Chemical Constituents from Fruits and Stem Bark of *Celtis australis* L.

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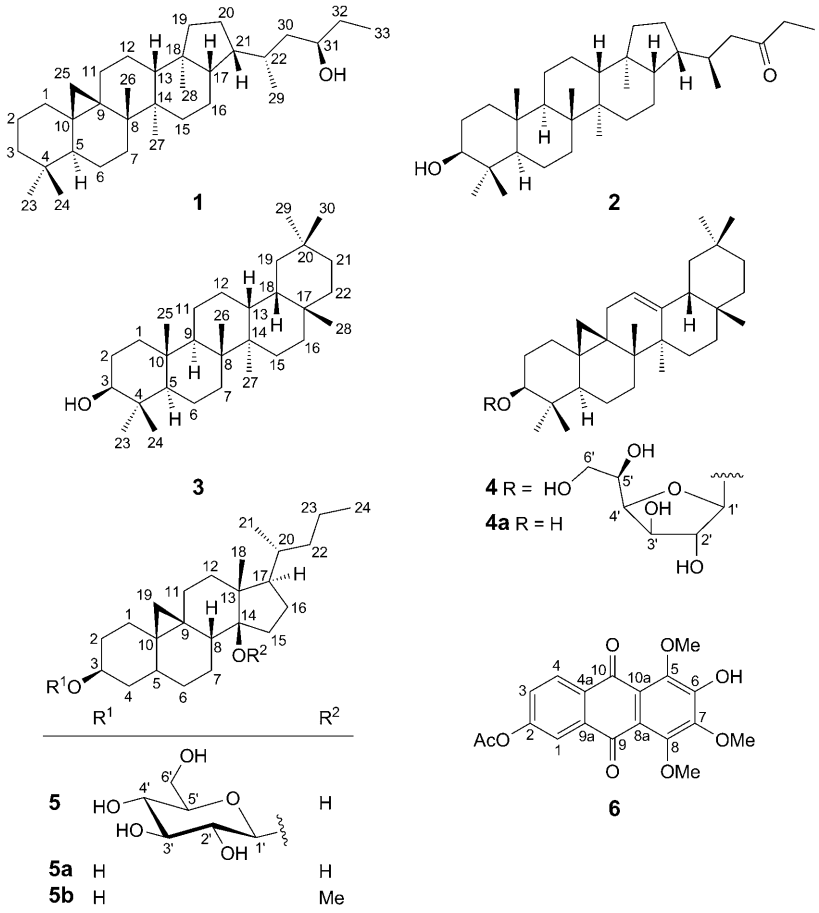
Four triterpenoids named (9*β*,31*R*)-9,25-cyclo-30-propylhopan-31-ol (**1**), (3*β*)-3-hydroxy-30-propylhopan-31-one (**2**), (3*β*)-oleanan-3-ol (**3**), and (3*β*,9*β*)-9,25-cycloolean-12-en-3-yl *β*-D-glucofuranoside (**4**), a steroid named (3*β*,9*β*,14*β*)-14-hydroxy-9,19-cyclocholan-3-yl *β*-D-glucopyranoside (**5**), and an anthraquinone named 6-hydroxy-5,7,8-trimethoxy-9,10-dioxo-9,10-dihydroanthracen-2-yl acetate (**6**) have been isolated from the fruits and bark of *Celtis australis* (Ulmaceae), along with apigenin, quercetin, and its glucoside. Their structures were elucidated by means of chemical and spectral analysis including COSY, NOESY, and HMBC experiments.

Introduction. – *Celtis australis* L. of Ulmaceae is a deciduous tree distributed from montane to submontane Himalaya. The plant has been used as remedy for bone fracture, pimples, contusions, sprains, and joint's pain in the traditional Indian medicine [1]. Previous studies on the plants of the genus *Celtis* led to the isolation of phenolic glycosides [2], steroids [3], terpenoids [4][5], and tannins, saponins, and alkaloids [6]. From the leaves of *C. australis*, three phenol derivatives, acacetin 7-*O*-glucoside, isovitexin, and cytisoside were reported [7]. Recently, we have isolated a novel sulfonated phenolic celtisanin from the fruits [8] and a bacteriohopanoid, (3*β*)-33-ethyl-3-hydroxy-34-methyl-35-(3-propanoylcyclohex-1-yl)bacteriohopane from the stem bark [9] of this plant. Here, we describe the isolation and structure elucidation of four triterpenoids, **1**–**4**, one steroid, **5**, and one anthraquinone, **6**, for the first time from this source.

