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MONOTERPENE, CHROMONE AND COUMARIN GLUCOSIDES OF *DIPLOLOPHIUM BUCHANANII*

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Key Word Index—*Diplolophium buchananii* ssp. *swynnertonii*; Apiaceae; monoterpene glycosides; chromone glycosides; coumarin glycosides; (*Z*)-4-*O*-β-D-glucopyranosyl-*p*-coumaric acid; exciton coupling; stereochemistry.

Abstract—A glycosidic fraction obtained from aerial parts of *Diplolophium buchananii* ssp. *swynnertonii* afforded 12 glucosides, of which three, or possibly four, are new. Thus, the main constituent is the new monoterpene, (1*S*, 2*R*,4*R*,5*S*)-bornan-2,4,5-triol 2-*O*-β-D-glucopyranoside, the absolute configuration of which was determined by use of the exciton chirality rule. The chromone, (3*S*)-3,4-dihydro-5-methoxy-3-β-D-glucopyranosyloxy-2,2,8-trimethyl-2H, 10H-benzo[1,2-*b*:3,4-*b*']dipyran-10-one or (2'*S*)-2'-hydroxy-7-*O*-methylallopeucenin 2'-*O*-β-D-glucopyranoside is new. So also is the coumarin, (2*R*)-2'-hydroxymarmesin 2'-*O*-β-D-glucopyranoside, with an unknown configuration at C-1'. (2'*R*)-7-Hydroxy-8-(2',3'-dihydroxy-3'-methylbutyl)-coumarin 7-*O*-β-D-glucopyranoside was also obtained, but a β-D-glucopyranoside, at least constitutionally identical to it, is known. The known 4-*O*-β-D-glucopyranoside of (*Z*)-*p*-coumaric acid was characterized for the first time, by ^{1}H and ^{13}C NMR spectra.

INTRODUCTION

Diplolophium buchananii is a stout perennial umbellifer native to the montane grasslands of South East Africa. The species has been divided [1] into two geographically separated subspecies, ssp. *buchananii* and ssp. *swynnertonii*. This report describes the isolation, from young aerial parts, of *D. buchananii*. ssp. *swynnertonii*, of 12 glucosides, and their identification by spectroscopic and chemical means.

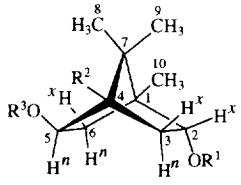
RESULTS AND DISCUSSION

A fraction containing the polar constituents of the plant material was chromatographed by a combination of polyamide 6, Amberlite XAD-2 and silica gel chromatography. Furthermore, some compounds were separated by reversed phase HPLC on ODS-silica. In this way glycosides **1**, **7**–**12**, **14**–**16** and **21**–**22** were obtained.

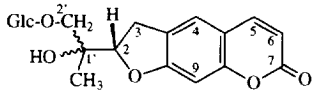
The main glycoside **1** was obtained in substantial quantity, amounting to 0.3% of the dry plant material. On enzymic hydrolysis it released one mol of D-glucose and a 10 carbon aglycone **2**. The ^{1}H NMR spectrum of **2** showed three sharp C-methyl singlets, δ0.75, δ0.81 and δ0.87, at once pointing to a bicyclic monoterpene structure. From a closer study of the ^{1}H NMR spectra of **1** and **2**, supported by extensive decoupling experiments, and a comparison with known NMR data of bornane systems [2], it could then be concluded that **1** is a mono β-D-glucopyranoside of 2-*endo*,4,5-*exo*-bornantriol, or possibly, with interchangement of bowsprit -OH and -Me groups, of 2-*exo*,4,5-*endo*-bornantriol. This ambiguity, and the problem of placement of the glucose moiety, was solved chemically, as it was shown that **1** easily forms a diacetonide **3**, connecting the 4- and 6-OH groups of glucopyranose into a dioxane ring, and the 4- and 5-OH groups of the aglycone part of the structure into a dioxolane ring. As formation of an acetonide from a 4,5-*endo* diol grouping is unlikely, **1** must be the 2-*O*-β-D-glucopyranoside of one of the 2-*endo*,4,5,-*exo*-bornantriol enantiomers. In support of this structure, it may be mentioned also that the ^{1}H NMR spectrum of **1** (Table 1) showed a fairly strong NO enhancement of the signal corresponding to the anomeric proton, upon irradiation of its nearby proton, H-2, and that this proton from its long range coupling with 6-*exo*-H is known to be the 2-*exo* proton.

The absolute configuration of the aglycone **2** was determined with the exciton chirality rule as a basis [3]. To this end, the 4,5-*O*-acetonide (**4**), prepared from **2**, was *O*-methylated and the acetonide grouping again hydrolysed. The resulting 2-*endo*-methoxy-4,5-*exo*-bornandiol (**5**) was then transformed into its diester **6** with *p*-bromobenzoic acid and subjected to CD spectroscopy. As bisignate Cotton effects corresponding to a positive chirality were observed, **6** and accordingly **2** and **1** must possess the stereochemistry, 1*S*,2*R*,4*R*,5*S*. Thus **1** is (1*S*,2*R*,4*R*,5*S*)-bornan-2,4,5-triol 2-*O*-β-D-glucopyranoside.

