A Novel Dimeric Podophyllotoxin-Type Lignan and a New Withanolide from *Withania coagulans*

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A novel dimeric lignan, bispicropodophyllin glucoside (**1**) and a highly oxygenated new withanolide, coagulin S (**2**) were isolated from the ethanolic extract of *Withania coagulans*. The structures were established on the basis of the spectroscopic data and have been identified as (5*S**,5a*R**,8a*R**,9*S**,15*S**,15a*S**,18a*S**,19*S**)-9,19-di-β-D-glucopyranosyl-5,8a,9,15,15a,18,18a,19-octahydro-5,15-bis(3,4,5-trimethoxyphenyl)bis([1,3]dioxolo-[4′,5′:6,7]naphtho)[2,3-*c*:2,3-*h*][1,6]dioxecin-6,16(5a*H*,8*H*)-dione (**1**) and (20*S**,22*R**)-5α,6β,14α,15α,17β,20,27-heptahydroxy-1-oxowith-24-enolide (**2**), respectively.

1. Introduction. – *Withania coagulans* DUNAL. (Solanaceae), a small, evergreen shrub, abundantly grows in India and Pakistan. The plant has been reported to be used for the treatment of dyspepsia, flatulent colic, and other intestinal diseases. The fruits of the plant are claimed to have diuretic effect and coagulating properties [1][2]. A number of withanolides (steroidal lactones) has been isolated from this plant, and many of them show antitumor, antibacterial, antifungal, anti-inflammatory, cytotoxic, hepatoprotective, and immunosuppressive activities [3]. In continuation of our work on the bioactive constituents of *W. coagulans* [4–9], we report here the isolation of a novel dimeric podophyllotoxin-type lignan, bispicropodophyllin glucoside (**1**) and a new highly oxygenated withanolide, coagulin S (**2**). Many members of this class of lignans were found to be potent antitumour agents, and their derivatives to be useful in cancer chemotherapy [10–12]. The withanolides isolated from this genus have also attracted a lot of attention because of their interesting bioactivities [13] as well as their structures [4][5][8]. The structures of compounds **1** and **2** were determined by a combination of spectroscopic methods, including 2D-NMR techniques and chemical transformations.

2. Results and Discussion. – Bispicropodophyllin glucoside (**1**) was isolated as an amorphous powder from the EtOH extract of the whole plant of *W. coagulans* with $CHCl_3$/MeOH 8.5:1.5. The intense absorption at 1740 cm^{-1} in the IR spectrum indicated the presence of an ester C=O group, whereas the absorption bands at 206, 240, 280, and 324 nm in the UV spectrum were characteristic of a podophyllotoxin-type lignan skeleton [14].

The negative FAB-MS of **1** displayed a pseudo M^+ at *m*/*z* 1151.3795 corresponding to the formula $C_{56}H_{64}O_{26}$ (calc. 1151.3686), with 25 degrees of unsaturation. The highest peak in EI-MS at *m*/*z* 576 represented only one half of the molecule, whereas the peak