Results and Discussion. – Compound **1** was obtained as white crystals (0.132 g) with a melting point of 220–222°, and from the molecular-ion peak at *m*/*z* 468.40 (calc. 468.43) in the MS (positive-ion mode), the molecular formula $C_{33}H_{56}O$ was deduced. The IR spectrum exhibited an absorption band at 3460 cm^{-1} characteristic of a OH group. The ^{13}C-NMR and DEPT spectra showed 33 C-atom signals including those for seven Me, fourteen CH_2, six CH groups, and six quaternary C-atoms. Six degrees of unsaturation for $C_{33}H_{56}O$ indicated six rings in the structure. Detailed spectral studies and their comparison to those of similar triterpenoids [10][11] gave the evidence for a hopane-type structure for **1**. A broad signal at *δ*(H) 3.41 in the ^{1}H-NMR (*Table 1*) and a downfield value at *δ*(C) 73.1 in the ^{13}C-NMR (*Table 2*) were due to a OH (confirmed by IR)-substituted C-atom. Often, a OH group at C(3) is observed in triterpenoids, but in compound **1**, the OH group is positioned in the side chain, which was confirmed by long-range correlations of H–C(31) (*δ*(H) 3.41) to C(22) (*δ*(C) 30.1) and C(33) (*δ*(C)



8.5) in the HMBC spectrum. In addition, the correlation $CH_2(1)/CH_2(6)$ to C(4) (δ(C) 42.8) and $CH_2(1)$/H–C(5) to C(3) (δ(C) 30.8) clearly evidenced the structure of ring *A* without OH substitution at C(3). From the HMBC of H–C(21) to C(29) (δ(C) 17.9) and C(30) (δ(C) 34.2), the position of the side chain at C(21) was determined (*Fig.*). The size of the side chain was determined by MS which showed a base peak at *m*/*z* 409 (a hopane ion) after the loss of H_2O and C_3H_4 from the parent ion (*m*/*z* 468). The configuration of compound **1** was determined by NOESY experiments which showed α-configuration of the side chain at C(21) (δ(H) 1.20 (H–C(17)) to 1.05 (H–C(21))). In addition, the configuration of substituted Me groups were also confirmed by NOESY experiments (*Fig.*). The configuration at C(31) has been assumed to be (*R*) due to biogenetic considerations. On the basis of the above discussion, the structure of **1** was elucidated as (9β,31*R*)-9,25-cyclo-30-propylhopan-31-ol.

Compound **2** was isolated as white crystals (0.177 g) with a melting point of 249°, and the molecular formula $C_{33}H_{56}O_2$ was deduced from the molecular-ion peak at *m*/*z* 485 in the MS (positive-ion mode). The bands at 3472 and 1705 cm^{-1} in the IR

