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POLYPHENOLIC CONSTITUENTS OF THE FLOWERS OF TAMARIX NILOTICA: THE STRUCTURE OF NILOCITIN, A NEW DIGALLOYLGLUCOSE

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Summary
The new compounds nilocitin (2,3-digalloyl-D-glucopyranose), methyl gallate 4-methyl ether and the known methyl gallate were isolated; nilocitin is the first example of a galloyl glucose not substituted at the anomeric position.

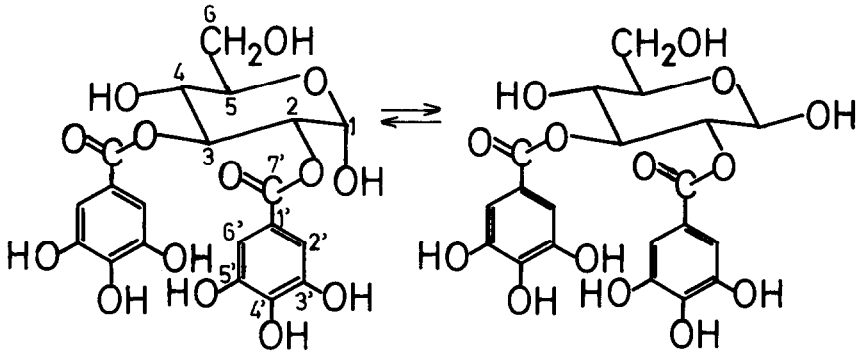
In continuation of our investigation on the constituents of Tamarix nilotica[1,2,3], we have now isolated two new compounds, nilocitin (I) and methyl gallate 4-methylether (II), and one known compound, methyl gallate (III). Isolation of the compounds from the aqueous acetone extract was achieved by a series of separations on polyamide columns and by paper chromatography.

Nilocitin (I) was eluted from the column by MeOH:H_2O (2:8). For purification PPC on Whatman paper No.3MM using solvent A (n-BuOH:AcOH:H_2O = 4:1:5, upper layer) as solvent system was applied followed by repeated precipitation from acetone by ether. The pure material showed chromatographic properties similar to those of galloyl esters. R_f-values: 0.65 (6% AcOH), 0.75 (15% AcOH), 0.50 (solvent A). On acidic hydrolysis by 2 N aq. HCl for three hrs at 100°C, gallic acid [CoPC, UV λ_{max}(CH_3OH):272 nm, ^{1}H-NMR (DMSO-d_6):δ(ppm) 6.98 (s, 2-H, 6-H)] and D-glucose (CoPC) have been obtained.

Partial hydrolysis of I by 0.1 N aq. HCl for three hrs at 100 °C gave besides glucose and gallic acid, an intermediate Ia with chromatographic properties similar to galloyl esters. R_f-values: 0.72 (6% AcOH), 0.83 (15% AcoH), 0.33 (solvent A). Ia was separated by PPC and shown to have a molecular weight of 332 (pos. FAB-MS, MH^+:333) and a λ_{max} (CH_3OH) at 273 nm; these data show Ia to be monogalloyl glucose, the site of attachment being unknown.

Compound I has a molecular weight of 484 as shown by pos. FAB-MS (MH^+: 485). The UV-spectrum shows λ_{max} = 276 nm (CH_3OH). The ^{1}H-NMR-spectrum (CD_3COCD_3) was registered at 270 MHz and assigned on the basis of the coupling constants; the assignments were confirmed by decoupling experiments. The two sets of signals due to the sugar moieties are: δ (ppm) 5.78 (dd, J = 9.6 and 9.0 Hz, 3-H_α), 5.47 (d, J = 3.3Hz, 1-H_α), 5.41 (t, J = 8.5 Hz, 3-H_β), 5.08 (dd, J = 8.5 and 7.5 Hz, 2-H_β), 4.98 (d, J = 7.5 Hz, 1-H_β), 4.92 (dd, J = 9.6 and 3.3 Hz, 2-H_α), 4.0-4.1 (m, 5-H_β), 3.6-3.95 (m,4-H_α and 4-H_β, 6-H_α and 6-H_β), and the signals of the galloyl moieties appear at: δ (ppm) 7.05, 7.07, 7.1 (each as s, ratio 1:1:2).

