194. Allobetonicoside and 6-*O*-Acetylmioporoside: Two New Iridoid Glycosides from *Betonica officinalis* L.

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Dedicated to Prof. *Robert Hegnauer* on the occasion of his 70th birthday

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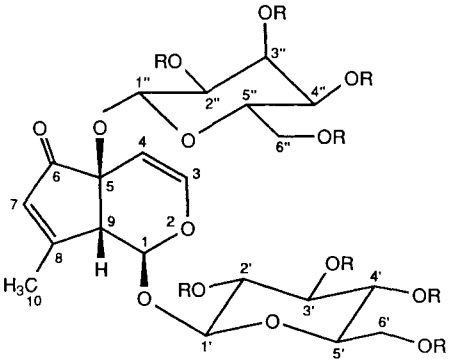
A new allose-containing iridoid diglycoside, allobetonicoside (**1**), and a new acyl iridoid glucoside, 6-*O*-acetylmioporoside (**2**) have been isolated from the aerial parts of *Betonica officinalis* L. in addition to two known iridoid glucosides, acetylharpagide (**3**) and reptoside (**4**). Their structures have been determined by spectroscopic methods as well as by means of chemical evidence.

1. Introduction. – *Betonica* L. (Lamiaceae) includes about twelve species with the main centre of diversity in middle, south, and southeast Europe as well as in Turkey. It seems natural and advisable to separate the genus *Betonica* L. from the polymorphic genus of *Stachys* L. [1].

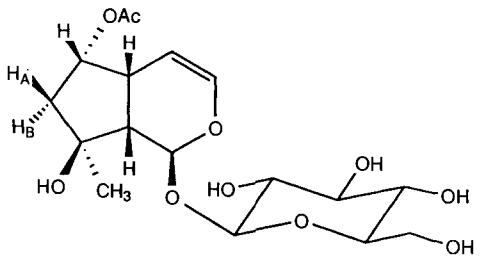
Earlier biosystematic investigations of *Stachys recta* L. and *Stachys anisochila* VIS. et PANCIC have resulted in the isolation of iridoids such as ajugol, ajugoside, melittoside, harpagide, and acetylharpagide [2], in addition to several allose-containing flavonoid glycosides [3] [4].

In the course of chemotaxonomic studies on *Betonica officinalis* L., we have isolated, besides acetylharpagide (**3**) and reptoside (**4**), as the main compound a new iridoid diglycoside which we name allobetonicoside (**1**) and a new acyl iridoid glucoside, 6-*O*-acetylmioporoside (**2**). Allobetonicoside which represents the main iridoid glycoside in the aerial parts of *Betonica officinalis* can be used as taxonomic marker for biosystematic investigations [5].

2. Results and Discussion. – Allobetonicoside (**1**) was obtained as a colourless, amorphous substance with the mol. wt. 506 (FAB-MS: 507 ($[M + H]^+$)) compatible with the molecular formula $C_{21}H_{30}O_{14}$. Its structure was deduced from UV, IR, ^{1}H-NMR, ^{13}C-NMR, COSY, and FAB-MS data and confirmed by chemical transformations. Thus, hydrolysis of **1** produced glucose and allose which were detected as their trimethylsilyl derivatives by GLC in a 1:1 molar ratio. Acetylation of **1** with Ac_2O/pyridine afforded the octa-*O*-acetyl derivative **5** (FAB-MS: 865 ($[M\ (C_{37}H_{46}O_{22}) + Na]^+$)).



1 R=H[1])
5 R=COCH$_3$



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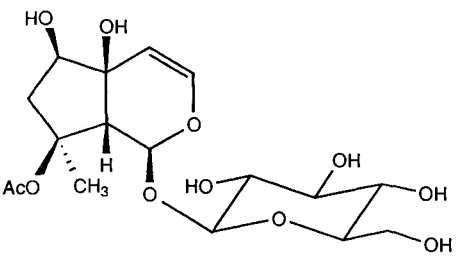

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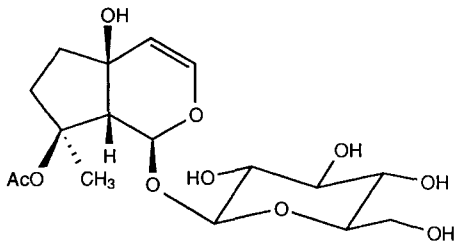