Table 1. *^{1}H-NMR* (400 MHz) *Data of Compounds* **1**–**6**

H-Atom	**1**[a])	**2**[a])	**3**[a])	**4**[b])	**5**[b])	**6**[b])
1	0.93–0.95 (*m*), 2.37–2.40 (*m*)	0.94–0.97 (*m*), 2.30–2.32 (*m*)	0.91–0.94 (*m*), 2.28–2.31 (*m*)	1.12–1.16 (*m*), 1.44–1.47 (*m*)	0.93–0.97 (*m*)	–
2	1.32–1.34 (*m*), 2.33–2.35 (*m*)	1.32–1.35 (*m*), 2.34–2.36 (*m*)	1.91–1.94 (*m*), 2.28–2.31 (*m*)	2.32–2.37 (*m*), 1.92–1.95 (*m*)	1.32–1.35 (*m*)	–
3	1.32–1.34 (*m*), 2.29–2.32 (*m*)	3.65 (br.)	3.66 (br. *s*)	3.61 (*t*, *J* = 2.5)	3.65 (br.)	–
4	–	–	–	–	0.90–0.92 (*m*)	–
5	0.93–0.95 (*m*)	0.94–0.97 (*m*)	0.98–1.01 (*m*)	0.89–0.92 (*m*)	0.93–0.97 (*m*)	7.68 (*s*)
6	1.36–139 (*m*), 2.24–2.26 (*m*)	1.32–1.35 (*m*), 2.24–2.27 (*m*)	1.37–1.40 (*m*), 2.20–2.24 (*m*)	1.79–1.83 (*m*), 0.94–0.97 (*m*)	1.32–1.35 (*m*)	–
7	1.47–1.51 (*m*), 2.21–2.23 (*m*)	1.47–1.49 (*m*), 2.24–2.27 (*m*)	1.47–1.51 (*m*), 2.28–2.31 (*m*)	1.44–1.47 (*m*), 1.79–1.83 (*m*)	1.64–1.67 (*m*)	7.22 (*d*, *J* = 8.5)
8	–	–	–	–	1.49–1.52 (*m*)	7.94 (*d*, *J* = 8.5)
9	–	0.98–1.01 (*m*)	0.98–1.01 (*m*)	–	–	–
11	0.93–0.95 (*m*), 1.71–1.73 (*m*)	0.92–0.94 (*m*), 1.08–1.10 (*m*)	0.87–0.90 (*m*), 1.10–1.13 (*m*)	1.89–1.92 (*m*)	1.95–1.99 (*m*)	
12	0.88–0.90 (*m*), 1.88–1.91 (*m*)	0.88–0.90 (*m*), 1.71–1.73 (*m*)	0.87–0.90 (*m*), 1.60–1.63 (*m*)	5.30 (br. *s*)	1.20–1.23 (*m*)	
13	2.27–2.28 (*m*)	2.29–2.31 (*m*)	0.91–0.94 (*m*)	–	–	
15	0.98–1.01 (*m*), 2.27–2.28 (*m*)	0.94–0.97 (*m*), 2.24–2.27 (*m*)	0.87–0.90 (*m*), 1.84–1.86 (*m*)	2.32–2.37 (*m*), 1.44–1.47 (*m*)	1.58–1.61 (*m*)	
16	0.88–0.90 (*m*), 2.21–2.23 (*m*)	0.80–0.83 (*m*), 2.24–2.27 (*m*)	0.80–0.84 (*m*), 2.20–2.24 (*m*)	2.10–2.13 (*m*)	1.49–1.52 (*m*)	
17	1.20 (overlap)	1.21 (overlap)	–	–	1.12–1.14 (*m*)	
18	–	–	1.58–1.60 (*m*)	2.49 (*s*)	0.86 (overlap)	
19	0.88–0.90 (*m*), 2.21–2.23 (*m*)	0.80–0.83 (*m*), 2.22–2.24 (*m*)	0.80–0.84 (*m*), 2.28–2.31 (*m*)	0.89–0.92 (*m*), 2.10–2.13 (*m*)	0.85 (overlap)	
20	0.85–0.87 (*m*), 2.17–219 (*m*)	0.78–0.80 (*m*), 2.19–2.21 (*m*)	–	–	1.58–1.61 (*m*)	
21	1.05 (overlap)	1.10 (overlap)	1.37–1.40 (*m*), 2.16–2.18 (*m*)	1.92–1.95 (*m*), 2.50–252 (*m*)	0.98 (overlap)	
22	1.83–1.86 (*m*)	1.11–1.13 (*m*)	0.87–0.90 (*m*), 1.81–1.83 (*m*)	2.88–2.91 (*m*), 2.10–2.13 (*m*)	1.20–1.23 (*m*)	
23	0.95–0.97 (*m*)	0.87 (overlap)	0.85 (overlap)	0.80 (overlap)	0.94 (overlap)	
24	0.95–0.97 (*m*)	0.88 (overlap)	0.87 (overlap)	0.87 (overlap)	1.32–1.35 (*m*)	
25	0.81–0.83 (*m*)	0.88 (*s*)	0.82 (overlap)	0.89–0.92 (*m*)		
26	0.88 (*s*)	0.90 (*s*)	0.79 (overlap)	0.76 (overlap)		
27	0.91 (*s*)	0.91 (*s*)	0.78 (overlap)	0.79 (overlap)		
28	0.81 (*s*)	0.85 (*s*)	0.85 (overlap)	0.63 (overlap)		
29	0.79 (*s*)	1.18 (*s*)	0.88 (overlap)	0.80 (overlap)		
30	1.94–1.97 (*m*)	1.94–1.97 (*m*)	0.89 (overlap)	0.87 (overlap)		
31	3.41 (br. *s*)	–				
32	1.16–1.18 (*m*)	1.67–1.70 (*m*)				
33	0.88–0.90 (*m*)	0.88–0.90 (*m*)				
1′				4.21 (*d*, *J* = 7.5)	5.10 (*d*, *J* = 8.5)	
2′				2.88–2.91 (*m*)	3.24–3.27 (*m*)	
3′				3.08–3.10 (*m*)	3.64–3.66 (*m*)	
4′				3.02–3.05 (*m*)	4.00–4.02 (*m*)	
5′				3.13–3.16 (*m*)	3.09–3.13 (*m*)	
6′				3.11–3.12 (*m*)	4.45–4.46 (*m*)	
AcO						2.10 (*s*)
MeO–C(1)						3.61 (*s*)
MeO–C(3)						3.70 (*s*)
MeO–C(4)						3.30 (*s*)
HO–C(2)						10.20 (*s*)

[a]) Measured in $CDCl_3$. [b]) Measured in (D_6)DMSO.

