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A NEO-CLERODANE GLUCOSIDE AND NEO-CLERODANE DITERPENOIDS FROM *TEUCRIUM FLAVUM* SUBSP. *GLAUCUM*

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Key Word Index—*Teucrium flavum* subsp. *glaucum*; Labiatae; diterpenoids; diterpenoid glucoside; neo-clerodane derivatives; teuflavoside; teuflavin; teuflin.

Abstract—From the aerial part of *Teucrium flavum* subsp. *glaucum* a new neo-clerodane diterpenoid, teuflavin, and a new 19-nor-neo-clerodane glucoside, teuflavoside, have been isolated, besides the previously known diterpene teuflin. The structures of teuflavin (19-acetoxy-4α,18:15,16-diepoxy-6β-hydroxy-3-keto-neo-cleroda-13(16),14-diene-20ξ,12*S*-hemiacetal) and teuflavoside (18-acetoxy-15,16-epoxy-19-nor-neo-cleroda-4,13(16),14-trien-20,12*S*-olid-6β-yl-2′-*O*-acetyl-β-D-glucopyranoside) were established by chemical and spectroscopic means and by correlation with known compounds. In addition, the previously known flavone salvigenin has also been obtained from the same source.

INTRODUCTION

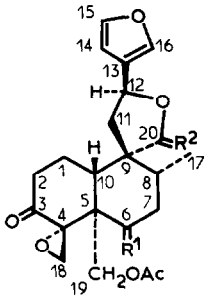
In continuation of our studies on diterpenic compounds from *Teucrium* species [1–4], we have now investigated *T. flavum* L. subsp. *glaucum* (Jordan & Fourr.) Ronniger from the aerial parts of which we have isolated a new neo-clerodane diterpenoid, teuflavin (**1**), besides a new 19-nor-neo-clerodane glucoside, teuflavoside (**5**). In addition, the previously known neo-clerodane diterpene teuflin [5] and the flavone salvigenin (5-hydroxy-6,7,4′-trimethoxy-flavone) [6] have also been obtained from the same source. The structures and absolute configurations of the new substances (**1** and **5**) were established on the basis of spectroscopic evidence and by chemical correlation with previously described compounds.

RESULTS AND DISCUSSION

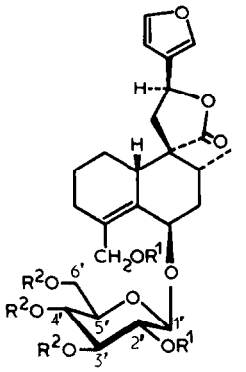
Teuflavin (**1**) had a molecular formula of $C_{22}H_{28}O_8$ and its IR spectrum showed furanic (3150, 3140, 1505, 880 cm^{-1}), hydroxyl (3420 cm^{-1}), acetate (1745, 1240 cm^{-1}) and ketone (1720 cm^{-1}) absorptions. Examination of the ^1H and ^{13}C NMR spectra of teuflavin (**1**, Tables 1 and 2, respectively) showed that the oxygen functions are a β-substituted furan ring, an α,α-disubstituted oxirane ring, a ketone, a secondary hydroxyl group, an acetoxymethylene group attached to a fully substituted sp^3 carbon atom and a hemiacetalic grouping. The ^1H and ^{13}C NMR spectra of teuflavin also contained resonances attributable to a secondary methyl group (δ1.01, 3H, *d*, *J* = 6.5 Hz; δ17.5 *q*, see Tables 1 and 2). Bearing in mind the isolation of neo-clerodanes from *Teucrium* species [1–5, 7] all the above data can be accommodated in the structure **1** for teuflavin. In agreement with this hypothesis, chromium trioxide–pyridine treatment of teuflavin for 2 hr yielded, besides starting material (**1**), three derivatives (**2**, **3** and **4**), one of which (**4**) was identical in all respects with the epoxy-derivative of tafricanin A, a neo-clerodane diterpenoid recently isolated from *T. africanum*, the structure and absolute configuration of which were firmly established by X-ray diffraction analysis [7]. This correlation firmly established that teuflavin (**1**) possessed a neo-clerodane [8] hydrocarbon skeleton with a 4α,18-oxirane ring, a C-19 acetoxyl group, a 20ξ,12*S*-hemiacetal function and a C-13–C-16 furan ring, whereas its ketone and secondary hydroxyl functions must be placed at the C-3 and C-6 positions.

