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# CHEMICAL CONSTITUENTS OF THE FLORA OF JORDAN, PART V-B.[1] THREE NEW ARYLNAPHTHALENE LIGNAN GLUCOSIDES FROM *HAPLOPHYLLUM BUXBAUMII*

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ABSTRACT.—*Haplophyllum buxbaumii* has yielded three new lignan type A glucosides: majidine [**2**], qudsine [**3**], and arabelline [**4**]. Cleistanthin B [**1**] is also reported for the first time from this family. Temperature-dependent nmr studies have provided insight into the conformational equilibria existing in **1**, **2**, and **4**.

In continuation of our systematic phytochemical investigation of *Haplophyllum buxbaumii* A. Juss. (Rutaceae) (1), we now report the isolation and structure elucidation of four diphyllin glucosides, three of which (**2–4**) are new. These are cleistanthin B [**1**], 4-*O*-[β-D-xylopyranosyl(1↦2)β-D-apiofuranosyloxy]-6,7-dimethoxy-1-(3′,4′-methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (majidine) [**2**], 4-*O*-[β-D-glucopyranosyl(1↦3)α-L-arabinopyranosyl(1↦5)(2-*O*-acetyl-β-D-apiofuranosyloxy]-6,7-dimethoxy-1-(3′,4′- methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (qudsine) [**3**], and 4-*O*-[α-L-arabinopyranosyl(1↦6)β-D-glucopyranosyloxy]-6,7-dimethoxy-1-(3′,4′-methylenedioxyphenyl)-3-hydroxymethylnaphthalene-2-carboxylic acid lactone (arabelline) [**4**].

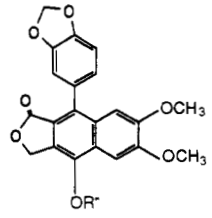
The bluish fluorescence of the four lignan glucosides under uv light as well as their similar uv spectra (λ max 261.6 nm) indicated that all these compounds bear an arylnaphthalene nucleus (2). The acid hydrolysis of the four lignan glucosides afforded the same aglycone, which was identified by spectral data as diphyllin [**11**] (12). The sugar residues, identified by tlc comparison with authentic samples, were found to be glucose of compound **1**, apiose and xylose of compound **2**, apiose, arabinose, and glucose of compound **3**, and arabinose and glucose of compound **4**.

The uv, ir, ms, and $^1$H-nmr spectra were reported for cleistanthin B (3). As the $^1$H-nmr assignments were not fully made, we present in Table 1 the $^1$H-nmr spectrum with the assignments of the individual aromatic protons. The $^{13}$C-nmr chemical shifts and multiplicity assignments of cleistanthin B are shown in Table 2.

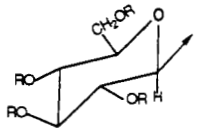
Compound **2** was assigned the molecular formula $C_{31}H_{32}O_{15}$) positive fabms *m/z* 645 $[M+H]^+$). The $^1$H-nmr spectrum of the acetylated derivative **6** of compound **2** showed five 3 H singlets in the region between δ 2.02 and 2.14, corresponding to the aliphatic acetoxy groups, indicating the presence of five aliphatic hydroxyl groups. The $^{13}$C-nmr spectrum (DMSO-$d_6$, 75.43 MHz) of **2** showed the presence of 31 carbons.

The sequence of the sugar units in compound **2** was determined by spectral analysis. The positive ion fabms exhibited ions at *m/z* 645, 513, and 381, which were assigned to $[M+H]^+$, $[M+H-\text{pentose}]^+$, and $[M+H-2\text{ pentose}]^+$, respectively. The $^{13}$C-nmr spectrum of compound **2** showed that there were 10 carbon resonances corresponding to the sugar moiety. Of these, two were the anomeric carbons resonating at δ 109.8 and 105.0, while the rest resonated in the region δ 62.5 to 84.5. DEPT experiments (5) showed one quaternary carbon at δ 79.7 and three methylene carbons at δ

[1]For part A, see Al-Abed *et al.* (1).

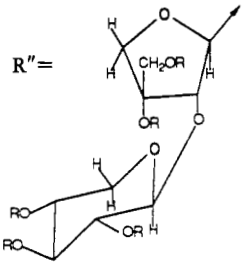



R''=



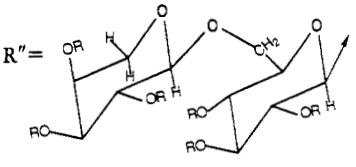
**1** R=H
**5** R=Ac

R''=



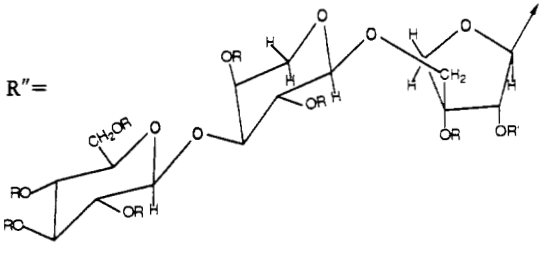
**2** R=H
**6** R=Ac

R''=



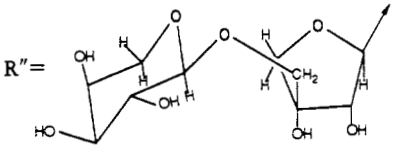
**4** R=H
**10** R=Ac

R''=



**3** R=H, R'=Ac
**7** R=R'=Ac
**8** R=R'=H

R''=



**11** R'=H

**9**

62.5, 66.1, and 47.7. The hetero COSY showed that two anomeric carbons resonating at δ 109.80 (furanoside-type sugar) and 105.00 (pyranoside-type sugar) (4) were coupled to the protons (each 1H) at δ 5.56 (these exist in pairs at 26°) (d, $J = 2.9$ Hz) and δ 4.38 (d, $J = 7.6$ Hz), respectively.