A known monoterpene glucoside, (1*S*,2*S*,4*R*,5*S*)-bornan-2,5-diol 2-*O*-β-D-glucopyranoside (**7**) [4, 5] was also obtained, together with the known coumarin glucos-



	R^1	R^2	R^3
1	β-D-Glucopyranosyl	OH	H
2	H	OH	H
3	4,6-O-isopropylidene β-D-Glucopyranosyl	-O—C(CH$_3$)$_2$—	
7	β-D-Glucopyranosyl	H	H



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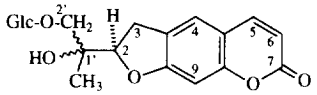

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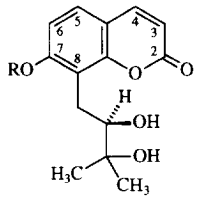
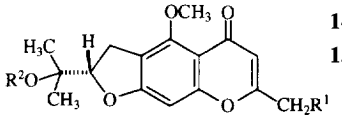
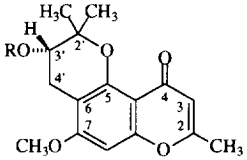


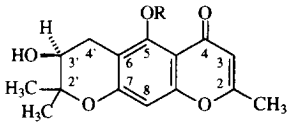
12 R = Glc
13 R = H

	R^1	R^2
14	O-Glc	H
15	H	Glc





16 R = Glc
19 R = H



17 R = CH_3
18 R = H

Table 1. ^{13}C NMR and ^{1}H NMR data (δ values) of **1** (D_2O)

Pos.	^{13}C	^{1}H	$J_{H,H}$ (Hz)
1	48.8		
2	82.3	*exo* 4.08 *dm*	$J_{2x,3x} = 9.8$
3	40.0	*exo* 2.16 *dd*	$J_{3x,3n} = 13.3$
		endo 1.14 *dd*	$J_{2x,3n} = 2.8$
4	83.6		
5	75.2	*endo* 3.69 *dd*	$J_{5n,6n} = 8.3$
			$J_{5n,6x} = 3.4$
6	37.6	*exo* 1.32 *ddd*	$J_{2x,6x} = 1.7$
		endo 2.38 *dd*	$J_{6n,6x} = 13.8$
7	47.3		
8	17.7*	0.87 *s*	
9	17.6*	0.75 *s*	
10	13.9	0.86 *s*	
G1	101.8	4.33 *d*	$J_{1',2'} = 7.9$
G2	73.8	3.17 *dd*	$J_{2',3'} = 9.0$
G3	76.8		
G4	70.5	3.3–3.5 *m*	
G5	76.5		
G6	61.5	a 3.83 *dd*	$J_{6a',6b'} = 12.5$
		b 3.66 *dd*	$J_{5',6a'} = 2.8$
			$J_{5',6b'} = 5$

*Interchangeable assignments.

ides, scopolin (**8**), (2*S*,3*R*)-3-hydroxymarmesin 1′-*O*-β-D-glucopyranoside (**9**) [6] and a third, **10**, which may be designated: (2*S*)-2′-hydroxymarmesin 2′-*O*-β-D-glucopyranoside, with an unknown stereochemistry at C-1′ [6]. This glycoside **10** and another coumarin glycoside **11** with similar chromatographic properties were separated only by means of HPLC.

Compound **11** is new. It released glucose upon enzymic hydrolysis and showed UV and IR spectra virtually identical to those of **10**. Also the ^{1}H and ^{13}C NMR spectra (Table 2) were extremely similar, the small differences being compatible only with **10** and **11** being diastereomers. In particular, the idea of glucose being positioned at the tertiary oxygen function of **11** must be rejected as in this case the signal corresponding to the anomeric carbon would have appeared at a 4–5 ppm lower δ value [6]. The difference in stereochemistry between **10** and **11** was obvious from their CD spectra (Fig. 1), which were nearly antipodal. From these spectra it was concluded that the asymmetric centre C-2, connected directly to the 7-oxycoumarin chromophore, has opposite configurations in the two compounds. Thus **11** is (2*R*)-2′-hydroxymarmesin 2′-*O*-β-D-glucopyranoside, with a stereochemistry at C-1′ as yet unknown.

Still another coumarin glycoside **12** was obtained as an amorphous powder. Upon enzymic hydrolysis it afforded 1 mol of -D-glucose and the known coumarin (2′*R*)-7-hydroxy-8-(2′,3′-dihydroxy-3′methylbutyl)-coumarin (**13**) [7]. As evident, for instance, from the UV spectrum of **12**, which showed no shift by addition of sodium acetate, 12 did not have a free phenolic group. Thus **12** is (2′*R*)-7-hydroxy-8-(2′,3′-dihydroxy-3′-methylbutyl)-coumarin 7-*O*-β-D-glucopyranoside. A crystalline glucoside at least constitutionally identical with **12** has earlier been isolated from a Mongolian umbellifer [8]. No rotation value was reported for this glucoside nor for its aglycone. It is still uncertain if the slight differences in the ^{13}C NMR spectra of the Mongolian glucoside and of **12** may be interpreted to mean that they are β-D-glucopyranosides of enantiomeric aglycones.