Table 2. *^{13}C-NMR* (100 MHz) *Data of Compounds* **1**–**6**

C-Atom	**1**[a])	**2**[a])	**3**[a])	**4**[b])	**5**[b])	**6**[b])
1	38.4	41.8	32.8	38.4	37.8	163.8
2	28.3	30.0	27.8	28.9	27.3	153.2
3	30.8	72.9	72.5	82.0	81.1	154.2
4	42.8	37.5	37.5	40.5	38.3	161.7
4a						110.4
5	49.2	59.4	56.0	57.1	43.5	113.4
6	18.9	22.2	17.9	24.2	26.9	158.2
7	32.0	32.0	30.6	33.7	33.5	121.6
8	39.8	42.9	40.6	44.3	42.1	128.9
8a						124.5
9	24.8	53.1	50.9	25.8	20.6	179.3
9a						115.1
10	24.2	39.9	35.6	23.7	27.8	182.0
10a						132.6
11	21.5	31.9	33.4	27.6	22.4	
12	31.8	35.7	29.6	126.2	31.8	
13	39.9	49.7	51.0	140.1	39.9	
14	41.5	38.4	41.2	44.5	72.4	
15	32.8	32.9	33.3	32.9	34.7	
16	36.2	36.0	34.9	36.4	22.8	
17	58.2	58.2	39.3	44.7	47.6	
18	42.1	42.2	47.0	45.0	16.5	
19	39.2	39.5	30.1	50.2	25.9	
20	30.0	30.5	33.9	44.3	28.7	
21	59.8	61.3	29.9	30.5	17.8	
22	30.1	35.0	33.1	43.3	32.3	
23	20.1	28.2	28.8	21.6	17.1	
24	29.3	35.3	14.7	30.5	29.4	
25	41.9	20.1	15.3	41.9		
26	18.2	18.8	16.0	16.8		
27	17.5	18.0	16.4	16.7		
28	14.6	17.9	15.6	33.7		
29	17.9	14.8	26.0	34.3		
30	34.2	35.7	14.2	24.0		
31	73.1	213.5				
32	32.3	41.2				
33	8.5	7.3				
1′				105.8	101.2	
2′				75.1	75.7	
3′				78.5	76.1	
4′				66.1	70.5	
5′				60.4	72.9	
6′				61.2	63.5	
CO(Ac)						168.9
Me(Ac)						24.3
*Me*O–C(1)						56.1
*Me*O–C(3)						56.5
*Me*O–C(4)						56.3

[a]) Measured in $CDCl_3$. [b]) Measured in (D_6)DMSO.

