Natural Product Sciences
3(2) : 127 ~ 134 (1997)

New Dimeric Phenolic Conjugates from the Wood of *Tamarix tetragyna*

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Abstract – Two new dimeric phenolic conjugates, 2,3-di-O-dehydrodigallicmonocarboxyl-(α,β)-$^4C_1$-glucopyranose and ellagic acid 3,3'-dimethylether-4-O-SO_3K were isolated from the debarked heart wood of *Tamarix tetragyna* (Tamaricaceae) along with the known phenolic compounds, isoferulic acid, ferulic acid, gallic acid, gallic acid 4-methyl ether, syringic acid, ellagic acid 3,3'-dimethyl ether and ellagic acid. All structures were determined mostly by ESI-MS, 1D and 2D-NMR spectroscopy.

Key words – *Tamarix tetragyna*, tamaricaceae, debarked heart wood, dimeric phenolics, 2,3-di-O-dehydrodigallicmonocarboxyl-(α/β)-$^4C_1$-glucopyranose, ellagic acid 3,3'-dimethyl ether 4-potassium sulphate; ESI-MS, NMR.

Introduction

Dimeric and oligomeric galloyl derivatives are the biogenetic products of intramolecular oxidative C-O or C-C coupling among two or more galloyl moieties in hydrolyzable tannins (Haslem, 1977).

A diversity of these derivatives are widely spreaded among several plant families (Nawwar *et al.*, 1997) including Tamaricaceae (Nawwar *et al.*, 1994a). Many of these derivatives have remarkable biological activities where by they act as host-mediated anti-tumor agents (Miyamoto *et al.*, 1987), as inhibitors of reverse transcriptase of retro-virus (Kakiuchi *et al.*, 1985) and as anti-inflammatory, anti-pyretic agents (Barakat *et al.*, 1996).

In Egypt, three *Tamarix* species, namely, *T. aphylla, T. nilotica*, and *T. tetragyna* are growing wild in marshy habitat mainly along the Mediterranean Coastalstrip, in Sinai peninsula and at the coast of Qarun lake in Upper Egypt. Extracts of these plants are used in traditional medicine for treating edema of spleen and mixed with ginger to treat uterus affections (Boulos, 1983). Several intensive phytochemical investigations of the constitutive phenolics of *T. aphylla* and *T. nilotica* proved that both are capable of synthesizing and accumulating high contents of dimeric phenolic ellagitannins in their galls, leaves, bark, flowers and roots (Nawwar *et al.*, 1994a; Nawwar *et al.*, 1984a&b; Nawwar *et al.*, 1982 and Souleman *et al.*, 1991). However, the third Egyptian *Tamarix* species, *T. tetragyna* Ehronb, a small tree or tall shrub up to about 3 m height which produces large pink flowers, in long slender recemes springing up from old woody branches, has not been subjected previously to any phytochemical study concerning its chemical constituents. In the present work, the isolation and characterization of the new natural products 2,3-di-O-dehydrodigallicmonocarboxyl-(α/β)-$^4C_1$-glucopyranose (**6**) and ellagic acid 3,3'-dimethyl ether 4-O-KSO_3 (**7**), from the aqueous alcoholic debarked heart wood extract of *T. tetragyna* were carried out.

The occurrence of the known phenolic acids, gallic acid (**1**), gallic acid 4-methyl ether (**2**),

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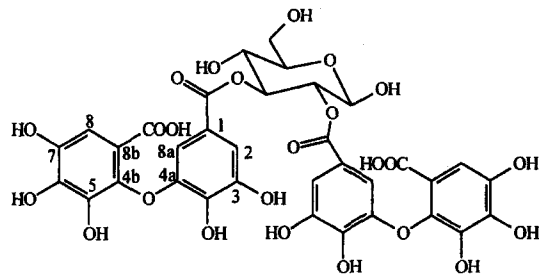
syringic acid (**3**), ferulic acid (**4**), isoferulic acid (**5**), ellagic acid (**8**) and ellagic acid 3,3'-dimethyl ether (**9**) in the extract is also reported herewith.

