Compound H (Me *tritriacontanoate*). Removal of solvent from the latter fractions of hexane (41–50) furnished a residue, 10 mg, mp 80–82° (Me_2CO). IR ν_{max} (cm^{-1}): 2910, 2825, 1735, 1470, 1380, 1180, 740 and 730. MS *m/z* (rel. int.) 508 (M^+, $C_{34}H_{68}O_2$, 1), 423 (4), 409 (2), 395 (4), 381 (2), 367 (3), 353 (2), 339 (2), 311 (2), 297 (2), 283 (2), 255 (2), 241 (3), 227 (2), 213 (2), 199 (7), 185 (6), 171 (2), 157 (3), 143 (23), 129 (12), 115 (4), 101 (7), 99 (12), 87 (63), 85 (36), 74 (77), 71 (53), 59 (4), 57 (100), 55 (42), 43 (75). H (5 mg) was hydrolysed with 5% alcoholic KOH (2 ml) for 4 hr. The reaction mixture was then diluted with H_2O (20 ml), acidified with dil. HCl and extrd with Et_2O (4 × 25 ml). The Et_2O extract was washed with H_2O (2 × 50 ml) and dried (Na_2SO_4). Removal of solvent provided a residue identified as tritriacontanoic acid. IR ν_{max} (cm^{-1}): 2900, 2840, 3500–3000, 1705, 1185 and 920.

Compound G [*8-hydroxytriacontan-25-one* (**1**)]. The latter fractions (132–140) of hexane–C_6H_6 (1:3) gave a residue, 20 mg, mp 95° (MeOH). IR ν_{max} (cm^{-1}): 3440, 2920, 2840, 1710, 1465, 1380, 1175, 730 and 720. MS *m/z* (rel. int.) 452 (M^+, $C_{30}H_{60}O_2$, 8), 396 (3), 381 (5), 353 (2), 339 (3), 325 (3), 297 (2), 283 (2), 269 (2), 241 (3), 227 (3), 213 (2), 199 (3), 185 (8), 183 (3), 171 (5), 169 (3), 157 (3), 155 (4), 143 (7), 141 (5), 129 (21), 127 (6), 114 (8), 99 (11), 85 (35), 71 (55), 58 (5), 57 (100), 43 (85). G (15 mg) was treated with pyridine (1 ml) and AC_2O (1 ml) overnight at room temp. When worked up it afforded a residue, mp 76–78° (Me_2CO). IR ν_{max} (cm^{-1}): 2920, 2850, 1735, 1710, 1460, 1370, 1260, 730 and 720.

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5,7-BISDEOXYCYNANCHOSIDE, AN IRIDOID GLUCOSIDE FROM *MACFADYENA CYNANCHOIDES*

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Key Word Index—*Macfadyena cynanchoides*; Bignoniaceae; iridoid glucosides; 5,7-bisdeoxycynanchoside; ^1H NMR; ^{13}C NMR.

Abstract—A new iridoid glucoside from *Macfadyena cynanchoides* leaves has been identified by spectral (^1H and ^{13}C NMR) and chemical procedures as 5,7-bisdeoxycynanchoside.

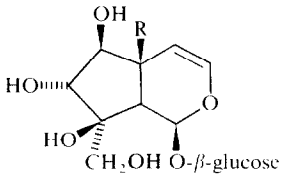
INTRODUCTION

Macfadyena cynanchoides is a well-known wall-creeper which is grown as an ornamental plant. Previous investigations on the iridoid glucosides of the species demonstrated the presence of macfadyenoside [1] and cynanchoside (**1**) [2].

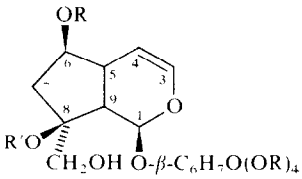
The present communication describes the isolation and structure elucidation of a new iridoid, 5,7-bisdeoxycynanchoside (**2**), which was isolated from the aerial part of the plant.

