Phytochemistry, Vol. 20, No. 8, pp. 1891–1893, 1981.
Printed in Great Britain.

0031-9422/81/081891-03 $02.00/0

FURTHER EUDESMANOLIDES AND XANTHANOLIDES FROM *TELEKIA SPECIOSA**

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(*Received* 18 *November* 1980)

Key Word Index—*Telekia speciosa*; Compositae; sesquiterpene lactones; eudesmanolides; xanthanolides.

Abstract—The re-investigation of the aerial parts of *Telekia speciosa* afforded five new sesquiterpene lactones, two eudesmanolides and three xanthanolides, all closely related to those isolated before from this species or from related genera. The structures were elucidated by ^{1}H NMR spectroscopy.

Telekia, at one time included as part of *Buphthalmum* (Compositae, tribe Inuleae), is a small genus, chemically characterized by the occurrence of sesquiterpene lactones similar to those from *Inula* species. *Telekia speciosa* (Schreber) Baumg. has already been investigated [1]. A re-investigation of more material, however, afforded further constituents, some not isolated before from nature. In addition to phytol, nerolidol, 2-*E*- and 2-*Z*-farnesal, **1** and **2**, the sesquiterpene lactones **3** [2], **4** [2], **5** [3], **8** [1], **9** [1], **10** [4] and **11** [4], were present. Furthermore, two additional eudesmanolides, the diols **6** and **7** and three further xanthanolides, the isomeric ketones **12–14**, were isolated.

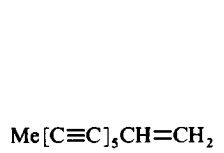
The ^{1}H NMR data of **6** (Table 1) were very close to those of asperilin (**5**) [3]. However, the H-3α and the H-7 signals showed a considerable downfield shift indicating that a second hydroxyl group had to be α-orientated at C-5. The stereochemistry at C-1 followed from the observed couplings of H-1. The IR spectrum of the second eudesmanolide (**7**) as well as the molecular formula indicated the presence of an additional keto group. The ^{1}H NMR data (Table 1) showed that this group must be placed at C-2. Consequently the H-3 signals were shifted downfield. These assignments could be deduced from the allylic coupling with H-15 observed for one of these protons, while the other H-3 signal was a broadened doublet only. A coupling between H-1 and H-3 showed that the hydroxyl at C-1 was β-orientated. The corresponding signal was a double doublet so that a H, OH-coupling was present. The missing couplings between H-5 and H-6 indicated the presence of the second hydroxyl at C-5, which also was α-orientated since the H-7 signal was shifted downfield due to the deshielding effect of the axial 5-OH group. The ^{1}H NMR spectrum of **12** (Table 1) was very close to that of tomentosin [4]; a broadened doublet at 4.48 ppm, however, indicated the presence of an additional hydroxyl, which was obviously at C-2 as the H-3 signals were now only double doublets. The stereochemistry at C-8 followed from the chemical shift of H-7 [4], which was typically shifted to lower fields. The spectral data of **13** were close to those of 8-*epi*-tomentosin [4]. Again an additional signal at 4.51 ppm (*dd*, J = 10, 2.5 Hz) and the H-3 double doublets indicated a hydroxyl group at C-2, while from the upfield

Table 1. ^{1}H NMR spectral data of compounds **6**, **7** and **12–14** (270 MHz, $CDCl_3$, TMS as internal standard)

