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Unique Phenolic Sulphate Conjugates from the Flowers of *Tamarix amplexicaulis*

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Abstract – The unique sulphated phenolics, gallic acid 3-methyl ether 5-potassium sulphate, isoferulic acid 3-potassium sulphate, and ellagic acid 4,4'-dimethyl ether 3-potassium sulphate have been isolated from the flowers of *Tamarix amplexicaulis* Ehrenb. (Tamaricaceae). The hitherto unknown natural phenolic acid, gallic acid 3-methyl ether, together with the known phenolic, gallic acid, gallic acid 4-methyl ether, isoferulic acid, ferulic acid, ellagic acid, and ellagic acid 4,4'-dimethyl ether have been also separated and characterized. The structures were established by conventional methods, including electrophoretic analysis and cofirmed by ESI-MS, ^{1}H- and ^{13}C-NMR.

Key words – *Tamarix amplexicaulis*, Tamaricacaea, flowers, sulphated phenolics, gallic acid 3-methyl ether 3-potassium sulphate, isoferulic acid 3-potassium sulphate, ellagic acid 4,4'-dimethyl ether 3-potassium sulphate, ESI-MS, ^{1}H- and ^{13}C-NMR.

Introduction

The distinct feature which characterizes the constitutive phenolics of *Tamarix* plants, is the presence, in their extracts, of partially methylated hydroxycinnamic acids (e.g. ferulic and isoferulic acids), gallic acid (e.g. gallic acid 4-methyl ether), and ellagic acid (e.g. ellagic acid 3,3'-dimethyl ether). These acids were found to exist in both free and conjugated forms (Nawwar *et al.*, 1982 & 1984a; Souleman *et al.*, 1991 and Barakat *et al.*, 1987). Among these conjugates, the 4-potassium sulphate of ellagic acid 3,3'-dimethyl ether, recently isolated from the woods of *T. tetragyna* (Hussein, 1997) was quite interesting as it represents the first natural gallic acid derivative coupled at one of its phenolic OH groups to a potassium bisulphite radical. Generally, phenolic sulphates are rare in nature and of the few of these conjugates which have been previously fully characterized the 2',3'- and 4'-sulphates of 1-caffeoylglucose, found in different ferns and the 3-sulphate of caffeic acid, detected in several members of the Polygonaceae (Barron *et al.*, 1988) could be noted. In our series of studies on the constitutive phenolics of Egyptian medicinal plants, we have previously investigated extracts of three Tamaricaceous plants, namely *T. aphylla, T. nilotica* and *T. tetragyna* (Nawwar *et al.*, 1982, 1984a, b & c, and 1994a & b; Souleman *et al.*, 1991; Barakat *et al.*, 1987 and Hussein, 1997).

The present paper deals with the isolation and structure elucidtion of the new natural phenolics, gallic acid 3-methyl ether (**3**), gallic acid 3-methyl ether 5-potassium sulphate (**4**), isoferulic acid 3-potassium

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sulphate (**7**), and ellagic acid 4,4'-dimethyl ether 3-potassium sulphate (**10**) from the aqueous ethanolic (3:1) flower extract of *Tamarix amplexicaulis* Ehrenb. (=*T. paucio-vulata* J. Gay. teste Baum, *T. balansae* J. Gay ex batt. et Trab, *T. traubutii* Maire), a bushy tree with fleshy small scale-like leaves and flowers in long dense racemes, which grows wild in the Nile delta and in all the deserts of Egypt as well. The known phenolics, gallic acid (**1**), isoferulic acid (**2**), ferulic acid (**5**), gallic acid 4-methyl ether (**6**), ellagic acid (**8**), and ellagic acid 4,4'-dimethyl ether (**9**), also were isolated and identified.

Results and Discussion

Compounds **1-10** were isolated from an aqueous ethanolic flower extract of *T. amplexicaulis* by applying a combination of CC on polyamide followed by Sephadex LH-20. The known compounds **1, 2, 5, 6, 9** and **10** showed chromatographic, UV absorption and hydrolytic data identical with those reported for gallic acid, isoferulic acid, ferulic acid, gallic acid 4-methyl ether, ellagic acid, and ellagic acid 4,4'-dimethyl ether, respectively. These structures were confirmed by EI-MS, ^{1}H- and ^{13}C-NMR spectral analysis (Nawwar *et al.*, 1982; 1997 and Sato, 1987).