RESULTS AND DISCUSSION

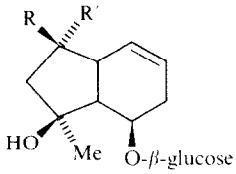
Compound **2** was obtained as a colourless powder with molecular formula $C_{15}H_{24}O_{10}$, and $[\alpha]_D$ −126°. It gave a colour with vanillin characteristic of an iridoid and was hydrolysed in the presence of β-glucosidase. Its UV (204 nm, log ε 3.4) and IR (1670 (C=C) and 1090 cm^{-1}) spectra indicated the presence of a non-conjugated enol–ether system. The ^1H and ^{13}C NMR spectra (see Experimental and Table 1) indicated that the new iridoid had structure **2** with unknown stereochemistry at C-6 and C-8. Acetylation of **2** under mild conditions gave the hexaacetate (peracetate) **4**. The ^1H NMR spectrum of **2** was rather similar (apart from the signals due to the different substitution at C-10) to those of mioporoside **5** and its C-6 epimer ajugol **6** (see data in Experimental). Comparison of the ^{13}C NMR data for **2** and **6** (Table 1, those of **5** were not available) corroborated the above structure for **2**, but did not clarify the stereochemistry at C-6. However, the data



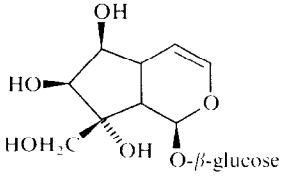
1 R = OH
8 R = H



2 R = R′ = H
3 R = Ac, R′ = H
4 R = R′ = Ac



5 R = OH, R′ = H
6 R = H, R′ = OH



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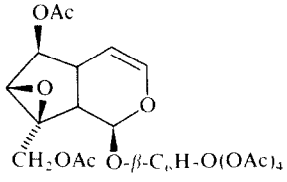

9

confirmed that **2** was indeed a 10-hydroxy derivative of **5** or **6**.

The β-configuration of the hydroxyl group at C-8 was confirmed by the C-9 resonance value which is a known diagnostic tool [2, 3] for establishing the configuration at C-8 in epimeric couples at this chiral centre. In fact, of the two values of C-9 resonance found in the model compounds 10-*des*cynnamoylglobularinin (**7**) (δ 43.70, α-OH and β-CH_2OH at C-8) and 10-*des*cynnamoylglobularimin (**8**) (δ 48.04, β-OH and α-CH_2OH at C-8) [3], the latter was in good agreement with the corresponding value (δ 50.38) of **2** considering that the small difference was caused by the shielding γ-effect ($\simeq$ 2 ppm) exerted on C-9 resonance of **8** by the hydroxyl group at C-7.

Unambiguous evidence for the structure of **2** was obtained by synthesis. Reduction of catalpol hexa-acetate (**9**) with lithium aluminium hydride gave **2** in excellent yield by a regiospecific cleavage of the oxirane ring giving the alcohol at C-8. Therefore the hydroxyl group at C-6 of **2** was shown to be in the β-configuration and the structure of the new iridoid was established as 5,7-bisdeoxycynanchoside.

Table 1. ^{13}C NMR data* of compounds **2**, **3** and **6**

Carbon	**2** (D_2O)	**3**‡ ($CDCl_3$)	**6**† (D_2O)
1	93.28 *d*	91.40 *d*	93.88 *d*
3	140.14 *d*	140.13 *d*	139.47 *d*
4	105.28 *d*	103.68 *d*	105.87 *d*
5	40.82 *d*	38.53 *d*	39.66 *d*
6	76.56 *d*	78.19 *d*	76.77 *d*
7	44.15 *t*	42.75 *t*	49.03 *t*
8	82.14 *s*	79.66 *s*	79.31 *s*
9	50.38 *d*	50.27 *d*	50.50 *d*
10	67.00 *t*	69.02 *t*	24.91 *q*
1′	98.93	95.57	98.92
2′	73.54	70.76	73.56
3′	76.56	72.24	76.56
4′	70.50	68.34	70.52
5′	76.98	72.63	77.06
6′	61.63	61.70	61.63

*Spectra recorded at 20 MHz with dioxane (67.4 ppm) as internal standard. Chemical shifts are in ppm relative to TMS.

†From ref. [6]

‡Additional signals from acetoxy groups at δ 170.48 (C=O) 21.27 and 20.67 (Me).

EXPERIMENTAL

Fractions (I–III) containing iridoids were isolated from *M. cynanchoides* as described in ref. [2]. ^1H NMR: 90 MHz.

Compound **2** (R_f 0.16, grey-violet with vanillin) corresponds to compound *D* of ref. [2].