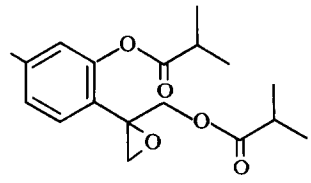
	6	**7**	**12**	**13**	**14**
H-1	4.04 *dd*	3.37 *dd*	—	—	—
H-2	2.00 *m*	—	4.49 *br d*	4.51 *dd*	—
H-2′	1.55 *m*	—			—
H-3	2.24 *br d*	2.95 *dddd*	2.64 *dd*	2.74 *dd*	2.75 *dd*
H-3′	2.65 *ddd*	2.71 *d*	2.76 *dd*	2.59 *dd*	2.86 *dd*
H-4	—	—	—	—	3.63 *ddq*
H-5	—	—	5.76 *dd*	5.86 *dd*	7.05 *dd*
H-6 }	1.8 *m*	1.94 *dd*	2.30 *ddd*	2.13 *ddd*	2.82 *ddd*
H-6′ }		1.85 *dd*	2.47 *ddd*	2.56 *ddd*	2.3 *m*
H-7	3.33 *ddddd*	3.40 *m*	3.38 *m*	2.45 *m*	2.54 *m*
H-8	4.64 *ddd*	4.68 *ddd*	4.65 *ddd*	4.30 *ddd*	4.31 *ddd*
H-9	2.20 *dd*	2.45 *dd*	2.10 *ddd*	2.23 *ddd*	2.34 *ddd*
H-9′	2.35 *dd*	2.23 *dd*	1.86 *ddd*	1.71 *ddd*	1.74 *ddd*
H-10	—	—	2.70 *m*	2.83 *m*	2.3 *m*
H-13	6.17 *d*	6.20 *d*	6.28 *d*	6.17 *d*	6.23 *d*
H-13′	5.60 *d*	5.62 *d*	5.54 *d*	5.45 *d*	5.51 *d*
H-14	0.88 *s*	1.01 *s*	1.19 *d*	1.20 *d*	1.24 *d*
H-15	4.92 *br s*	5.02 *br d* }	2.22 *s*	2.22 *s*	1.08 *d*
H-15′	4.78 *br s*	4.76 *br d* }			
OH		2.78 *d*			

J(Hz): Compound **6**: 1,2 = 11; 1,2′ = 4.5; 2,3′ = 3,3′ = 13; 2′,3′ = 5; 6,7 ~ 10; 6′,7 ~ 5; 7,8 = 5; 7,13 = 1; 8,9 = 5; 8,9′ = 1.5; compound **7**: 1,OH = 1,3 = 2.5; 3,3′ = 16.5; 3,15 = 2; 6,7 = 10; 6′,7 = 7; 7,8 = 5; 7,13 = 1.5; 7,13′ = 1.2; 8,9 = 5; 8,9′ = 5; 8,9′ = 1.5; compound **12**: 2,3 = 9; 2,3′ = 3; 3,3′ = 17; 5,6 = 8.5; 5,6′ = 5.5; 6,6′ ~ 13; 6,7 ~ 10; 6,7′ ~ 4; 7,8 = 9; 8,9 = 3; 8,9′ = 12; 9,9′ = 13; compound **13**/**14**: 5,6 = 8.5; 5,6′ = 3.3; 6,6′ = 15; 6,7 = 10; 6′,7 = 5; 7,8 = 10; 7,13 = 3.5; 7,13 = 3; 8,9 = 3; 8,9′ = 12; 9,9′ = 12; 10,14 = 7 (**13**: 2,3 = 10; 2,3′ = 3; 3,3′ = 17; **14**: 3,4 = 3.5; 3′,4 = 8.5; 4,15 = 7).

* Part 348 in the series "Naturally Occurring Terpene Derivatives". For Part 347 see Bohlmann, F., Gupta, R. K., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20** (in press).



1



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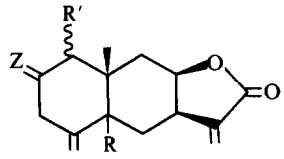
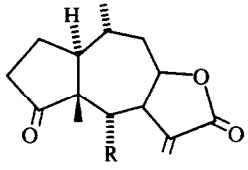
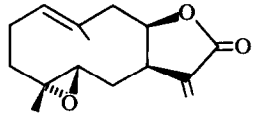


	3	4	5	6	7
R	H	OH	H	OH	OH
R'	H	H	β-OH	β-OH	α-OH
Z	H_2	H_2	H_2	H_2	=O



8 R = H
9 R = OH



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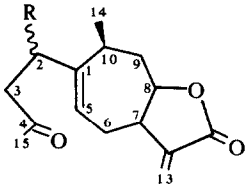
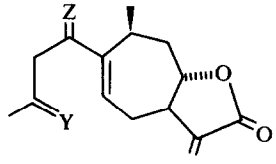


11 R = H
12 R = OH



13 Z = H, OH; Y = O
14 Z = O; Y = H, OH

shift of the H-7 signal an 8,12-*trans*-lactone was proposed [4]. The spectral data of the last lactone (Table 1) clearly showed that the keto group was at C-2 since the signal of the olefinic proton was drastically shifted downfield. The situation at C-4 also clearly followed from the ^{1}H NMR data by the methyl doublet at 1.08 and the *ddq* at 3.63 ppm. Spin decoupling allowed the assignment of these signals as irradiation at 3.63 collapsed the double doublets at 2.75 and 2.86 ppm as well as the methyl doublet at 1.08 ppm to a singlet. Again the chemical shift of H-7 indicated an 8,12-*trans*-lactone. Although all these lactones were isolated in minute amounts, their structures were based only on the ^{1}H NMR data. Probably some of these compounds should be obtained in larger amounts in order that their structures can be confirmed. The compounds now isolated are all closely related to those reported before from this species. Therefore no new chemotaxonomic conclusions can be drawn.