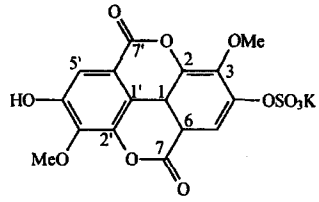
Results and Discussion

The aqueous ethanolic (3:1) extract of the heart woods of *Tamarix tetragyna* Ehronb was shown by preliminary 2D-PC screening to contain a complicated phenolic mixture from which nine compounds (**1-9**) were isolated and purified by polyamide column chromatography using H_2O-EtOH solvent systems of decreasing polarities as eluents. The two compounds **6** and **7** were isolated for the first time from natural sources. The remaining compounds (**1-5**, **8** and **9**) are known and gave chromatographic, UV spectral properties (Table 1), ESI-MS and NMR data identical with those of gallic acid (Nawwar *et al.*, 1982), gallic acid 4-methyl ether (Nawwar *et al.*, 1984b), syringic acid (Harborne, 1973), ferulic acid (Souleman *et al.*, 1991), ellagic acid 3,3'-dimethyl ether (Nawwar *et al.*, 1982), ellagic acid (Nawwar *et al.*, 1984b), respectively.

The new compound **6** was eluted from the polyamide column by EtOH-H_2O (4:6). For purification of **6**, preparative PC was applied, followed by precipitation of the obtained material from its concentrated acetone solution by addition of ether. Repetition of the precipitation process (three times) afforded a pure light brown amorphous sample of **6**. It showed chromatographic properties (Table 1) and results of colour reactions similar to those of polar polyphenolics (dark purple spot on PC under UV light, high Rfs in aqueous solvents and low Rfs in organic solvents and dark blue $FeCl_3$ reaction), but gave



Compound **6** : β–form



Compound 7

Table 1. Chromatographic and UV data of compounds 1-9

Compound	Chromatographic properties Rf- (×100)			UV spectral data λmax (MeOH), nm
	H_2O	HOAc-H_2O	4:1:5	
1-Gallic acid	53	56	78	272
2-Gallic acid 4-methyl ether	51	48	85	270
3-Syringic acid	48	48	88	268
4-Ferulic acid	34	55	90	235, 324
5-Isoferulic acid	30	52	92	240, 295, 325
6-2,3-Di-O-dehydrodigallic-monocarboxyloyl-(α/β)-^{4}C1-glucopyranoseglucose	54	52	32	270
6a-Monodehydrodigallic-monocarboxyloylglucose	58	60	25	271
Dehydrodigallic acid	45	58	72	270
7-Ellagic acid 3,3'-dimethyl ether 4-O-KSO_3	59	56	38	254, 291*, 352, 370*
8-Ellagic acid 3,3'-dimethyl ether	0	16	91	251,362*, 375
9-Ellagic acid	0	09	48	255,361

*inflection.

no response towards aqueous KIO_3, specific for galloyl ester (Haddock *et al.*, 1982) or towards nitrous acid, specific for ellagitannins containing hexahydroxydiphenyl moieties (Gupta *et al.*, 1982). Compound **6** showed a UV spectrum with a maximal absorption band at 270 nm in MeOH similar to galloyl derivatives (Nawwar *et al.*, 1994b) and exhibited a molecular ion peak at $[M-H]^-$; 819 in negative ESI-MS, corresponding to a molecular weight of 820 amu.

