Two New Octulosonic Acid Derivatives and a New Cyclohexanecarboxylic Acid Derivative from *Erigeron bonariensis* L.

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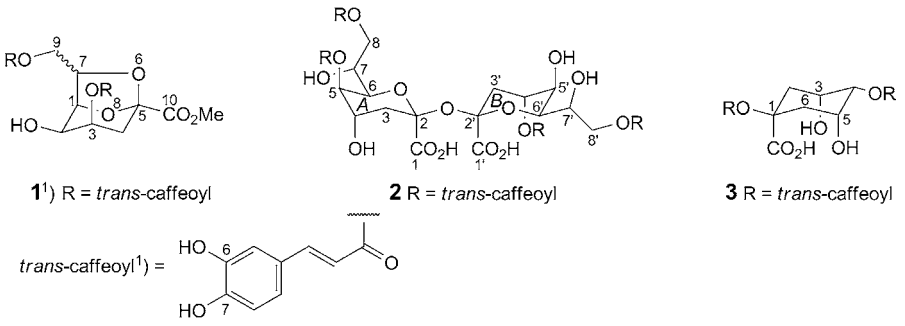
The AcOEt-soluble part of a MeOH extract from the whole plant of *Erigeron bonariensis* yielded two new rare-class octulosonic acid derivatives, *rel*-methyl (1*R*,2*S*,3*S*,5*R*)-3-(*trans*-caffeoyloxy)-7-[(*trans*-caffeoyloxy)methyl]-2-hydroxy-6,8-dioxabicyclo[3.2.1]octane-5-carboxylate (**1**) and 5,8-di[*O*-*trans*-caffeoyl]-3-deoxy-β-D-*gluco*-oct-2-ulopyranosonosyl 4,8-di[*O*-*trans*-caffeoyl]-3-deoxy-β-D-*gluco*-oct-2-ulopyranosidonic acid (**2**) along with a cyclohexanecarboxylic acid derivative, (1α,3β,4β,5β)-1,4-di-3,5-dihydroxy-bis(*trans*-caffeoyloxy)cyclohexanecarboxylic acid (**3**). The structures of these compounds were elucidated through ESI-MS, and 1D- and 2D-NMR spectroscopic techniques including ^{1}H- and ^{13}C-NMR, HMQC or HSQC, and HMBC experiments.

Introduction. – Asteraceae is one of the largest plant families of Pakistan, containing *ca.* 650 species distributed in 15 tribes [1]. The genus *Erigeron* (Asteraceae) comprises *ca.* 50 species [2]. *Erigeron bonariensis* L. (syn. *Conyza bonariensis* (L.) CRONQUIST), locally called 'gulava' or 'mirch booti' and traditionally used in urine problems, is a common weed distributed from plains to *ca.* 1800 m height in Pakistan [3][4]. The plant causes skin-contact dermatitis and asthma. Our previous investigation led to the isolation of aromatic glycosides from *E. bonariensis* [5]. Here we report the isolation and structure elucidation of the two rare-class octulosonic acid derivatives **1** and **2** along with the cyclohexanecarboxylic acid derivative **3** from the same plant.

Results and Discussion. – Compound **1** was isolated as a yellowish green gum. Its molecular formula was deduced to be $C_{27}H_{26}O_{13}$ from its high-resolution electrospray-ionization quadrupole time-of-flight mass spectrum (HR-ESI-Q-TOF-MS) (pos. mode) which gave a quasimolecular-ion peak at m/z 559.1426 ($[M+H]^+$). The molecular formula was also supported by the IR, UV, and NMR data. Compound **1** gave IR absorption bands for OH groups (3425 cm^{-1}), an α,β-unsaturated C=O moiety (1686 cm^{-1}), and olefinic (1603 cm^{-1}), aromatic C=C (1443 cm^{-1}), and C–O bonds (1114 cm^{-1}). The UV spectrum of **1** in MeOH showed the characteristic maxima at 217.6, 244.4, and 328 nm [6][7]. The ^{1}H- and ^{13}C-NMR spectra (*Table 1*) as well as comparison with literature revealed data that the basic skeleton of compound **1** was