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The UV (λ_{max} 211 and 230 nm) and IR absorption ($\tilde{\nu}$ = 1705, 1645, and 1620 cm^{-1}) of **1** and its ^{1}H-NMR spectrum[1]) (D_2O; 6.45 (*d*, $^3J(3,4)$ = 6.4 Hz, H–C(3)), 5.04 (*dd*, $^3J(4,3)$ = 6.4, $^4J(4,9)$ = 1.1 Hz, H–C(4)), and 6.13 (*'t'*, $^4J(7,9) \approx {}^4J(7,10) \approx$ 1.5 Hz, H–C(7))) indicate a non-conjugated iridoid enol-ether system and a conjugated enone system in a cyclopentane ring. The multiplicity of the 2 signals at 6.45 and 5.04 ppm, assigned to H–C(3) and H–C(4), support C(5) to be substituted. The complete interpretation of the ^{1}H-NMR spectrum (see *Exper. Part*) is based on a homonuclear COSY experiment. The starting point for the analysis of the iridoid protons is the *d* at 6.45 ppm (H–C(3)). It shows a correlation peak only with the *dd* at 5.04 ppm which confirms its assignment to H–C(4). The latter is coupled to the *m* at 3.97 ppm (H–C(9)). Moreover, H–C(9) exhibits correlations to both the *s* at 2.30 ppm (3H), assigned to CH_3(10), and to the *'t'* at 6.13 ppm (^4J = 1.5 Hz, 1H) which is, therefore, assigned to H–C(7). This significant coupling pattern suggests a 7-ene-6-one structure, and the experimental data are also in good agreement with the reported data for teucardoside and teuhircoside with a similar iridoid skeleton [6–8]. The ^{13}C-NMR spectrum of **1** fully confirms this assumption as the chemical shifts of the relevant iridoid C-atoms are similar to the ones of teucardoside [6]; particularly informative are the signals at 178.5 (C(8)) and 204.9 ppm (C(6)). The ^{1}H-NMR signals of **1** at 5.29 (*d*, *J* = 8.3 Hz) and 4.77 ppm (*d*, *J* = 8.0 Hz) are assigned to the anomeric protons of *β*-D-allopyranose and *β*-D-glucopyranose, respectively.

The IR spectrum of **5** shows no OH absorption band. Complete ^{1}H-NMR spectral assignments of **5** are obtained from the homonuclear COSY experiment. In **1**, the OH groups of the two sugar moieties are all unsubstituted, since all protons of glucose and allose are shifted paramagnetically upon acetylation, proposing a diglycoside structure.

This suggestion is also corroborated by the ^{13}C-NMR spectrum of **1** showing no glycosydation shift for the C-atoms of the sugar moieties. The allose signals are also in good agreement with those reported [9]. Comparison of the ^{13}C-NMR spectrum of **1** with those of teuhircoside and its 5-*O*-rhamnopyranosyl derivative, teucardoside [6–8], shows very good accordance, indicating glycosidation at C(5) and C(1) of the aglycone moiety. In the FAB-MS of **1** and **5**, a peak at *m/z* 147 corresponding to that of an ion arising from the aglycone moiety [6], also supports the structure of **1** indicating the same aglycone than that of teucardoside as well as the same glycosidation sites mentioned above. The glycosidation pattern of **1**, is confirmed by the ^{1}H-coupled ^{13}C-NMR spectra. The

[1]) Numbering used currently for the aglycone moiety.

resonances of C(1), C(1'), and C(1'') are assigned as follows: C(1') of the glucose moiety appears at 98.9 (br. *d*, ^1J = 163.2 Hz) C(1'') of the allose moiety at 96.7 (*dt*, ^1J = 165.3, $^3J \approx 5$ Hz), and C(1) of the aglycone at 92.3 ppm (*dq*, ^1J = 176.0, ^2J(C(1), *H*–C(9)) ≈ ^3J(C(1), *H*–C(3)) ≈ ^3J(C(1), *H*–C(1')) ≈ 5 Hz). Selective ^{1}H-decoupling at 4.77 ppm (*H*–C(1') of glucose) simplifies the signal of C(1) (*dt*, $^3J \approx 5$ Hz) establishing the position of the glucose moiety at C(1), and consequently of the allose moiety at C(5).