Final assignment of the different protons was done using spin echo correlated spectroscopy (SECSY) (Figure 1), which allowed some of the interactions to be determined with greater clarity than COSY and showed that the anomeric proton resonating at δ

TABLE 1. $^1$H-nmr Chemical Shifts of the Aglycone Part of Compounds **1**, **2**, **3**, **4**, and **11**.

| Proton | Compound | | | | |
|---|---|---|---|---|---|
| | **1** | **2** | **3** | **4** | **11** |
| H-5 | 8.17[a] (s)<br>8.16 (s) | 7.61 (s) | 7.54 (s) | 8.19 (s) | 7.62 (s) |
| H-8 | 6.967[a] (s)<br>6.972 (s) | 6.99[a] (s)<br>7.00 (s) | 6.99 (s) | 6.98[a] (s)<br>6.99 (s) | 6.95 (s) |
| H-2′ | 6.90[a] (d, $J$ = 1.6 Hz)<br>6.94 (d, $J$ = 1.6 Hz) | 6.89[a] (d, $J$ = 1.6 Hz)<br>6.91 (d, $J$ = 1.6 Hz) | 6.91 (d, $J$ = 1.7 Hz) | 6.90[a] (d, $J$ = 1.6 Hz)<br>6.93 (d, $J$ = 1.6 Hz) | 6.85 (d, $J$ = 1.6 Hz) |
| H-5′ | 7.02[a] (d, $J$ = 7.9 Hz)<br>7.03 (d, $J$ = 7.9 Hz) | 7.02 (d, $J$ = 7.9 Hz) | 7.04 (d, $J$ = 8.0 Hz) | 7.03[a] (d, $J$ = 7.9 Hz)<br>7.032 (d, $J$ = 7.9 Hz) | 7.00 (d, $J$ = 7.9 Hz) |
| H-6′ | 6.77[a] (dd, $J$ = 8.0, 1.7 Hz)<br>6.80 (dd, $J$ = 8.0, 1.7 Hz) | 6.77[a] (dd, $J$ = 7.9, 1.7 Hz)<br>6.79 (dd, $J$ = 7.9, 1.7 Hz) | 6.78 (dd, $J$ = 8.0, 1.7 Hz) | 6.79[a] (dd, $J$ = 7.9, 1.7 Hz)<br>6.81 (dd, $J$ = 7.9, 1.7 Hz) | 6.74 (dd, $J$ = 7.9, 1.7 Hz) |
| 6-OMe | 3.95 (s) | 3.95 (s) | 3.98 (s) | 3.95 (s) | 3.93 (s) |
| 7-OMe | 3.67 (s) | 3.66 (s) | 3.67 (s) | 3.67 (s) | 3.64 (s) |
| 2H-3a | 5.76[a] (d, $J$ = 20.6 Hz)<br>5.47 (dd, $J$ = 20.6, 2.2 Hz) | 5.45 (s) | 5.48 (s) | 5.69[a] (d, $J$ = 15.4 Hz)<br>5.44 (dd, $J$ = 15.4, 1.7 Hz) | 5.35 (s) |
| 3′,4′-$OCH_2O$ | 6.12 (s) | 6.11 (s) | 6.12 (s) | 6.12 (s) | 6.10 (s) |

[a]Exist in pairs at nmr room temperature (26°).

TABLE 2. $^{13}$C-nmr Chemical Shifts (ppm) and Multiplicity Assignments of Compounds **1–4**.