The secondary hydroxyl group of teuflavin (**1**) and its derivative **3** is axially oriented because its geminal proton appeared as a narrow multiplet ($W_{1/2}$ = 8 Hz, δ3.83 and 3.80, respectively) in the ^1H NMR spectra of these compounds (Table 1). Since the ^1H NMR spectra of compounds **1** and **3** showed no long-range coupling between the lower field signal (δ4.13 and 3.93, respectively) of the oxiranic protons and the C-3α (axial) proton [3, 4, 7, 9], the secondary hydroxyl group can be placed at the C-3α (axial) position in a 6-keto-neo-clerodane structure or, alternatively, at the C-6β (axial) position of a 3-keto-neo-clerodane derivative. However, the ^{13}C NMR spectrum of teuflavin (**1**, Table 2) clearly established that the second possibility prevails, because the C-1–C-10, C-18 and C-19 carbon atom resonances of this new diterpenoid (**1**) are only compatible with that arrangement, as can be inferred comparing the data of Table 2 with the ^{13}C NMR spectra of compound **4** [7] and teucjaponin A, a neo-clerodane diterpenoid possessing a 6β-hydroxyl group [3, 9]. The unusual down-field resonance of the C-18B proton in teuflavin (**1**, δ4.13, Table 1) also confirmed this point [3, 9]. Thus, teuflavin is 19-acetoxy-4α,18:15,16-diepoxy-6β-hydroxy-3-keto-neo-cleroda-13(16),14-diene-20ξ,12*S*-hemiacetal (**1**).

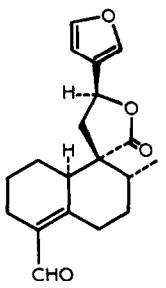
The new 19-nor-neo-clerodane glucoside isolated from *T. flavum* subsp. *glacum* was named teuflavoside (**5**) and it had a $C_{29}H_{38}O_{12}$ molecular formula and possessed two acetyl groups [ν_{max} 1725, 1250 cm^{-1}, two three-proton singlets at δ2.09 and 2.08 (Table 3) and ^{13}C NMR signals at δ171.0 *s*, 170.1 *s*, 21.0 *q* and 20.8 *q* (see Table 4)].Acetic



	R^1	R^2
1	αH, βOH	H, OH
2	O	H, OH
3	αH, βOH	O
4	O	O



	R^1	R^2
5	Ac	H
6	Ac	Ac
7	H	H



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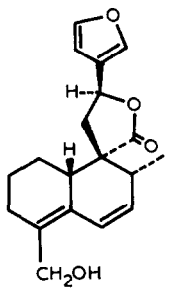

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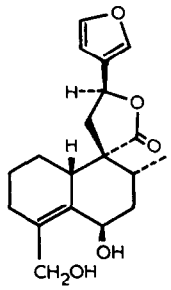

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anhydride–pyridine treatment of teuflavoside (**5**) yielded the peracetyl derivative **6** ($C_{35}H_{44}O_{15}$), whereas when it was subjected to alkaline hydrolysis with Amberlite IRA-400 a bis-deacetyl derivative (**7**, $C_{25}H_{34}O_{10}$) was obtained. Moreover, acetylation of **7** gave the peracetyl derivative **6**; thus, it is evident that teuflavoside (**5**) possessed two acetyl groups.

On the other hand, acid hydrolysis of the derivative **7** yielded glucose (see Experimental) and two isomeric aglycones **8** and **9** ($C_{19}H_{22}O_4$), whereas enzymic hydrolysis of **7** with β-D-glucosidase also yielded D-glucose and only an aglycone (**10**, $C_{19}H_{24}O_5$) which was identical with montanin B, a diterpenoid previously found in *T. montanum* [10]. These results clearly established that teuflavoside (**5**) was a β-D-glucoside of montanin B (**10**) and the appearance of compounds such as **8** and **9** by acid hydrolysis of the derivative **7** must be rationalized on the basis of a dehydration reaction of montanin B (**10**) to yield the dehydroderivative **9** [ν_{OH} 3430 cm^{-1}; λ_{max} 225, 233 and 238 nm (log ε4.13, 4.18 and 4.21, respectively); see Table 3 for its ^1H NMR data and also Experimental] and of a pinacol–pinacolone rearrangement of montanin B (**10**) to give the α,β-unsaturated aldehyde **8** [δ_{CHO} 10.22 *s*; λ_{max} 253.5 nm (log ε4.09), see Table 3 and Experimental]. A H-10α configuration in compound **8** was supported by the fact that this proton appeared at δ3.63 in its ^1H NMR spectrum (Table 3), which is typical of compounds of the teucvidin (H-10α) series [7, 11]. The H-10α configuration of compound **8** must be formed from montanin B (**10**) by an acid-catalysed epimerization involving the α,β-unsaturated aldehyde in which the driving force is the relief of the H-10β–H-8β and H-10β–H-11 *pro S* interactions.