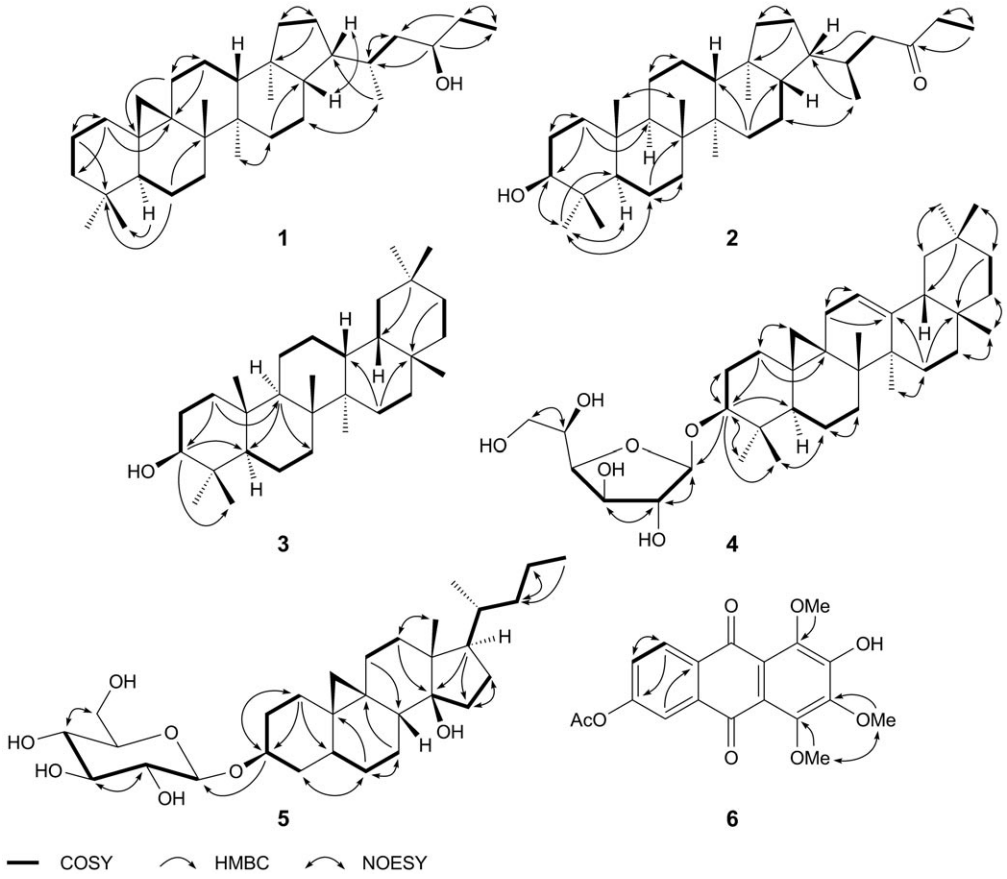


Figure. *Important 2D-NMR correlations of* **1**–**6**

spectrum were characteristic for a OH and a CO group, respectively. Six degrees of unsaturation for $C_{33}H_{56}O_2$ indicated the presence of five rings and one C=O bond. The ^{13}C-NMR and DEPT spectra showed 33 C-atom signals for eight Me, twelve CH_2, seven CH groups, and six quaternary C-atoms. The signals at δ(H) 3.65 in the ^{1}H-NMR and δ(C) 72.9 in the ^{13}C-NMR spectra indicated an O-bearing aliphatic C-atom in the structure. The correlation of H–C(3) to C(4) (δ(C) 37.5), C(5) (δ(C) 59.4), C(23) (δ(C) 28.2), and C(24) (δ(C) 35.3) in the HMBC clearly evidenced the position of OH at C(3). A highly downfield *singlet* at δ(C) 213.5 in the ^{13}C-NMR spectrum is due to the presence of a CO function, which must be located in the side chain, since Me(33) (δ(H) 0.88–0.90) showed a long range correlation with C(31) (δ(C) 213.5) in the HMBC spectrum. The signals at δ(C) 35.3, 28.2, 20.1, 18.8, 18.0, 17.9, 14.8, and 7.3 are due to the presence of eight Me groups. The signal at δ(C) 7.3 is typical for a terminal Me group in the side chain. The above evidence, including 2D-NMR studies, led us to deduce that **2** is a hopane-type triterpene (pentacyclic) with a side chain with a CO function. The long-range correlations of H–C(21) (δ(H) 1.10) to C(16) (δ(C) 36.0) and C(18) (δ(C)

42.2) in the HMBC spectrum suggested that the side chain must be attached to C(21), which confirmed the hopane-type structure of **2**. The strong NOESY correlation of H–C(3) (δ(H) 3.65) to Me(23) (δ(H) 0.87) indicated that the OH group is β-oriented. The MS showed a base peak at m/z 485 (M^+) which fragmented to an ion with the peak at
m/z 466 by loss of a H_2O molecule, whereas an important fragment-ion peak at m/z 367 was due to the loss of the side chain ($C_6H_{11}O$) from the m/z 466 fragment. On the basis of the above discussion and the comparison of spectral data to those of similar hopanoids [12][13], the structure of **2** was elucidated as (3β)-3-hydroxy-30-propylhopan-31-one.

Compound **3** was isolated as a white powder (0.099 g) with a melting point of 276–278°, and with a molecular formula of $C_{30}H_{52}O$ deduced from m/z 428 in the MS. The compound was recognized as a triterpenoid by positive *Libermann–Burchard* and *Salkowski* tests. The IR spectrum exhibited a band at 3423 cm^{-1} characteristic of a OH group. The ^{13}C-NMR and DEPT spectra exhibited 30 C-atom signals for eight Me, eleven CH_2, five CH groups, and six quaternary C-atoms. A downfield signal at δ(C) 72.5 (C(3)) in the ^{13}C-NMR indicated the presence of an O-bearing substituted C-atom. The HMBC spectrum showed correlations of H–C(5) (δ(H) 0.98–1.01) to C(1) (δ(C) 32.8), C(7) (30.6), C(23) (28.8), and C(24) (14.7). In addition, the correlations of CH_2(2) (δ(H) 1.91–1.94) to C(4) (δ(C) 37.5) and C(10) (35.6) afforded the complete structure of ring *A* in triterpenoid, whereas the correlation of CH_2(1) (δ(H) 0.91–0.94) to C(3) (72.5) confirmed the position of a OH group at C(3). The NOESY correlation of H_α–C(3) to Me(23) indicated that the OH group in C(3) was β-oriented. The MS showed a base peak at m/z 372 by the loss of C_4H_8 from the molecular ion (m/z 428), and, in addition, the fragments at m/z 205 and 192 are characteristic for triterpenoids. From the spectral evidence and the comparison with reported data of similar compounds [14][15], the structure of **3** was elucidated as (3β)-oleanan-3-ol.