| Carbon | Multiplicity[a] | Chemical shift (ppm) | | | |
|---|---|---|---|---|---|
| | | **1** | **2** | **3** | **4** |
| C-1 | s | 134.85, 134.89[b] | 134.8 | 134.6 | 135.5 |
| C-2 | s | 118.8 | 119.0 | 118.9 | 119.4 |
| C-3 | s | 126.8 | 126.7 | 126.3 | 127.3 |
| C-4 | s | 144.87, 144.84[b] | 144.4 | 143.9 | 145.15, 145.20[b] |
| C-5 | d | 101.7 | 101.11 | 100.6 | 102.2 |
| C-6 | s | 151.5 | 151.9 | 151.6 | 152.0 |
| C-7 | s | 150.0 | 150.3 | 150.1 | 150.5 |
| C-8 | d | 105.4 | 106.2 | 105.7 | 105.9 |
| C-9 | s | 129.93, 129.81[b] | 130.0 | 128.36, 128.49[b] | 130.51, 130.68 |
| C-10 | s | 129.7 | 129.0 | 129.6 | 120.2 |
| C-1′ | s | 128.3 | 128.5 | 128.2 | 128.7 |
| C-2′ | d | 110.74, 110.88[b] | 110.95, 110.99[b] | 110.8 | 111.13, 111.41[b] |
| C-3′ | s | 146.9[c] | 147.2 | 146.94[c] | 147.4 |
| C-4′ | s | 147.0[c] | 147.2 | 146.97[c] | 147.4 |
| C-5′ | d | 107.9 | 108.3 | 108.0 | 108.6 |
| C-6′ | d | 123.55, 123.60[b] | 123.9 | 123.6 | 124.13, 124.26[b] |
| C-2a | s | 169.2 | 169.5 | 169.0 | 170.1 |
| C-3a | t | 67.4 | 67.16 | 66.7 | 68.0 |
| 6-OMe | q | 55.8 | 56.4 | 55.7 | 56.4 |
| 7-OMe | q | 55.2 | 55.6 | 55.3 | 55.7 |
| $OCH_2O$ | t | 101.1 | 101.4 | 101.1 | 101.6 |
| C-1″ | d | 105.0 | 109.8 | 108.4 | 105.3 |
| C-2″ | d | 73.8 | 84.5 | 78.7 | 74.1 |
| C-3″ | | 76.4 (d) | 79.7 (s) | 78.1 (s) | 75.8 |
| C-4″ | | 70.1 (d) | 74.7 (t) | 75.1 (t) | 70.2 (d) |
| C-5″ | | 77.3 (d) | 66.1 (t) | 71.3 (t) | 76.4 (d) |
| C-6″ | | 61.62 (t) | | | 68.8 (t) |
| C-1‴ | d | | 105.0 | 103.9[d] | 103.6 |
| C-2‴ | d | | 73.7 | 72.0 | 70.7 |
| C-3‴ | d | | 76.1 | 87.7 | 72.7 |
| C-4‴ | d | | 69.7 | 68.2 | 67.7 |
| C-5‴ | t | | 62.5 | 65.1 | 65.4 |
| C-1⁗ | d | | | 103.6[d] | |
| C-2⁗ | d | | | 73.8 | |
| C-3⁗ | d | | | 76.1 | |
| C-4⁗ | d | | | 70.2 | |
| C-5⁗ | d | | | 67.9 | |
| C-6⁗ | t | | | 61.1 | |
| $CH_3CO$ | q | | | 20.7 | |
| MeCO | s | | | 170.1 | |

[a]Symbols: s-singlet; d-doublet; t-triplet; q-quartet.
[b]Exist in pairs at room temperature (26°).
[c,d]Assignments in the same column with the same superscript are interchangeable.

5.56 was coupled with the proton resonating at δ 4.62, the two protons not being coupled further with any other protons.

The protons of one of these two methylene groups resonated at δ 3.78 (d, $J$ = 9.4 Hz, Hα) and 4.22 (existing in pairs at 26°) (d, $J$ = 9.4 Hz, Hβ). From the SECSY spectrum these two protons were coupled to each other. The protons of one of the other two methylene groups resonated as two doublets at δ 3.47 ($J$ = 11.4 Hz) and 3.57 ($J$ = 11.4 Hz). These two protons were also not coupled to any other protons, as evident from the SECSY spectrum. The above data are typical for apiose furanoside.

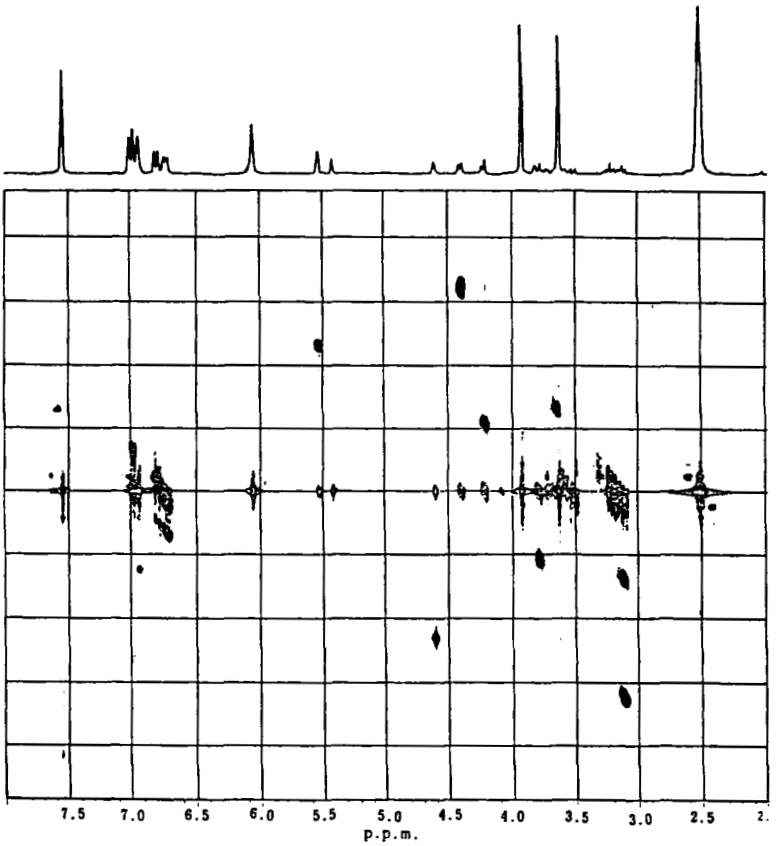



FIGURE 1. Spin echo correlated spectrum of compound **2**.

The third methylene carbon (δ 62.5) could be clearly assigned from its characteristic chemical shift value and acid hydrolysis data to the C-5‴ of the xylose moiety (6). The NOESY spectrum showed that the anomeric proton of apiose (δ 5.56) was seen to interact through space with the lactone methylene proton (δ 5.45). This proved that apiose is bound directly to the aglycone. Assignment of the connectivity between the sugar xylose and apiose followed also from the study of SECSY and HX-COSY spectra.