The glucoside 6-*O*-acetylmioporoside (**2**) was obtained as an amorphous, colourless powder (mol.wt. 390 by FAB-MS: (391, $[M(C_{17}H_{26}O_{10}) + H]^+$)). Its structure was deduced similarly to that of **1**.

The UV (λ_{max} 207 and 232 nm) and IR ($\tilde{\nu}$ = 1725 and 1660 cm^{-1}) absorptions of **2** suggest the presence of a non-conjugated iridoid enol-ether system as well as that of a saturated ester function.

The ^{1}H-NMR spectrum of **2** supports an iridoid structure closely related to that of 8-*O*-acetylmioporoside [10] [11] and mioporoside [12], the major difference being a significant paramagnetic shift of the H–C(6) signal. The signal corresponding to that of H–C(6) in mioporoside (a complex *m* at 4.60 ppm) [12] appears in **2** as a *q*-like signal at 5.33 ppm indicating acylation at *O*–C(6).

The relative configuration of **2** is proved by the observed NOE's, together with spin-spin decoupling experiments. Two selected spin-decoupling experiments fully confirm these assignments. Irradiation of the complex *m* (*dddd*) centred at 3.21 ppm (H–C(5)) modifies the spectrum in four regions: the *dd* at 2.40 ppm (H–C(9)) becomes a broad *s*, the *'q'* at 5.33 ppm (H–C(6)) is simplified to a broad *'t'*, and the 2 *dd* at 6.40 (H–C(3)) and 4.95 ppm (H–C(4)) are simplified to two sharp *d* with ^3J(3,4) = 6.4 Hz, showing that the removed small couplings (2.0 and 2.9 Hz, resp.) are due to interactions with H–C(5).

As expected, irradiation of the signal of H–C(6) (5.33 ppm) modifies the complex *m* at 3.21 ppm (H–C(5)) into a broad *dd*. By the same irradiation, the eight-line spin system at *ca.* 2.16 and 1.99 ppm (*AB* of *ABX*) is changed to a simple *AB* system with the typical geminal coupling constant ($^2J_{AB}$ = 13.8 Hz). This result confirms the assignment of the signal at 5.33 ppm (H–C(6)) as the *X* part of an *ABX* system.

Furthermore, the relative configuration of **2** is established unambiguously by NOE difference spectroscopy: Irradiation of H–C(6) produces a strong enhancement of both the H–C(5) signal (3.21 ppm) and the low-field proton of the *AB* system CH_2(7) (2.16 ppm, H_A–C(7)), thus establishing their *cis* relationship. A small long-distance NOE is also observed with H–C(9) (2.40 ppm) in this experiment. On the other hand, irradiation of the CH_3(10) *s* (1.45 ppm) exhibits significant NOE effects with the high-field part of the *AB* system CH_2(7) (1.99 ppm, H_B–C(7)) and with H–C(1) (5.55 ppm), hence establishing another *cis* arrangement. As a consequence, OH–C(8) is located *trans* to AcO–C(6). The proposed structure **2** is also supported by the ^{13}C-NMR spectrum (see *Exper. Part*) and its comparison with those of 8-*O*-acetylmioporoside [10], ajugol, and its 6-*O*-acyl derivative nemoroside [13]. The chemical shifts of C(8), C(9), and C(10) of **2** are comparable with those of ajugol which has a similar substitution at C(8). Moreover, C(6) (77.4 ppm) is shifted paramagnetically by *ca.* 7 ppm as compared with 8-*O*-acetylmioporoside (70.5 ppm) [10], thus supporting the acylation site *A* [δ (C(3))-δ (C(4))] for **2** (39.6 ppm) is larger than in the case of the 6,8-*cis*-epimers ajugol (33.7 ppm) and nemoroside (35.9 ppm) [13], confirming the 6,8-*trans*-epimer structure as has been demonstrated in similar cases by *Damtoft et al.* [14] [15].