Table 2. ^{13}C NMR and ^{1}H NMR data (δ values) of **10** and **11** (D_2O)

	^{13}C		^{1}H	
Pos.	**10**	**11**	**10**	**11**
2	87.9	88.0	5.01, *t* (8.4)	5.02, *t* (8.4)
3	29.4	29.4	*ca* 3.3*	*ca* 3.3†
3a	126.9	126.8		
4	125.0	125.0	7.40, *s*	7.43, *s*
4a	114.0	114.0		
5	147.3	147.2	7.88, *d* (9.5)	7.91, *d* (9.5)
6	111.5	111.4	6.22, *d* (9.5)	6.25, *d* (9.5)
7	163.7	163.6		
8a	155.7	155.5		
9	98.1	98.0	6.75, *s*	6.78, *s*
9a	165.9	165.7		
1′	74.52	74.61		
2′	74.45	74.29	3.89,*d* (10.6)	3.99, *d* (10.6)
			3.67, *d* (10.6)	3.56, *d* (10.6)
1′-Me	19.4	19.4	1.21 *s*	1.20, *s*
1G	103.7	103.7	4.44, *d* (7.9)	4.39, *d* (8.0)
2G	74.1	74.0		
3G	76.8	76.7	3.2–3.5* *m*	3.2–3.5† *m*
4G	70.6	70.6		
5G	76.5	76.4		
6G	61.6	61.6	3.85, *dd*, (12.2, 2.0)	3.86, *dd*, (12.1, 2)
			3.64, *dd*, (12.2, 5.5)	3.64, *dd* (12.1, 5.6)

*† Overlapping signals.

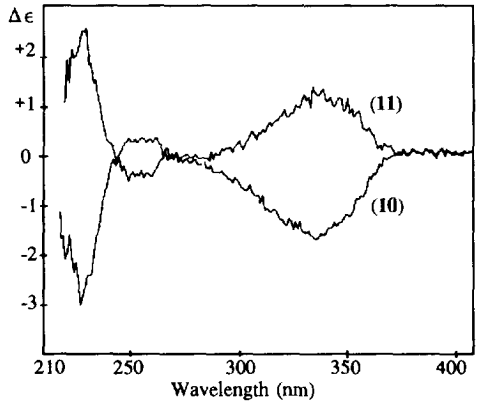


Fig. 1. CD spectra of diastereomers **10** and **11** (methanol solution).

Also three chromone glycosides were obtained. One of these, **14**, which was nearly as abundantly present as glycoside **1**, was the known cimifugin prim. -*O*-β-D-glucopyranoside [9], and another one, **15**, was the known 5-*O*-methylvisamminol β-D-glucopyranoside [10]. The third chromone glycoside **16**, which released D-glucose upon enzymic hydrolysis, from its ^{1}H NMR spectrum appeared to possess a dihydropyranochromone structure isomeric with the dihydrofuranochromone structure in **15**, and from the similarity of UV spectra, most likely also with a corresponding oxygenation pattern of the chromone nucleus. On this basis three structural possibilities could be suggested for **16**. Two compounds were prepared for comparison with its aglycone. Thus 5-*O*-methylhamaudol (**17**), prepared by methylation of authentic hamaudol (**18**), was similar, but not identical, with the aglycone of **16**. On the other hand, (±)-2′-hydroxy-7-*O*-methylallopeucenin [(±)-**19**], prepared by epoxidation and acid catalysed cyclization of 6-γ,γ-dimethylallyl-5-hydroxy-7-methoxy-2-methylchromone (peucenin 7-*O*-methyl ether) (**20**), showed ^{1}H and ^{13}C NMR data, identical with those of the aglycone.

As to the stereochemistry of **16**, its aglycone may be compared with the related compound **17**, which is known to be the (*S*)-enantiomer [11]. As the fairly large shifts of their rotation values upon acetylation were in the same direction, an (*S*)-configuration **19** may tentatively be assigned also to the aglycone of **16**. In conclusion, **16** is (2′*S*)-2′-hydroxy-7-*O*-methylallopeucenin 2′-*O*-β-D-glucopyranoside.

Two of the compounds obtained, **21** and **22**, were shown to be the (*E*)- and the (*Z*)-4-*O*-β-D-glucopyranosyl-*p*-coumaric acids, which are well known plant constituents [12]. Of these, the (*Z*)-diastereomer **22** has not been properly characterized before, being known almost only as chromatographic peak. Its spectral data have now been recorded (see the Experimental).

EXPERIMENTAL

Mps: corr.; TLC of glucose: NaH_2PO_4–silica gel [13], with CH_2Cl_2–96% EtOH–H_2O (10:8:1) as eluent (2

runs); ^{1}H and ^{13}C NMR: 200 MHz and 50.3 MHz respectively, spectra in D_2O with MeCN as int. standard (δ2.00 and δ1.70, respectively). Multiplicities in ^{13}C NMR spectra have been deduced from DEPT spectra.

Plant material. Green aerial parts of *Diplolophium buchananii* (Benth. ex Oliv.) ssp. *swynnertonii* were collected in the month of January at the top of Vumba Hills near Mutare, eastern Zimbabwe. A voucher specimen is deposited at the Department of Pharmacognosy, Royal Danish School of Pharmacy.