The anomeric proton of apiose was seen to be coupled (through bond) with the C-2″ proton which resonated at δ 4.62. From the hetero-COSY spectrum, this proton was found to be coupled with the carbon which resonated at δ 84.50. In the absence of the linkage between the two sugar units, this carbon is normally expected to resonate at δ 76.00 (7,8), the downfield shift being indicative of the presence of the *O*-glucoside linkage at C-2″. From these data the sequence of connectivity was determined to be xylopyranoside(1↦2)apiofuranosyloxy.

The $^{1}$H-nmr and $^{13}$C-nmr spectra of **2** were useful in determining the configuration of the glucosidic linkage from the magnitude of the coupling constant of the anomeric

protons (9) and the chemical shift of the anomeric carbons (4). These data established β configurations for apiofuranosyl and xylopyranosyl.

Compound **3** was assigned the molecular formula $C_{39}H_{44}O_{21}$ (positive fabms $[M+H]^+$ 849). It was optically active with specific rotation $[\alpha]^{24}D$ −60.53 ($c$ = 0.38, MeOH). The $^1$H-nmr spectrum of the acetylated derivative **7** of compound **3** in $CDCl_3$ showed 8 singlets, each integrating for 3H, corresponding to the aliphatic acetoxy groups in the region between δ 1.90 and 2.14.

The $^{13}$C-nmr spectrum (DMSO-$d_6$, 75.43 MHz) of **3** showed the presence of 39 carbons, 18 of which corresponded to the sugar moiety and the rest to the aromatic moiety. The 18 carbons of the sugar moiety consisted of two quaternary carbons, one Me carbon, four $CH_2$ carbons and 11 CH carbons. The $^{13}$C-nmr chemical shifts and multiplicity assignments of compound **3** are shown in Table 2. The $^1$H/$^{13}$C correlation experiment allowed the identification of individual proton-bearing carbons.

The sequence of sugar units in compound **3** was determined by spectral analysis. The positive ion fabms exhibited ions at *m/z* 849, 687, 555, and 381, which were assigned to $[M+H]^+$, $[M+H-162]^+$, $[M+H-132]^+$, and $[M+H-162-132-174]^+$, respectively. The losses of 162, 132, and 174 mu corresponded to the loss of hexose, pentose, and acetylated pentose, respectively. The presence of an acetyl group was confirmed from the 3H signal for the acetyl methyl protons at δ 2.16.

The $^1$H/$^{13}$C-nmr correlated spectrum showed three anomeric carbons resonating at δ 108.40, 103.90, and 103.60, each of which was coupled with corresponding protons resonating at δ 5.69 (d, $J$ = 2.3 Hz), 4.36 (d, $J$ = 7.4 Hz), and 4.36 (d, $J$ = 7.4 Hz), respectively (these exist in pairs at 26°).

The $^1$H-$^1$H-COSY spectrum showed that the anomeric proton resonating at δ 5.69 (H-1″) was scalar-coupled only with the proton resonating at δ 5.53 (H-2″) and that the two protons were not coupled to any other protons. The chemical shift of the corresponding attached anomeric carbon (C-1″) was consistent with that expected for it in a furanoside pentose sugar (4). From these spectral data and the identification of the sugar after acid hydrolysis, the sugar was established as apiose. The C-2″ proton which resonated at δ 5.53 was coupled with the carbon resonating at δ 78.7. This carbon usually resonates at δ 76.0 when a free hydroxyl group is attached to it (7,8). The downfield shift of this carbon is consistent with the presence of an acetate group on it (1,10). These data showed that the monoacetylated apiose (174 mu) was bound directly to the aglycone. The C-3″ quaternary carbon in the apiose moiety resonated at δ 78.1 at its normal chemical shift value when bearing a hydroxyl group (7,8). This data gave confirmatory evidence that the arabinose unit was linked to apiose through C-5″, which resonated downfield at δ 71.3 (rather than at its normal chemical shift of δ 63.8 when it bears a free OH group). The arabinose moiety was, on the other hand, bound to the glucose moiety through C-3‴, which caused downfield shift for this carbon to δ 87.7 as against its normal value of 73.0 when it bears a free OH group (11). The C-2‴ and C-4‴ carbons of arabinose resonated at their normal chemical shifts (δ 72.0 and 68.2 respectively) (11). From the spectral data of the anomeric protons and their carbons, the configuration of the sugar moieties was established as β configurations for the apiofuranosyl and glucopyranosyl and α configuration for the arabinopyranosyl.

Compound **4** was assigned the molecular formula $C_{32}H_{34}O_{16}$ (positive fabms $[M+H]^+$ 675). It was optically active with specific rotation $[\alpha]^{24}D$ −30.78 ($c$ = 0.26, MeOH) and showed a splitting pattern similar to that of compound **2** in the aromatic region.

The $^1$H-nmr spectrum of the acetylated derivative **7** of compound **4** in $CDCl_3$ showed six singlets each integrating for 3H, corresponding to the aliphatic acetoxy groups in the region δ 1.90 to 2.15. The $^{13}$C-nmr spectrum (DMSO-$d_6$, 75.43 MHz)

of **4** showed the presence of 32 carbons, 11 of which corresponded to the sugar moiety and the rest to the aromatic moiety. The $^{13}$C-nmr chemical shifts and multiplicity assignments of compound **4** are shown in Table 2.

