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NILOTICOL, A PHENOLIC GLYCERIDE AND TWO PHENOLIC ALDEHYDES FROM THE ROOTS OF *TAMARIX NILOTICA*

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Key Word Index—*Tamarix nilotica*; Tamaricaceae; roots; phenolic glyceride; 1-feruloyl-3-pentacosanoylglycerol; phenolic aldehydes; isoferulaldehyde; ferulaldehyde; ^{13}C NMR.

Abstract—From the petrol extract of the roots of *Tamarix nilotica* the novel glyceride, niloticol, and the hitherto unknown aldehyde, isoferulaldehyde, together with the known aldehyde, ferulaldehyde, were isolated.

INTRODUCTION

In a previous paper we have reported the occurrence of five gallic acid derivatives, a lignan (syringaresinol) and isoferulic acid in the benzene and ethyl acetate extract of the debarked roots of *Tamarix nilotica* [1]. In the present paper, characterization of the new phenolic glyceride, 1-feruloyl-3-pentacosanoylglycerol, for which we suggest the name niloticol (**1**), the unknown aldehyde, 3-hydroxy-4-methoxycinnamaldehyde (isoferulaldehyde, **2**), and its known isomer, 4-hydroxy-3-methoxycinnamaldehyde (ferulaldehyde, **3**), all isolated from the petroleum extract of the same plant part, are described. The new glyceride is interesting because it contains a normal fatty acid moiety. Previously reported phenolic glycerides of similar structures contain ω-hydroxyfatty acid moieties [2]. Furthermore, this is the first reported occurrence of isoferuladehyde. Its isomer, ferulaldehyde (coniferaldehyde) is a known degradation product of lignins [3]. The parent aldehyde 3,4-dihydroxycinnamaldehyde was reported to occur in *Phytolacca americana* [4].

RESULTS AND DISCUSSION

1, contaminated with **2** and **3**, was precipitated as an amorphous white powder from a concentrated petrol extract of the roots, by standing overnight at 4°. Isolation and identification of individual compounds were achieved through silica gel CC, followed by a series of PTLC of the received crude eluate which desorbed from the column.

Niloticol (**1**) was separated as colourless cubic crystals from acetone and exhibited no optical activity when dissolved in chloroform. Its colour on the chromatograms under UV light (blue, turning bright blue with ammonia) and its UV data are closely similar to those of ferulic acid [5]. The elemental analysis and MS data ($[M]^+$ at m/z 632) showed the molecular formula of **1** to be $C_{38}H_{64}O_7$. On alkaline hydrolysis, **1** yielded ferulic acid (CoPC, UV data, ^{1}H and ^{13}C NMR); pentacosanoic acid (GC of the methyl ester, [6]) and glycerol (CoPC). These data suggest a monoferuloyl monopentacosanoyl glycerol structure for **1**. Formation of a diacetate and a monotrimethylsilyl ether [7] proved the presence of one alcoholic and one phenolic group in **1**. The ^{1}H NMR of **1**, measured at 100 MHz in DMSO-d_6 showed signals assignable to the feruloyl, pentacosanoyl and glycerol protons. In this spectrum, the multiplet in the aliphatic region at δppm 3.65, integrated to one proton was assigned to a glycerol methine proton, bearing a free OH group (shifted downfield by *ca* 1.7 ppm on acetylation of **1**), while the AB-type multiplet at δppm 4.15 wa assigned to the four methylene protons of a 1,3-diesterified glycerol. Also, the measured coupling constant (15 Hz) for the doublet signals of the α- and β-feruloyl protons ensured a *trans* form for this moiety. Consequently, **1** is 1-(*E*)-feruloyl-3-pentacosanoylglycerol. The ^{13}C NMR spectrum of **1**, measured at 25 MHz in DMSO-d_6 confirmed this structure. The spectrum proved the presence of a free OH group at position 2 of the glycerol moiety (C-2 at δ ppm 68.4) and proved esterification at positions 1 and 3 of the same moiety (C-1 and C-3 at δppm 64.63 and 65.05).

Isoferulaldehyde (**2**) was isolated as a pale yellow oil which appears on TLC under UV light as a dull yellow spot, turning brownish yellow with ammonia and gave UV data similar to those of isoferulic acid [8]. The IR spectrum of (**2**) showed absorption bands at 1660 and 1610 cm^{-1}, consistent with α, β unsaturated carbonyl group. The ^{1}H NMR spectrum of **2**, measured in $CDCl_3$, with a doublet at δppm 9.6 (1H, J = 8 Hz), a doublet at 7.38 (1H, J = 16 Hz) and a double doublet at 6.55 (1H, J = 8 and 16 Hz) indicated the presence of a *trans* CH=CH–CHO moiety. In this spectrum, the presence of a 1,3,4-trisubstituted benzene moiety is indicated by the three signals located at δppm 7.16 (1H, *d*, J = 2 Hz), 6.8 (1H, *dd*, J = 2 and 7 Hz) and 6.76 (1H, *d*, J = 7 Hz). Also the presence of a methoxyl group was proved by the signal at δppm 3.8. The MS spectrum of **2** showed a molecular ion peak at m/z 178 and a fragmentation pattern consistent with a monomethoxy monohydroxy cinnamaldehyde. On the other hand, spots of **2** on different TLC were treated with ammoniacal silver nitrate solution, left to dry and dipped in different solvent systems, whereby isoferulic acid was detected (CoPC, UV and MS data).