Extraction and isolation. The dried and powdered material (310 g) was extracted in a Soxhlet apparatus for 6 hr with $CHCl_3$–MeOH (87:13). The extract was partitioned in the system of $CHCl_3$–MeOH–H_2O (8:4:3) and the polar phase evapd. The residue (13 g) was passed through a column of polyamide 6 (80 g) with H_2O (2.5 l). Upon evapn, the residue (11.6 g) was subjected to CC on macroreticular polystyrene, XAD-2, (160 g) with a CH_2Cl_2–MeOH–H_2O–HOAc (0.5:10:88.5:1) → (4:80:15:1) gradient, rechromatography on XAD-2, and CC on silica gel with CH_2Cl_2–MeOH (95:5) or (92.5:7.5) gradually changed to (85:15). A few compounds were finally sepd by rev. phase prep. HPLC on Lichrosorb RP18, with MeOH–H_2O–HOAc (20:79:1) ~ syst. A, or (22:77:1) ~ syst. B, as eluents.

Yields, mentioned in the approximate order of elution from XAD-2: **1** (*ca* 0.9 g), 21 (2 mg), **22** (6 mg), **12** (19 mg), **7** (76 mg), **8** (70 mg), **14** (*ca* 0.8 g), **10** (2.5 mg), **11** (1.3 mg), **9** (15 mg), **15** (16 mg), **16** (20 mg).

(1S,2R,4R,5S)-*Bornan*-2,4,5-*triol* 2-O-β-D-*glucopyranoside* (**1**). Crystalline (EtOH); ill-def. mp; $[\alpha]_D^{21}$ − 46 (MeOH; *c* 0.4); ^{1}H and ^{13}C NMR: see Table 1.

Enymic hydrolysis of **1**. To **1** (82 mg) in H_2O (8 ml) was added 0.6 ml of *Helix pomatia* β-glucuronidase-sulphatase (crude solution, Sigma). After 3 days, evapn on silica gel (1 g) and CC [silica gel; CH_2Cl_2–MeOH (85:15)] afforded **2** (24 mg). Elution with CH_2Cl_2–MeOH–H_2O (78:20:1) afforded D-glucose, identified by TLC and by the D-glucose oxidase test.

(1S,2R,4R,5S)-*Bornan*-2,4,5-*triol* (**2**). Crystalline (MeCN); ill-def. mp; $[\alpha]_D^{24.8}$ − 8.9, $[\alpha]_{436}^{24.8}$ − 22 (MeOH; *c* 0.8); ^{1}H NMR (D_2O): δ3.91 (1H, *ddd*, *J* = 10.3, 3.3, 2.0 Hz, H-2x), 3.66 (1H, *dd*, *J* = 8.3, 3.4 Hz, H-5n), 2.23 (1H, *dd*, *J* = 14.4, 8.3 Hz, H-6n), 2.19 (1H, *dd*, *J* = 13.4, 10.3 Hz, H-3x), 1.34 (1H, *ddd*, *J* = 14.4, 3.4, 2.0 Hz, H-6x), 0.97 (1H, *dd*, *J* = 13.4, 3.3 Hz, H-3n), 0.87 (3H, *s*, H-8), 0.81 (3H, *s*, H-10), 0.75 (3H, *s*, H-9); ^{13}C NMR (pyridine-d_5): δ83.5 (C-4), 75.4 (C-5), 74.0 (C-2), 48.6 (C-1 or C-7), 47.9 (C-7 or C-1), 43.5 (C-3), 38.4 (C-6), 18.8 (C-8), 18.0 (C-9), 14.7 (C-10).

Conversion of **1** *into di*-O-*isopropylidene derivative* **3**. Compound **1** (40 mg), dry $CuSO_4$ (0.4 g), 2,2-dimethoxypropane (1.5 ml) and Me_2CO (1.5 ml) were mixed and agitated for 2 hr. After filtration and evapn, the residue was subjected to gradient CC on Al_2O_3, basic (grade I) with CH_2Cl_2–EtOAc–tert. BuOH (75:20:5) → EtOAc–tert. BuOH–H_2O (75:25:0.5), which afforded 32 mg of amorphous **3**. ^{1}H NMR (pyridine-d_5): δ4.84 (1H, *d*, *J* = 7.7 Hz, H-1G), 4.44 (1H, *dd*, *J* = 7.9, 4.3 Hz, H-5n), 4.29 (1H, *dm*, *J* = 9.1 Hz, H-2x), 4.2–4.0 (5H, *m*, residual H_G), 3.62 (1H, *ddd*, *J* = 9.6, 9.6, 5.5 Hz, H-5G), 2.57 (1H, *dd*, *J* = 12.0, 9.1 Hz, H-3x), 2.54 (1H, *dd*, *J* = 12.8, 7.9 Hz, H-6n), 1.84 (1H, *ddd*, *J* = 12.8, 4.3, *ca* 1.3 Hz, H-6x), 1.75 (1H, *dd*, *J* = 12.0, 1.8 Hz, H-3n), 1.54, 1.53, 1.53 and 1.32 (12H, *ssss*, isopropylidene Me), 1.07 (3H, *s*, H-8), 1.02 (3H, *s*, H-10), 0.81 (3H, *s*, H-9).

(1S,2R,4R,5S)-4-O,5-O-*Isopropylidene-bornan*-2,4,5-*triol* (**4**). Amorphous; ^{1}H NMR (Me_2CO-d_6): δ4.17 (1H, *dd*, *J* = 8.0, 4.3 Hz, H-5n), 4.05 (1H, *d*, *J* = 4.3 Hz, 2n-OH), 3.90 (1H, *dm*, *J* = 9.5 Hz, H-2x), 2.39 (1H, *dd*, *J* = 11.9, 9.5 Hz, H-3x), 2.24 (1H, *dd*, *J* = 12.8, 8.0 Hz, H-6n), 1.64 (1H, *ddd*, *J* = 12.8, 4.3, 1.5 Hz, H-6x), 1.44 and 1.31 (6H, *ss*, isopropylidene Me), 1.12 (1H, *dd*, *J* = 11.9, 2.0 Hz, H-3n), 0.96 (3H, *s*, H-8), 0.86 (3H, *s*, H-10), 0.75 (3H, *s*, H-9), was prepd from **2**, approximately as **3** from **1**.