Compound **4** was isolated as a white crystalline solid (0.129 g) with a melting point of 296–298°, and showed a molecular-ion peak at 586 in the EI-MS (positive-ion mode), corresponding to the molecular formula $C_{36}H_{58}O_6$. It gave positive tests with *Salkowski*, *Liebermann–Burchard*, and *Molisch*'s reagents, characteristic for a triterpenoid glycoside. In the IR spectrum, the bands at 3412 and 1640 cm^{-1} indicated OH groups and an olefinic function, respectively. In the ^{1}H-NMR spectrum, a *doublet* at δ(H) 4.21 (J = 7.5, anomeric H–C(1′)) pointed to a β-configuration of the glycoside unit. A *triplet* at δ(H) 3.61 (H–C(3)) in the ^{1}H-NMR, and δ(C) 82.0 (C(3)) in the ^{13}C-NMR indicated the presence of an O-bearing C-atom. The ^{13}C-NMR spectrum and DEPT experiments showed 36 C-atoms signals for seven Me, twelve CH_2, nine CH groups, and eight quaternary C-atoms, including one O-bearing C-atom (δ(C) 82.0, C(3)) and two olefinic C-atoms (δ(C) 126.2 and 140.1, C(12) and C(13), resp.). In the COSY experiments, the correlation of CH_2(1) to CH_2(2), CH_2(6) to CH_2(7), CH_2(11) to H–C(12), CH_2(15) to CH_2(16), and CH_2(21) to CH_2(22) are characteristic for oleanene-type triterpenoids. The acid hydrolysis of **4** produced an aglycone, **4a**, and D-glucofuranose (co-PC and R_f value), whereas the methanolysis afforded **4a** and 2,3,4,6-tetra-*O*-methyl-D-glucofuranose. The structure of **4a** was elucidated as (3β,9β)-9,25-cycloolean-12-en-3-ol based on IR and NMR data. Seven degrees of unsaturation for $C_{30}H_{48}O$, **4a**, indicated the presence of six rings and a C=C bond. The structure of the

aglycone was found to be similar to that of olean-12-en-3-ol [16][17], except for an additional ring (9β,25-cyclo). The position of this ring was confirmed by the NOESY correlation of CH_2(1) to CH_2(25). Hence, the structure of **4** was elucidated as (3β,9β)-9,25-cycloolean-12-en-3-yl β-D-glucofuranoside.

Compound **5** was isolated as a muddy white powder with a melting point of 220–222° and a molecular formula $C_{30}H_{50}O_7$ deduced from the molecular-ion peak at *m*/*z* 522 in the EI-MS (positive-ion mode). It was recognized as steroidal glycoside by detailed spectral analysis, along with its positive tests with *Salkowski*, *Liebermann–Burchard*, and *Molisch*'s reagents. The IR band at 3486 cm^{-1} showed indicated the presence of OH groups. In the ^{1}H-NMR spectrum, the coupling constant of the *doublet* at δ(H) 5.10 (J = 8.5, anomeric H–C(1′)) indicated β-configuration at the anomaric center of a sugar moiety. In addition, the other sugar H-atoms resonated at δ(H) 3.09–4.46 (H–C(2′), H–C(3′), H–C(4′), H–C(5′), and CH_2(6′)). A signal at δ(C) 81.1 (C(3)) in the ^{13}C-NMR spectrum indicated the presence of an O-bearing C-atom. The presence of three Me, thirteen CH_2, ten CH groups, and four quaternary C-atoms were confirmed by the ^{13}C-NMR and DEPT spectra. The signals at δ(C) 81.1 (C(3)) and δ(C) 72.4 (C(14)) in the ^{13}C-NMR spectrum indicated the presence of two O-bearing C-atoms. The COSY spectrum showed correlation of CH_2(1) to CH_2(2), CH_2(2) to H–C(3), CH_2(6) to CH_2(7), and CH_2(11) to CH_2(12). The HMBC of H–C(3) (δ(H) 3.65) to C(1′) (δ(C) 101.2) indicated that the sugar residue was at C(3). The acid hydrolysis of **5** gave an aglycone, **5a**, and D-glucopyranose (co-PC and R_f value), whereas the methanolysis produced an aglycone, **5b**, and 2,3,4,6-tetra-*O*-methyl-D-glucopyranose. The structures of **5a** and **5b** were elucidated as (3β,9β,14β)-9,19-cyclocholane-3,14-diol and (3β,9β,14β)-14-methoxy-9,19-cyclocholan-3-ol, respectively, by spectral analysis and by comparison with similar steroids reported earlier [18–20]. Hence, the structure of **5** was characterized as (3β,9β,14β)-14-hydroxy-9,19-cyclocholan-3-yl β-D-glucopyranoside.