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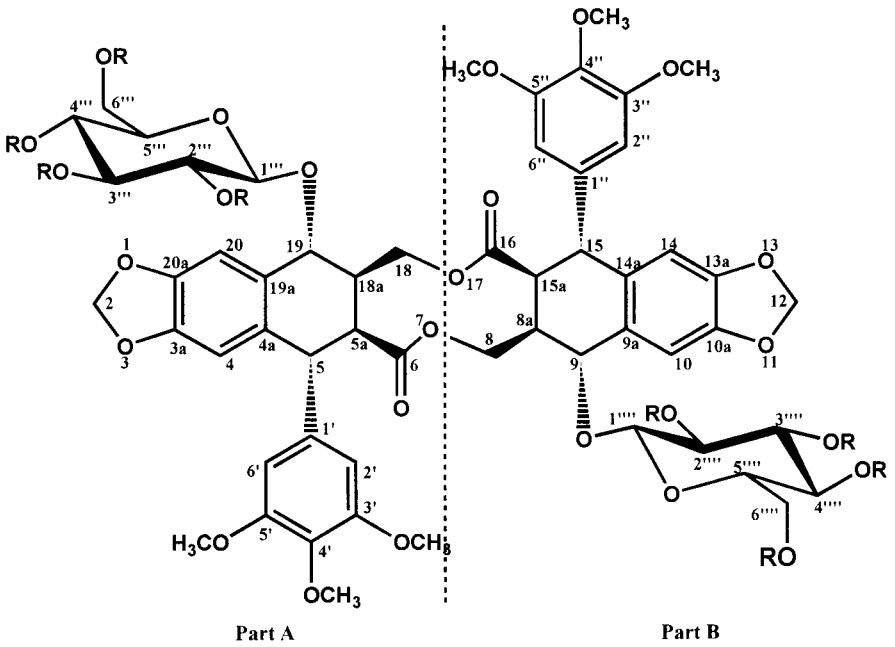
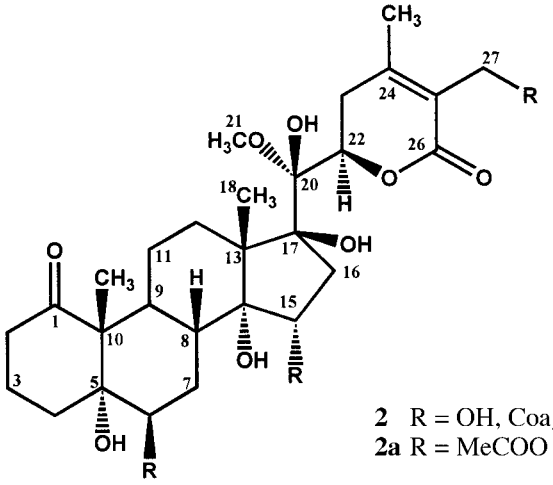


1 R = H, Bispicrodophyllin glucoside
1a R = MeCO



2 R = OH, Coagulin S
2a R = MeCOO

at *m*/*z* 414 was due to the loss of a sugar moiety from it. The subsequent loss of H_2O from *m*/*z* 414 generated the base peak at *m*/*z* 396. The fragment ion at *m*/*z* 167 indicated the presence of a three *O*-Me-substituted aryl system in the molecule.

The ^{1}H-NMR spectrum of **1** (C_5D_5N, 500 MHz) indicated the presence of two equivalent parts (Parts A and B) in the molecule that were apparently symmetrical through a C_2 axis. The representation of each signal for two equivalent H-atoms in the

^{1}H-NMR spectrum indicated the dimeric nature of the molecule. The ^{1}H-NMR spectrum showed two signals at δ 5.23 (*dd*, $J = 9.5, 2.5$ Hz) and 4.51 (*dd*, $J = 6.5, 2.5$ Hz) for C(8)/C(18) CH_2 H-atoms and two resonances at δ 6.49 (C(4)/C(14), *s*) and 7.91 (C(10)/C(20), *s*) for four CH H-atoms in the monomer. The H-atoms of the sugar moiety were observed as seven signals. This again indicated the dimeric nature of the molecule. The signals in the aromatic regions at δ 6.49 (*s*) and 7.91 (*s*) were attributed to H–C(4) (H–C(14)) and H–C(20) (H–C(10)), respectively. Two aromatic signals for H–C(2′) (H–C(6″)) and H–C(6′) (H–C(2″)) resonated at δ 6.87 (2 H, *s*). The two OCH_2O H-atoms (H–C(2α)/H–C(2β) and H–C(12α)/H–C(12β)) were observed as *doublets* at δ 5.86 ($J = 1.5$ Hz), and 5.88 ($J = 1.5$ Hz). The *singlets* at δ 3.73 (6 H) and 3.87 (3 H) were due to the six MeO groups at C(3′) (C(5″)), C(5′) (C(3″)) and C(4′) (C(4″)), respectively. The four CH signals at δ 4.33 (*d*, $J = 6.5$ Hz), 3.62 (*dd*, $J = 9.5$, 6.5 Hz), 3.16 (*dddd*, $J = 11.0, 9.0, 6.0, 2.0$ Hz), and 5.16 (*d*, $J = 9.0$ Hz) were assigned to H–C(5) (H–C(15)), H–C(5a) (H–C(15a)), H–C(18a) (H–C(8a)), and H–C(9) (H–C(19)), respectively. The signal at δ 5.22 (*d*, $J = 7.5$ Hz) represented H–C(1‴) (H–C(1⁗)) anomeric sugar H-atoms in the monomer of the molecule and indicated the β-configuration of the sugar.