The sequence of sugar connectivity for compound **4** was deduced from the positive fabms and other spectral data. The positive ion fabms of **4** exhibited ions at *m/z* 675, 543, and 381 assigned to $[M+H]^+$, $[M+H-\text{pentose}]^+$, and $[M+H-\text{pentose}-\text{hexose}]^+$, respectively. These data provided evidence that the pentose (arabinose) is the terminal sugar while hexose (glucose) is the inner sugar.

Normally C-6 of the glucosyl pyranoside is expected to resonate at δ 60.0 (DMSO-$d_6$) (1) but C-6″ in compound **4** (from BB $^{13}$C-nmr, HX-COSY, and DEPT) resonated at δ 68.8. The downfield shift of this carbon established that the linkage to the pentose monosaccharide occurred through C-6″. From these data the sequence of connectivity was determined to be arabinopyranosyl(1↦6)glucopyranosyloxy.

The configuration of the sugar linkages was established from the coupling constants of the anomeric protons and chemical shifts of the anomeric carbons, which revealed β and α configurations for glucopyranosyl and arabinopyranosyl, respectively.

Most of the aromatic protons of the compounds cleistanthin B, **2**, and **4** exist as pairs of signals, and some of the aromatic carbons exist as pairs of signals due to the equilibrium between two conformational isomers resulting from the slow rotation of the sugar unit at room temperature around the glucosidic linkage with the aglycone. The aromatic protons are hence exposed to two different environments because two different conformational isomers predominate, so the protons of a sugar unit can exist in two different orientations resulting from the restricted rotation, i.e., either above or below the plane of the naphthalide ring system.

The $^1$H-nmr spectrum (DMSO-$d_6$) of cleistanthin B showed similar doubling of all aromatic protons at 26°. The corresponding $^{13}$C-nmr spectrum (DMSO-$d_6$) showed a similar doubling of signals of C-1, C-4, C-9, C-2′, and C-6′. Temperature-dependent $^1$H-nmr studies showed that the C-5, C-8, C-2′, C-5′, and C-6′ protons coalesced at 50°, 50°, 70°, 50°, and 70°, respectively (Figure 2). The anomeric proton of cleistanthin B resonated at δ 5.95 at room temperature (26°). There was a noticeable upfield shift in the chemical shift of this proton as the temperature was increased. The chemical shifts recorded were δ 5.96, 5.91, 5.82, 5.74, 5.66, 5.61 and 5.64 at 26°, 30°, 40°, 50°, 60°, 70°, and 80°, respectively (Figure 2). The upfield shifts suggest that, in the optimum conformation, the C-1″ proton becomes increasingly exposed to the shielding influence of the π-electronic clouds of the naphthalene nucleus.

Subsequently, in compounds **2** and **4** the C-2′, C-6′, and C-8 protons showed similar doubling of signals; the temperature-dependent $^1$H-nmr studies showed that their protons coalesced around 60°, 60°, and 50°, respectively, for compound **2** while for compound **4** around 70°, 70°, and 60°.

The lack of conformational equilibirum in **3** may be explained by the presence of steric hindrance induced by the acetyl group present at C-2″ of the apiose moiety, which reduces the influence of the sugar units on the aromatic portion of the molecule by moving them farther away into a position of least non-bonded interaction. This was proven by alkaline hydrolysis of the acetyl group of **3** because the $^1$H-nmr spectrum of the corresponding hydrolyzed glucoside **9** again showed pairing of signals in a part of the aromatic region (C-8, C-2′, and C-6′ protons).

The H-5 appeared downfield in cleistanthin B and compound **4** (δ 8.16 and 8.19, respectively) as compared to other diphyllin glucosides such as **2** and **3** (δ 7.61 and 7.54, respectively) in which the sugar directly attached was of the furanoside type. This may be attributed to the differential interaction due to the change from pyranose to the furanose sugar. Interestingly, acetylation of the hydroxyl groups in cleistanthin B and **4**