Isolation of 5,7-*bisdeoxycynanchoside* (**2**). Fractions I and II (8 g) were chromatographed on cellulose (250 g) in *n*-BuOH satd with H_2O (BW) to give **2** contaminated with *C* [fraction (a), 500 mg]. Fraction III (2.5 g) was chromatographed on cellulose (100 g) in BW to give the following fractions: (b) *A*, *B* and *C* (250 mg); (c) **2** and macfadyenoside (600 mg); (d) macfadyenoside (900 mg); (e) macfadyenoside and **1** (300 mg). Fractions (a) and (c) were bulked and rechromatographed on Si gel (80 g) in BW to give pure **2** (700 mg) as a hygroscopic amorphous powder, $[\alpha]_D^{25}$ −126° (MeOH; *c* 0.3) UV λ_{max}^{MeOH} nm (log ε): 204 (3.4); IR ν_{max}^{KBr} cm^{-1}: 3320, 2900, 1670, 1090, 1020. (Found: C, 49.25; H, 6.70. $C_{15}H_{24}O_{10}$ requires: C, 49.45; H, 6.64%). ^1H NMR (D_2O): δ 6.24 (1 H, *dd*, $J_{3,4}$ = 6.3, $J_{3,5}$ = 2.0 Hz, H-3), 5.60 (1 H, *d*, $J_{1,9}$ = 2.5 Hz, H-1), 4.93 (1 H, *dd*, $J_{3,4}$ = 6.3, $J_{4,5}$ = 3.0 Hz, H-4), 4.02 (1 H, *m*, H-6), 3.68 and 3.56 (2 H, AB, J_{AB} = 12.5 Hz, 2H-10), 2.82 (1 H, *bd*, $J_{5,9}$ = 10.0 Hz, H-5), 2.62 (1 H, *bd*, $J_{5,9}$ = 10.0, Hz, H-9), 1.95 (2 H, *o*, J_{AB} = 15.0, J_{AX} = 6.0, J_{BX} = 3.3 Hz, 2 H-7).

^1H *NMR* (D_2O) *of* **5** [4]: δ 6.44 (1 H, *dd*, *J* = 6.5/2.0 Hz, H-3), 5.58 (1 H, *d*, *J* = 2.5 Hz, H-1), 5.15 (1 H, *dd*, *J* = 6.5/2.5 Hz, H-4), 4.60 (1 H, *cm*, H-6), 2.96 (1 H, *cm*, H-5), 2.38 (1 H, *dd*, *J* = 7.5/2.5 Hz, H-9), 2.30 and 1.60 (2 H, *dq*, J_{AB} = 13.5 Hz, 2 H-7), 1.44 (3 H, *s*, Me-8).

^1H *NMR* (D_2O) *of* **6** [5]: δ 6.28 (1 H, *dd*, *J* = 6.5/1.5 Hz, H-3), 5.55 (1 H, *d*, *J* = 1.0 Hz, H-1), 5.02 (1 H, *dm*, *J* = 6.5 Hz, H-4), 4.08 (1 H, *dt*, *J* = 5.5/2.0 Hz, H-6), 2.73 (1 H, H-5), 2.68 (1 H, *d*, *J* = 1.0 Hz, H-9), 2.02 (2 H, *dq*, *J* = 13.8/5.5/5.5 Hz, 2 H-7), 1.35 (3 H, *s*, Me-8).

Hexa-acetate (**3**) *of* **2**. Compound **2** (80 mg) was treated with dry pyridine (0.4 ml) and Ac_2O (0.8 ml) for 30 min at room temp. After addition of MeOH the soln was left for 30 min and then

evapd to dryness. The residue was then chromatographed on Si gel in Et_2O to give the hexa-acetate (**3**) of **2** (37 mg) as an amorphous powder, $[\alpha]_D^{25}$ −103° (MeOH; *c* 0.4). (Found: C, 52.63; H, 5.83. $C_{27}H_{36}O_{16}$ requires: C, 52.59; H, 5.88%.) ^{1}H NMR ($CDCl_3$): δ 6.20 (1 H, *dd*, $J_{3,4}$ = 6.3, $J_{3,5}$ = 2 Hz, H-3), 5.50 (1 H, *d*, $J_{1,9}$ = 2.5 Hz, H-1), 5.3–4.8 (H-6), 4.95 (1 H, *dd*, $J_{3,4}$ = 6.3 Hz, H-4), 4.20 (2 H, *br s*, 2 H-10), 2.80 (2 H, *br s*, H-5 and H-9), 2.2–1.9 (2 H-7 and AcO signals).