All spectral data (UV, IR, ^{1}H-NMR, ^{13}C-NMR, FAB-MS) obtained for **3** and **4** are in good agreement with the data reported for 8-*O*-acetylharpagide and reptoside, respectively [16] [17].

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Experimental Part

General. Gel filtration: *Sephadex® LH-20 (Pharmacia).* MPLC: *Sepralyte® C18,* 40 μm *(Analytichem).* TLC: silica gel *60 F_{254} (Merck)* plates; iridoids were detected by spraying with 1% vanillin/H_2SO_4, followed by heating at 100° for 5 min.

GLC: *HP 58809A* apparatus; column, *BP-5* fused silica, 25 m × 0.3 mm; 0.4 atm H_2, flow 15 min; temp. 190° isothermal. UV spectra (λ_{max}): *Beckman DU-7* spectrophotometer; spectroscopic-grade MeOH *(Merck).* IR spectra (cm^{-1}): *Perkin-Elmer-782* instrument; KBr pellets. Optical rotations: *Perkin-Elmer-141* polarimeter. ^{1}H- and ^{13}C-NMR spectra (δ [ppm], *J* [Hz]): at 300.13 and 400 MHz (^{1}H) and at 75.47 and 100 MHz (^{13}C) in FT mode using *Bruker WM 300* (1D) and *AM 400* (1D and 2D) instruments with TMS as internal standard. FAB-MS: *Kratos AEI-MS 50* in glycerol and *Finnigan MAT 90* mass spectrometers in thioglycerol.

Extraction and Purification. The plant material of *Betonica officinalis* L. was collected in the neighbourhood of Weesen, Walenstadterberg, and Flums in Switzerland. Dried aerial parts of the plant (1.5 kg) were extracted with $CHCl_3$ (8 l) at r.t. (12 h). After filtration, the residue was pressed out, extracted with $CHCl_3$ (2 ×), AcOEt (3 ×), and MeOH (1 ×). All extracts were concentrated *in vacuo* and lyophilized ($CHCl_3$ extract, 55.8 g; AcOEt extract, 7.27 g; MeOH extract, 144.45 g). MeOH extracts were dissolved in H_2O and extracted with BuOH saturated with H_2O (4 ×). The combined BuOH extracts were concentrated and lyophilized (54.79 g). The whole residue was partitioned by *Craig* distribution (160 steps, shaking 50 × /step, separation time 10 min) with AcOEt/PrOH/H_2O 4:2:7 as solvent system, and 4 fractions were collected: *A* (14.03 g), *B* (4.6 g), *C* (14.33 g), and *D* (21.58 g).

Isolation of Allobetonicoside (**1**). In a typical procedure, an aliquot of *Fraction B* (3.8 g) was rechromatographed over *Sephadex LH-20* (column 3.6 cm × 92 cm) using gradient elution with H_2O/MeOH (0–100% MeOH; 48 h) and 13 fractions were collected. *Fr. B3* (0.9065 g) was subjected to MPLC (*Sepralyte C18;* column 2.4 × 71 cm) applying again gradient elution with H_2O/MeOH (0–100% MeOH; 68 h) and 6 fractions were collected. Diglycoside **1** was obtained in *Fr.B3.3* (40.8 mg). Similarly, **1** was isolated also from other fractions of the *Craig* distribution (TLC control), yielding a total amount of 4.3 g of pure **1**.

Isolation of Acetylharpagide (**3**). The AcOEt extract (totally 7.27 g) was divided into two parts (4.74 g and 2.26 g) which were subjected separately to DCCC using the upper phase of $CHCl_3$/MeOH/H_2O 43:37:20 as mobile phase (separation times 96 and 48 h, resp.; flow rate 1.5–2 ml/min; fractionation time 12 min). Each application resulted in the isolation of **3** (totally 840 mg).

Isolation of 6-O-Acetylmioporoside (**2**) *and Reptoside* (**4**). An aliquot of *Fraction C* (6.9 g) obtained by *Craig* distribution (see above) was applied to *Sephadex LH-20* using H_2O as eluent to give a crude fraction mainly composed of **2** and **4**. This mixture was subjected to MPLC (*Sepralyte C18*, column 26 mm × 73 cm) applying gradient elution with H_2O/MeOH (0–20% MeOH; 24 h). Early fractions gave **2** (40 mg) while **4** (21 mg) was isolated from the slower running band.