Methylation of **4**, *followed by hydrolysis.* Under argon and with stirring, **4** (13 mg) in THF (0.1 ml) was added during 15 min to 58% NaH-in-oil dispersion (13.6 mg) and MeI (20 μl) in THF (0.1 ml) at 40–50°. After standing for a further 15 min, dilute HCl was added. Evapn and CC on silica gel with CH_2Cl_2–tert. BuOH (97:3) → CH_2Cl_2–EtOAc–tert. BuOH (92:5:3) afforded **5** (5 mg).

(1S,2R,4R,5S)-2-*Methoxy-bornan*-4,5-*diol* (**5**). Amorphous; ^{1}H NMR (Me_2CO-d_6): δ4.00 (1H, *d*, *J* = 3.7 Hz, 5x-OH), 3.59 (1H, *ddd*, *J* = 8.1, 3.7, 3.4 Hz, H-5*n*), 3.47 (1H, *s*, 4-OH), 3.40 (1H, *ddd*, *J* = 9.4, 2.9, 1.9 Hz, H-2x), 3.24 (3H, *s*, 2n-OMe), 2.34 (1H, *dd*, *J* = 13.2, 8.1 Hz, H-6n), 2.08, partially covered by solvent (1H, *dd*, *J* = 12.9, 9.4 Hz, H-3x), 1.29 (1H, *ddd*, *J* = 13.2, 3.4, 1.9 Hz, H-6x), 1.01 (1H, *dd*, *J* = 12.9, 2.9 Hz, H-3n), 0.93 (3H, *s*, H-8), 0.87 (3H, *s*, H-10), 0.78 (3H, *s*, H-9).

4-*Bromobenzoylation of* **5**. Under argon, **5** (5 mg), 4-dimethylaminopyridine (50 mg) and 4-bromobenzoylchloride (50 mg) were dissolved in pyridine (250 μl) and *N*-ethyldiisopropylamine (50 μl). After standing for 1 day with occasional agitation, addition of H_2O (25 μl), standing for 5 min, work-up as usual and CC on silica gel with CH_2Cl_2 as eluent, gave **6** (10 mg).

(1S,2R,4R,5S)-2-*Methoxy-bornan*-4,5-*diol di*-(4-*bromobenzoate*) (**6**). Amorphous; UV λ_{max}^{MeOH} nm (log ε): 242 (4.56); ^{1}H NMR (Me_2CO-d_6): δ7.94/7.68 and 7.75/7.56 (8H, AA′, BB′-systems, aromatic H), 5.57 (1H, *dd*, *J* = 8.1, 3.4 Hz, H-5n), 3.68 (1H, *ddd*, *J* = 9.3, 3.5, 1.8 Hz, H-2x), 3.37 (3H, *s*, 2n-OMe), 2.78 (1H, *dd*, *J* = 13.9, 81 Hz, H-6n), 2.43 (1H, *dd*, *J* = 13.6, 9.3 Hz, H-3x), 2.13, partly covered by solvent, (1H, *dd*, *J* = 13.6, 3.5 Hz, H-3n), 1.62 (1H, *ddd*, *J* = 13.9, 3.4, 1.8 Hz, H-6x), 1.28 (3H, *s*, H-8), 1.10 (3H, *s*, H-9), 1.00 (3H, *s*, H-10); CD extrema: $\Delta\varepsilon_{237}$ − 6.9, $\Delta\varepsilon_{253}$ + 6.8 (MeCN; *c* 2.8 × 10^{-5} M).

(1S,2R,4S,5S)-*Bornan*-2,5-*diol* 2-O-β-D-*glucopyranoside* (**7**). Amorphous; $[\alpha]_D^{24.8}$ − 44 (MeOH; *c* 0.6) lit. [4]: $[\alpha]_D^{20}$ − 26.3 (MeOH); [5]: $[\alpha]_D$ − 66 (MeOH); ^{1}H and ^{13}C NMR data as reported [4].

Scopolin (**8**). Mp 220–222°; $[\alpha]_D^{20}$ − 86 (pyridine; *c* 0.5); ^{13}C NMR data as reported [14]; tetraacetate: mp 168° and ^{1}H NMR data as reported [15].

(2S,3R)-3-*Hydroxymarmesin* 1′-O-β-D-*glucopyranoside* (**9**). Mp 235–240°; $[\alpha]_D^{23.5}$ − 18 (pyridine; *c* 0.5). Identified by comparison with IR, ^{1}H NMR and ^{13}C NMR

data of an authentic sample [6]. (Assignments, C-1′ and C-3 in ref. [6] should be reversed.)

(2S)-2′-*Hydroxymarmesin* 2′-O-β-D-*glucopyranoside* (**10**). Unknown configuration at C-1′. Crystalline (H_2O); mp 184–188°; $[\alpha]_D^{20.4}$ − 25, $[\alpha]_{436}^{20.4}$ − 87 (MeOH; *c* 0.08). Identified by comparison with UV, IR, CD and ^{1}H NMR data of an authentic sample [6]. Sepd from **11** by HPLC in syst. A (k′ = 12.2).