On complete acid hydrolysis of **6** (2N aqueous HCl, 3 hours, 100 ℃), dehydrodigallic acid (Co-PC, UV λ_{max} MeOH, ^1H and ^{13}C-NMR) was produced as the only phenolic hydrolysis product together with D-glucose (Co-PC). Partial acid hydrolysis of the compound (0.1 N aqueous HCl, 3 hours, 100℃) gave besides dehydrodigallic acid and glucose (Co-PC), an intermediate **6a** (isolated from an ethyl acetate extract of the hydrolysate by preparative PC) with chromatographic (colour on PC under UV light) and UV spectroscopic properties similar to those of the parent compound **6**, but possesses distinctly different Rfs (Table 1). **6a** was shown to have a molecular weight of 500 amu (negative ESI-MS, $[M-H]^-$: 499) and λ_{max} in MeOH at 271 nm. These data show **6a** to be monodehydrodigallicmonocarboxyl glucose. However, the attachment site is still unknown in this step.

The ^1H-NMR spectrum of **6** (CD_3COCD_3, room temp.) was assigned on the basis of the mode of resonance splitting and coupling constants. The assignments were then confirmed by measurement of ^1H-^1H COSY spectrum. In this spectrum, the recognition of two distinct patterns of glucose proton resonance attributable to α- and β-anomeric glucose moieties confirmed the absence of substitution at the anomeric glucose hydroxyl group. The anomeric protons were found, therefore, resonating at δ 5.32 (d, J=3 Hz, H-1α) and at 4.68 (d, J=7.5 Hz, H-1β).

Esterification of the glucose hydroxyl grpoups at C-2 and C-3 of both glucose anomers was determined from the downfield shift of the geminal H-2α, H-2β, H-3α and H-3β protons in comparison with the corresponding signals in the spectrum of α- and β-glucose (Table 2) (Nawwar *et al.*, 1984b). The characteristically shielded H-8a protons in both dehydrodigallicmonocarboxyl moieties of **6** (see formulae) have revealed their resonances, each in douplicate, as meta coupled doublets detected in this spectrum at δ 6.72, 6.75, 6.78 and 6.80. The resonances of the remaning aromatic protons (H-2 and H-8) appears as an unresolved multiplet centred at δ 7.15 and integrated to 4 H.

Table 2. ^1H-NMR chemical shifts (δppm) and coupling constant (J in Hz) of compound 6

Compound	Proton of the glucose moiety						
	H-1	H-2	H-3	H-4	H-5	H-6	H-6'
6β	4.68	5.0	5.35	3.6	4.15	3.6	3.6
	(d, J=7.5)	(d, d, J=7.5, 8.5)	(t, J=8.5)	(m)	(m)	(m)	(m)
β-D-	4.65	3.27	3.45	3.35	3.42	3.83	3.77
glucopyranose	$J_{1,2}$=7.9	$J_{2,3}$=9.1	$J_{3,4}$=9.0	$J_{4,5}$=9.8	$J_{5,6}$=2.0	$J_{5,6}$=5.8	$J_{6,6'}$=12.0
6α	5.32	4.72	5.53	3.6	4.15	3.6	3.6
	(d, J=3)	(d, d, J=9.5, 3.0)	(t, J=9.5)	(m)	(m)	(m)	(m)
α-D-	5.23	3.5	3.71	3.36	3.82	3.89	3.72
glucopyranose	$J_{1,2}$=3.7	$J_{2,3}$=10	$J_{3,4}$8.8	$J_{4,5}$=9.8	$J_{5,6}$=2.0	$J_{5,6'}$=5.8	$J_{6,6'}$12.0
6α/β: Aromatic dehydrodigallicmonocarboxyloyl protons							
6.72, 6.75, 6.78 and 6.8 (each as d, J=2.5 Hz, H-8a in 2- and 3-dehydrodigallicmonocarboxyloyl moicties in both α and β-anomers)							
7.15 (m, H-2 & H-8 in 2- and 3-dehydrodigallicmonocarboxyloyl moieties in both α- and β-anomers)							

Table 3. ^{13}C-NMR chemial shifts (δ ppm), multiplicities and coupling constants (J in Hz) of compounds **6**, **7**, dehydrodigallic acid and ellagic acid 3,3'-dimethyl ether