Allobetonicoside (= *(1*R*,*4a*R*,*7a*S*)*-4-[(β-*D*-Allopyranosyl)oxy]-1-[(β-*D*-glucopyranosyl)oxy]-4a,6,7,7a-tetrahydrocyclopenta[*c*]pyran-5(1H)-one*; **1**). Amorphous, colourless powder. $[\alpha]_D^{20} = -53.3$ (MeOH, $c = 0.34$). UV (MeOH): 211 (3.84), 230 (3.71). IR (KBr): 3400 (br., OH), 1705 (C=O), 1645 (C=C–O), 1620 (C=C). ^{1}H-NMR[1]) (400 MHz, D_2O): aglycone: 5.95 (*d*, $^3J(1,9) = 1.2$, H–C(1)); 6.45 (*d*, $^3J(3,4) = 6.4$, H–C(3)); 5.04 (*dd*, $^3J(4,3) = 6.4$, $^4J(4,9) = 1.1$, H–C(4)); 6.13 ('*t*', $^4J(7,9) \approx {}^4J(7,10) \approx 1.5$, H–C(7)); 3.97 (*m*, $w_{1/2} \approx 6$, H–C(9)); 2.30 (*s*, CH_3(10)); glucose: 4.77 (*d*, $^3J(1',2') = 8.0$, H–C(1')); 3.39 (*dd*, $^3J(2',1') = 8.0$, $^3J(2',3') = 9.0$, H–C(2')); 3.42, 3.48 ('*t*' each, overlapping, H–C(3'), H–C(4')); 3.50 (*X* of *ABXY*, *m*, overlapping, H–C(5')); 3.94 (*A* of *ABXY*, '*dd*', $^2J(6'A,6'B) = 12.3$, $^3J(6'A,5') = 2.1$ H_A–C(6')); 3.72 (*B* of *ABXY*, '*dd*', $^2J(6'B,6'A) = 12.3$, $^3J(6'B,5') = 5.9$, H_B–C(6')); allose: 5.29, (*d*, $^3J(1'',2'') = 8.3$, H–C(1'')); 3.47 (*dd*, $^3J(2'',1'') = 8.3$, $^3J(2'',3'') = 2.9$, H–C(2'')); 4.20 (*t*, $^3J(3'',2'') = {}^3J(3'',4'') = 2.9$, H–C(3'')); 3.60 (*dd*, $^3J(4'',3'') = 2.9$, $^3J(4'',5'') = 10.1$, H–C(4'')); 3.72 (*X* of *ABXY*, *m*, overlapping, H–C(5'')); 3.85 (*A* of *ABXY*, *dd*, $^2J(6''A,6''B) = 12.3$, $^3J(6''A,5'') = 2.1$, H_A–C(6'')); 3.64 (*B* of *ABXY*, *dd*, $^2J(6''B,6''A) = 12.3$, $^3J(6''B,5'') = 5.4$, H_B–C(6'')). ^{13}C-NMR[1]) (100 MHz, D_2O): aglycone: 92.3 (*d*, C(1)); 144.2 (*d*, C(3)); 102.8 (*d*, C(4)); 77.5 (*s*, C(5)); 204.9 (*s*, C(6)); 127.9 (*d*, C(7)); 178.5 (*s*, C(8)); 55.0 (*d*, C(9)); 17.7 (*q* C(10)); glucose: 98.9 (*d*, C(1')); 73.7 (*d*, C(2')); 75.7 (*d*, C(3')); 69.6 (*d*, C(4')); 76.3 (*d*, C(5')); 60.8 (*t*, C(6')); allose: 96.7 (*d*, C(1'')); 71.3 (*d*, C(2'')); 70.7 (*d*, C(3'')); 66.8 (*d*, C(4'')); 72.8 (*d*, C(5'')); 61.2 (*t*, C(6'')). FAB-MS: 545 ($[M + K]^+$), 529 ($[M + Na]^+$), 507 ($[M + H]^+$), 327 ($[M + H]^+ -$ hexose), 183, 165, 147 ($[M + H]^+ -$ glucose – allose).