that of a methyl 6,8-dioxabicyclo[3.2.1]octane-5-carboxylate containing two *trans*-caffeoyl (=(2*E*)-3-(3,4-dihydroxyphenyl)-1-oxoprop-2-en-1-yl) moieties [8]. The presence of a *trans*-caffeoyl moiety in the molecule was also supported by the MS/MS of the $[M+H]^+$ peak at *m*/*z* 559 which gave a product ion peak at *m*/*z* 163 (*trans*-caffeoyl$^+$, base peak). The MS/MS experiment also yielded a peak at *m*/*z* 397 showing the loss of a *trans*-caffeoyl moiety from the molecule. The direct attachments between H- and C-atoms were revealed by a HSQC experiment. The constitution of the 6,8-dioxabicyclo[3.2.1]octane-5-carboxylate moiety was determined from the ^{1}H,^{1}H-COSY plot. For this purpose, the H-atoms of CH_2(4) were selected as starting point. The H-atom at δ(H) 4.55 (H–C(1) and H–C(7)) showed HMBC cross-peaks with the anomeric C-atom (δ(C) 104.5 (C(5)); *Fig. 1*) indicating the presence of a ketal group at C(5); this was supported by the downfield shift of the anomeric C-atom signal and two tertiary C-atom signals at δ(C) 81.0 (C(7)) and 78.0 (C(1)) in the ^{13}C-NMR spectrum [7]. The ^{1}H- and ^{13}C-NMR spectra also indicated the presence of two *trans*-caffeoyl moieties in the molecule. The ^{1}H-NMR signals of one *trans*-caffeoyl moiety were observed at δ(H) 6.42 and 7.56 (each *d*, $J=15.8$ Hz) showing the presence of a *trans* C=C bond, and the aromatic signals at δ(H) 6.98 (br. *d*, $J=8.0$ Hz), 6.77 (*d*, $J=$ 8.1 Hz), and 7.13 (*d*, $J=1.6$ Hz). These observations indicated the presence of OH groups at the C(6′) and C(7′) positions[1]) of the benzene ring (*i.e.*, of a *trans*-caffeoyl moiety). The other acyl moiety was also a *trans*-caffeoyl group as observed from its NMR data (*cf. Table 1*). The points of attachment of these *trans*-caffeoyl moieties to the sugar unit were suggested by the downfield shift of the C(3) and C(9) signals at δ(C) 67.8 and 64.1, respectively, and confirmed by the HMBC interactions of CH_2(3) (δ(H) 5.46) with δ(C) 168.7, and H–C(9) (δ(H) 4.59 and 5.29) with δ(C) 169.1. The MeO group (δ(H) 3.79) showed a HMBC with a C=O group at δ(C) 169.3 indicating that the COOH group of 6,8-dioxabicyclo[3.2.1]octane-5-carboxylic acid moiety was esterified with a Me group.

The relative configuration of the 6,8-dioxabicyclo[3.2.1]octane-5-carboxylate unit of compound **1** was assigned on the basis of coupling constants and the NOESY data (*Fig. 1*). The *trans*-caffeoyl group at C(3) was preferentially oriented axially because of the coupling constants of H–C(3) (br. *dd*, $J=5.38$ and 5.4 Hz) and H_b–C(4) (*dd*, $J=5.39$ and 15.5 Hz). Both $J_{ax,eq}$ and $J_{eq,eq}$ values fall in the same range, therefore, the

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[1]) Arbitary atom numbering; for systematic names, see *Exper. Part.*

Table 1. *^{1}H- and ^{13}C-NMR Data* (CD_3OD; 500 and 125 MHz, resp.) *of* **1**. δ in ppm, J in Hz.

Position[1])	δ(H)	δ(C)
6,8-Dioxabicyclo[3.2.1]octane-5-carboxylate moiety:		
H–C(1)	4.55 (*dd*, *J* = 2.6, 4.9)	78.0
H–C(2)	4.24 (*dd*, *J* = 4.8, 5.0)	67.9
H–C(3)	5.46 (br. *dd*, *J* = 5.38, 5.4)	67.8
CH_2(4)	2.26 (br. *d*, *J* = 15.4), 2.40 (*dd*, *J* = 5.39, 15.5)	38.8
C(5)		104.5
H–C(7)	4.55 (*dd*, *J* = 2.6, 4.9)	81.0
CH_2(9)	4.59 (*dd*, *J* = 2.6, 11.6), 5.29 (*dd*, *J* = 8.6, 11.9)	64.1
C(10)		169.3
trans-Caffeoyl moiety I:		
C(1′)		168.7
H–C(2′)	6.42 (*d*, *J* = 15.8)	115.6
H–C(3′)	7.56 (*d*, *J* = 15.8)	147.1
C(4′)		127.9
H–C(5′)	7.13 (*d*, *J* = 1.6)	115.3
C(6′)		146.7
C(7′)		149.5
H–C(8′)	6.77 (*d*, *J* = 8.1)	116.5
H–C(9′)	6.98 (br. *d*, *J* = 8.0)	123.3
trans-Caffeoyl moiety II:		
C(1″)		169.1
H–C(2″)	6.32 (*d*, *J* = 15.8)	114.9
H–C(3″)	7.62 (*d*, *J* = 15.8)	147.3
C(4″)		127.8
H–C(5″)	7.0 (*d*, *J* = 1.6)	115.2
C(6″)		146.7
C(7″)		149.5
H–C(8″)	6.72 (*d*, *J* = 8.1)	116.4
H–C(9″)	6.98 (br. *d*, *J* = 8.0)	123.0
MeO	3.79 (*s*)	53.3