Compound **6** was isolated as a brownish yellow powder with a melting point of 247–249°, and showed molecular-ion peak at 372 (calc. 372) in the EI-MS, corresponding to the molecular formula $C_{19}H_{16}O_8$. The IR bands at 3448, 1610, and 1729 cm^{-1} indicated OH, CO, and AcO functions, respectively. The UV absorption maxima at 270, 315, and 406 nm were suggestive of a typical anthraquinone. This finding was supported by a positive color reaction (deep red) with Zn dust and aqueous NaOH. The downfield signals at δ(H) 7.22, 7.68, and 7.94 in the ^{1}H-NMR spectrum were due to three aromatic H-atoms. A *singlet* at δ(H) 2.10 was observed for the AcO H-atoms, whereas three sharp *singlet*s at δ(H) 3.30, 3.61, and 3.70 were due to the presence of three MeO substituents. The ^{13}C-NMR and DEPT spectra showed 19 C-atom signals for four Me (δ(C) 24.3, 56.1, 56.3, and 56.5) and three CH groups (δ(C) 113.4, 121.6, and 128.9), and twelve quaternary C-atoms (δ(C) 110.4, 115.1, 124.5, 132.6, 153.2, 154.2, 158.2, 161.7, 163.8, 168.9, 179.3, and 182.0). The highly downfield shifted signals at δ(C) 168.9 (CO of AcO), 179.3 (C(9)), and 182.0 (C(10)) were assigned to three CO functions. The MS showed a molecular-ion peak at *m*/*z* 372, along with a base peak at *m*/*z* 192 arising from the loss of $C_9H_8O_4$. All the spectral data for **6** were found to be similar to those of 2-hydroxy-1,3,4-trimethoxyanthraquinone [21], except for the additional AcO group. A *singlet* (δ(H) 7.68) and two *doublet*s (δ(H) 7.22 and 7.94) in the ^{1}H-NMR spectrum in the aromatic region clearly indicated the position of the AcO

group at ring *A*, either at C(6) or C(7). The NOESY correlation between (δ(H) 3.70) MeO–C(3) and MeO–C(4) (δ(H) 3.30) clearly showed that the two MeO groups must be placed at adjacent C-atoms. The further confirmation for the position of substituents, including the AcO group, was established by a HMBC experiment. The correlation of H–C(8) (δ(H) 7.94) with C(6) (δ(C) 158.2) clearly evidenced the position of the AcO group at C(6) [22]. Hence, the structure of **6** was elucidated as 9,10-dihydro-6-hydroxy-5,7,8-trimethoxy-9,10-dioxoanthracen-2-yl acetate.

Experimental Part

General. TLC (0.5 mm thick layer): silica gel (10–40 μ, *Merck*) pre-coated plates, spots were visualized by spraying with 7% H_2SO_4. M.p.: *Perfit* melting point apparatus. UV Spectra: *Perkin-Elmer Lambda-25* spectrometer in MeOH. IR Spectra: *Perkin-Elmer Spectrum RX I* FT-IR spectrometer (KBr discs). NMR Spectra: *JEOL AL 300* NMR spectrometer (300 MHz for ^{1}H and 75 MHz for ^{13}C, TMS as internal standard) and *Bruker-400 Ultra Shield*™ NMR spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C; TMS as internal standard). MS: *LC-MS Q-TOF Micro* mass spectrometer (LC/MS) and *LC-MS-LCQ*, *Finnigan*, MAT mass spectrometer.

Plant Material. Fresh bark (5 kg) and fruits (3 kg) of *Celtis australis* were collected from the village Bhatwara, District Tehri Garhwal, during November and identified at the Taxonomical Laboratory, Department of Botany, H. N. B. Garhwal University Srinagar. A voucher specimen (GUH-17595) of the plant has been deposited with the Departmental Herbarium for future records.

Extraction and Isolation. Bark. Air-dried powder of bark was extracted exhaustively with 95% EtOH at 30–50° (for 15 h × 3) on a heating mantle. The extraction mixture was filtered and solvent evaporated to dryness under reduced pressure to yield a black residue (350 g). This was pre-adsorbed onto SiO_2 (200 g, 60–120 mesh, *Merck*) and then allowed to run over a SiO_2 (500 g) packed column. The elution was started with $CHCl_3$/MeOH by increasing polarity of MeOH (6 → 20%). The fractions (100 ml) obtained from this column were collected and combined on the basis of TLC. The elution with $CHCl_3$/MeOH (23 : 2 → 43 : 7) afforded three compounds **1**–**3**.

Fruits. Air-dried powdered fruits were extracted similarly as in the case of bark and yielded black brown residue (300 g). This residue was fractionated with AcOEt in a *Soxhlet* apparatus which yielded an AcOEt-soluble (130 g) and an AcOEt-insoluble (170 g) fraction. The vacuum-dried fractions were pre-adsorbed onto SiO_2 (60–120 mesh, 100 g, *Merck*) and allowed to run over a SiO_2 (300 g) packed column. The column of the AcOEt-soluble fraction was eluted with hexane/$CHCl_3$ by increasing polarity of $CHCl_3$ (10 → 100%), $CHCl_3$/AcOEt by increasing polarity of AcOEt (1 → 100%), and finally with AcOEt/MeOH by increasing polarity of MeOH (1 → 5%), whereas the column of the AcOEt-insoluble fraction was eluted with $CHCl_3$/MeOH by increasing polarity of MeOH (10 → 20%). The column of the AcOEt-soluble fraction afforded two compound **4** and **5** in pure form, whereas the AcOEt-insoluble fraction produced a single compound, **6**, purified by recrystallization from MeOH.