To establish the complete structure of teuflavoside (**5**) required the knowledge of the site of glycosidation (C-6 or C-18 of the aglycone) and the position of the two acetyl groups, and these were established as follows.

Comparison of the ^1H and ^{13}C NMR data of montanin B [10, 12], teuflavoside (**5**) and its derivatives **6** and **7** (Tables 3 and 4) clearly established that the new diterpenoid glucoside was 18-acetyl-montanin B-6-2′-*O*-acetyl-β-D-glucopyranoside (**5**). Effectively, the C-18 protons of montanin B (**10**) appeared in its ^1H NMR spectrum as an AB system at δ3.86 and 4.20 [10], whereas they appeared paramagnetically shifted in teuflavoside (**5**) and its peracetate **6** (δ4.54 and 4.81, and 4.66 and 4.69, respectively; both AB systems centered at δ4.67), thus establishing that one of the acetyl groups of teuflavoside was at the C-18 aglycone position and, consequently, that the site of attachment of the glucose moiety was the C-6β position of montanin B (**10**). These conclusions were also supported by comparing the ^{13}C NMR data (Table 4) of compounds **5** and **6** with those of **7**, because deacetylation at C-18 caused the expected [13, 14] diamagnetic shifts on the C-18 and C-5 carbon atoms (Δδ −2.4 and −2.9, respectively) and a paramagnetic shift on C-4 (Δδ +5.0, Table 4). Moreover, the differences between compound **7** (Table 4) and montanin B (**10**) [12] in the C-5, C-6 and C-7 carbon atom chemical shifts (Δδ −2.2, +9.7 and −1.2,

Table 1. ^{1}H NMR data of compounds **1**–**4** (90 MHz, TMS as int. standard)*

	1 (pyridine-d_5)	**2** ($CDCl_3$)	**3** ($CDCl_3$)	**4** ($CDCl_3$)
H-6α	3.83 *m*	—	3.80 *m*	—
H-7α	†	†	†	3.22 *t*
H_A-11	†	†	†	2.52 *dd*
H_B-11	†	†	†	2.65 *dd*
H-12	5.47 *ddd*	5.37 *ddd*	5.46 *ddd*	5.53 *t* (*br*)
H-14	6.67 *dd*	6.48 *dd*	6.42 *dd*	6.40 *dd*
H-15	7.63 *dd*	7.42 *dd*	7.43 *dd*	7.47 *m*
H-16	7.73 *ddd*	7.50 *ddd*	7.47 *ddd*	7.47 *m*
Me-17	1.01 *d*	1.03 *d*	1.03 *d*	1.10 *d*
H_A-18‡	2.98 *d*	2.60 *d*	2.70 *d*	2.48 *d*
H_B-18§	4.13 *d*	3.73 *d*	3.93 *d*	3.92 *d*
H_A-19	4.30 *d*	4.72 *d*	4.22 *d*	4.80 *d*
H_B-19	4.77 *d*	4.83 *d*	5.20 *d*	5.07 *d*
H-20	5.72 *s*	5.72 *s*	—	—
OAc	1.97 *s*	1.93 *s*	1.93 *s*	1.97 *s*

J (Hz) **1**–**4**: 8,17 = 6.5; 14,15 = 1.8; 14,16 = 0.9; 16,12 = 0.75; 18A,18B = 6.6; 19A,19B = 11. **1** and **2**: 11A,12 = 9.6; 11B,12 = 6.6. **3** and **4**: 11A,12 = 11B,12 = 8.4. **1** and **3**: 6α,7α + 6α,7β = 8. **4**: 7α,7β = 7α,8β = 13.5; 11A,11B = 13.5.

*Spectral parameters were obtained by first order approximation. All these assignments have been confirmed by double resonance experiments.

†Could not be identified.

‡*Exo* hydrogen with respect to ring B.

§*Endo* hydrogen with respect to ring B.

Table 2. ^{13}C NMR chemical shifts of compound **1** (pyridine-d_5, TMS as int. standard)

C	**1**		**1**
1	22.7 *t**	C-12	70.2 *d*
2	42.5 *t*	C-13	127.1 *s*
3	206.5 *s*	C-14	110.0 *d*
4	68.8 *s*	C-15	143.7 *d*
5	47.6 *s*	C-16	139.9 *d*
6	66.2 *d*	C-17	17.5 *q*
7	37.5 *t*	C-18	56.8 *t*
8	35.9 *d*	C-19	63.0 t
9	54.1 s	C-20	100.0 *d*
10	45.4 *d*	$CH_3\underline{C}OO$	170.2 *s*
11	46.2 *t*	$\underline{C}H_3COO$	20.7 *q*

*SFORD multiplicity.

respectively) were in complete agreement with the presence in the C-6β position of **7** of a β-D-glucopyranosyl moiety [15, 16].