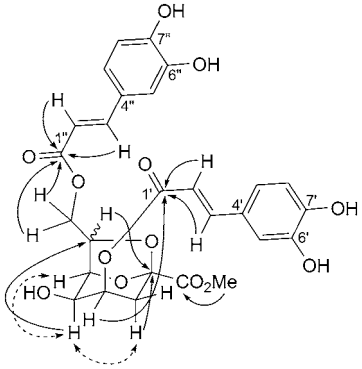

Fig. 1. *Important HMBC* (H → C) *and NOESY* (H ←- - → H) *correlations of* **1**

orientation of the OH group at C(2) could not be determined on the basis of the coupling constant of H–C(2) (*dd*, $J = 4.8$ and 5.0 Hz). However, OH–C(2) was oriented equatorially because of the correlations of H–C(2) with H_b–C(4) in the NOESY plot. The H–C(1) was oriented equatorially due to its correlations with H–C(2) in the NOESY plot as well as the smaller coupling constant of H–C(1) ($J_{1,2} =$ 4.9 Hz). The chemical shifts of H–C(1) and H–C(7) were the same; therefore, their correlations could not be observed in the NOESY plot. Hence the configuration at C(7) could not be determined by spectroscopy. The configurationsat all the positions in the 6,8-dioxabicyclo[3.2.1]octane-5-carboxylate moiety of compound **1** were similar to those of phenylpropanoyl 2,7-anhydro-3-deoxy-2-octulosonic acid derivatives exept for C(7), which could not be defined [8]. Thus the structure of compound **1** was deduced to be methyl *rel*-(1*R*,2*S*,3*S*,5*R*)-3-(*trans*-caffeoyloxy)-7-[(*trans*-caffeoyloxy)methyl]-2-hydroxy-6,8-dioxabicyclo[3.2.1]octane-5-carboxylate. Compound **1** and erigoster A [7] have the same planar structure but differ in the configuration at C(2). In compound **1**, OH–C(2) is oriented equatorially, while in erigoster A it is oriented axially. Thus compound **1** is a diastereoisomer of erigoster A and is unprecedented.