Hepta-acetate (**4**) *of* (**2**). Compound **2** (120 mg) was treated with dry pyridine (0.5 ml) and Ac_2O (1 ml) for 3 days at room temp. The usual work-up gave a residue which when chromatographed on Si gel in Et_2O–C_6H_6 (7:3) gave the hepta-acetate (**4**) of **2** (70 mg) as an amorphous powder, $[\alpha]_D^{25}$ −116° (MeOH; *c* 0.4). (Found: C, 52.77; H, 5.71. $C_{29}H_{38}O_{17}$ requires: C, 52.88; H, 5.82%.) ^{1}H NMR ($CDCl_3$): δ 6.20 (1 H, *dd*, $J_{3,4}$ = 6, $J_{3,5}$ = 2 Hz, H-3), 5.90 (1 H, *br s*, H-1), 5.3–4.5 (H-6), 5.0–4.6 (H-4), 4.5–4.0 (2 H-10), 3.05 (1 H, *br d*, H-9), 2.80 (1 H, *br d*, $J_{5,9}$ = 8.3 Hz, H-5), 2.4–2.1 (2 H-7), 2.1–1.9 (AcO signals).

Reduction of catalpol-hexa-acetate (**9**) *with* $LiAlH_4$. **9** (100 mg) was dissolved in dry THF (7 ml) and then treated with $LiAlH_4$ (20 mg) at 70° with stirring for 5 hr. After cooling in an ice-bath, MeOH was added (3 ml) and the soln neutralized with 6 M HCl. After addition of H_2O (8 ml) the soln was evapd to an aq. suspension, which was treated with charcoal and stratified on a Gooch funnel. After removal of salts with H_2O, elution with MeOH gave a residue (70 mg) which was chromatographed on Si gel in $CHCl_3$–MeOH (7:3) to give small amounts (8 mg) of catalpol and the reduction product (45 mg) whose physical data (^{1}H and ^{13}C NMR) were identical to those of **2**.

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NOTE ADDED IN PROOF

The unexpected coincidence observed for C-4 C.S. values in **2** and **6** (in epimers at C-6 this value differs by *ca* 3 ppm) prompted us to check the correct stereochemistry of ajugol. The succesful transformation of ajugol penta-acetate to give linaride (10-deoxyaucubin) penta-acetate unequivocally proves that the configuration at C-6 of ajugol must be reversed (data of next publication).

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(+)-*ENT*-EPICUBENOL FROM THE LIVERWORT *SCAPANIA UNDULATA*

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Key Word Index—*Scapania undulata*; Hepaticae; liverwort; sesquiterpene alcohol; (+)-*ent*-epicubenol.

Abstract—(+)-*Ent*-epicubenol has been isolated from the liverwort *Scapania undulata*.

The liverwort *Scapania undulata* (L.) Dum. (Family: Scapaniaceae) has been analysed several times and the following sesquiterpenes have been found: (−)-longifolene [1–4], (−)-longiborneol [1–3], (−)-α-longipinene [2–4], (+)−α−himachalene [2–4], γ-himachalene, (−)-α-ylangene, β-farnesene, (−)-longicyclene, sativene, sibirene, (−)-β-longipinene, (−)-α-caryophyllene, (−)-α-helmiscapene, β-helmiscapene, α_1-bisabolene, α_2-bisabolene, aequilobene, scapanene, β-gymnomitrene, (+)-α-chamigrene, β-chamigrene, γ-cadinene, asperene, undulatene and (−)-longipinanol [3]. During the course of a chemotaxonomic study of European *S. undulata* (Huneck, S., Jänicke, S. and Meinunger, L., unpublished work), we found a chemical race containing a further sesquiterpene alcohol which could be isolated from the essential oil by column chromatography. This alcohol was shown to be the hitherto unknown (+)-*ent*-epicubenol (**1**) by comparison of the spectroscopic data with the data of (−)-epicubenol which was isolated from the oil of *Piper cubeba* L. several years ago [5]. The identity with epicubenol was confirmed by conversion of **1** into (+)-cubenene (**2**). The isolation of **1**