Finally, the presence of an acetyl group at the C-2′ position of the sugar part of teuflavoside (**5**) was firmly supported by its ^{1}H NMR spectrum (Table 3), in which the C-2′ proton appeared at δ4.73 as a double doublet ($J_{2',1'}$ = 8 Hz, $J_{2',3'}$ = 9.6 Hz), whereas the H-3′ and H-4′ sugar protons showed signals at higher field than H-2′ (both at δ3.81). Comparison of ^{1}H NMR data of compounds **5** and **6** (Table 3) also confirmed this point and provided conclusive proof on the β-glucopyranosyl nature of the sugar moiety of teuflavoside (**5**), since all the glucose protons showed signals in complete agreement with this structure (Table 3 [15, 16]). Moreover, inspection of ^{13}C NMR spectra of compounds **5** and **7** (Table 4) showed that the acetyl group was not placed at the C-6′ position, because the C-6′ carbon atom resonance was almost identical in both compounds [17, 18]. On the other hand, comparison of the ^{13}C NMR data of teuflavoside (**5**, Table 4) with those reported for 3′-*O*-acetyl-β-D-glucose [19] clearly confirmed that one of the acetyl groups of the new diterpenoid (**5**) must be placed at the C-2′ position.

It is important to note that in this work we have utilized boric acid as an aid for the study of the ^{13}C NMR spectra of compounds **5** and **7** (Table 4). It is known [20] that boric acid produces induced shifts and broadening of the signals of some of the carbon atoms of substances possessing 1,2-glycol functions. Table 4 shows that only the signals of the sugar carbon atoms of teuflavoside (**5**) and its derivative **7** experienced noticeable shifts and broadening by the effect of boric acid, thus excluding a mistake with other signals of the aglycone moiety.

EXPERIMENTAL

Mps are uncorr. For general details on methods see refs [1–4]. Assignments of ^{13}C NMR chemical shifts were made with the aid of off-resonance, noise-decoupled ^{13}C NMR spectra and INEPT experiments. Observation of H_3BO_3 ^{13}C NMR induced shifts was made as previously described [20]. Plant materials were collected in September 1982, at Gennargentu Mountains, Sardinia, Italy, and voucher specimens were deposited in the Herbarium of the 'Dipartimento di Biologia' of the University of Milan, Italy.

Extraction and isolation of the components. Dried and finely powdered *T. flavum* L. subsp. *glaucum* aerial parts (900 g) were extracted with Me_2CO (10 l.) at room temp. for a week. The extract (86 g) was chromatographed on a silica gel column (Merck, No. 7734, deactivated with 15% H_2O, 1 kg). Elution with *n*-hexane, *n*-hexane–EtOAc mixtures and pure EtOAc yielded, in order of elution, salvigenin (1 g), teuflin (100 mg), teuflavin (**1**, 3 g) and teuflavoside (**5**, 9 g). The previously known compounds, salvigenin [6] and teuflin [5], were identified by their physical (mp, [α]) and spectroscopic (IR, UV, ^{1}H NMR, mass spectra) data and by comparison (TLC, mmp) with authentic samples.

Teuflavin (**1**). Mp 197–200° (from EtOAc–*n*-hexane); $[\alpha]_D^{17}$ + 5.2° (pyridine; *c* 0.305); IR ν_{max}^{KBr} cm^{-1}: 3420, 3150, 3140, 2970, 2900, 1745, 1720, 1505, 1480, 1390, 1370, 1240, 1160, 1095, 1030, 980, 895, 880, 795, 690; UV λ_{max}^{EtOH} nm (log ε): 212 (3.56); ^{1}H NMR (90 MHz, pyridine-d_5): see Table 1; ^{13}C NMR (20.15 MHz, pyridine-d_5): see Table 2; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 420 $[M]^+$ (0.2), 389 (2), 360 (1), 359 (1.8), 323 (6), 317 (12), 262 (7), 203 (36), 190 (24), 189 (40), 171 (52), 159 (20), 145 (16), 133 (12), 119 (18), 110 (21), 105 (18), 95 (79), 94 (20), 91 (22), 81 (18), 67 (14), 55 (22), 43 (100). (Found: C, 62.52; H, 6.91. $C_{22}H_{28}O_8$ requires: C, 62.84; H, 6.71%.)