Compound **2** was isolated as a yellowish green gum. The HR-ESI-Q-TOF-MS (pos. mode) showed an unusual molecular-ion peak at *m*/*z* 1106.2620 (M^+) instead of $[M + H]^+$ peak indicating the molecular formula $C_{52}H_{50}O_{27}$. This formula was also supported by the IR and NMR spectra. Compound **2** gave IR-absorption bands typical for OH groups (3440 cm^{-1}) and olefinic bonds (1643 cm^{-1}), while its UV-absorption maxima were observed at 202 and 283 nm. The ESI-MS/MS of the M^+ peak at *m*/*z* 1106 resulted in the fragment ion peaks at *m*/*z* 562 (loss of one di(*O*-*trans*-caffeoyl)glycosyl moiety along with the bridging O-atom), 545 (loss of the other di(*O*-*trans*-caffeoyl)glycosyl moiety without the bridging O-atom), and 163 (*trans*-caffeoyl moiety). The ^{13}C-NMR spectra suggested the presence of six C=O groups (δ(C) 169.3, 169.0, 169.0, 168.9, 167.9, and 167.9), and the ^{1}H- and ^{13}C-NMR spectra (*Table 2*) established the presence of four *trans*-caffeoyl moieties and two octulosonic acid moieties in the molecule. A HMQC experiment revealed the direct attachments between H- and C-atoms. The constitutions of the octulosonic acid moieties were determined from the ^{1}H,^{1}H-COSY and HMBC experiments. For the assignment of the ^{1}H,^{1}H-COSY data, the H-atoms of CH_2(3) and CH_2(3′) of each sugar moiety were, respectively, selected as starting points. The two octulosonic acid moieties were linked to each other at the anomeric C-atoms *via* a bridging O-atom. This linkage was established on the basis of the downfield shift of the anomeric C-atoms of both sugar moieties. Each octulosonic acid moiety was esterified with two *trans*-caffeic acid moieties. The subunit *A* was esterified at C(5) and C(8), while the subunit *B* was esterified at C(4′) and C(8′). The points of attachment of the *trans*-caffeoyl moieties at these positions were established on the basis of the downfield shifts of the esterified C-atoms of both sugar moieties as by well as the HMBC interactions of the sugars H-atoms at esterified C-atoms with those of the C=O C-atoms of the *trans*-caffeoyl moieties. Thus the signals of C(5) and C(8) of subunit *A* were shifted downfield to δ(C) 72.1 and 64.4, respectively, while the signals of C(4′) and C(8′) of subunit *B* were shifted downfield to δ(C) 68.4 and 64.7, respectively. The H–C(5) (δ(H) 5.18) showed HMBC interactions with C(1″)[1]) (δ(C) 167.9), while CH_2(8) (δ(H) 4.86 and 5.01) showed interactions with C(1‴)[1]) (δ(C) 169.0) (*Fig. 2*). Similarly, H–C(4′) (δ(H) 4.44 – 4.45) showed HMBC interactions with C(1⁗) (δ(C)

Table 2. *^{1}H- and ^{13}C-NMR Data* (CD_3OD; 600 and 150 MHz, resp.) *of* **2**. δ in ppm, J in Hz.

Position	δ(H)	δ(C)
Octulosonic acid I:		
C(1)		167.9
C(2)		107.0
CH_2(3)	2.30–2.35 (*m*), 2.38–2.41 (*m*)	38.1
H–C(4)	4.32 (*dd*, *J* = 5.1, 4.9)	64.6
H–C(5)	5.18 (*dd*, *J* = 4.9, 4.9)	72.1
H–C(6)	4.66 (*dd*, *J* = 4.0, 4.0)	76.1
H–C(7)	4.44–4.45 (*m*, overlap)	79.3
CH_2(8)	4.86 (masked), 5.01 (*dd*, *J* = 6.8, 11.2)	64.4
Octulosonic acid II:		
C(1′)		168.9
C(2′)		106.3
CH_2(3′)	2.30–2.35 (*m*), 2.38–2.41 (*m*)	39.5
H–C(4′)	4.44–4.45 (*m*, overlap)	68.4
H–C(5′)	4.24 (*dd*, *J* = 5.0, 5.0)	68.6
H–C(6′)	5.44 (*dd*, *J* = 5.0, 5.1)	78.1
H–C(7′)	4.53 (*ddd*, *J* = 4.2, 4.5, 8.7)	80.0
CH_2(8′)	4.62 (*dd*, *J* = 3.1, 12.1), 5.27 (*dd*, *J* = 8.8, 12.0)	64.7
trans-Caffeoyl moiety I[1]):		
C(1″)		167.9
H–C(2″)	6.41 (*d*, *J* = 15.8)	116.3
H–C(3″)	7.58 (*d*, *J* = 15.8)	147.2
C(4″)		127.8
H–C(5″)	7.12 (*d*, *J* = 1.9)	115.2
C(6″)		146.72
C(7″)		149.53
H–C(8″)	6.77 (*d*, *J* = 8.2)	116.5
H–C(9″)	6.95 (*dd*, *J* = 1.9, 8.2)	123.3
trans-Caffeoyl moiety II[1]):		
C(1‴)		169.0
H–C(2‴)	6.21 (*d*, *J* = 15.8)	114.7
H–C(3‴)	7.56 (*d*, *J* = 15.9)	147.1
C(4‴)		127.68
H–C(5‴)	7.00 (*d*, *J* = 2.0)	115.12
C(6‴)		146.6
C(7‴)		149.6
H–C(8‴)	6.68 (*d*, *J* = 8.2)	116.40
H–C(9‴)	6.76 (*dd*, *J* = 2.0, 8.4)	123.0
trans-Caffeoyl moiety III[1]):		
C(1⁗)		169.0
H–C(2⁗)	6.15 (*d*, *J* = 15.8)	114.6
H–C(3⁗)	7.46 (*d*, *J* = 15.8)	146.9
C(4⁗)		127.64
H–C(5⁗)	6.92 (*d*, *J* = 1.9)	114.9
C(6⁗)		146.79
C(7⁗)		149.56
H–C(8⁗)	6.70 (*d*, *J* = 8.1)	116.42
H–C(9⁗)	6.76 (*dd*, *J* = 2.0, 8.4)	123.0

Table 2 (cont.)