(2R)-2′-*Hydroxymarmesin* 2′-O-β-D-*glucopyranoside* (**11**). Unknown configuration at C-1′. Crystalline (H_2O); mp 152–154.5°; $[\alpha]_D^{20.5}$ − 22, $[\alpha]_{436}^{20.5}$ − 13 (MeOH; *c* 0.06). UV and IR data virtually identical to those of **10**. ^{1}H NMR data, see Table 2. CD extrema: $\Delta\varepsilon_{228}$ − 3.0, $\Delta\varepsilon_{254}$ + 0.3, $\Delta\varepsilon_{282}$ 0.0, $\Delta\varepsilon_{335}$ + 1.4 (MeOH; *c* 7 × 10^{-5} M). Sepd from **10** by HPLC in syst. A (k′ = 12.5). Upon enzymic hydrolysis as described for **1**, glucose was detected by TLC.

(2′R)-7-*Hydroxy*-8-(2′,3′-*dihydroxy*-3′-*methylbutyl*)-*coumarin* 7-O-β-D-*glucopyranoside* (**12**). Amorphous, slightly contaminated material; $[\alpha]_D^{25}$ − 55, $[\alpha]_{436}^{25}$ − 130 (MeOH; *c* 0.3); UV λ_{max}^{MeOH} nm (log ε): 315 (4.02), 253 (sh) (3.53), no shift with NaOAc. ^{1}H NMR (DMSO-d_6 + 10% CF_3COOD): δ7.99 (1H, *d*, *J* = 9.6 Hz, H-4), 7.54 (1H, *d*, *J* = 8.7 Hz, H-5), 7.18 (1H, *d*, *J* = 8.7 Hz, H-6), 6.31 (1H, *d*, *J* = 9.6 Hz, H-3), 4.94 (1H, *d* with fine splitting, *J* = 7.3 Hz, H-1G), 3.83–3.13 (7H, *m*, residual H_G and H-2′), 3.13–2.85 (2H, *m*, H-1′), 1.19 and δ1.17 (6H, *ss*, *gem*-dimethyl); ^{13}C NMR (DMSO-d_6): δ161.4 (C-2), 158.2 (C-7), 153.0 (C-8a), 144.6 (C-4), 126.6 (C-5), 117.5 (C-4a), 113.3 (C-8), 112.7 (C-6), 111.0 (C-3), 100.8 (C_G-1), 77.1 (C_G-5), 76.9 (C_G-3), 76.0 (C-2′), 73.3 (C_G-2), 72.3 (C-3′), 69.5 (C_G-4), 60.5 (C_G-6), 25.1 (C-1′), 26.9 and 23.6 (*gem*-dimethyl). Enzymic hydrolysis and CC as described for **1** afforded **13** and D-glucose, identified by TLC and the D-glucose oxidase test.

(2′R)-7-*Hydroxy*-8-(2′,3′-*dihydroxy*-3′-*methylbutyl*)-*coumarin* (**13**). Crystalline (toluene); mp 134–137°; $[\alpha]_D^{25}$ + 63, $[\alpha]_{436}^{25}$ + 155 (MeOH; *c* 0.1); ^{1}H NMR (CD_3OD): δ7.86 (1H, *d*, *J* = 9.5 Hz, H-4), 7.35 (1H, *d*, *J* = 8.5 Hz, H-5), 6.84 (1H, *d*, *J* = 8.5 Hz, H-6), 6.19 (1H, *d*, *J* = 9.5 Hz, H-3), 3.68 (1H, *dd*, *J* = 10.3, 2.3 Hz, H-2′), 3.17 (1H, *dd*, *J* = 13.8, 2.3 Hz, H-1a′), 2.93 (1H, *dd*, *J* = 13.8, 10.3 Hz, H-1b′), 1.30 and 1.29 (6H, *ss*, *gem*-dimethyl). Identified by comparison ($[\alpha]_D$, ^{13}C NMR) with lit. data [7].

Cimifugin prim.-O-β-D-*glucopyranoside* (**14**). Amorphous; $[\alpha]_D^{25}$ + 16 (MeOH; *c* 0.4). Identified by comparison ($[\alpha]_D$, ^{1}H and ^{13}C NMR) with lit. data [10].

5-O-*Methylvisamminol* β-D-*glucopyranoside* (**15**). Crystalline (H_2O); mp 151–156°; $[\alpha]_D^{25}$ + 104, $[\alpha]_{436}^{25}$ + 234 (MeOH; *c* 0.05); UV λ_{max}^{MeOH} nm (log ε): 289 (4.06), 250 (4.20), 243 (4.23), 229 (4.27). Identified by comparison ($[\alpha]_D$, ^{1}H and ^{13}C NMR) with lit. data [10].