Carbon No.	**6**	Dehydrodigallic acid	**7**	Ellagic acid 3,3' -dimethyl ether
1	119.5, 119.6, 119.86	120.6 (t, 1.6)	115.0	111.8
2	106.5	107.1 (d, 165.5; d, 7.0)	140.8	141.1
3	145.6, 145.5, 145.3, 145.2	146.1 (d, 1.0; d, 2.9)	143.6	140.2
4	138.9, 138.5	139.6 (t, 7.0)	153.15	153.0
4a	147.1, 147.3	148.0 (d, 1.0; d, 3.4)		
4b	136.2, 136.1, 136.4	136.6 (d, 12.5)	113.23	111.4
5	139.9, 139.7	140.0 (d, 1.0)	113.23	112.0
6	139.7, 139.7	139.7 (d, 10.4)	158.7	158.3
8	142.4	143.0 (d, 3.5)		
7	108.8, 108.7, 108.6	109.0 (d, 166)		
8a	113.6, 113.4	115.7 (d, 1.5)		
8b	112.9, 112.7	111.3 (d, 165; d, 7.5)		
8c	167.6, 167.47, 167.3	167.1 (d, 4.9)		
10	162.6, 162.7, 162.9, 162.94	168.2 (t, 4.4)		
1'			111.4	111.8
2'			140.8	141.1
3'			140.4	140.2
4'			153.15	153.0
5'			111.8	111.4
6'			111.8	112.0
7'			158.7	158.3
α&β-glucose				
1	89.5 and 94.5			
2	72.2 and 73.3			
3	72.2 and 75.5			
4	68.4 and 68.5			
5	72.2 and 76.9			
6	60.5 and 60.6			
Methoxy groups			61.28 and 61.75	60.9

The coupling constant of the sugar in the recorded ^{1}H-NMR spectrum (see Table 2) confirmed that the glucose moiety of 6 is adopting a $^4C_1$ conformation. Other glucose conformation, known in association with tannin chemistry do not have $J_{1,2}$, $J_{2,3}$, $J_{3,4}$ values similar to those measured for glucose moiety of 6 (Nawwar *et al.*, 1994b). From the data given above it becomes cleared that compound **6** is an anomeric mixture of 2,3-di-O-dehydrodigallicmonocarboxyl-$^4C_1$-glucose.

The ^{13}C-NMR data (Table 3) of **6** are in accordance with the achived structure, whereby the α- and β-glucose anomers are recognized from the signals at δ 89.2 and δ 94.4, respectively. The attachment of the two dehydrodigallicmono-carboxyl moieties to positions 2 and 3 of the sugar can be identified from the upfield shift of the resonances of the glucose carbons C-1 and C-4 compared to the corresponding signals in D-glucopyranose itself (Breitmaier, 1974). These β-effects range from 0.6 to 2.7 ppm and are in accordance with that reported for C-1 and C-4 in the analogeons compound, nilocitin, 2,3-di-O-galloyl-(α/β)-$^4C_1$-glucopyranose (Nawwar *et al.*, 1982). The upfield shifts of the signals of the glucose carbons C-2 and C-3, in the spectrum of **6**, are caused by both α- and β-effects. Assignments of the remaining glucose carbon resonances were aided by comparison with the recorded chemical shift of nil-