Position	δ(H)	δ(C)
trans-Caffeoyl moiety IV[1]):		
C(1′′′′′)		169.3
H–C(2′′′′′)	6.30 (*d*, *J* = 15.9)	115.9
H–C(3′′′′′)	7.62 (*d*, *J* = 15.8)	147.6
C(4′′′′′)		127.9
H–C(5′′′′′)	7.06 (*d*, *J* = 1.9)	115.17
C(6′′′′′)		146.79
C(7′′′′′)		149.4
H–C(8′′′′′)	6.72 (*d*, *J* = 8.2)	116.47
H–C(9′′′′′)	6.88 (*dd*, *J* = 1.9, 8.2)	123.2

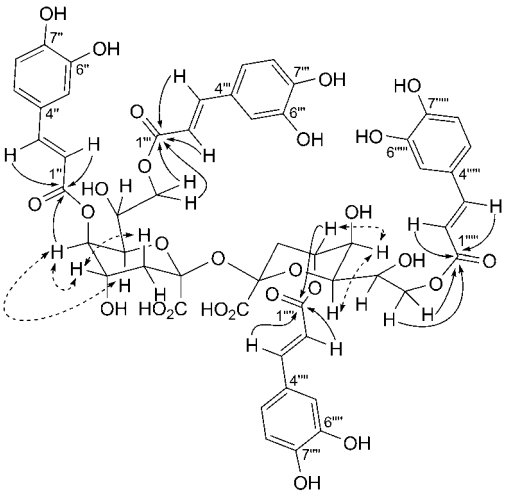

Fig. 2. *Important HMBC* (H → C) *and NOESY* (H ← - - → H) *correlations of* **2**

169.0), while the CH_2(8′′) (δ(H) 4.62 and 5.27) showed interactions with C(1′′′′′)[1]) (δ(C) 169.3). The relative configuration of the sugar moieties was established on the basis of NOESY experiments as well as the coupling constants of the sugars H-atoms. The coupling constants of H–C(4) (*dd*, *J* = 4.9 and 5.1 Hz), H–C(5) (*dd*, *J* = 4.9 and 4.9 Hz), and H–C(6) (*dd*, *J* = 4.0 and 4.0 Hz) as well as the NOESY interactions H–C(4) H_b–C(3) and H–C(5), and H–C(5) with H–C(6) indicated that OH–C(4) and the *trans*-caffeoyl group at C(5) were oriented axially in subunit *A* (*Fig. 2*). Similarly, the coupling constants of H–C(5′) (*dd*, *J* = 5.0 and 5.0 Hz) and H–C(6′) (*dd*, *J* = 5.0 and 5.1 Hz) in subunit *B* as well as the NOESY interactions H–C(4′)/H–C(5′), and H–C(5′)/H–C(6′) indicated that the *trans*-caffeoyl group at C(4′) and the OH group at C(5′) were oriented axially in subunit *B*. On the basis of these observations, the structure of **2** was proposed to be 5,8-di[*O*-*trans*-caffeoyl]-3-deoxy-β-D-*gluco*-oct-2-ulopyranosonosyl 4,8-di[*O*-*trans*-caffeoyl]-3-deoxy-β-D-*gluco*-oct-2-ulopyranosidonic acid (2 ↔ 2 likage) which is unprecedented.