The new compound (**3**) was isolated as an amorphous off-white powder from the EtOH/H_2O (2:8) fraction of the major polyamide column by refractionation over Sephadex LH-20 column, using *n*-BuOH saturated with H_2O for elution. It showed chromatographic properties (Table 1) similar to those of gallic acid derivatives [itense blue spot on PC uder short UV light, which turned dark blue in visible light when sprayed with $FeCl_3$ and reddish brown when sprayed with KIO_3, specific for gallic acid derivatives (Haddock *et al.*, 1982)]. Compound **3** possesses a molecular weight (Mr) of 184 amu corresponding to a molecular ion, M^+: 184 in EI-MS and exhibited UV absorption maxima, in MeOH at 262 and 292 (inflection nm.). It resisted normal acid hydrolysis, thus recovered unchanged after being refluxed with 2N aqueous HCl at 100°C for 3 hours. However, it yielded gallic acid (CoPC, UV and ^{1}H-NMR) on hydrolytic cleavage by heating under reflux with HI/$(AcO)_2O$ at 145°C for 1/2 an hour. This data suggested compound **3** to be gallic acid mono methyl ether. In the ^{1}H-NMR spectrum, recorded for **3** (DMSO-d_6, room temp.), only two meta coupled (J=2.5 Hz) aromatic proton resonances, each integrated to one proton revealed themselves at δ 7.24 and 7.15 ppm, thus proving a departure of the high symmetry which characterizes the structure of gallic acid. The presence, in the same spectrum, of only one methoxyl proton resonance, appearing as singlet at δ 3.8 ppm wolud therefore prove that **3** is gallic acid 3-methyl ether, which is the only unsymmetric mono methyl ether of gallic acid. Consequently, the resonance located at δ 7.24 ppm is assigned to the H-2 proton, while that located at δ 7.15 ppm is attributed to the H-6 proton in the molecule of compound **3**.

^{13}C-NMR spectral analysis finally confirmed the achieved structure. The received spectrum revealed eight distinct carbon resonances (see experimental), with chemical shift values which are in close agrement with the values calculated for gallic acid 3-mono methyl ether by applying the substituent additive rules (Kalinowski *et al.*, 1984) on the ^{13}C-NMR data of gallic acid, itself, thus confirming the structure of **3** to be gallic acid 3-mono methyl ether, a natural phenolic which has not reported before in the literature.

The new compound (**4**) was isolated as an amorphous white powder from the EtOH/H_2O (3:7) fraction of the polyamide major column fraction using Sephadex LH-20 column fractionation and H_2O as an eluent. It exhibited the known chromatographic and

Table 1. Chromatographic, electrophoretic and UV data of compouds **1-10**

Compound	Chromatographic properties R_f- (×100)			Electrophoretic mobility*	UV spectral data λ_{max} (MeOH) nm
	H_2O	HOAc	4:1:5		
1-Gallic acid	53	56	78	-	272
2-Isoferulic acid	33	50	92	-	240, 295, 325
3-Gallic acid 3-methyl ether	52	54	85	-	272
4-Gallic acid 3-methyl ether 5-$OKSO_3$	97	86	51	6	266, 295**
5-Gallic acid 4-methyl ether	51	49	85	-	270
6-Ferulic acid	34	55	90	-	235, 324
7-Isoferulic acid 3-$OKSO_3$	76	68	74	5.2	292, 307
8-Ellagic acid	0	0.9	48	-	255, 361
9-Ellagic acid 4,4'-dimethyl ether	0	16	50	-	244**, 255, 360
10-Ellagic acid 4,4'-dimethyl ether 3-$OKSO_3$	66	52	43	5	246, 255**, 344, 384

*: Electrophoretic analysis: on Whatman No. 3 MM paper, buffer sol. of pH 2, H_2O-HOAc-HCOOH (89:8.5:2.5), 2 hr, 50 v/cm.
**: Inflection.