coitin, as well as with those reported for similar esterified glucoses (Haddoch *et al.*, 1982). In this spectrum, the recognition of two distinct resonances for most of the carbons of the two dehydrodigallicmonocarboxyl moieties confirmed the presence of α/β-anomeric mixture of a di-dehydrodigallicmonocarboxyl glucose. Among these carbons, only one of the carboxyl carbons of each dehydrodigallic-monocarboxyl moiety has revealed its signal in duplicate, thus producing four resonances at δ 162.5, 162.58, 162.7 and 162.9, a location which is remarkably upfield when compared with that of the free dehydrodigallic acid carboxyl carbon signals (see experimental) and is obviously due to the esterification of these carboxyl groups with the glucose hydroxyl groups at positions 2 and 3. Each of these upfield carboxyl carbon signals have appeared as a triplet of (J=4.5 Hz) in the gated decoupled ^{13}C-NMR spectrum of **6** indicating that they belong to carboxyl carbon (C-7) which is coupled to H-2 and H-8a protons to result in the detected triplet signals (one for each dehydrodigallicmonocarboxyl moiety in each anomer). The second carboxyl carbons of the dehydrodigallicmonocarboxyl moieties revealed Their signal as two intense downfield signals located at δ 167.4 and 167.47. Thus proving non-esterification of this carboxyl groups. Furthermore, the chemical shifts of the sugar carbons in this spectrum confirmed that the sugar moiety in the molecule of **6** exists in the pyranose form. Consequently, **6** is 2,3-di-O-dehydrodigallic-monocarboxyl-(α/β)-$^4C_1$-glucopyranose, which has not been reported from nature source.

The second new dimeric phenol **7** eluted from the polyamide column by EtOH- H_2O (6:4), was separated as a white amorphous powder, showing characteristic properties (rosy buff fluorescence on PC under UV light which turning yellow with ammonia vapour, high Rfs in aqueous solvents and low Rfs in organic solvents and UV spectral data, Table 1) similar to those of ellagic acid 3,3'-dimethyl ether 4-O-β-glucoside, isolated previously from the roots of *T. nilotica* (Nawwar et al., 1982). However, on electrophoretic analysis (buffer soln. of pH 2, H_2O-HOAc-HCOOH, 89:5.8:2.5, 1 hour, 50 v/cm) of compound **7**, it was shifted towards the anode, thus proving its anionic character. Complete acid hydrolysis of **7** gave ellagic acid 3,3'-dimethylether which precipitated from the cold aqueous acidic hydrolysate, filtered off and was then identified through Co-PC, UV spectral (Table 1), ^{1}H and ^{13}C-NMR analysis. No other phenolics or sugars have been detected in the received hydrolysate, which gave a white precipitate with aqueous $BaCl_2$. Same results are given on partial acid hydrolysis (traced perodically by PC) of the compound, thus proving the presence of sulphate, existing as potassium bisulphate as deduced from the result of atomic absorption analysis of an aqueous solution of **7** as well as from the yellow precipitate given on treating this solution with an aqueous solution of sodium cobaltnitrite (Feigel, 1956). Compound **7** exhibited a molecular weight of 448 as confirmed by ESI-MS (negative mode) which gave an anion at m/z 409 $[M-K]^-$ and a base peak ion at m/z 329 $[M-KSO_3]^-$. These data proved that compound **7** is ellagic 3,3'-dimethyl ether monopotasium sulphate.

To find out the site of attachment of the inorganic radical (KSO_3) to the organic moiety in the molecule of **7**, both ^{1}H and ^{13}C-NMR analysis were then carried out. The recorded ^{1}H-NMR spectrum (DMSO-d_6, room temp.) exhibited two aromatic proton singlets, each 1H at δ 7.6 and 8.1, together with two methoxyl singlets at δ 4.05 and 4.1. Unambiguous assignments could be achieved by comparison with the ^{1}H-NMR spectra of the aglycone, ellagic acid 3,3'-dimethyl ether and that of its 4-O-glucoside as well. This led to the assignment of the aromatic singlets to the H-5' and H-5 protons, respectively in an 4-sulphated ellagic acid 3,3'-dimethyl ether.

Comparison of the ^{13}C-NMR data (Table 3)

of **7** with those of the aglycone, ellagic acid 3, 3'-dimethyl ether reflected 4-O-substitution in the molecule which results in loss of symmetry that characterizes the molecule of the aglycone. The absence of any carbon signals other than those of the 4-O-substituted aglycone **7** in this spectrum confirmed the structure of ellagic acid 3,3'-dimethyl ether 4-mono -potassium sulphate. This compound was isolated for the first time from natural source.