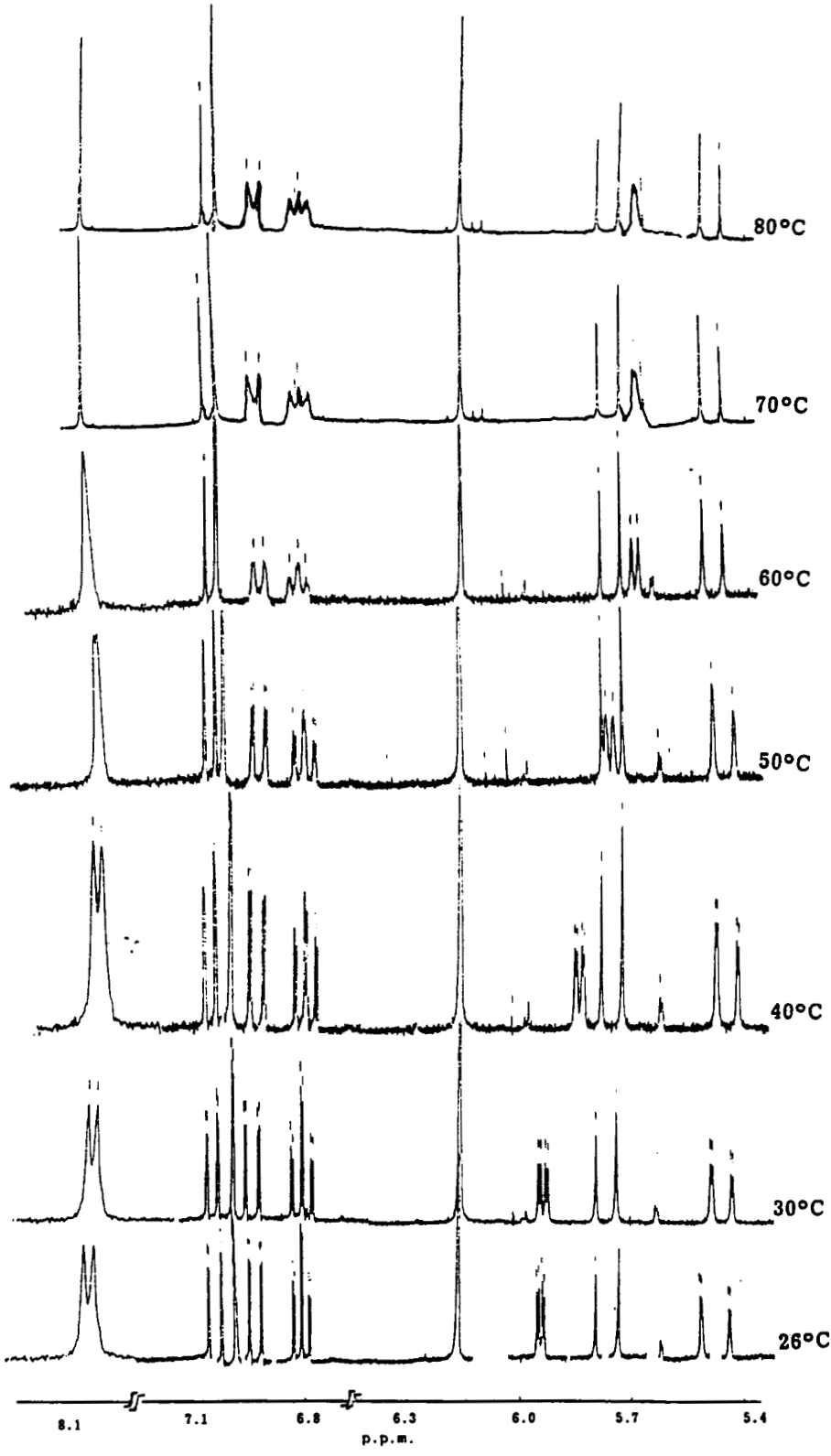



FIGURE 2. $^1$H nmr of **4** (δ 5.4–δ 8.1 region) with temperature variation.

resulted in the appearance of the H-5 at its normal value (δ 7.51 and 7.53, respectively).

Another influence of the pyranosyl moiety was observed in the $^1$H-nmr spectra of cleistanthin B and **4**, which showed the C-3a methylene protons as an AB system while they appeared as an $A_2$ system for compounds **2** and **3**.

## EXPERIMENTAL

PLANT MATERIAL, EXTRACTION, AND ISOLATION.—The whole plant of *H. buxbaumii* (20 kg, dry wt) was collected around the campus of Jordan University of Science and Technology ( JUST) near Irbid (Roman Arabella), Jordan in April 1986. The plant was identified by Prof. D. El-Isawi, and a voucher specimen was deposited in the herbarium of the University of Jordan, Amman. The dried and ground whole plant was defatted with petroleum ether and then extracted with cold EtOH. The crude EtOH extract (1 kg) was partitioned between $CHCl_3$ and $H_2O$. The organic layer was separated and the solvent evaporated. The residue was partitioned between hexane and 10% $H_2O$/MeOH. The aqueous MeOH residue, obtained after evaporation, was fractionated using Si gel cc. $CHCl_3$ gradually enriched with MeOH was the eluent. Final purification of the compounds was done by tlc on Si gel plates, using any of the following systems: MeOH-EtOAc (15:85), EtOH-$C_6H_6$ (3:7), or MeOH-$CHCl_3$ (4:6) (in an atmosphere of $NH_3$).

Nmr spectra are reported either in DMSO-$d_6$ or $CDCl_3$ at 300 or 400 MHz in the case of $^1$H nmr and 75.43 MHz in the case of $^{13}$C nmr. Chemical shifts are on the δ scale, and coupling constants are in Hz. Instrumentation and chromatographic methods are given in Al-Abed *et al.* (1).

ACID HYDROLYSIS OF THE GLUCOSIDES.—Each lignan glucoside was dissolved in 20% aqueous HCl solution and refluxed for 1 h. It was filtered to remove the aglycone. The aqueous layer was concentrated at reduced pressure, and the residue obtained was compared with standard sugar on tlc [Si gel, $H_2O$-MeOH-HOAc-EtOAc (15:15:20:65)]. Spots were detected by spraying with sugar reagent (orcinol + $H_2SO_4$ + $FeCl_3$).

ACETYLATION OF THE GLUCOSIDES.—Each lignan glucoside was dissolved in pyridine and treated with excess $Ac_2O$. The mixture was kept for 24 h at 26° and then for 1 h at 100°. The solvent and excess reagent were evaporated under high vacuum. The residual material was purified by preparative tlc over Si gel using one of the appropriate solvent mixtures: $CHCl_3$-MeOH (98:2), EtOAc-MeOH (95:5), or $C_6H_6$-MeOH (95:5).