Compound **3** was obtained as a pale yellow gummy solid. Its molecular formula was deduced to be $C_{25}H_{24}O_{12}$ on the basis of HR-ESI-Q-TOF-MS (pos. mode) which gave a quasi-molecular-ion peak at *m/z* 517.1392 ($[M+H]^+$). The HR-ESI-Q-TOF-MS also revealed a peak at *m/z* 499.1167 ($[M+H-H_2O]^+$). The MS/MS of *m/z* 499 ($[M+H-H_2O]^+$) gave diagnostic fragment-ion peaks at *m/z* 319 ($[M-(18+179)]$) (loss of H_2O + *trans*-caffeoyl) and 163 ([*trans*-caffeoyl]$^+$). The formula deduced by HR-ESI-Q-TOF-MS (pos. mode) was also supported by the UV, IR, and NMR spectra. Compound **3** showed UV-absorption maxima at 220 and 330 nm, while it gave IR absorption bands typical for OH groups (3435 cm^{-1}), CH stretching vibrations (2924 cm^{-1}), acid CO (1740 cm^{-1}), olefinic bonds (1692 cm^{-1}), and aromatic C=C bonds (1518 and 1450 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra (*Table 3*) and their comparison with literature data indicated the presence of two *trans*-caffeoyl moieties and a cyclohexanecarboxylic acid skeleton in the molecule [9][10]. The direct attachments between H- and C-atoms were revealed by the HSQC experiment. The constitution of the cyclohexane moiety was established on the basis of the ^{1}H,^{1}H-COSY experiment. A H-atom at δ(H) 5.11 (H–C(4)) showed HMBC interactions with a

Table 3. *^{1}H- and ^{13}C-NMR Data* (CD_3OD; 500 and 125 MHz, resp.) *of* **3**. δ in ppm, *J* in Hz.

Position	δ(H)	δ(C)
Cyclohexanecarboxylic acid:		
C(1)		79.4
CH_2(2)	2.11 (br. *d*, *J* = 12.4), 2.29 (br. *d*, *J* = 9.5)	38.4
H–C(3)	4.37 (br. *s*)	69.6
H–C(4)	5.11 (*d*, *J* = 7.1)	76.0
H–C(5)	5.63 (br. *s*)	69.0
CH_2(6)	2.23 (br. *d*, *J* = 10.2), 2.29 (br. *d*, *J* = 9.5)	39.6
COOH		176.9
trans-Caffeoyl moiety I[1]):		
C(1′)		168.3
H–C(2′)	6.17 (*d*, *J* = 15.8)	114.8
H–C(3′)	7.50 (*d*, *J* = 15.8)	147.5
C(4′)		127.8
H–C(5′)	6.98 (*s*)	115.2
C(6′)		146.7
C(7′)		149.6
H–C(8′)	6.72 (*d*, *J* = 7.7)	116.5
H–C(9′)	6.89 (br. *d*, *J* = 8.9)	123.1
trans-Caffeoyl moiety II[1]):		
C(1″)		168.5
H–C(2″)	6.27 (*d*, *J* = 15.8)	114.8
H–C(3″)	7.58 (*d*, *J* = 15.8)	147.6
C(4″)		127.7
H–C(5″)	7.00 (*s*)	115.2
C(6″)		146.7
C(7″)		149.6
H–C(8″)	6.73 (*d*, *J* = 7.9)	116.5
H–C(9″)	6.89 (br. *d*, *J* = 11.5)	123.1

C-atom at δ(C) 168.5 (*Fig. 3*) indicating that a *trans*-caffeoyloxy moiety was attached at C(4). The point of attachment of the *trans*-caffeoyloxy moiety at C(4) was also supported by the downfield shift of the C(4) signal δ(C) 76. A second *trans*-caffeoyloxy moiety was assumed to be attached with to C(1) as there were no HMBC interactions of the C=O C-atom of this *trans*-caffeoyl moiety (δ(C) 168.3) with any H-atom of the cyclohexane ring; this was confirmed by comparison with the literature data of cyclohexanecarboxylic acids substituted at C(1) by a *trans*-caffeoyloxy moiety [10][11]. The H–C(5) signal was shifted downfield as compared to the H–C(3) signal, probably due to H-bonding between OH–C(5) and the C=O group of COOH [9]. The COOH signal was also shifted downfield to δ(C) 176.9 due to the same H-atom bonding. The analysis of the NOESY plot and coupling constants helped in the assignment of the relative configuration of the cyclohexane ring of **3**. The H–C(3) showed NOESY interactions with H–C(4) which in turn showed interactions with H–C(5) indicating that these H-atoms are in the same plane (*Fig. 3*). The coupling constant between H–C(3) (br. *s*, equatorial) and H–C(4) ($J_{ax,eq} = 7.1$ Hz), and between H–C(4) and H–C(5) (br. *s*, equatorial) revealed that in the cyclohexane moiety, the H-atoms were H_β–C(3), H_β–C(4), and H_β–C(5). On the basis of the described spectral evidences and comparison with the literature data, the basic skeleton of **3** was proposed to be *neo*-quinic acid (=(1α,3β,4β,5β)-1,3,4,5-tetrahydroxycyclohexanecarboxylic acid) [12] having a conformation in which the COOH group is axial, and containing a *trans*-caffeoyloxy moiety at C(1) and another *trans*-caffeoyloxy moiety at C(4). Thus the structure of compound **3** was assigned to be (1α,3β,4β,5β)-1,4-bis(*trans*-caffeoyloxy)-3,5-dihydroxycyclohexanecarboxylic acid. Compound **3** is a diastereoisomer of 1,4-di[*O-trans*-caffeoyl]quinic acid [13] and is unprecedented.