The ^{13}C-NMR (C_5D_5N, 125 MHz, broad-band, DEPT) spectra showed 25 signals for 28 C-atoms (total 56 C-atoms in the molecule). This further indicated the presence of two equivalent halves in **1**. The interpretation of the ^{13}C-NMR spectra showed three Me, three CH_2, eight CH, and nine quaternary C-atoms in the monomer. The signal of the anomeric C-atom was observed at δ 105.6, whereas the ester C=O C-atom resonated at δ 178.3. The signal at δ 101.4 was characteristic of the OCH_2O C-atom.

The couplings between various H-atoms were further confirmed with the help of HOHAHA and COSY-45° spectra, which indicated the presence of two main spin systems in the monomer. The geminally coupled H–C(18α) (δ 5.23) and H–C(18β) (δ 4.51) resonances showed vicinal couplings with H–C(18a) (δ 3.16), while H–C(18a) and H–C(18) further showed couplings with H–C(19) (δ 5.16) and H–C(5a). H–C(5) (δ 3.62) showed cross-peaks with H–C(5a). All the assignments of the ^{1}H- and ^{13}C-NMR chemical shifts were confirmed by their respective interactions observed in 2D-HMQC and HMBC spectra. The HMBC spectrum (*Fig.*) provided informations about the long-range couplings between H- and C-atoms, leading to a further confirmation of the structure **1**. The key HMBC interaction between H–C(8) (CH_2 H-atom of part B) and C(6) (δ 178.3) indicated the dimeric nature of the molecule. The CH_2(18) (δ 5.23 and 4.51) showed couplings with C(5a) (δ 45.3) and C(19) (δ 78.6). The H–C(5a) (δ 3.62) showed HMBC cross-peaks with C(6′)/C(2′) (δ 107.1), C(6) (δ 178.3), C(18a) (δ 42.7), and C(4) (δ 108.4). The H–C(19) (δ 5.16) showed interactions with C(1″) (δ 105.6), C(20) (δ 108.1), C(5a) (δ 45.3), and C(18) (δ 70.2) in the HMBC spectrum. The OCH_2O H-atoms (δ 5.86 and 5.88) exhibited connectivities with C(3a) (δ 147.5) and C(20a) (δ 147.6).

On the basis of the NOESY and NOE spectra, the relative configurations at the stereogenic centers C(5), C(5a), C(18a), and C(19) were deduced. The strong interactions between H–C(5) and H–C(19), and H–C(5a) and H–C(18a) were due to the *syn*-configurations of the respective H-atoms, whereas no interactions between H–C(5) and H–C(5a), and H–C(18a) and H–C(19) were observed, indicating the *anti*-configuration of these respective H-atoms. The dimeric nature of the molecule was