UV absorption (MeOH) features which characterize gallic acid derivatives (Table 1). However, its exceptionally high $R_{f\text{-}s}$ in aqueous solvents H_2O (0.95) was quite abnormal and could only be interpreted in terms of ionic property. Electrophoretic analysis (on 3MM Whatman paper, HOAc-HCO_2H buffer, of pH 2, 90 minutes, 50 v/cm) supported this view and migration of **4** towards the anode proved its anionc property. Mild acid hydrolysis (aqueous 0.1N HCl at 100°C, 5 minutes) of **4** yielded gallic acid 3-methyl ether (CoPC, ^{1}H- and ^{13}C-NMR) as the only released phenolics. The hydrolysate was found to be free from any sugar material (CoPC), but it gave a heavy white precipitate with aqueous $BaCl_2$, thus proving the presence of a sulphate in the molecule of **4**. That the sulphate is existing in the form of potassium bisulphite was then confirmed by the results of atomic absorption analysis as well as by the yellow precipitate given on treatig the aqueous solution of **4** by sodium cobltinitrite (Feigel, 1956). On negative FAB-MS, compound **4** was found to possess an anion signal at m/z 263, thus proving its structure to be gallic acid 3-methyl ether mono potassium sulphate. To find out the site of attachment of the sulphate substituent in the molecule of **4**, ^{1}H- and ^{13}C-NMR spectral analyses were then engaged. The received ^{1}H-NMR spectrum (DMSO-d_6, room temp.) was similar to that of the parent compound, gallic acid 3-methyl ethet. however, a distinction can be made with respect to the chemical shift of one of the two aromatic meta coupled doublets. This value (7.55 ppm) reflected a downfield shift of the corresponding resonance, obviously due to sulphate substitution of the vicinal (ortho) hydroxyl group, which therefore must be OH-5. The chemical shift values of the remaining aromatic proton resonance and that of the methoxyl proton resonances (7.24 and 3.76 ppm, respectively) were similar, as expected to those of the corresponding resonances in the spectrum of the parent compound. Further confirmation of the achieved structure of **4** was then received through ^{13}C-NMR spectral analysis. In this spectrum, the chemical shift values of the detected eight carbon resonances were in good agrement with a calculated set of chemical shifts, obtained by applying the

substituent additive rules on the ^{13}C-MR data of gallic acid 3-methyl ether and by taking into consideration that the effect of a sulphate substituent on the shifts of the carbon resonance is similar to that of acetylation or glycosylation (Nawwar *et al.*, 1981). Consequently, compound **4** is confirmed to be gallic acid 3-methyl ether 5-potassium sulphate, a phenolic metabolite which has not been reported before in nature.

The third new compound (**7**) was isolated as cream-coloured amorphous powder from the EtOH/H_2O (9:1) fraction of the polyamide major colum through Sephadex LH-20 column fractionation, using *n*-BuOH saturated with H_2O for elution. Its chromatographic and electrophoretic behaviour (Table 1) suggested that it is an isoferulic acid potassium sulphate derivative (distinctive pale pink spot on PC under UV light which turned orange-yellow when fumed with ammonia vapour, high R_f in H_2O and migration towards the anode on electrophoretic analysis). The UV spectral properties of **7** (λ_{max}^{MeOH} nm: 292, 307; +HCl: 294, 315) showed that the phenolic hydroxyl group (OH-3) of isoferulic acid (λ_{max}^{MeOH} nm: 240, 295, 325) must be substituted. On negative FAB-MS, compound **7** exhibited an anionic signal at m/z 273, thus provig its structure as isoferulic acid mono potssium suphate. Mild acid hydroysis of **7** yieded only isofrulic acid (CoPC, UV, ^{1}H- and ^{13}C-NMR analysis). The hydrolysate gave a heavy white precipitate with aqueous $BaCl_2$, thus indicating the presence of a sulphate which was proved to exist as potassium bisulphite in the molecule of **7** (detection of potassium ion in atomic absorption analysis and formation of yellow precipitate on addition of aqueous sodium cobaltinitrite to the aqueous solution of the compound).