CrO_3–pyridine treatment of teuflavin (**1**) *to give compounds* **2**–**4**. CrO_3–pyridine treatment of **1** (200 mg) for 2 hr in the usual manner gave a mixture of compounds which was subjected to column chromatography (silica gel, EtOAc–*n*-hexane, 1:1) yielding, in order of elution, **2** (30 mg), starting material (**1**, 60 mg), **3** (27 mg) and **4** (40 mg).

Compound **2**. Mp 223–225° (Me_2CO–*n*-hexane); $[\alpha]_D^{19}$ + 26.6° ($CHCl_3$; *c* 0.290); IR ν_{max}^{KBr} cm^{-1}: 3430, 3160, 3140, 3030, 2990,

Table 3. ^{1}H NMR data of compounds **5**–**9** (int. standard TMS)*

	5 (360 MHz, $CDCl_3$)	**6** (360 MHz, $CDCl_3$)	**7** (90 MHz, pyridine-d_5)	**8** (90 MHz, $CDCl_3$)	**9** (90 MHz, $CDCl_3$)
H-6α	4.80 *t*	4.79 *t*	†	‡	—
H_A-11	2.31 *dd*	2.34 *dd*	‡	2.42 *dd*	2.48 *d*
H_B-11	2.53 *dd*	2.53 *dd*	‡	2.57 *dd*	2.48 *d*
H-12	5.38 *t*	5.37 *t*	†	5.39 *t*	5.43 *t*
H-14	6.40 *dd*	6.40 *dd*	6.60 *dd*	6.40 *dd*	6.39 *dd*
H-15	7.44 *t*	7.44 *t*	7.68 *t*	7.43†	7.42†
H-16	7.46 *m*	7.45 *m*	7.78 *m*	7.43†	7.42†
Me-17	0.96 *d*	0.95 *d*	0.98 *d*	1.02 *d*	0.98 *d*
H_A-18	4.54 *d*	4.66 *d*	†	10.22 *s*	4.23 *s* (*br*)
H_B-18	4.81 *d*	4.69 *d*	†	—	4.23 *s* (*br*)
H-1′	4.52 *d*	4.62 *d*	†	—	—
H-2′	4.73 *dd*	4.97 *dd*	†	—	—
H-3′	3.81†	5.19 *dd*	†	—	—
H-4′	3.81†	5.04 *dd*	†	—	—
H-5′	3.30 *m*	3.66 *ddd*	†	—	—
H_A-6′	3.56 *dd*	4.12 *dd*	†	—	—
H_B-6′	3.58 *dd*	4.18 *dd*	†	—	—
OAc	2.09 *s*	2.10 *s*	—	—	—
	2.08 *s*	2.08 *s*	—	—	—
	—	2.04 *s*	—	—	—
	—	2.03 *s*	—	—	—
	—	2.01 *s*	—	—	—
Other signals				H-10α: 3.63 *dd*	H-6 + H-7: 3.83 *m*

J (Hz) **5**–**9**: 8,17 = 6.6; 11A,11B = 13.8; 11A,12 = 11B,12 = 8.6; 14,15 = 1.6; 14,16 = 1.0; 15,16 = 1.6. **5**–**7**: 6α,7α = 6α,7β = 3.4; 18A,18B = 12.3; 1′,2′ = 8; 2′,3′ = 9.6; 3′,4′ = 9.8; 4′,5′ = 10; 6′A,6′B = 12.3; 6′A,5′ = 2.4; 6′B,5′ = 4.7. **8**: 1β,10α = 9; 1α,10α = 3. **9**: 11A,11B and18A,18B not observed; 6,7 + 6,8 + 7,8 $W_{1/2}$ = 10.

*Spectral parameters were obtained by first order approximation. All these assignments have been confirmed by double resonance experiments.

†Overlapped signal.

‡Could not be identified.

2970, 2880, 1730, 1715, 1503, 1460, 1435, 1385, 1250, 1230, 1160, 1110, 1040, 1025, 980, 900, 880, 875, 810; ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 418 $[M]^+$ (3), 400 (2), 390 (2), 372 (4), 358 (3), 354 (4), 346 (5), 327 (7), 312 (7), 301 (9), 299 (8), 282 (15), 281 (20), 217 (14), 200 (24), 175 (12), 163 (16), 147 (14), 145 (14), 134 (16), 121 (12), 110 (13), 107 (14), 105 (14), 97 (24), 95 (43), 94 (100), 91 (20), 81 (43), 69 (28), 55 (20), 43 (93). (Found: C, 63.32; H, 6.09. $C_{22}H_{26}O_8$ requires: C, 63.15; H, 6.26%.)