Experimental

General – For NMR analysis, A JEOL EX-270 NMR spectrometer, 270 MHz for ^{1}H-NMR and 67.5 MHz for ^{13}C-NMR, was used with superconducting magnet from Oxford and 5 mm Dual probehead for ^{1}H and ^{13}C-analysis. Typical conditions: Spectral width=4000 Hz for ^{1}H and 15000 Hz for ^{13}C, 32 K data points and a flip angle of 45°. The UV spectra were taken in MeOH using Shimadzu UV-240 spectrometer, ESI-MS (negative mode): The direct flow injection technique was applied, sample in MeOH was introduced (1.25 ml/min) together with MeOH sheath-liquid (5 ml/min) by a Harvard infusion pump 9 ml/min SF6 Sheath-gas into the ESI ion source of a Finnigan Mat 4,600 spectrometer. PC was carried out on Whatman No.1 paper using solvent systems [1] H_2O, [2] HOAc-H_2O (3:47), [3] *n*-BuOH-HOAc-H_2O (4:1:5, top layer), [4] C_6H_6-*n*-BuOH-H_2O-pyridine (1:5:3:3, top layer). Solvent [3] was used for prep. PC on Whatmann No. 3 MM paper and solvents [3] and [4] for sugar analysis.

Plant Material – A sample of *T. tetragyna* heart wood, collected from a mature tree, growing wild at the Coast of Qaroun lake, El-Fayyoum District, Egypt, in May 1996 was authenticated by Dr. Nabiel El-Hadeady, Prof. of Botany, Faculty of Science, Cairo University.

Extraction, isolation and identification – An aqu. EtOH extract (3:1) of the debarked ground heart wood sample was concentrated *in vacuo* and applied to a polyamide 6S-CC (Riedel-De H en AG, Seelze hanover, Germany) and eluted by EtOH-H_2O solvent in decreasing polarities. The successive eluates were individually dried *in vacuo* and subjected to 2D-PC. Compounds **1** (230 mg) and **2** (168 mg) were isolated in the pure state from the H_2O-EtOH (20:80) fraction, through Sephadex LH-20 column fractionation, using H_2O as an eluent. Compound **3** was crystallized from an aq. soln of the dried 30:70 polyamide column fraction. Filtered mother liquor was concentrated, followed by applying the Sepahdex LH-20 column chromatography to produce pure compounds **4** (38 mg) and **5** (97 mg). The new compound **6** was isolated by prep. PC of the material of the 40:60 column fraction, using solvent system [3], the eluted material corresponding to compound **6** was dried *in vacuo*, dissolved in acetone and treated with excess diethyl ether, whereby **6** was precipitated, the process (repeated three times) led to the isolation of a pure sample of **6** (142 mg). Compound **7** was separated from a cold conc. aq. soln. of the 60:40 column fraction. Recrystallization from water yield **7** in pure form (73 mg).

Compounds **8** and **9** were separated from the 90:10 column fraction through polyamide column fractionation using EtOAc saturated with H_2O for elution to yield pure samples of **8** (132 mg) and of **9** (169 mg).

2,3-*di-O-dehydrodigallicmonocarboxyl*-(α/β)-$^4C_1$-*glucopyranose* (**6**): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 819 $[M-H]^-$, Mr 820. Compound **6** yielded glucose and dehydrodigallic acid (Co-PC) on complete acid hydrolysis [40 mg of 6 were refluxed with 25 ml 2N aqu. HCl, 100°, 3 hr]. Dehydrodigallic acid was extracted by EtOAc from the aqu. hydrolysate. Dehydrodigallic acid Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 337 $[M-H]^-$, Mr 338. ^{1}H-NMR (DMSO-d_6), δ: 6.45 (d, *J*=2.5 Hz, H-8b), 6.93 (s, H-8); 7.05 (d, *J*=2.5 Hz, H-2). ^{13}C-NMR (Table 3). Partial acid hydrolysis of 6 [27 mg of 6 were refluxed with 20 ml 0.1 N aqu.