^{1}H- and ^{13}C-NMR analysis lent further support to this conclusion. In the recorded ^{1}H-NMR spectrum (DMSO-d_6, room temp.), substitution at the hydroxyl group no. 3 of the parent compound was evidenced by the recognizable downfield shift ($\Delta\delta$=0.56 ppm) of the meta-coupled H-2 proton resonance on comparison with the corresponding resonance in the ^{1}H-MR spectrum of isoferulic acid itself. Other signal in the recorded spectrum of **7** possess chemical shift values which were in accordance with the proposed structure as isoferulic acid 3-monopotassium sulphate. In the ^{13}C-NMR spectrum, substitution with sulphate was concluded from the upfield shift ($\Delta\delta$=3.9 ppm) detected for the resonance of C-3 as well as from the accompanying downfield shifts ($\Delta\delta$=5.3 and 2. 4 ppm) of the resonance of the ortho carbons (C-2 and C-4, respectively), all in comparison with the chemical shifts of the corresponding resonances in the spectrum of the free acid (see experimental). This data finally confirmed the structure of compound **7** to be isoferulic acid 3-mono potassium sulphate, an additional new natural phenolic.

The last new compound (**10**), eluted from the major polyamide column by EtOH was purified by refractionation on Sephadex LH-20 column and elution with *n*-BuOH saturated with H_2O which afforded an off-white amorphous powder of chromatographic and electrophoretic properties (Table 1, fluorescent white spot on PC under UV light, turning yellow when fumed with ammonia vapour, high R_f in H_2O, and migration towards the anode on electrophoretic analysis) and UV spectral features in MeOH (Table 1) similar to those reported for ellagic acid derivatives (Nawwar *et al.*, 1982 and Hussein, 1997). this view was supported by negative FAB-MS analysis, whereby, an anio peak at m/z 409 and a base peak ion at m/z 329, corresponding to ellagic acid dimethyl ether mono sulphate, and ellagic acid dimethyl ether, respectively were detected in the recorded spectrum. Compound **10** was totaly hydrolysed after being refluxed together with 0.1N aqueous HCl at 100°C for 5 minutes to yield ellagic

acid 4,4'-dimethyl ether only [UV, ^{1}H- and ^{13}C-NMR spectral analysis (Sato, 1987)]. The hydrolysate gave a positive sulphate test with aqueous $BaCl_2$, while the presence of potassium in the molecule of **7** was deduced from the results of atomic absorption analysis and that of the treatment with sodium cobaltinitrite as well.

The received ^{1}H-NMR spectrum of **10** (DMSO-d_6, room temp.) was similar to that reported for the analgous compound, ellagic acid 3,3'-dimethyl ether 4-potassium sulphate (Hussein, 1997). However, the ^{13}C-NMR spectrum of **10** was quite different from that of the analgous (see experimental) and finally confirmed the structure of which to be ellagic acid 4,4'-dimethyl ether 3-potassium sulphate, a phenolic compound which has not been reported previously, to occur in nature.

Experimental

General – For NMR analysis, A Jeol EX-270 NMR spectrometer, 270 M Hz 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. For FAB-MS (negative mode) a MM 7070 E mass spectrometer (VG analytical) has been used. PC wa 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 together with solvent [4] for sugar analysis.

Plant Material – A sample of *T. amplexicaulis* flowers were collected from a mature tree, growing in the marshy habitats near the Mediterranean coasts, 15 km east of El-Kantara city in sinai proper, Egypt, in March 1996 and authenticated by dr. N. El-Hadeady, prof. of Botany, faculty of Science, Cairo Uiversity.

Extraction, isolation and identification – An aqu. EtOH extract (3:1) of the fresh flower collected sample, concentrated *in vacuo* was applied to a polyamide 6S CC (Riedel-De Hen AG, Seelze Hannover, Germany) and eluted by H_2O followed by H_2O EtOH mixts. of decreasing polarities to yield nine fractions (I-IX) which were individually subjected to 2D-PC. Compoud **1** (143 mg) and **2** (125 mg) were isolated pure from the EtOH-H_2O (10:90) fraction by CC over Sephadex LH-20 using H_2O for elution. **3** was separated (245 mg) from fr. III (EtOH: H_2O, 20:80) by CC over Sephadex LH-20 using *n*-BuOH saturated with water as solvent system and **4** was obtained (288 mg) from fr. IV (EtOH:H_2O, 30:70) by Sephadex LH-20 using H_2O as an eluent. **5** (68 mg) and **6** (47 mg) were isolated individually from fr. V (EtOH:H_2O) by Sephadex LH-20 using *n*-BuOH saturated with H_2O for elution. **7** (156 mg) and **8** (132 mg) each was separated pure from fr. VII (EtOH:H_2O, 80:20) through crystallisation of its dried material from pyridine to afford yellow crystal of **7**. The mother liquor, dried *in vacuo* was applied to a Sephadex LH-20, using MeOH for elution to yield crude **8**. Purification was then engaged by crystallization from MeOH (off-white crystals). **9** (112 mg) was separated from fr. VIII (EtOH: H_2O, 90:10) by refractionation over Sephadex LH-20 using *n*-BuOH saturated with H_2O for elution and **10** (94 mg) was obtained from the last column fraction IX (EtOH) through sephadex LH-20 column fractionation using *n*-BuOH saturated with H_2O as an eluent.