Compound **3**. An amorphous solid, $[\alpha]_D^{19}$ +54.1° ($CHCl_3$; *c* 0.273); IR ν_{max}^{KBr} cm^{-1}: 3480, 3150, 3120, 3040, 2960, 2930, 2890, 1755, 1725, 1505, 1475, 1460, 1370, 1240, 1160, 1040, 1025, 915, 895, 880, 800; ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 418 $[M]^+$ (1), 400 (1), 390 (4), 372 (1), 358 (6), 345 (2), 330 (12), 327 (6), 317 (6), 264 (4), 236 (5), 220 (5), 189 (5), 178 (13), 161 (9), 147 (6), 133 (9), 121 (6), 119 (6), 107 (7), 105 (11), 95 (46), 94 (23), 91 (13), 81 (28), 79 (12), 69 (11), 55 (13), 43 (100). (Found: C, 63.08; H, 6.19. $C_{22}H_{26}O_8$ requires: C, 63.15; H, 6.26%.)

Compound **4**. Mp 210–212° (Me_2CO–*n*-hexane); $[\alpha]_D^{19}$ +110.1° ($CHCl_3$; *c* 0.218); IR ν_{max}^{KBr} cm^{-1}: 3140, 3120, 3030, 2990, 2970, 2930, 2880, 1760, 1745, 1720, 1503, 1455, 1430, 1415, 1385, 1370, 1350, 1340, 1320, 1230, 1208, 1170, 1155, 1135, 1060, 1045, 1025, 915, 890, 880, 815, 735, 690; ^{1}H NMR (90 MHz, $CDCl_3$): see Table 1; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 416 $[M]^+$ (3), 388 (3), 386 (3), 356 (7), 344 (26), 328 (14), 326 (12), 325 (12), 316 (4), 281 (5), 232 (10), 231 (9), 220 (10), 199 (13), 187 (16), 178 (17), 161 (10), 150 (20), 149 (30), 148 (60), 121 (11), 105 (8), 96 (45), 95 (46), 94 (22), 91 (14), 81 (30), 69 (22), 55 (60), 43 (100). (Found: C, 63.28; H, 5.67. Calc. for $C_{22}H_{24}O_8$: C, 63.45; H, 5.81%.) Identical in all respects with tafricanin A epoxide (**4**, mp 200°, $[\alpha]_D^{20}$ +112°) [7].

Teuflavoside (**5**). Mp 100–102° (from H_2O); $[\alpha]_D^{17}$ +25.0° (pyridine; *c* 3.02); IR ν_{max}^{KBr} cm^{-1}: 3530, 3420, 3150, 3120, 2970, 2940, 2920, 2870, 2840, 1750, 1725, 1635, 1515, 1450, 1430, 1380, 1330, 1270, 1250, 1165, 1075, 1050, 1030, 940, 880, 805, 720; ^{1}H NMR (360 MHz, $CDCl_3$): see Table 3; ^{13}C NMR (20.15 MHz, pyridine-d_5): see Table 4; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 578 $[M]^+$ (0.2), 560 (0.1), 518 (0.3), 458 (0.1), 409 (0.2), 394 (0.6), 356 (7), 330 (2), 325 (3), 314 (55), 297 (10), 296 (23), 269 (8), 251 (8), 228 (7), 220 (13), 205 (37), 187 (23), 159 (66), 145 (22), 127 (27), 109 (17), 105 (19), 96 (28), 95 (44), 91 (22), 85 (18), 81 (28), 73 (15), 69 (14), 67 (10), 61 (10), 57 (10), 55 (9), 53 (7), 43 (100). (Found: C, 56.54; H, 7.04. $C_{29}H_{38}O_{12}.2H_2O$ requires: C, 56.67; H, 6.89%.)

Peracetylteuflavoside (**6**). Ac_2O–pyridine treatment of **5** for 24 hr at room temp. yielded the derivative **6** as an amorphous solid which melted at 78–86°; $[\alpha]_D^{20}$ +37.2° ($CHCl_3$; *c* 0.813);

Table 4. ^{13}C NMR chemical shifts and H_3BO_3 induced shifts of compounds 5–7 (int. standard TMS)