HCl, 100°, 3 hr] yielded monodehydrodigallic-monocarboxyl glucose, Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 499 $[M-H]^-$, Mr 500; complete acid hydrolysis yielded dehydrodigallic acid and glucose (Co-PC). ^{1}H-NMR of 6: Table 2. ^{13}C-NMR of **6** : Table 3.

Ellagic acid 3,3'-dimethyl ether 4-monopotassium sulphate (**7**): Rfs: Table 1. Electrophoretic mobility: 6 cm. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 409 $[M-K]^-$, Mr 448. Compound **7** yielded ellagic acid 3,3'-dimethyl ether on complete or controlled acid hydrolysis [17 mg were hydrolysed completely and 21 mg were hydrolysed partially]. The released aglycone ellagic acid 3,3'-dimethyl ether: Rfs: Table 1; UV (MeOH) λ_{max}: Table 1. ^{1}H-NMR (DMSO-d_6) δ: 7.52 (s, 2H, H-5 & H-5'), 4.08 (s, OMe-3 & OMe-3'). ^{13}C-NMR: Table 3. ^{1}H-NMR of **7**: δ 7.50 (s, H-5'), 8.1 (s, H-5), 4.03 (s, OMe-3'), 4.1 (s, OMe-3). ^{13}C-NMR of **7**: Table 3.

Known compounds: *Gallic acid* (**1**): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 169 $[M-H]^-$, Mr 170; ^{1}H-NMR (DMSO-d_6): δ 6.9 (s, 2H, H-2 & H-6). *Gallic acid 4-methylether* (**2**): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 183 $[M-H]^-$, Mr 184; ^{1}H-NMR (DMSO-d_6): δ 6.92 (s, 2H, H-2 & H-6), 3.76 (s, 3H, methoxyl group). *Syringic acid* (**3**): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 197 $[M-H]^-$, Mr 198; ^{1}H-NMR (DMSO-d_6): δ 7.15 (s, 2H, H-2 & H-6), 3.8 (s, 6H, OCH_3-3, OCH_3-5). Ferulic acid (**4**): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 193 $[M-H]^-$, Mr 194; ^{1}H-NMR (DMSO-d_6): δ 6.32 (d, J=15 Hz, H-β), 6.8 (d, J=7.5 Hz, H-5), 7.08 (dd, J=7.5 Hz and 2 Hz, H-6), 7.24 (d, J=2 Hz, H-2), 7.52 (d, J=15 Hz, H-α), 3.8 (s, OCH_3). Isoferulic acid (5): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 193 $[M-H]^-$, Mr 194; ^{1}H-NMR (DMSO-d_6): δ 6.22 (d, J=15 Hz, H-β), 6. 95-7.10 (AB system, H-5 and H-6), 7.08 (d, J =2.5 Hz, H-2), 7.42 (d, J=15 Hz, H-α), 3.8 (s, OCH_3). *Ellagic acid 3,3'-dimethyl ether* (**8**): Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 329 $[M-H]^-$, Mr 330; ^{1}H-NMR (DMSO-d_6): δ 10.6 (br.s, OH-4, OH-4'), 7.52 (s, 2H, H-5 & H-5'), 4.08 (s, 6H, OCH_3-3, OCH_3-3'). *Ellagic acid* (**9**):Rfs: Table 1. UV (MeOH) λ_{max}: Table 1. ESI-MS, negative ion: m/z 301 $[M-H]^-$, Mr 302; ^{1}H-NMR (DMSO-d_6): d 7.5 (s, 2H, H-4 & H-4').

Acknowledgement

This work was executed through a project of Deutsch Forschunges-gemeinschaft, No. Wi 383/6-2, for which I would like to express my deep gratitude.

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(Accepted November 17, 1997)