal (H-3) was coupled with a broadened doublet at δ7 53 (H-4) The latter showed a further coupling with the double doublet at δ7 24 which itself was coupled with the doublet at 7 41 Thus the substitution pattern was clear The nature of the side chain at C-5 followed from the chemical shifts of the two proton doublets at δ4 32 and the triplet at 6 06 The down field shifted methyl singlet at δ1 63 required a hydroxy group at C-10 Accordingly, the natural compound was **9**, obviously closely related to the tremetone derivative **8** [5]

EXPERIMENTAL

The air dried aerial parts (200 g) were collected in Peru (voucher RMK 9098) and worked up in the usual fashion [6] The CC fraction eluted with Et_2O–petrol (1 4), gave by TLC (Et_2O–petrol, 1 9) 335 mg **1** and the CC fraction obtained with Et_2O–petrol (1 1), gave by repeated TLC (Et_2O–petrol, 1 1) of the polar band 2 6 mg **6** (R_f 0 55), 4 mg **8** (R_f 0 45) and 14 mg **3** (R_f 0 35) The CC fraction eluted with Et_2O gave 425 mg **2** The fraction obtained with Et_2O–MeOH (9 1) showed in the ^{1}H NMR spectrum no acetate methyl singlets and could not be separated Therefore it was acetylated (Ac_2O, 30 min, 70°) TLC (Et_2O–petrol, 3 2) of the acetates gave 23 mg **5** (R_f 0 4) and 15 mg **10** (R_f 0 3)

15-Hydroxyverbesin diol-6-O-cinnamate (**3**) (gum). IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1710, 1640 (C=CCO_2R), MS *m/z* (rel int) 355 227 [M − CH_2OH]$^+$ (10) (calc for $C_{23}H_{31}O_3$ 355 227), 238 [M − RCO_2H]$^+$ (10), 220 [238 − H_2O]$^+$ (30), 207 [238 − CH_2OH]$^+$ (72), 131 [PhCH=CHCO]$^+$ (100), 103 [131 − CO]$^+$ (37),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-14 \quad -15 \quad -17 \quad -36} \quad (c\ 0\,4,\ CHCl_3)$$

1β,15-Dihydroxyverbesin diol-6-O-cinnamate (**4**) Compound **4** was isolated as its diacetate **5** (gum) IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1740, 1240 (OAc), 1720, 1640 (C=CCO_2R), MS *m/z* (rel int) 486 262 [M]$^+$ (6) (calc for $C_{28}H_{38}O_7$ 486 262), 413 [M − CH_2OAc]$^+$ (8), 338 [M − RCO_2H]$^+$ (3), 278 [338 − HOAc]$^+$ (6), 260 [278 − H_2O]$^+$ (10), 131 [PhCH=CHCO]$^+$ (100), 103 [131 − CO]$^+$ (26),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-29 \quad -30 \quad -35 \quad -72} \quad (c\ 2\,3,\ CHCl_3)$$

Vernoeggersic acid (**6**) Isolated as a gum IR $\nu_{max}^{CCl_4}$ cm^{-1} 3500–2700, 1720 (CO_2H), 1710, 1640 (C=CCO_2H); MS *m/z* (rel int): 384 230 [M]$^+$ (1) (calc for $C_{24}H_{32}O_4$ 384 230), 366 [M − H_2O]$^+$ (0 2), 338 [M − HCO_2H]$^+$ (1 5), 236 [M − RCO_2H]$^+$ (10), 190 [236 − HCO_2H]$^+$ (6), 131 [PhCH=CHCO]$^+$ (100), 103 [131 − CO]$^+$ (22),

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-39 \quad -42 \quad -48 \quad -94} \quad (c\ 0\,2,\ CHCl_3)$$

2-[1′-Hydroxyisopropyl]-5-[1′,2′-dihydroxyethyl]-benzofuran (**9**) Compound **9** was isolated as its diacetate **10** (gum) IR $\nu_{max}^{CCl_4}$ cm^{-1} 3600 (OH), 1745, 1260 (OAc), MS *m/z* (rel int) 320 126 [M]$^+$ (22) (calc for $C_{17}H_{20}O_6$ 320 126), 305 [M − Me]$^+$ (20), 260 [M − HOAc]$^+$ (10), 247 [M − CH_2OAc]$^+$ (11), 218 [260 − ketene]$^+$ (44), 205 [247 − ketene]$^+$ (100), 203 [218 − Me]$^+$ (37), 187 [205 − H_2O]$^+$ (22), 131 [PhCH =CHCO]$^+$ (22); ^{1}H NMR ($CDCl_3$) 6 55 *d* (H-3, *J* = 1 Hz), 7 53 *br d* (H-4, *J* = 1 5 Hz), 7 24 *dd* (H-6, *J* = 8 5, 1 5 Hz), 7 41 *d*

(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

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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_6D_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