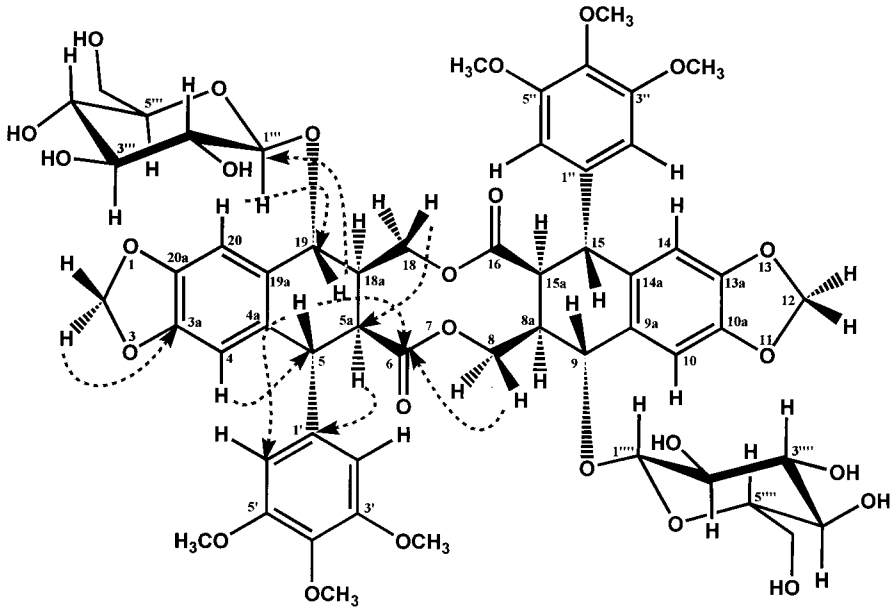


Figure. *Important HMBC interactions of* **1**

also inferred from $[\alpha]_D = -20.5$. This is approximately double the reported value for picropodophyllin glucoside ($[\alpha]_D = -11.5$) [15].

Hydrolysis and co-TLC of the sugars further confirmed their nature as glucose. For further confirmation, the sugar moiety was reduced by $NaBH_4$ and acetylated with Ac_2O. The acetylated product was then analyzed by GC, which showed similar retention time as the authentic acetylated β-D-glucose. The above spectroscopic data led to the structure of **1** as bispicropodophyllin glucoside. To the best of our knowledge, this represents the first example of a dimeric lignan from any natural source.

Coagulin S (**2**) was isolated as a white amorphous solid. The IR spectrum showed the presence of OH (3495 cm^{-1}), α,β-unsaturated δ-lactone (1717 cm^{-1}), and six-membered cyclic ketone (1692 cm^{-1}) moieties [16]. The UV spectrum displayed an absorption maximum at 215 nm, characteristic of cyclic-ketone and α,β-unsaturated δ-lactone chromophores present in other withanolides [17].

The pseudomolecular ion of **2** at *m/z* 539.2847 ($[M+H]^+$) in the (HR-FAB-MS) indicated the formula $C_{28}H_{42}O_{10}$. In EI-MS, the ion fragment at *m/z* 353.1873 ($C_{19}H_{29}O_6$) arose by the cleavage of the C(17)–C(20) bond, while the fragment at *m/z* 185.0817 ($C_9H_{13}O_4$) indicated the presence of a 20-hydroxywithanolide [18]. The fragment ion *m/z* 397.2218 ($C_{21}H_{33}O_7$) resulted from the cleavage of the C(20)–C(22) bond, while the fragment ion at *m/z* 141.0654 ($C_7H_9O_3$) indicated the presence of a six-membered δ-lactone substituent at C(20) of the steroidal skeleton [19].

The ^{1}H-NMR spectrum of **2** featured four *singlets* at δ 1.91, 1.55, 1.79, and 2.06 assigned to the Me(18), Me(19), Me(21), and Me(28) H-atoms, respectively. The appearance of the Me(21) H-atoms as a *singlet* indicated the absence of any H-atom at the vicinal C(20) [7]. The presence of a 2-H *AB doublet* at δ 4.75, 4.91 (J(27a,27b) =