(2′S)-2′-*Hydroxy*-7-O-*methylallopeucenin* 2′-O-β-D-*glucopyranoside* (**16**). Crystalline (H_2O), mp 238–241°; $[\alpha]_D^{24.8}$ − 69, $[\alpha]_{436}^{24.8}$ − 147 (MeOH; *c* 0.5); UV λ_{max}^{MeOH} nm (log ε): 283 (4.03), 255 (4.31), 247 (4.31), 233 (4.36), no shift with NaOAc; IR ν_{max}^{KBr} cm^{-1}: 3400, 1670, 1610; ^{1}H NMR (DMSO-d_6 + 10% CF_3 COOD): δ6.63 (1H, *s*, H-8), 5.94 (1H, *br s*, H-3), 4.35 (1H, *d*, *J* = 7.7 Hz, H-1G), 3.96 (1H, *dd*, *J* = 5.4, 6.4, H-3′), 3.90 (3H, *s*, 7-OMe), 3.71 (1H, *dd*, *J* = 1.5, 11.8 Hz, Ha-6G), 3.47 (1H, *dd*, *J* = 6.0, 11.8, Hb-6G), 3.25–2.92 (4H, *m*, residual H_G), 2.89 (1H, *dd*, *J* = 5.4, 17.3, Ha-4′), 2.56, partly covered by solvent, (1H, *dd*, *J* = 6.4, 17.3 Hz, Hb-4′), 2.27 (3H, *br s*, 2-Me), 1.34 and 1.28 (6H, *ss*, *gem*-dimethyl); before addition of CF_3COOD: signals at δ4.94 (3H, apparent *d*, *J* = 5 Hz, 2-, 3- and 4-OH of glucose), 4.45 (1H, *t*, *J* = 5.7 Hz, 6-OH of glucose); ^{13}C NMR (DMSO-d_6): 175.3 (*s*, C-4), 162.7 (*s*, C-2), 160.7 (*s* C-7 or C-5), 152.7 (*s*, C-5 or C-7), 157.8 (*s*, C-8a), 111.1 (*d*, C-3), 107.7 (*s*, C-4a), 104.9 (*s*, C-6), 100.4 (*d*, C_G-1), 91.1 (*d*, C-8), 76.9 (*doublets*, C_G-3 and C_G-5), 76.6 (*s*, C-2′), 72.4 (*d*, C-3′), 70.2 (*d*, C_G-4), 61.3 (*t*, C_G-6), 56.0 (*q*, 7-OMe), 25.2 and 21.2 (*qq*, 2′-Me), 22.4 (*t*, C-4′), 19.0 (*q*, 2-Me). Enzymic hydrolysis and CC, as described for **1**, afforded **19** and D-glucose, identified by TLC and the D-glucose oxidase test.

(2′S)-2′-*Hydroxy*7-O-*methylallopeucenin* (**19**). Crystalline (Me_2CO); mp 198° (dec.); $[\alpha]_D^{24}$ − 61, $[\alpha]_{436}^{24}$ − 32 (MeOH; *c* 0.2); $[\alpha]_D^{24.8}$ − 2, $[\alpha]_{436}^{24.8}$ + 2 ($CHCl_3$; *c* 0.2); [acetate: $[\alpha]_D^{24.8}$ − 94 ($CHCl_3$; *c* 0.2)]; UV λ_{max}^{MeOH} nm (log ε): 285 (sh) (4.02), 270 (4.06), 255 (4.36), 248 (sh) (4.37), 234 (4.32), no shift with NaOAc; ^{1}H NMR (CD_3OD); δ6.60 (1H, *s*, H-8), 6.01 (1H, *q*, *J* = 0.7 Hz, H-3), 3.92 (3H, *s*, 7-OMe), 3.76 (1H, *dd*, *J* = 7.2, 5.6 Hz, H-3′), 2.89 (1H, *dd*, *J* = 17.4, 5.6 Hz, Ha-4′), 2.54 (1H, *dd*, *J* = 17.4, 7.2 Hz, Hb-4′), 2.32 (3H, *d*, *J* = 0.7 Hz, 2-Me), 1.40 and 1.30 (6H, *ss*, *gem*-dimethyl); ^{13}C NMR (CD_3OD): 180.1 (*s*, C-4), 166.1 (*s*, C-2), 163.6 (*s*, C-7*), 160.3 (*s*, C-5*), 154.8 (*s*, C-8a*), 112.0 (*d*, C-3), 109.1 (*s*, C-4a), 107.4 (*s*, C-6), 92.1 (*d*, C-8), 79.7 (*s*, C-2′), 69.3 (*d*, C-3′), 56.7 (*q*, 7-OMe), 27.0 (*t*, C-4′), 25.2 (*q*, 2′-Me), 19.7 (*q*, 2′-Me†), 18.3 (*q*, 2-Me†), assignments marked* or † are exchangeable. ^{1}H NMR of acetate ($CDCl_3$): δ6.38 (1H, *s*, H-8), 5.96 (1H, *br q*, *J* = 0.7 Hz, H-3), 5.04 (1H, *dd*, *J* = 5.4, 5.0 Hz, H-3′), 3.87 (3H, 7-OMe), 2.96 (1H, *dd*, *J* = 17.8, 5.4 Hz, Ha-4′), 2.67 (1H, *dd*, *J* = 17.8, 5.0 Hz, Hb-4′), 2.26 (3H, *d*, *J* = 0.7 Hz, 2-Me), 2.06 (3H, *s*, MeCO–), 1.43 and 1.39 (6H, *ss*, *gem*-dimethyl).

Methylation of hamaudol (**18**). To **18** (6 mg) and Ag_2O (6 mg) in DMF (250 μl) was added MeI (30 μl). After stirring for 1 hr, the reaction was stopped and the mixt. worked up as usual. CC [silica gel, CH_2Cl_2–EtOAc–tert. BuOH–HCOOH (89:10:1:0.1) → (72:25:2.5:0.1)] afforded **17** (5 mg).