Acetylation of **1**. Treatment of **1** (10 mg) with Ac_2O (1 ml) and pyridine (1 ml) at r.t. overnight followed by usual workup yielded the octa-*O*-acetyl derivative **5**. Colourless needles from EtOH. M.p. 118–119°. UV (MeOH): 209 (3.33), 228 (3.17). IR (KBr): 2960 (C–H), 1755 (C=O), 1640 (C=C). ^{1}H-NMR[1]) (400 MHz, $CDCl_3$): aglycone: 5.36 (*d*, $^3J(1,9) = 3.1$, H–C(1)); 6.32 (*d*, $^3J(3,4) = 6.3$, H–C(3)); 5.04 (*dd*, $^3J(4.3) = 6.3$, $^4J(4,9) = 0.7$, H–C(4)); 5.99 (*sext.*-like, $^4J(7,9) \approx 1.5$, $^4J(7,10) = 1.2$, H–C(7)); 3.68 (*m*, $w_{1/2} \approx 6.0$, H–C(9)); 2.21 (*t*, $^4J(10,7) = {}^4J(10,9) = 1.2$, CH_3(10)); glucose: 4.94 (*d*, $^3J(1',2') = 8.2$, H–C(1')); 4.89 (*dd*, $^3J(2',1') = 8.2$, $^3J(2',3') = 9.2$, H–C((2')); 5.28 ('*t*', $^3J(3',2') = 9.2$, $^3J(3',4') = 9.4$, H–C(3')); 5.12 (*dd*, $^3J(4',3') = 9.4$, $^3J(4',5') = 10.0$, H–C(4')); 3.76 (*X* of *ABXY*, *dq*-like, $^3J(5',4') = 10.0$, $^3J(5',6'A) = 4.5$, $^3J(5',6'B) = 2.3$, H–C(5')); 4.33 (*A* of *ABXY*, *dd*, $^2J(6'A,6'B) = 12.5$, $^3J(6'A,5') = 4.5$, H_A–C(6')); 4.14 (*B* of *ABXY*, *dd*, $^2J(6'B,6'A) = 12.5$, $^3J(6'B,5') = 2.3$, H_B–C(6')); allose: 5.14 (*d*, $^3J(1'',2'') = 8.2$, H–C(1'')); 4.85 (*dd*, $^3J(2'',1'') = 8.2$, $^3J(2'',3'') = 3.1$, H–C(2'')); 5.68 (*t*, $^3J(3'',2'') = {}^3J(3'',4'') = 3.1$, H–C((3'')); 4.98 (*dd*, $^3J(4'',3'') = 3.1$, $^3J(4'',5'') = 10.1$, H–C(4'')); 4.11 (*X* of *ABXY*, *dt*-like, $^3J(5'',4'') = 10.1$, $^3J(5'',6''A) = 4.1$, $^3J(5'',6''B) = 3.2$, H–C(5'')); 4.26 (*A* of *ABXY*, '*dd*', $^2J(6''A,6''B) = 12.4$, $^3J(6''A,5'') = 4.1$, H_A–C(6'')); 4.24 (*B* of *ABXY*, '*dd*', $^2J(6''B,6''A) = 12.4$, $^3J(6''B,5'') = 3.2$, H_B–C(6'')). FAB-MS: 865 ($[M + Na]^+$), 823 ($[M + Na]^+ -$ ketene), 781 ($[M + Na]^+ - 2$ ketene).

Hydrolysis of **1** *and Silylation of the Sugar Components.* A soln. of **1** (5 mg) in 3% H_2SO_4 soln. (5 ml) was hydrolyzed at 90° for 3 h. After neutralization with $BaCO_3$ and filtration through *Celite*, the aglycone was extracted with Et_2O and the H_2O layer evaporated and dried *in vacuo* (2 h, 25°/10^{-3} Torr). The residue was dissolved in abs. pyridine (1 ml), hexamethyldisilazane (0.2 ml) and trimethylsilyl chloride (0.1 ml) were added, and the mixture was shaken vigourously for 30 s. After standing for 5 min at r.t., the mixture was dissolved with Et_2O and the pyridine removed by washing with sat. $CuSO_4$ soln. The Et_2O layer was dried ($MgSO_4$) and subjected to GLC [18]: Me_3Si derivatives of D-allose at t_R 5.91 (16%), 6.11 (23%), 6.38 (55%), and 6.78 min (6%); Me_3Si derivatives of α- and β-D-glucopyranose, resp., at t_R 7.54 (41%) and 10.31 min (59%). Silylated reference sugars: from D-allose, t_R 5.90 (3%), 6.09 (7%), 6.37 (84%), and 6.68 min (6%); from α- and β-D-glucopyranose, resp., t_R 7.49 (48%) and 10.30 min (52%).