11.9 Hz, H–C(27)) implied that the C(27) position is substituted with a OH group. The characteristic double *doublet* at δ 5.33 ($J(22\alpha,23\alpha) = 13.0$ Hz, $J(22\alpha,23\beta) = 2.9$ Hz) was assigned to the CH(22) H-atom of the lactone moiety. The multiplicity of the CH(22) signal also indicated the absence of any H-atom at vicinal C(20). No olefinic signal could be observed in the downfield region of the spectrum, and, hence, the characteristic 2-ene-1-one or 3,5-dien-1-one or 3-hydroxy-5-ene system in rings A and B of withanolide was considered absent. Two 1-H signals at δ 3.61 (br. *s*) and 4.57 (*d*, $J(15,16a) = 6.4$ Hz) were assigned to the H–C(6) of the 5α,6β-dihydroxy and H–C(15) of the 14α,15α-dihydroxy moieties [8]. Acetylation of this compound with Ac_2O in pyridine yielded a triacetate derivative [20]. Further evidence for the presence of the primary 27-OH, and secondary 6-OH and 15-OH groups was obtained by the analysis of the ^{1}H-NMR spectrum, which displayed three additional sharp Me *singlets* at δ 2.01, 2.04, and 2.06 for the three MeCOO groups. The CH_2(27) H-atoms geminal to the AcO group were shifted downfield to δ 4.83 and 4.87 (*AB doublet*, $J(27a,27b) =$ 12.0 Hz, H–C(27)), and a similar downfield shift of H–C(15β) to δ 4.79 (*d*, $J(15,16a) = 6.1$ Hz) and of H–C(6α) and to 4.57 (*t*, $J(6,7a) = 2.5$ Hz) have also been observed in the ^{1}H-NMR spectrum of the triacetate derivative [14]. Two 1-H *singlets* at δ 9.15 and 6.85, and one 2-H *singlet* at δ 6.25 disappeared on shaking the (D_5)pyridine solution with D_2O and were, therefore, identified as OH signals [21].

The DEPT spectra showed that there were four Me, nine CH_2, five CH, and, hence, 10 quaternary C-atoms. The quaternary C-atom signals resonated at δ 217.7, 166.5, 155.1, 127.1, 89.1, 83.6, 79.3, 78.1, 53.1, and 55.0 in the broad-band-decoupled spectrum [22]. Downfield signals at δ 217.7 and 166.5 were assigned to the olefinic C-atoms C(24) and C(25), respectively. The OH-bearing C-atoms C(5), C(6), C(14), C(15), C(17), C(20), and C(27) resonated at δ 78.1 (C), 73.1 (CH), 83.6 (C), 76.1 (CH), 89.1 (C), 79.3 (C), and 56.3 (CH_2), respectively. The configurations at various stereogenic centers were assigned on the basis of chemical-shift comparisons with related withanolides [8][18][23][24]. Me Signals at δ 21.0, 20.0, 15.1, and 20.2 were ascribed to C(28), C(21), C(19), and C(18), respectively. The ^{1}H- and ^{13}C-NMR spectra were consistent with a withanolide skeleton, in which a 5α,6β-dihydroxy-1-oxo functionality was clearly present, along with a substituted α,β-unsaturated δ-lactone in the side chain [25].

^{1}H,^{1}H and ^{1}H,^{13}C connectivities have been determined with the help of COSY-45° and HMQC. The long-range ^{1}H,^{13}C correlations were determined by an HMBC experiment and used to connect different structural fragments as well as to confirm the above chemical-shift assignments. For instance, starting from the ketone C=O at δ 217.7, three-bond (^3J) correlation could be observed with H–C(3) and H–C(19). The oxygenated quaternary C(5) resonating at δ 78.1 showed a ^2J coupling to H–C(4) and H–C(6), and a ^3J coupling to H–C(3) and H–C(9). H–C(15) showed a ^2J coupling to C(14), which, in turn, showed ^3J coupling to H–C(18). Likewise, H–C(21) showed ^2J and ^3J couplings with C(20) and C(17), respectively. Thus, the spectroscopic evidence led to the structure of this new withanolide as coagulin S (**2**).

Experimental Part

General. UV Spectra: *Hitachi U-3200* spectrophotometer. IR Spectra: *Jasco A-302* spectrophotometer. ^{1}H-NMR Spectra: *Bruker AMX-500* spectrometer with a UNIX data system at 500 MHz; ^{13}C-NMR spectra: at

125 MHz on the same instrument with $CDCl_3$ and C_5D_5N as solvents. Negative-ion FAB, LR-EI, and HR-EI mass spectra: *Jeol JMS HX 110* mass spectrometer with a *DA 5000* data system.