5-O-*Methylhamaudol* (**17**). Amorphous; $[\alpha]_D^{25}$ + 5, $[\alpha]_{436}^{25}$ + 15 (MeOH; *c* 0.2); $[\alpha]_D^{25}$ + 8, $[\alpha]_{436}^{25}$ + 27 ($CHCl_3$; *c* 0.2) (ref. [11] $[\alpha]_D^{22}$ + 0.6 in $CHCl_3$); [acetate: $[\alpha]_D^{25}$ − 39 ($CHCl_3$; *c* 0.2) (ref. [11] $[\alpha]_D^{22}$ − 43 in $CHCl_3$)]; UV λ_{max}^{MeOH} nm (log ε): 294 (4.04), 251 (4.15), 244 (4.18), 227 (4.27); ^{1}H NMR (CD_3OD): δ6.67 (1H, *s*, H-8), 6.02 (1H, *br q*, *J* = 0.6 Hz, H-3), 3.83 (3H, *s*, 5-OMe), 3.84 (1H, *dd*, *J* = 6.6, 5.1 Hz, H-3′), 3.05 (1H, *dd*, *J* = 17.3, 5.1 Hz, Ha-4′), 2.76 (1H, *dd*, *J* = 17.3, 6.6 Hz, Hb-4′), 2.33 (3H, *d*, *J* = 0.6 Hz, 2-Me), 1.35 and 1.33 (6H, *ss*, *gem*-dimethyl); ^{13}C NMR (CD_3OD): 179.5 (*s*, C-4), 167.0 (*s*, C-2), 160.2 (*s*, C-5*), 159.6 (*s*, C-7*), 159.2 (*s*, C-8a*), 114.3 (*s*, C-6), 112.1 (*s*, C-4a), 111.3 (*d*, C-3), 101.7 (*d*, C-8), 79.9 (*s*, C-2′), 69.3 (*d*, C-3′), 61.9 (*q*, 5-OMe), 26.7 (*t*, C-4′), 25.7 (*q*, 2′-Me), 21.8 (*q*, 2′-Me), 19.9 (*q*, 2′-Me), assignments marked * are exchangeable.

Synthesis of (±)-2′-hydroxy-7-O-*methylallopeucenin* [(±)-**19**]. 6-γ,γ-Dimethylallyl-5,7-dihydroxy-2-methylchromone (peucenin), isolated from roots of *Peucedanum ostruthium* [16], was methylated (MeI, 1 mol of NaH, DMF). Peucenin 7-*O*-methylether (**20**), obtained in this way, showed ^{1}H and ^{13}C NMR data identical to those reported [17]. H_2O_2 (40%) (10 μl) was added to **20** (33 mg) in HCO_2H (0.4 ml). After 3 hr at 0°, the reaction was quenched by addition of $(Me)_2S$ (10 μl) in MeOH (2 ml). After work up as usual and CC (silica gel, MeOH in CH_2Cl_2, 0.5% → 4%) 19 mg of (±)-**19** was obtained.

(±)-2′-*Hydroxy*-7-O-*methylallopeucenin* [(±)-**19**]. Crystalline (Me_2CO–MeOH); mp indef. (*ca* 190–245°). ^{1}H and ^{13}C NMR spectra identical with those of **19**.

(E)-4-O-β-D-*Glucopyranosyl*-p-*coumaric acid* (**21**). Mp 190–198°; $[\alpha]_D^{24.2}$ − 61, $[\alpha]_{436}^{24.2}$ − 131. Identified by comparison (^{1}H and ^{13}C NMR) with lit. data [18]. Compound **21** was sepd from **22** by HPLC in syst. B (k′ = 2.0).

(Z)-4-O-β-D-*Glucopyranosyl*-p-*coumaric acid* (**22**). Crystalline (EtOH–toluene); mp 133–140°; $[\alpha]_D^{24.8}$ − 60, $[\alpha]_{436}^{24.8}$ − 135 (MeOH; *c* 0.2); UV λ_{max}^{MeOH} nm (log ε): 264 (4.18), 5 nm hypsochromic shift upon add. of NaOAc; ^{1}H NMR (D_2O: δ 7.45 and 7.05 (4H, AA′,BB′-syst., H-2, H-3, H-5, H-6), 6.92 (1H, *d*, *J* = 12.5 Hz, H-β), 5.94 (1H, *d*, *J* = 12.5 Hz, H-α), 5.10 (1H, *d*, with fine splitting, *J* = 7.5 Hz, H-1G), 3.93–3.30 (6H, *m*, residual H_G); ^{13}C NMR (D_2O) δ 172.7 (*s*, –COOH), 157.8 (*s*, C-4), 141.5 (*d*, C-β), 131.7 (*d*, C-2, C-6), 130.6 (*s*, C-1), 120.3 (*d*, C-α), 117.0 (*d*, C-3, C-5), 100.7 (*d*, C_G-1), 77.0 (*d*, C_G-3 or C_G-5), 76.4 (*d*, C_G-5 or C_G-3), 73.7 (*d*, C_G-2), 70.3 (*d*, C_G-4), 61.4 (*t* C_G-6). Compound **22** was sepd from **21** by HPLC in syst. B (k′ = 2.6). Upon enzymic hydrolysis as described for **1**, glucose was detected by TLC.

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