C	5 (pyridine-d_5)	$\Delta\delta(H_3BO_3)$	6 ($CDCl_3$)	7 (pyridine-d_5)	$\Delta\delta(H_3BO_3)$
1	20.9 *t**	0.0	20.5 *t*	21.4 *t*	0.0
2	25.6 *t*	0.0	25.4 *t*	26.1 *t*	−0.1
3	28.6 *t*	0.0	28.4 *t*	28.5 *t*	0.0
4	131.8 *s*	+0.1	132.2 *s*	136.8 *s*	0.0
5	135.0 *s*	0.0	134.0 *s*	132.1 *s*	−0.1
6	73.5 *d*	+0.1	74.5 *d*	73.2 *d*	+0.2
7	35.2 *t*	−0.1	35.0 *t*	35.1 *t*	−0.2
8	33.0 *d*	0.0	32.8 *d*	32.9 *d*	0.0
9	53.7 *s*	0.0	53.5 *s*	53.6 *s*	0.0
10	41.2 *d*	0.0	40.7 *d*	41.6 *d*	−0.1
11	40.7 *t*	−0.1	40.7 *t*	40.9 *t*	−0.1
12	72.0 *d*	0.0	71.7 *d*	71.8 *d*	+0.1
13	126.3 *s*	0.0	125.6 *s*	126.5 *s*	−0.1
14	108.9 *d*	0.0	108.2 *d*	108.9 *d*	0.0
15	144.6 *d*	0.0	144.1 *d*	144.6 *d*	0.0
16	140.3 *d*	0.0	139.6 *d*	140.3 *d*	0.0
17	17.1 *q*	0.0	17.0 *q*	17.3 *q*	0.0
18	63.8 *t*	0.0	63.3 *t*	61.4 *t*	+0.2
20	177.3 *s*	+0.1	176.9 *s*	177.5 *s*	+0.1
1′	100.4 *d*	0.0†	99.7 *d*	103.3 *d*	−0.3†
2′	75.7 *d*‡	−0.4†	71.8 *d*	75.2 *d*	0.0†
3′	75.3 *d*‡	+0.2†	71.9 *d*	77.9 *d*	−0.2†
4′	71.5 *d*	+0.5†	68.6 *d*	71.8 *d*	+0.7†
5′	77.8 *d*	−1.1†	72.9 *d*	78.4 *d*	−0.5†
6′	62.3 *t*	+0.2†	62.3 *t*	62.9 *t*	+0.4†
OAc	171.0 *s*	+0.2	170.7 *s*, 20.9 *q*	—	
	170.1 *s*	+0.2	170.4 *s*, 20.5 *q*	—	
	21.0 *q*	0.0	170.0 *s*, 20.5 *q*	—	
	20.8 *q*	0.0	169.4 *s*, 20.5 *q*	—	
			169.1 *s*, 20.5 *q*	—	

*SFORD multiplicity.
†Broadened signal.
‡These assignments may be reversed.

IR ν_{max}^{KBr} cm^{-1}: 3150, 3130, 2970, 2950, 2880, 1760, 1740 (*br*), 1505, 1435, 1380, 1370, 1230, 1160, 1040, 950, 910, 880; ^1H NMR (360 MHz, $CDCl_3$): see Table 3; ^{13}C NMR (20.15 MHz, $CDCl_3$): see Table 4; EIMS (direct inlet) 10 eV *m/z* (rel. int.): 704 $[M]^+$ (0.2), 644 (0.4), 584 (0.3), 524 (0.4), 464 (0.6), 451 (0.5), 422 (0.4), 409 (0.4), 404 (0.3), 394 (2), 356 (10), 343 (2), 331 (74), 314 (19), 297 (50), 296 (38), 271 (11), 269 (7), 251 (12), 229 (8), 228 (12), 211 (9), 202 (11), 187 (10), 169 (70), 159 (64), 157 (27), 145 (27), 127 (32), 115 (29), 109 (71), 96 (44), 95 (62), 91 (24), 81 (48), 69 (17), 67 (14), 55 (11), 43 (100). (Found: C, 59.29; H, 6.40. $C_{35}H_{44}O_{15}$ requires: C, 59.65; H, 6.29%.)

18,2′-*Bis-deacetylteuflavoside* (7). A suspension of teuflavoside (5, 250 mg), MeOH (20 ml), H_2O (10 ml) and Amberlite IRA-400 (OH^- form, 7.5 g) was stirred and heated at 75° for 1 hr. The soln was cooled, filtered and the solvents removed, yielding the derivative 7 (200 mg), an amorphous solid which melts at 110–119°; $[\alpha]_D^{21}$ +52.1° ($CHCl_3$; *c* 0.815); IR ν_{max}^{KBr} cm^{-1}: 3400 (*br*), 2930, 2880, 1760, 1505, 1475, 1430, 1385, 1350, 1320, 1190, 1160, 1080, 1020, 990, 965, 950, 900, 880, 790, 755; ^1H NMR (90 MHz, pyridine-d_5): see Table 3; ^{13}C NMR (20.15 MHz, pyridine-d_5): see Table 4; EIMS (direct inlet) 10 eV *m/z* (rel. int.): $[M]^+$ absent, 331 (33), 314 (10), 262 (23), 231 (100), 204 (10), 194 (12), 174 (14), 169 (37), 148 (25), 135 (30), 123 (11), 107 (9), 96 (10), 72 (27), 58 (26). (Found: C, 60.58; H, 6.87. $C_{25}H_{34}O_{10}$ requires: C, 60.72; H, 6.93%.) Treatment of 6 as previously described for 5 also yielded 7.