Plant Material. The whole plant of *Withania coagulans* DUNAL. (Solanaceae) was collected from the suburban areas of Karachi (Pakistan) in April 1991. Mr. *T. Ali*, plant taxonomist, Department of Botany, University of Karachi, identified the plant. A voucher specimen was deposited in the herbarium (KUH-46528) of the University of Karachi.

Extraction and Isolation. The dried plant (25 kg) was extracted with EtOH (60 l) at r.t. for two weeks, and the resulting extract was concentrated to a gum. This gum (1.0 kg) was partitioned between hexane and MeOH. The defatted MeOH extract was evaporated and suspended in dist. H_2O, which was extracted with $CHCl_3$ at different pH values (pH 9–10, 2–3, and 7) adjusted by the addition of NH_4OH and AcOH solns. The fraction obtained at pH 9–10 was subjected to column chromatography (CC) on silica gel. Elution with $CHCl_3$ and then with $CHCl_3$/MeOH yielded several fractions. A fraction obtained from elution with $CHCl_3$/MeOH 9:1 was found to contain **1**, which was further purified by TLC with $CHCl_3$/MeOH 85:15. Compound **2** was isolated from the fraction obtained at pH 7. A subfraction obtained from extraction at pH 7 followed by CC with $CHCl_3$/MeOH 95:5 yielded coagulin S (**2**), which was purified by TLC with $CHCl_3$/MeOH 9:1.

*(5*S**,5a*R**,8a*R**,9*S**,15*S**,15a*S**,18a*S**,19*S**)-9,19-Di-β-*D*-glucopyranosyl-5,8a,9,15,15a,18,18a,19-octahydro-5,15-bis(3,4,5-trimethoxyphenyl)bis([1,3]dioxolo[4′,5′:6,7]naptho)[2,3-*c*:2,3-*h*][1,6]dioxecin-6,16(5a*H*,8*H*)-dione (Bispicropodophyllin glucoside*; **1**): 17.5 mg (7×10^{-5}%). Amorphous powder. R_f ($CHCl_3$/MeOH 85:15) 0.45. $[\alpha]_D = -20.5$ ($c = 0.1$, (D_5)pyridine). UV (MeOH): λ_{max} 206 (4.13), 240 (3.91), 280 (3.76), 324 (3.34). IR (KBr): 3610–3125, 2920, 1768, 1590, 1475. ^{1}H- and ^{13}C-NMR: *Table*. HR-FAB-MS (neg. ion): 1151.3795 ($[M-H]^+$, $C_{56}H_{63}O_{26}$; calc. 1151.3686). LR-EI-MS: 576 (99), 414 (38), 396 (76), 167 (17), and 63 (100).

Acetylation of **1**. A soln. of **1** (8 mg) in pyridine (1 ml) was treated with Ac_2O (1 ml) and left overnight at r.t. The reagents were removed *in vacuo*, and the residue was purified on a prep. TLC plates with $CHCl_3$/MeOH 99:1 and characterized as compound **1a**: 9.1 mg. Amorphous powder. R_f ($CHCl_3$/MeOH 99:1) 0.61. $[\alpha]_D = -18.3$ ($c = 0.1$, pyridine). UV (MeOH): λ_{max} 205 (4.26), 243 (3.85), 270 (3.61), 318 (3.13). IR (KBr): 2915, 1772, 1765, 1762, 1758, 1755, 1595, 1470. ^{1}H- and ^{13}C-NMR: *Table*. HR-FAB-MS (neg. ion): 1487.4489 ($[M-1]^+$, $C_{72}H_{79}O_{34}$; calc. 1487.4531). LR-EI-MS: 744 (27), 414 (12), 396 (100), 167 (61), 109 (71).

Acid Hydrolysis. The nature of the carbohydrates was further confirmed by hydrolysis. Compound **1** (5 mg) was dissolved in MeOH (2 ml) and 3% H_2SO_4 (2 ml). This mixture was heated at 100° for 4 h. The soln. was neutralized with $BaCO_3$ and extracted with AcOEt. Co-TLC identified the sugars in aq. phase as glucose with authentic sample of glucose and galactose, with BuOH/AcOH/H_2O 7:2:5. For further confirmation, the sugar moiety was reduced with $NaBH_4$ and acetylated with Ac_2O. The acetylated product was then analyzed by GC. The gas chromatogram was identical to that of the authentic β-D-glucose.