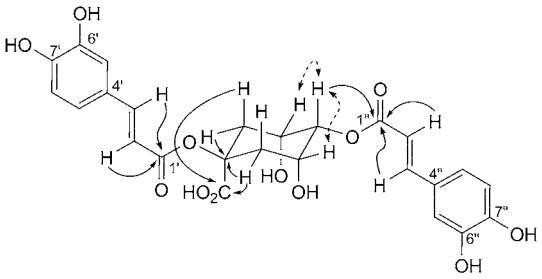

Fig. 3. *Important HMBC* (H → C) *and NOESY* (H ←- - → H) *correlations of* **3**

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Experimental Part

General. Column chromatography (CC): silica gel *60* (SiO_2, 230–400 mesh; *Macherey–Nagel*), *Sephadex LH-20* (25–100 μm; *Sigma–Aldrich*). MPLC: *Eyela VSP-3050* instrument with a 25 × 200 mm column (*Eyela*) filled with *Polygroprep C-18* (25–40 μm, 10 nm; *Macherey–Nagel*). Recycling Prep. HPLC: *LC-908W* instrument (*Japan Analytical Industries* (*JAI*) *Co., Ltd.*), equipped with a *J'sphere ODS-M80* column (S-4 μm, 8 nm, 20 × 250 mm; *YMC*) a *JAI RI-5* refractive index detector and a *JAI UV-310* detector (254 nm); t_R in min. TLC: *RP-18-F*$_{254s}$ plates (*Merck*); detection first under UV light

(254/366 nm), and then with cerium(IV) sulfate spray reagent in 10% H_2SO_4 soln. followed by and heating. UV Spectra: *Hitachi-U-3200* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Bruker Vector 22* FT-IR spectrometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. Optical rotations: *Jasco-DIP-360* digital polarimeter or *Polartronic-D* polarimeter. 1D- and 2D-NMR Spectra: *Bruker-Avance* 500 or 600 MHz instrument; δ in ppm with ref. to the residual non-deuterated solvent peaks (δ(H) 3.31 and δ(C) 49.0 from CD_3OD), *J* in Hz. ESI-MS (pos.): *QStar XL Hybrid* LC/MS/MS spectrometer (*Applied Biosystems*); in *m*/*z*. Collision-induced-dissociation (CID) MS: collision energy of 20 or 40 eV with N_2 as collision gas.

Plant Material. The whole plants of *Erigeron bonariensis* (Asteraceae) were collected from Oghi, Mansehra, Pakistan, in November 2002, and identified by Mr. *Jan Alam* (taxonomist) at the Botany Department, University of Karachi, Pakistan. A voucher specimen (KUH G. H. No. 68220) has been deposited with the herbarium of the above department.