From the data given above it becomes evident that compound I is an anomeric mixture of 2,3-digalloyl-D-glucopyranose. The attachment of the two galloyl residues to the positions C-2 and C-3 unequivocally follows from the strong downfield shift of the signals of 2-H and 3-H, a shift which is not observed for the signals of 4-H an 6-H. The ratio of the anomers in CD_3COCD_3 is α:β = 2:1.



The ^{13}C-NMR data (see table) are in accordance with the proposed structures; the α and β anomers are recognized from the signals at 89.3 and 94.5 ppm, resp. The attachment of the two galloyl moieties to the positions 2 and 3 of the sugar follows from the upfield shift of the signals of C-1 and C-4 compared to the corresponding signals in D-glucopyranose itself[4]. These β-effects range from 1.7 to 3.7 ppm and are in agreement with the 2.5 ppm upfield shift observed for C-1 in 2"-galloyl kaempferol 3-O-β-D-glucopyranoside[5] compared to C-1 in kaempferol 3-O-β-D-glucopyranoside[6]. The upfield shifts of the signals of C-2 and C-3 are caused by both α- and β-effects.

It should be noted that nilocitin, amongst the various naturally occurring galloyl esters of ß-D-glucose[7] is, to our knowledge, the first example of a galloyl ester not substituted at the anomeric position.

Methyl gallate 4-methylether (II) was isolated by PPC from the MeOH/H_2O (2:8) column fraction. It exhibited chromatographic properties similar to galloyl esters. R_f-values: 0.58 (6% AcOH), 0.68 (15% AcOH), 0.79 (solvent A). It possesses a molecular weight of 198 (EI-MS, M^+:198) and UV λ_{max} (CH_3OH) at 262 and 295 (inflection) nm. It yielded gallic acid (CoPC) on hydrolytic cleavage by HI/$(AcO)_2O$ at 145 °C for 1/2 hr. The simple ^1H- and ^{13}C-NMR spectra are in accord with the highly symmetric structure of methyl gallate 4-methylether. ^1H-NMR (DMSO-d_6):δ(ppm) 6.92 (s, 2-H, 6-H), 3.76 (s, OCH_3), 3.72 (s, CH_3OCO). ^{13}C-NMR (DMSO-d_6):δ(ppm), 166.0 (C=O), 150.6 (C-3, C-5), 139.7 (C-4), 124.4 (C-1), 108.5 (C-2, C-6), 59.6 ($O-CH_3$) 51.8 ($O-CO-CH_3$).

Methyl gallate (III) was also separated by PPC of the same column fraction. Its analytical data (^1H- and ^{13}C-NMR) were found to be identical to those reported for methyl gallate[7].

Table
Comparison of ^{13}C-NMR data (^{25}MHz, solvent:DMSO-d_6) of nilocitin and D-glucose[4]

	C-1	C-2	C-3	C-4	C-5	C-6
α-nilocitin, glucose moiety*	89.3	72.2	72.2	68.3	72.2	60.6
α-D-glucopyranose	93.0	72.8	73.4	71.0	72.6	61.9
ß-nilocitin, glucose moiety*	94.5	73.1	75.5	68.3	76.7	60.6
ß-D-glucopyranose	96.2	75.4	77.1	71.0	77.1	61.9

*The signals of the galloyl moieties have nearly the same chemical shifts as those of methylgallate[7] (the deviations are less than 1 ppm) with exception of the carbons of the carbonyl-groups which resonate at δ (ppm) 165.4 and 165.5 (α-anomer) and 164.8 and 165.2 (ß-anomer).

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