Acid hydrolysis of 18,2′-*bis-deacetylteuflavoside* (7) *to give* D-*glucose and compounds* 8 *and* 9. Compound 7 (400 mg) was subjected to acidic hydrolysis with 2 N H_2SO_4 (50 ml) for 30 min at 95°, then diluted with H_2O and extracted with Et_2O. The aq. soln was neutralized with Amberlite MB-3 and evaporated to yield the sugar fraction from which D-glucose was identified by comparison (PC, TLC, HPLC and GC of its trimethylsilyl ether) with an authentic sample. The Et_2O phase was dried, filtered and evaporated to yield a complex mixture (TLC) of compounds from which only derivatives 8 (15 mg) and 9 (104 mg) were isolated after chromatography on a silica gel column eluted with *n*-hexane–EtOAc (3:1).

Compound 8. Less polar component, mp 141–143° (from EtOAc–*n*-hexane); $[\alpha]_D^{22}$ +266.3° ($CHCl_3$; *c* 0.303); IR ν_{max}^{KBr} cm^{-1}: 3140, 3120, 2990, 2970, 2940, 2870, 2830, 1760, 1665, 1630, 1603, 1505, 1470, 1460, 1370, 1350, 1320, 1255, 1190, 1160, 1135, 1020, 990, 955, 900, 880, 805, 790, 750, 725, 620; UV λ_{max}^{EtOH} nm (log ε): 211 (3.62), 253.5 (4.09); ^1H NMR (90 MHz, $CDCl_3$): see Table 3; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 314 $[M]^+$ (55), 269 (45), 251 (10), 218 (63), 187 (100), 175 (37), 157 (75),

145 (36), 131 (34), 117 (35), 105 (50), 95 (98), 91 (86), 81 (55), 79 (60), 77 (65), 67 (35), 65 (40), 55 (30), 41 (70). (Found: C, 72.43; H, 7.12. $C_{19}H_{22}O_4$ requires: C, 72.59; H, 7.05%.)

Compound **9**. An amorphous solid which melts at 55–62°; $[\alpha]_D^{22}$ + 21.0° ($CHCl_3$; *c* 0.821); IR ν_{max}^{KBr} cm^{-1}: 3430, 3150, 3040, 2930, 2890, 2835, 1760, 1650, 1600, 1505, 1475, 1430, 1385, 1360, 1320, 1220, 1200, 1170, 1150, 1115, 1020, 940, 910, 900, 880, 830, 790, 750, 720; UV λ_{max}^{EtOH} nm (log ε): 225 (sh) (4.13), 233 (sh) (4.18), 238 (4.21); ^{1}H NMR (90 MHz, $CDCl_3$): see Table 3; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 314 $[M]^+$ (6), 296 (24), 281 (2), 251 (22), 233 (10), 228 (14), 218 (10), 202 (12), 201 (13), 200 (14), 199 (13), 197 (12), 187 (20), 183 (21), 169 (42), 157 (56), 143 (45), 129 (33), 128 (30), 117 (24), 115 (28), 107 (21), 105 (38), 96 (76), 95 (100), 91 (51), 81 (49), 79 (36), 77 (40), 65 (22), 53 (22), 43 (36), 41 (53). (Found: C, 72.67; H, 7.16. $C_{19}H_{22}O_4$ requires: C, 72.59; H, 7.05%.)

Enzymic hydrolysis of 18,2′-*bis-deacetylteuflavoside* (**7**) *to give* D-*glucose and montanin B* (**10**). A soln of **7** (100 mg) in 0.1 M Pi buffer (pH 7, 100 ml) and β-D-glucosidase (Sigma, 40 mg) was left at 29° for 48 hr. Work-up in the usual manner yielded a sugar fraction from which D-glucose was identified (see above). The aglycone fraction gave a unique spot on TLC and crystallization from EtOAc–*n*-hexane yielded a compound (26 mg), mp 165–167°; $[\alpha]_D^{21}$ + 76.8° ($CHCl_3$; *c* 0.31), identical in all respects (IR, ^{1}H NMR and mass spectra) with montanin B (**10**). Lit. [10] mp 164–165°, $[\alpha]_D$ + 79°.

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