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Thus 2 is (*E*)-3-hydroxy-4-methoxycinnamaldehyde. The ^{13}C NMR spectrum of 2 confirmed this structure [9, 10].

Ferulaldehyde (3) was isolated as a pale yellow oil of chromatographic properties similar to those of isoferulaldehyde and UV data similar to those of ferulic acid. Its structure as (*E*)-4-hydroxy-3-methoxy cinnamaldehyde [(*E*)-ferulaldehyde] was proved by reduction test, MS, ^{1}H and ^{13}C NMR analysis.

EXPERIMENTAL

^{1}H and ^{13}C NMR chemical shifts were measured relative to TMS. Typical conditions: spectral width 5000 Hz, 8k data points and a flip angle of 45°. TLC was carried out on silica gel plates of 20 mm thickness for normal investigation and of 25 mm thickness for prep. TLC. Solvent systems for TLC: 1—ether–*n*-hexane, 3:7; 2—EtOAc–*n*-hexane, 2:8; 3—BAW (*n*-BuOH–HOAc–H_2O, 4:1:5, upper layer).

Plant material and fractionation. Proceeding as described in ref. [1], the concentrated petrol (40/60°) extract was left to cool overnight at 4°. The white amorphous powder thus precipitated was filtered off, applied to a silica gel (S, 0.063–0.2 mm for CC, Riedel-De Haën AG Seelze-Hannover) column and eluted with *n*-hexane–EtOAc (19:1) to eliminate the nonphenolic constituents.

Isolation and identification. The phenolics were desorbed as a fluorescent band (under UV light), dried *in vacuo* and subjected to repeated PTLC, whereby pure samples of 1, 2 and 3 were individually obtained.

Niloticol 1. R_f values: 0.32 (solvent 1), 0.85 (solvent 2), 0.98 (solvent 3). UV λ_{max}^{MeOH} nm: 235, 245, 300 (inflection), 325. EI-MS, *m/z* (%): 632 (45), 269 (37), 194 (10), 177 (26), 137 (8). Alkaline hydrolysis of 1 (5% alcoholic KOH, 100°, 2 hr, followed by acidification) gave: (a) pentacosanoic acid, extracted with petrol (40/60°), dried and esterified by MeOH as described in ref. [4]. GC of the methyl ester (Varian 3700, standard conditions) showed t_R 69 min; (b) ferulic acid, extracted with ether, R_f values: 0.11 (solvent 1), 0.22 (solvent 2), 0.94 (solvent 3), UV λ_{max}^{MeOH} nm: 235, 295 (inflection), 324, ^{1}H NMR: δ(ppm) 6.32 (*d*, *J* = 15 Hz, β-H), 6.8 (*d*, *J* = 7 Hz, 5-H), 7.08 (*dd*, *J* = 7 and 2 Hz, 6-H), 7.24 (*d*, *J* = 2 Hz, 2-H), 7.52 (*d*, *J* = 15 Hz, α-H), 3.8 (*s*, OCH_3), ^{13}C NMR: δ(ppm) 168.2 (C-γ), 149.2 (C-3), 148.0 (C-4), 125.9 (C-1), 122.9 (C-6), 115.7 (C-5), 111.3 (C-2), 144.5 (C-α), 115.7 (C-β); (c)-glycerol, extracted with EtOAc, CoPC [11]. Acetylation of 1 by acetic anhydride–pyridine [12] gave an acetate which crystallized from acetone: mp (uncorr.) 68°, UV λ_{max}^{MeOH} nm; 225 (inflection), 240, 280, 315 (inflection), EI-MS, *m/z* (%): 716 (85), 494 (6), 311 (38), 219 (32), ^{1}H NMR: δ(ppm) 0.92 (broad *t*, terminal pentacosanoic CH_3), 1.2 [intense broad *s*, $(CH_2)_{21}$ in pentacosanoic], 1.65 (*m*, CH_2 β to the C=O in pentacosanoic), 2.28 (*t*, *J* = 7 Hz, CH_2 α to the C=O in pentacosanoic), 2.06 (*s*, CH_3CO), 2.1 (*s*, CH_3CO), 3.8 (*s*, aromatic OCH_3), 4.1 (*m*, glycerol H_2-1 and H_2-3), 5.4 (*m*, glycerol H-2), 6.26 (*d*, *J* = 15 Hz, feruloyl H-β), 6.88–7.05 (*m*, feruloyl H-2, H-5, H-6), 7.6 (*d*, *J* = 15 Hz, feruloyl H-α), 3.84 (OCH_3). On silylation [7], only the phenolic OH of 1 was derivatized, EI-MS, *m/z* (%): 704 (67), 341 (28), 249 (100). ^{1}H NMR of 1, pentacosanoyl moiety: δ(ppm) 0.84 (broad *t*, terminal CH_3), 1.2 [intense broad *s*, $(CH_2)_{21}$], 1.8 (*m*, CH_2 group β to the C=O), 2.3 (*t*, *J* = 7 Hz, CH_2 group α to the C=O); feruloyl moiety: δ(ppm) 6.28 (*d*, *J* = 15 Hz, H-β), 6.88 (*d*, *J* = 7 Hz, H-5), 7.08 (*dd*, *J* = 7 and 2.5 Hz, H-6), 7.32 (*d*, *J* = 2.5 Hz, H-2), 7.64 (*d*, *J* = 15 Hz, H-α), 3.92 (*s*, OMe); glycerol moiety: δ(ppm) 3.65 (*m*, H-2), 4.15 (AB-type *m*, 4 protons at C-1 and C-3). ^{13}C NMR of 1, pentacosanoyl moiety: δ(ppm) 173.9 (C=O), 34.1 (C-α), 26.0 (C-β), 14.0 (Me terminal), intense broad signal centred at 29.6 (CH_2 groups); feruloyl moiety: δ(ppm) 167.4 (C=O), 147.8 (C-3), 146.7 (C-4), 144.6 (C-α), 125.9 (C-1), 123.0 (C-6), 115.7 (C-5), 114.7 (C-β), 109.2 (C-2), 55.9 (Me); glycerol moiety: δ(ppm) 64.63 and 65.05 (C-1 and C-3), 68.4 (C-2).