(−)-*Cleistanthin B* [**1**].—Compound **1** (65 mg): $^1$H nmr δ (sugar moiety) 3.00–5.70 (10H, m), 5.92 (pairs at 26°) (1H, d, $J$ = 7.2 Hz, H-1″), $\delta_H$ values of the aglycone part see Table 1; $^{13}$C nmr see Table 2.

*Tetra-O-acetyl derivative* **5**: $^1$H nmr δ (aglycone part) 3.80 (s, 7-OMe), 4.06 (s, 6-OMe), 5.39 (dd, $J$ = 14.7, 2.4 Hz, H-3a), 5.51 (dd, $J$ = 14.7, 1.3 Hz, 2H-3a), 6.06 (m, 3′-, 4′-$OCH_2O$), 6.78 (m, H-6′), 6.81 (d, $J$ = 1.7 Hz, H-2′), 6.95 (d, $J$ = 7.8 Hz, H-5′), 7.07 (s, H-8), 7.51 (s, H-5), (sugar part) δ 2.04 (s, Ac), 2.05 (s, Ac), 2.06 (s, Ac), 2.10 (s, Ac), 3.76 (1H, m), 4.14 (1H, m), 4.26 (1H, m), 5.18 (2H, m,), 5.32 (1H, m), 5.51 (1H, dd, $J$ = 9.6, 7.9 Hz).

(−)-*Majidine* [**2**].—Compound **2** (40 mg): $[\alpha]^{24}_D$ −32.26 ($c$ = 0.62, MeOH), uv (MeOH) λ max 261.6 nm (log ε 4.53); ir (KBr) ν max 3510 (OH), 1740 (γ-lactone) cm$^{-1}$; positive fabms *m/z* 645, 513, 381; $^1$H nmr (sugar part) 3.08–3.18 (3H, m), 3.47 (1H, d, $J$ = 11.4 Hz), 3.57 (1H, d, $J$ = 11.4 Hz), 3.67 (1H, m), 3.78 (1H, d, $J$ = 9.4 Hz, H-4″α), 4.22 (1H, d, $J$ = 9.4 Hz, H-4″β), 4.38 (1H, d, $J$ = 7.6 Hz, H-1‴), 4.62 (1H, d, $J$ = 2.9, H-2″), 5.56 (pairs at 26°) (1H, d, $J$ = 2.9 Hz, H-1″); $\delta^H$ values of aglycone part see Table 1; $^{13}$C nmr see Table 2.

*Penta-O-acetyl derivative* **6**.—$^1$H nmr (aglycone part) δ 3.80 (s, 7-OMe), 4.08 (s, 6-OMe), 5.45 (m, 2H-3a), 6.06 (m, $OCH_2O$), 6.80 (m, H-6′), 6.80 (m, H-2′), 7.08 (s, H-8), 6.94 (pairs at 26°) (d, $J$ = 8.1 Hz, H-5′), 7.46 (s, H-5), (sugar moiety) 2.02 (s, Ac), 2.04 (s, Ac), 2.07 (s, Ac), 2.09 (s, Ac), 2.14 (s, Ac), 3.40 (1H, dd, $J$ = 7.8, 12.1 Hz), 4.04 (1H, dd, $J$ = 5.0, 12.0 Hz), 4.15 (1H, d, $J$ = 9.9 Hz), 4.47 (1H, d, $J$ = 9.9 Hz), 4.70 (1H, s), 4.82 (1H, m), 4.84 (1H, s), 4.88 (1H, d, $J$ = 7.2 Hz), 4.92 (1H, d, $J$ = 12.8 Hz), 4.98 (1H, dd, $J$ = 8.6, 6.3 Hz), 5.16 (1H, m), 5.64 (1H, s).

(−)-*Qudsine* [**3**].—Compound **3** (25 mg): $[\alpha]^{24}_D$ −60.53 ($c$ = 0.38, MeOH); uv (MeOH) λ max 261.6 nm (log ε 4.41); positive fabms *m/z* 849, 687, 555, 381; $^1$H nmr δ (sugar part) 3.0–5.7 (m), 2.16 (3H, s, 2″-Ac), 4.36 (2H, d, $J$ = 7.4 Hz, H-1‴ and H-1⁗), 5.52 (1H, d, $J$ = 2.4 Hz, H-2″), 5.69 (pairs at 26°) (1H, d, $J$ = 2.34 Hz, H-1″), $\delta_H$ values of the aglycone part see Table 1; $^{13}$C nmr data see Table 2.

*Hepta-O-acetyl derivative* **7**.—$^1$H nmr δ (aglycone part) 3.79 (s, 7-OMe), 4.11 (s, 6-OMe), 5.37 (dd, $J$ = 14.8, 1.1 Hz, H-3a), 5.49 (dd, $J$ = 14.8, 1.5 Hz, H-3a), 6.05 (m, 3′-, 4′-$OCH_2O$), 6.79 (m, H-6′),

6.8 (m, H-2′), 6.94 (d, $J$ = 7.7 Hz, C-5′H), 7.08 (s, H-8), 7.55 (s, H-5), (sugar part) δ 1.97, 2.00, 2.01, 2.03, 2.06, 2.10, 2.11, 2.14 (each 3H, s, Ac), 3.35 (1H, dd, $J$ = 11.0, 8.1 Hz), 3.70 (1H, m), 3.86 (1H, dd, $J$ = 8.1, 8.1 Hz), 3.97 (2H, m), 4.16 (1H, d, $J$ = 11.0 Hz), 4.25 (1H, d, $J$ = 10.2 Hz), 4.32 (1H, dd, $J$ = 12.3, 4.7 Hz), 4.49 (1H, d, $J$ = 6.9 Hz), 4.57 (2H, dd, $J$ = 10.9, 6.0 Hz), 4.63 (1H, d, $J$ = 8.0 Hz), 4.90–5.20 (5H, m), 5.49 (1H, d, $J$ = 1.3 Hz), 5.73 (1H, d, $J$ = 1.4 Hz).