*(20*S**,22*R**)-5α,6β,14α,15α,17β,20,27-Heptahydroxy-1-oxowith-24-enolide* (*Coagulin S*; **2**). 48.3 mg (5.1×10^{-5}%). Amorphous powder. R_f 0.45. $[\alpha]_D = +94$ ($c = 45$, MeOH). UV (MeOH): λ_{max} 215 (4.21). IR (KBr): 3495, 1717, 1692. ^{1}H-NMR (C_5D_5N, 400 MHz): 5.33 (*dd*, $J(22\alpha,23\alpha) = 13.0$, $J(22\alpha,23\beta) = 2.9$, H–C(22)); 4.91, 4.75 (*AB d*, $J(27a,27b) = 11.9$, 2 H–C(27)); 4.57 (*d*, $J(15,16a) = 6.4$, H–C(15)); 3.61 (br. *s*, H–C(6)); 2.06 (*s*, Me(28)); 1.91 (*s*, H–C(18)); 1.79 (*s*, MeO); 1.55 (*s*, Me(19)). ^{13}C-NMR ((D_6)DMSO, 125 MHz): 217.7 (C(1)); 166.5 (C(26)); 155.1 (C(24)); 127.1 (C(25)); 89.1 (C(17)); 83.6 (C(14)); 81.8 (C(22)); 79.3 (C(20)); 78.1 (C(5)); 76.1 (C(15)); 73.1 (C(6)); 56.3 (C(27)); 55.0 (C(13)); 53.1 (C(10)); 48.2 (C(16)); 40.1 (C(2)); 35.6 (C(4)); 33.9 (C(12)); 33.6 (C(3)); 33.4 (C(8)); 32.8 (C(23)); 32.7 (C(7)); 30.3 (C(9)); 22.9 (C(11)); 21.0 (C(28)); 20.2 (C(18)); 20.0 (C(21)); 15.1 (C(19)). HR-FAB-MS: 539.2847 ($[M+H]^+$, $C_{28}H_{43}O_{10}$; calc. 539.2855). HR-EI-MS: 397.2218 (8), 353.1873 (15), 185.0817 (18), 169.0896 (25), 141.0645 (85), 124.0523 (100).

Acetylation of **2**. A soln. of **2** (10 mg) was dissolved in pyridine (1 ml) in a 10-ml round-bottom flask, and then Ac_2O (1 ml) was added to this soln. The flask was covered with a quickfit stopper, and the solution was stirred at r.t. for 24 h. The reaction was quenched with dist. H_2O (10 ml), and the aq. layer was extracted with $CHCl_3$. The $CHCl_3$ layer was separated and dried (Na_2SO_4). The acetylated product was then purified on TLC with $CHCl_3$ to yield the triacetate derivative **2a** (8.0 mg, 80%). $[\alpha]_D = +71$ ($c = 0.51$, $CHCl_3$). UV (MeOH): λ_{max} 213 (4.17). IR ($CHCl_3$): 3445, 1735, 1718, 1702. ^{1}H-NMR ($CDCl_3$, 500 MHz): 4.89 (*dd*, $J(22\alpha,23\alpha) = 13.1$, $J(22\alpha,23\beta) = 3.5$, H–C(22)); 4.87, 4.83 (*Ab d*, $J(27a,27b) = 12.0$, 2 H–C(27)); 4.79 (*d*, $J(15,16a) = 6.1$, H–C(15)); 4.57 (*t*, $J(6,7a) = 2.5$, H–C(6)); 2.06, 2.04, 2.01 (*s*, 3 Ac); 2.01 (*s*, Me(28)); 1.33 (*s*, Me(18)); 1.12 (*s*, MeO); 1.04 (*s*, Me(19)). HR-FAB-MS: 665.3136 ($[M+H]^+$, $C_{34}H_{49}O_{13}$; calc. 665.3173). HR-EI-MS: 592.2668 (8), 574.2562 (11), 124.0523 (100).