Kown compounds: Gallic acid (1): R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. EI-MS: m/z 170 [M^+]. ^{1}H-MR (DMSO-d_6): δ 6.9 (s, 2H, H-2 & H-6). ^{13}C-NMR: Table 2. **Isoferulic acid (2):** R_fs: Table 1. UV (MeOH) λ_{max}:

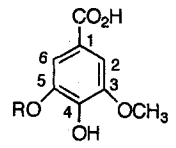
Table 2. ^{13}C-NMR chemical shifts (δ ppm) of compound **1-10**

C. No.	1	2	3	4	5	6	7	8	9	10
1	120.6	127.2	120.9	119.4	124.4	125.9	126.9	112.3	107.2	107.7
2	108.8	113.8	105.2	108.5	108.5	109.2	114.2	136.4	140.6	143.6
3	145.5	146.7	148.2	148.7	150.6	147.8	146.7	140.2	136.1	128.9
4	138.1	147.1	139.5	141.1	139.7	146.7	150.2	153.0	150.0	154.6
5	145.5	112.7	145.5	143.7	150.6	115.7	112.5	111.4	106.8	107.9
6	108.8	122.4	111.2	117.0	108.5	123.0	121.4	107.7	113.2	113.1
7	167.7	-	167.1	167.2	166.9	-	-	159.2	158.9	158.6
a	-	146.2	-	-	-	144.6	144.9	-	-	-
b	-	116.9	-	-	-	114.7	114.6	-	-	-
g	-	167.4	-	-	-	167.5	167.0	-	-	-
1′	-	-	-	-	-	-	-	112.3	107.2	107.7
2′	-	-	-	-	-	-	-	136.4	140.6	141.1
3′	-	-	-	-	-	-	-	140.2	136.1	134.8
4′	-	-	-	-	-	-	-	153.0	150.0	147.7
5′	-	-	-	-	-	-	-	111.4	106.8	107.9
6′	-	-	-	-	-	-	-	107.7	113.2	111.8
7′	-	-	-	-	-	-	-	159.2	158.9	158.7
MeO	-	55.95	56.1	56.6	59.6	55.9	55.7	-	56.65	56.9
MeO	-	-	-	-	-	-	-	-	56.65	56.2

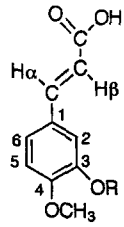
Table 1. EI-MS: m/z 194 [M$^+$]. ^{1}H-NMR (DMSO-d_6): δ 6.22 (d, J=15 Hz, H-β), 6.95-7.10 (AB system, H-5 and H-6), 7.08 (d, J= 2.5 Hz, H-2), 7.42 (d, J=15 Hz, H-α), 3.8 (s, 3H, OCH_3). ^{13}C-NMR Table 2. **Ferulic acid (5):** R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. EI-MS: m/z 194 [M$^+$]. ^{1}H-MR (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, 3H, OCH_3). ^{13}C-NMR Table 2. **Gallic acid 4-methyl ether (6)**: R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. EI-MS: m/z 184 [M$^+$]. ^{1}H-MR (DMSO-d_6): δ 6.92 (s, 2H, H-2 and H-6), 3.76 (s, 3H, OCH_3). ^{13}C-NMR Table 2. **Ellagic acid (8)**: R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. EI-MS: m/z 302 [M$^+$]. ^{1}H-MR (DMSO-d_6): δ 7.5 (s, 2H, H-5 and H-5'). ^{13}C-NMR Table 2. **Ellagic acid 4,4'-dimethyl ether (9):** s: Table 1. UV (MeOH) λ_{max}: Table 1. EI-MS: m/z 330 [M$^+$]. ^{1}H-MR (DMSO-d_6): δ 7.7 (s, 2H, H-5 and H-5'), 3.96 (s, 6H, 4-OCH_3 and 4'-OCH_3). ^{13}C-NMR Table 2.