*Compound* **8**.—Compound **3** (10 mg) in 10 ml of 0.5% KOH/EtOH (w/w) was kept at room temperature for 30 min. It was then neutralized with 3% HCl and evaporated to dryness at room temperature. The residue was dissolved in MeOH and chromatographed on tlc using EtOAc-MeOH (8:2) to give **8**: uv (MeOH λ max 261.6 nm (MeOH); ir ν max 3510 (OH), 1740 (γ-aromatic lactone) $cm^{-1}$, positive fabms *m/z* 807, 645, 513, 381; $^1$H nmr (aglycone moiety) δ 3.67 (s, 7-OMe), 3.97 (s, 6-OMe), 5.48 (s, H-3a), 6.11 (s, 3′-, 4′-$OCH_2O$), 6.78 (pairs at 26°) (dd, $J$ = 7.9, 1.6 Hz, H-6), 6.89 (pairs at 26°) (d, $J$ = 1.6 Hz, H-2′), 7.02 (d, $J$ = 7.9 Hz, H-5′), 7.00 (s, H-8), 7.67 (s, H-5), (sugar moiety) 3.00–3.90 (m), 4.25 (1H, d, $J$ = 9.3 Hz), 4.31 (1H, d, $J$ = 7.4 Hz, H-1‴), 4.37 (1H, d, $J$ = 7.4 Hz, H-1⁗), 4.46 (1H, d, $J$ = 4.0 Hz, H-2″), 5.45 (pairs at 26°) (1H, d, $J$ = 4.0 Hz, H-1″).

*Compound* **9**.—Compound **8** (7 mg) was dissolved in 12 ml of pH 5 buffer (an aqueous 0.5 M NaOAc solution adjusted to pH 5 with HOAc), and 7 mg of β-glucosidase was added. The mixture was allowed to stand overnight at 37°. The solution was concentrated under high vacuum, and the hydrolyzed product **9** was obtained by preparative tlc using MeOH-EtOAc (2:8). $^1$H nmr δ (aglycone moiety) 3.66 (s, 7-OMe), 3.96 (s, 6-OMe), 5.49 (s, H-3a), 6.11 (s, 3′-, 4′-$OCH_2O$), 6.77 (pairs at 26°) (dd, $J$ = 8.0, 1.7 Hz, H-6′), 6.89 (pairs at 26°) (d, $J$ = 1.7 Hz, H-2′), 7.02 (d, $J$ = 7.9 Hz, H-5′), 6.98 (s, H-8), 7.67 (s, H-5), (sugar moiety) 3.00–3.80 (m), 41.9 (d, $J$ = 7.6 Hz, H-1‴), 4.43 (d, $J$ = 3.9 Hz, H-2″), 5.46 (pairs at 26°) (d, $J$ = 3.9 Hz, H-1″).

(−)-*Arabelline* [**4**].—Compound **4** (100 mg): $[\alpha]^{24}_D$ −30.78 ($c$ = 0.26, MeOH), uv (MeOH) λ max 261.6 nm (log ε 4.33); positive fabms *m/z* 675, 543, 381; $^1$H-nmr δ (sugar part) 3.2–4.05 (17H, m), 4.17 (1H, d, $J$ = 5.6 Hz, H-1‴), 4.78 (pairs at 26°) (1H, d, $J$ = 7.7 Hz, H-1″), $\delta_H$ values of aglycone part see Table 1: $^{13}$C nmr see Table 2.

*Hexa-O-acetyl derivative* **10**.—$^1$H-nmr (aglycone part) δ 3.80 (s, 7-OMe), 4.07 (s, 6-OMe), 5.48 (m, 2H-3a), 6.05 (m, $OCH_2O$), 6.78 (pairs at 26°) (m, H-6′), 6.78 (pairs at 26°) (m, H-2′), 7.08 (s, H-8), 6.93 (pairs at 26°) (d, $J$ = 8.2 Hz, H-5′), 7.53 (s, H-5), (sugar moiety) 1.90 (s, Ac), 2.00 (s, Ac), 2.04 (6H, s, Ac), 2.09 (3H, s, Ac), 2.15 (3H, s, Ac), 3.52 (1H, m), 3.63 (1H, dd, $J$ = 10.8, 5.4 Hz), 3.72 (1H, m), 3.88 (1H, m), 3.98 (1H, m), 4.31 (1H, dd, $J$ = 10.6, 7.1 Hz), 4.88 (1H, m), 5.13 (3H, m), 5.22 (1H, m), 5.31 (1H, m), 5.50 (1H, m).

*Diphyllin* [**11**].—$^1$H-nmr chemical shift values in DMSO-$d_6$ are given in Table 1, and $^1$H- and $^{13}$C-nmr data in $CDCl_3$ are reported in the literature (12).

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