(E)-*Isoferulaldehyde* (2). R_f values: 0.48 (solvent 1), 0.9 (solvent 2), 0.99 (solvent 3). UV λ_{max}^{MeOH} nm: 245, 305, 337. EI-MS, *m/z* (%): 178 (31), 167 (40), 165 (53), 149 (31), 137 (10), 119 (28), 107 (22), 91 (41). ^{1}H NMR: δ(ppm) 9.6 (*d*, *J* = 8 Hz, H-γ), 7.38 (*d*, *J* = 16 Hz, H-α), 6.55 (*dd*, *J* = 8 and 16 Hz, H-β), 7.16 (*d*, *J* = 2 Hz, H-2), 6.80 (*dd*, *J* = 2 and 7 Hz, H-6), 6.76 (*d*, *J* = 7 Hz, H-5), 3.8 (*s*, OMe). Oxidation: concentrated spots of 2 on TLC were oxidized by drops of ammoniacal silver nitrate. The plates were left to dry at room temp. and dipped in solvents 1, 2 or 3. The developed chromatograms were examined under UV light, whereby mauve spots, turning yellow with ammonia or isoferulic acid were detected. Elution of these spots by cold MeOH and evaporation of the solvent *in vacuo* afforded pure sample of isoferulic acid: R_f values, 0.08 (solvent 1), 0.19 (solvent 2), 0.88 (solvent 3); UV λ_{max}^{MeOH} nm, 242, 294, 324; MS; *m/z* (%): 194 (35), 177 (46), 150 (100), 149 (12), 137 (18), 135 (12), 107 (14). ^{13}C NMR of (2): δ(ppm) 194 (C-γ), 153.13 (C-α), 148.4 (C-4), 147.33 (C-3), 126.7 (C-1), 121.2 (C-6), 116.8 (C-β), 114.09 (C-2), 111.02 (C-5), 56.4 (OMe).

(E)-*Ferulaldehyde* (3). R_f values: 0.49 (solvent 1), 0.93 (solvent 2), 0.99 (solvent 3). UV λ_{max}^{MeOH} nm: 240, 250 (inflection), 305 (inflection), 338. EI-MS, *m/z* (%): 178 (43), 177 (9), 167 (12), 149 (50), 137 (4), 135 (24), 107 (22). ^{1}H NMR: δ(ppm) 9.6 (*d*, *J* = 8 Hz, H-γ), 7.58 (*d*, *J* = 16 Hz, H-α), 6.6 (*dd*, *J* = 8 and 16 Hz, H-β), 7.3 (*d*, *J* = 2.5 Hz, H-2), 7.18 (*dd*, *J* = 2 and 7 Hz, H-6), 6.8 (*d*, *J* = 7 Hz, H-5), 3.79 (*s*, OMe). ^{13}C NMR: δ(ppm) 194.6 (C-γ), 153.98 (C-α), 150.13 (C-3), 147.38 (C-4), 125.71 (C-1), 123.96 (C-6), 115.63 (C-5), 111.48 (C-2), 115.33 (C-β), 55.73 (OMe).

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