EXPERIMENTAL

The fresh aerial parts (1.05 kg) (grown from seeds, voucher 1456/79) were extracted with Et_2O–petrol (1:2) and the extract was separated by column chromatography (Si gel) and further by repeated TLC (Si gel). Finally 3 mg **1**, 15 mg 2-*Z*-, 8 mg 2-*E*-farnesal, 10 mg nerolidol, 10 mg **2**, 50 mg phytol, 250 mg **3**, 150 mg **4**, 150 mg **5**, 1.5 mg **6** (Et_2O–petrol, 3:1), 2 mg **7** (Et_2O–petrol, 3:1), 150 mg **8**, 500 mg **9**, 100 mg **10**, 100 mg **11**, 1 mg **12**

(Et_2O–petrol, 3:1), 8 mg **13** (Et_2O–petrol, 3:1) and 3 mg **14** (Et_2O–petrol, 3:1) were isolated. The known compounds were identified by comparing the IR and ^1H NMR spectra with those of authentic material.

5α-Hydroxyasperilin (**6**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (lactone); MS *m/z* (rel. int.): 264.136 $[M]^+$ (3) ($C_{15}H_{20}O_4$), 246 $[M - H_2O]^+$ (19), 231 $[246 - Me]^+$ (46), 228 $[246 - H_2O]^+$ (10), 55 (100); CI (*iso*-butane): 265 $[M + 1]^+$ (25), 247 $[265 - H_2O]^+$, (100), 229 $[247 - H_2O]$ (27).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\,nm}{+94 \quad +113 \quad +135} (c = 0.13, CHCl_3).$$

5α-Hydroxy-2-oxoasperilin (**7**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1775 (lactone), 1730 (C=O); MS *m/z* (rel. int.): 278 $[M]^+$ (1), 236 $[M - ketene]^+$ (7), 218 $[M - HOAc]^+$ (3), 203 $[218 - Me]^+$ (4), 57 (100); CI (*iso*-butane): 279 $[M + 1]^+$ (2), 249 $[279 - CH_2O]^+$ (72), 231 $[249 - H_2O]^+$ (100).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+64 \quad +70 \quad +84 \quad +137} (c = 0.14, CHCl_3).$$

2-Hydroxytomentosin (**12**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (lactone), 1725 (C=O); MS *m/z* (rel. int.): 264.136 $[M]^+$ (8) ($C_{15}H_{20}O_4$), 246 $[M - H_2O]^+$ (8), 231 $[246 - Me]^+$, (6), 55 (100); CI (*iso*-butane): 265 $[M + 1]^+$ (33), 247 $[265 - H_2O]^+$ (100), 205 $[247 - ketene]^+$ (51).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{+9 \quad +12 \quad +12 \quad +27} (c = 0.2, CHCl_3).$$

2-Hydroxy-8-epi-tomentosin (**13**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (lactone), 1720 (C=O); MS *m/z* (rel. int.): 264.136 $[M]^+$ (3), 246 $[M - H_2O]^+$ (11), 228 $[246 - H_2O]^+$ (16), 55 (100); CI (*iso*-butane): 265 $[M + 1]^+$ (100), 247 $[265 - H_2O]^+$ (98), 229 $[247 - H_2O]^+$ (19).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546\,nm}{-3 \quad -6 \quad -11} (c = 0.5, CHCl_3).$$

4-Hydroxy-2-oxo-4-desoxo-8-epi-tomentosin (**14**). Colourless gum, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1770 (lactone), 1670 (C=CCO); MS *m/z* (rel. int.): 264.136 $[M]^+$ (22), 246 $[M - H_2O]^+$ (11), 231 $[246 - Me]^+$ (20), 204 $[M - MeCH(OH)Me]^+$ (39), 176 $[204 - CO]^+$ (54), 69 (100); CI (*iso*-butane): 265 $[M + 1]^+$ (100), 247 $[265 - H_2O]^+$ (19).

$$[\alpha]_{24°}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,nm}{-19 \quad -19 \quad -22 \quad -47} (c = 0.27, CHCl_3).$$

Acknowledgement—We thank the Deutsche Forschungsgemeinschaft for financial support.

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