Extraction and Isolation. The air died whole plant of *Erigeron bonariensis* (24 kg) was ground into fine powder which was percolated with MeOH (50e × 7d) three times at rt and filtered. The solvent was evaporated under reduced pressure to fernish a dark green residue (550 g) which was dissolved in H_2O and partitioned between hexane (190 g), $CHCl_3$ (70 g), AcOEt (120 g), BuOH (90 g), and H_2O (80 g). The AcOEt fraction was subjected to CC (SiO_2, hexane, hexane/AcOEt gradient, and AcOEt) to obtain six fractions. The fraction eluted with AcOEt /hexane 3 : 1 was further subjected to CC (*Sephadex LH-20*, MeOH/H_2O 1 : 1): *Fractions 1–3*. *Fr. 2* was subjected to MPLC (*Polygroprep C-18,* H_2O followed by a gradient 0 → 100% MeOH/H_2O) to give a semi-pure compound which was then purified by prep. recycling HPLC (*J'Sphere ODS-M80*, MeOH/H_2O 1 : 1, flow rate 3 ml/min): **1** (25 mg; t_R 45). *Fr. 3* was subjected to MPLC (*Polygroprep C-18*, H_2O followed by a gradient 0 → 100% MeOH/H_2O) to give a semi-pure compound which when subjected to prep. recycling HPLC (*J'Sphere ODS-M80*, MeOH/H_2O 1 : 1, flow rate 3 ml/min): **2** (4.0 mg; t_R 25). The fraction from the main column eluted with AcOEt/hexane 1 : 1 was subjected to CC (*Polygroprep C-18*, H_2O followed by a gradient 0 → 100% MeOH/H_2O) to give a semi-pure compound which was again subjected to MPLC (*Polygroprep C-18*) to get a more purified compound showing one major spot with impurities on reversed-phase TLC. That fraction was further purified by prep. recycling HPLC (*J'Sphere ODS-M80*, MeOH/H_2O 1 : 1, flow rate 3 ml/min): **3** (6.0 mg; t_R 34). The elution of **1**–**3** was simultaneously monitored by the refractive-index and UV detectors.

Methyl rel-*(1*R,*2*S,*3*S,*5*R*)-3-{[(2*E*)-3-(3,4-Dihydroxyphenyl)-1-oxoprop-2-en-1-yl]oxy}7-{[(2*E*)-3-(3,4-dihydroxyphenyl)-1-oxoprop-2-en-1-yl]oxy}-methyl}-2-hydroxy-6,8-dioxabicyclo[3.2.1]octane-5-carboxylic acid* (**1**): Yellowish green, gummy solid (25 mg). $[\alpha]_D^{29} = -18$ ($c = 0.25$, MeOH). UV (MeOH): 328.0, 244.4, 217.6. IR (KBr): 3425, 1686, 1603, 1443, 1114. ^{1}H- and ^{13}C-NMR: *Table 1*. HR-ESI-Q-TOF-MS: 559.1426 ($[M+H]^+$, $C_{27}H_{27}O_{13}^+$; calc. 559.1443). ESI-Q-TOF-MS/MS (pos.): 559 ($[M+H]^+$, 6), 541 (4), 397 (1.5), 379 (6), 163 (100), 145 (2).

*3-Deoxy-5,8-bis{*O*-[(2*E*)-3-83,4-dihydroxyphenyl)-1-oxoprop-2-en-1yl]}-β-*D-gluco*-oct-2-ulopyranosonosyl 3-Deoxy-4,8-bis{*O*-[(2*E*)-3-(3,4-dihydroxyphenyl)1-oxoprop-2-en-1-yl]}-β-*D-gluco*-oct-2-ulopyranosidonic Acid* (**2**): Yellowish green, gummy solid (4 mg). $[\alpha]_D^{29} = +33$ ($c = 0.41$, MeOH). UV (MeOH): 283, 202. IR (KBr): 3440, 1643. ^{1}H- and ^{13}C-NMR: *Table 2*. HR-ESI-Q-TOF-MS: 1106.2620 (M^+, $C_{52}H_{50}O_{27}^+$; calc. 1106.2523). ESI-Q-TOF-MS/MS (pos.): 1106 (M^+, 13.5), 1089 (5.8), 562 (100), 545 (71), 163 (5.8).

*(1α,3β,4β,5β)-1,4-Bis{[(2*E*)-3-(3,4-dihydroxyphenyl)-1-oxoprop-2-en-1-yl]oxy}-3,5-dihydroxycyclohexanecarboxylic Acid* (**3**): Pale yellow, gummy solid (6 mg). $[\alpha]_D^{29} = -22$ ($c = 0.30$, MeOH). UV (MeOH): 330, 220. IR (KBr): 3435, 2924, 1740, 1692, 1518, 1450. ^{1}H- and ^{13}C-NMR: *Table 3*. HR-ESI-Q-TOF-MS: 517.1392 ($[M+H]^+$, $C_{25}H_{25}O_{12}^+$; calc. 517.1338; 66.5), 499.1167 (100). ESI-Q-TOF-MS/MS (pos.): 499 ($[M+H-H_2O]^+$, 6), 319 (21.5), 163 (100).

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