Gallic acid 3-monomethyl ether (3) – R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. EI-MS: m/z 184 [M$^+$]. Compound **3** recovered unchanged (Co-PC) on normal acid hydrolysis (22 mg of **3** were heated under reflux with 15 ml 2N aqu. HCl at 100°C, 3 hr). 3 yielded gallic acid (Co-PC, UV, ^{1}H-NMR). On demethylation with HI/$(AcO)_2O$ (31 mg of **3** were refluxed over a heating mantel with 1/2 ml conc. HI and 1/2 ml $(AcO)_2O$ at 145°C, 1/2 hr, the reaction mixture was diluted by adding 20 ml aqu. saturated $NaHSO_3$. The released phenol was extracted with ethyl acetate. ^{1}H-NMR (DMSO-d_6) δ 7.15 (d, J=2.5 Hz, H-6), 7.24 (d, J=2.5 Hz, H-2), 3.8 (s, 3H, 3-OCH_3). ^{13}C-NMR Table 2.

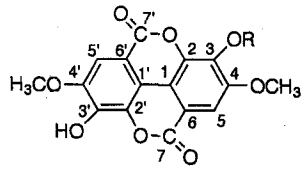
Gallic acid 3-monomethyl ether 5-monopotassium sulphate (4) – R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. Electrophoretic



Compound **3** : R=H
Compound **4** : R=KSO_3



Compound **2** : R=H
Compound **7** : R=KSO_3



Compound **9** : R=H
Compound **10** : R=KSO_3

mobility: Table 1. mild acid hydrolysis of **4**, (38 mg of **4** refluxed with 15 ml aqu. 0.1 N HCl at 100°C, 5 min.), yielded gallic acid 3-methyl ether (Co-PC, ^{1}H- and ^{13}C-NMR). FAB-MS, negative ion: m/z 263 $[M-K]^-$, Mr 302. ^{1}H-NMR (DMSO-d_6): δ 7.55 (d, J=2 Hz, H-6), 7.24 (d, J=2 Hz, H-2), 3.76 (s, 3H, 3-OCH_3). ^{13}C-NMR Table 2.

Isoferulic acid 3-monopotassium sulphate (7) – R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. Electrophoretic mobility: Table 1. mild acud hydrolysis of **7**, (47 mg of **7** refluxed with 20 ml aqu. 0.1 N HCl at 100°C, 5 min.), yielded isoferulic acid (Co-PC, UV, ^{1}H- and ^{13}C-NMR). FAB-MS, negative ion: m/z 273 $[M-K]^-$, Mr 312. ^{1}H-NMR (DMSO-d_6): δ 7.64 (d, J=2.5 Hz, H-2), 7.45 (d, J=15 Hz, H-a), 7.32 (dd, J=7.5 Hz, J=2.5 Hz, H-6), 7.0 (d, J=7.5 Hz, H-5), 6.18 (d, J=15 Hz, H-b). ^{13}C-NMR Table 2.

Ellagic acid 4,4'-dimethyl ether 3-monopotassium sulphate (10) – R_fs: Table 1. UV (MeOH) λ_{max}: Table 1. Electrophoretic mobility: Table 1. mild acid hydrolysis of **10**, (56 mg of **10** refluxed with 15 ml aqu. 0.1 N HCl at 100°C, 5 min.), yielded ellagic acid 4, 4'-dimethyl ether (UV, ^{1}H- and ^{13}C-NMR). FAB-MS, negative ion: m/z 409 $[M-K]^-$, Mr 448 and at m/z 329 $[M-KSO_3]^-$. ^{1}H-NMR (DMSO-d_6): δ 7.64 (s, H-5), 7.60 (s, H-5'), 3.94 (s, 3H, OCH_3), 4.0 (s, 3H, OCH_3). ^{13}C-NMR Table 2.

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