*(9β,31*R*)-9,25-Cyclo-30-propylhopan-31-ol* (=(α*R*,γ*S*,*4a*S,*6a*S,*6b*R,*8a*S,*9*R,*11a*S,*11b*R,*13a*R,*14a*R)-α-*Ethyloctadecahydro-*γ*,4,4,6a,6b,11a-hexamethyl-1*H,*14*H-*cyclopenta[*a*]cyclopropa[*n*]chrysene-9-propanol*; **1**). White crystalline solid (0.132 g). M.p. 220–222°. IR: 3460, 2827. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 468 (6.2), 449 (19), 409 (100), 381 (53), 353 (60), 202 (13). Anal. calc. for $C_{33}H_{56}O$: C 84.55, H 12.04; found: C 84.09, H 12.20.

(3β)-3-Hydroxy-30-propylhopan-31-one (=*(5*R*)-5-[(3*R,*3a*S,*5a*R,*5b*R,*7a*R,*9*S,*11a*R,*11b*R,*13a*R,*13b*S*)-Eicosahydro-9-hydroxy-5a,5b,8,8,11a,13b-hexamethyl-1*H*-cyclopenta[*a*]chrysen-3-yl]hexan-3-one*; **2**). White crystals (0.177 g). M.p. 249°. UV: 276. IR: 3472, 2910, 1705, 1426. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 485 (100, M^+), 466 (10), 367 (10), 219 (22), 191 (12), 135 (7). Anal. calc. for $C_{33}H_{56}O_2$: C 81.76, H 11.64; found: C 81.49, H 11.03.

(3β)-Oleanan-3-ol (**3**). White powder (0.099 g). M.p. 276–278°. IR: 3423, 2884, 1427. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 428 (13.5, M^+), 372 (100), 205 (6), 192 (72). Anal. calc. for $C_{30}H_{52}O$: C 83.91, H 12.31; found: C 84.04, H 12.23.

*(3β,9β)-9,25-Cycloolean-12-en-3-yl β-*D*-Glucofuranoside* (**4**). White crystalline solid (0.129 g). M.p. 296–298°. IR: 3412, 1640, 2834, 1465. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 586 (6, M^+), 411 (30), 367 (100), 302 (20), 103 (10). Anal. calc. for $C_{36}H_{58}O_6$: C 73.68, H 9.96; found: C 73.46, H 9.53.

Acid Hydrolysis of **4**. Compound **4** (10 mg) was refluxed with 10% aq. HCl (10 ml) for 5 h, which afforded an aglycone and D-glucose identified by co-PC ($BuOH/H_2O/AcOH$ 4 : 1 : 5; $R_f = 0.18$) with an authentic sample.

Methanolysis of **4**. Compound **4** (10 mg) was refluxed with NaH (25 mg) and MeI (2 ml) in DMSO (10 ml) for 3 h, which afforded a methylated product. The acid hydrolysis of (10% HCl, 5 h, reflux) furnished the aglycone and 2,3,4,6-tetra-*O*-methyl-D-glucose (R_f, co-PC).

*(3β,9β,14β)-14-Hydroxy-9,19-cyclocholan-3-yl β-*D*-Glucopyranoside* (**5**). Muddy white powder (0.089 g). M.p. 220–222°. IR: 3486, 2818, 1424. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 522 (10, M^+), 360 (100), 325 (50), 282 (12), 234 (14), 202 (9). Anal. calc. for $C_{30}H_{50}O_7$: C 68.93, H 9.64; found: C 69.01, H 9.58.

Acid Hydrolysis of **5**. The acid hydrolysis of compound **5** was carried out by following same method as described for compound **4** and afforded an aglycone and D-glucose (co-PC, R_f).

Methanolysis of **5**. The methylation of compound **5** followed by hydrolysis was carried out by similar method as described for compound **4** and furnished aglycone and 2,3,4,6-tetra-*O*-methyl-D-glucose (co-PC, R_f).

9,10-Dihydro-6-hydroxy-5,7,8-trimethoxy-9,10-dioxoanthracen-2-yl Acetate (**6**). Brownish-yellow powder (0.097 g). M.p. 247–249°. UV: 270 (71,000), 315 (44,000), 406 (25,000). IR: 3448, 1729, 1610. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 372 (68, M^+), 339 (9), 209 (4), 192 (100), 177 (3). Anal. calc. for $C_{19}H_{16}O_8$: C 61.29, H 4.33; found: C 61.50, H 4.78.

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