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Table. *^{1}H- and ^{13}C-NMR Assignments of* **1** *and its Acetylated Derivative* **1a**[a])

C-Atom	**1**		**1a**	
	δ(H) (C_5D_5N)	δ(C)	δ(H) ($CDCl_3$)	δ(C)
C(2)/C(12)	5.88 (*d*, *J* = 1.5), 5.86 (*d*, *J* = 1.5)	101.4	5.89 (*d*, *J* = 1.5), 5.91 (*d*, *J* = 1.5)	101.1
C(3a)/C(13a)	–	147.5	–	146.8
C(4)/C(14)	6.49 (*s*)	108.4	6.28 (*s*)	108.7
C(4a)/C(14a)	–	132.1	–	129.3
C(5)/C(15)	4.33 (*d*, *J* = 6.5)	44.8	4.03 (*d*, *J* = 5.5)	43.8
C(5a)/C(15a)	3.62 (*dd*, *J* = 6.5, 9.5)	45.3	3.11 (*dd*, *J* = 5.5, 8.5)	45.5
C(6)/C(16)	–	178.3	–	177.2
C(8)/C(18)	5.23 (*dd*, *J* = 2.5, 9.5) 4.51 (*dd*, *J* = 2.5, 6.5)	70.2	4.33 (*dd*, *J* = 6.0, 9.5) 3.33 (*dd*, *J* = 2.0, 9.5)	68.9
C(8a)/C(18a)	3.16 (*dddd*, *J* = 2.0, 6.0, 9.0, 11.0)	42.7	2.79 (*dddd*, *J* = 2.0, 6.0, 8.5, 11.0)	41.5
C(9)/C(19)	5.16 (*d*, *J* = 9.0)	78.6	4.52 (*d*, *J* = 8.5)	78.3
C(9a)/C(19a)	–	132.5	–	130.6
C(10)/C(20)	7.91 (*s*)	108.1	7.14 (*s*)	107.0
C(10a)/C(20a)	–	147.6	–	147.6
C(1′)/C(1″)	–	139.4	–	139.0
C(2′),C(6′)/ C(2″),C(6″)	6.87 (*s*)	107.1	6.40 (*s*)	106.0
C(3′),C(5′)/ C(3″),C(5″)	–	154.2	–	153.6
C(4′)/C(4″)	–	137.5		135.1
C(1‴)/C(1⁗)	5.22 (*d*, *J* = 7.5)	105.6	4.83 (*d*, *J* = 8.0)	101.2
C(2‴)/C(2⁗)	4.14 (*m*)	75.4	5.14 (*t*, *J* = 8.5)	72.1
C(3‴)/C(3⁗)	3.99 (*m*)	78.6	5.23 (*t*, *J* = 8.5)	72.9
C(4‴)/C/4⁗)	4.25 (*m*)	71.7	5.09 (*dd*, *J* = 9.5, 7.5)	68.9
C(5‴)/C(5⁗)	4.28 (*m*)	78.7	3.71 (*ddd*, *J* = 3.0, 5.0, 8.0)	72.4
C(6‴)/C(6⁗)	4.34 (*m*), 4.52 (*m*)	62.8	4.21 (*dd*, *J* = 5.0, 12.5), 4.14 (*dd*, *J* = 2.5, 12.5)	61.8
MeO at C(3′), C(5′)/C(3″),C(5″)	3.73 (*s*)	56.3	3.83 (*s*)	56.2
MeO at C(4′)/C(4″)	3.87 (*s*)	60.5	3.80 (*s*)	60.8
Me(2‴)	–	–	2.00 (*s*)*	20.5*
C=O(2‴)	–	–	–	168.9*
Me(3‴)	–	–	2.01 (*s*)*	20.5*
C=O(3‴)	–	–	–	168.8*
Me(4‴)	–	–	2.03 (*s*)*	20.5*
C=O(4‴)	–	–	–	170.2*
Me(6‴)	–	–	2.04 (*s*)*	20.5*
C=O(6‴)	–	–	–	170.3*

[a]) *: Values may be interchanged.

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