6-O-Acetylmioporoside (= *(1R*,4aS*,5R*,7R*,7aR*)-1-[(β-D-Glucopyranosyl)oxy]-1,4a,5,6,7,7a-hexahydro-7-hydroxy-7-methylcyclopenta[c]pyran-6-yl Acetate;* **2**). Amorphous, colourless powder. $[\alpha]_D^{20} = -165.3$ (MeOH, $c = 0.33$). UV (MeOH): 207 (3.18), 232 (2.71). IR (KBr): 3400 (br., OH), 1725 ($COCH_3$), 1660 (C=C–O). ^{1}H-NMR[1]) (400 MHz, D_2O): aglycone: 5.55 (*d*, $^3J(1,9) = 2.9$, H–C(1)); 6.40 (*dd*, $^3J(3,4) = 6.4$, $^3J(3,5) = 2.0$, H–C(3)); 4.95 (*dd*, $^3J(4,3) = 6.4$, $^3J(4,5) = 2.9$, H–C(4)); 3.21 (*dddd*, $^3J(5.3) = 2.0$, $^3J(5,4) = 2.9$, $^3J(5,6) = 6.8$, $^3J(5,9) = 8.5$, H–C(5)); 5.33 (*X* of *ABX*, *q*-like, $|^3J_{AX} + {}^3J_{BX}| = 15.5$, H–C(6)); 2.16 (*A* of *ABX*, *dd*, $^2J(7A,7B) = 13.8$, $^3J(7A,6) = 6.8$, H_A–C(7)); 1.99 (*B* of *ABX*, '*dd*', $^2J(7B,7A) = 13.8$, $^3J(7B,6) = 8.6$, H_B–C(7)); 2.40 (*dd*, $^3J(9,1) = 2.9$, $^3J(9,5) = 8.5$, H–C(9)); 1.45 (*s*, CH_3(10)); 2.14 (*s*, AcO–C(6)); glucose: 4.82 (*d*, $^3J(1',2') = 8.0$, H–C(1')); 3.33 (*dd*, $^3J(2',1') = 8.0$, $^3J(2',3') = 9.1$, H–C(2')); 3.43, ('*t*', $^3J(3',2') \approx {}^3J(3',4') = 9.1$, H–C(3')); 3.53 (*dd*, $^3J(4',3') \approx {}^3J(4',5') = 9.1$, H–C(4')); 3.50 (*X* of *ABXY*, *m*, overlapping, H–C(5')); 3.96 (*A* of *ABXY*, '*dd*', $^2J(6'A,6'B) = 12.3$, $^3J(6'A,5') = 2.0$, H_A–C(6')); 3.76 (*B* of *ABXY*, '*dd*', $^2J(6'B,6'A) = 12.3$, $^3J(6'B,5') = 5.9$, H_B–C(6')). ^{13}C-NMR[1]) (75 MHz, D_2O): aglycone: 95.5 (*d* C(1)); 142.9 (*d*, C(3)); 103.3 (*d*, C(4)); 36.6 (*d* C(5)); 77.4 (*d* C(6)); 47.2 (*t*, C(7)); 79.5 (*s*, C(8)); 52.4 (*d*, C(9)); 27.4 (*q*, C(10)); 176.7 (*s*, $COCH_3$); 23.1 (*q*, $COCH_3$); glucose: 100.6 (*d*, C(1')); 75.3 (*d*, C(2')); 78.3 (*d*, C(3')); 72.3 (*d*, C(4')); 78.8 (*d*, C(5')); 63.3 (*t*, C(6')). FAB-MS: 483 ($[M + H]^+$ + glycerol), 413 ($[M + Na]^+$), 391 ($[M + H]^+$).

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