

BIOLOGICALLY ACTIVE COMPOUNDS FROM *Tamarix hispida*. II.N. A. Sultanova,¹ Zh. A. Abilov,¹ E. E. Shul'ts,²
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In continuation of research on the chemical composition of the aerial part of *T. hispida* [1], **1-11** were isolated pure by adsorption-partition gel-chromatography. Compounds **4-6** and **10** are new for this genus.

Compounds **1-4** were identified by physicochemical constants and comparison with authentic samples as gallic (**1**), ellagic (**2**), dehydrodigallic (**3**), and caffeic (**4**) acids. Compounds **5-11** were identified by chemical (acid hydrolysis, acylation) and spectral (IR, UV, mass, PMR, and ¹³C NMR spectroscopies) analyses as:

β -Carotene (5): mp 184-186°C, PMR (500 MHz, CDCl₃, δ , ppm, J/Hz): 1.47 (m, H-2, H-2'), 1.62 (m, H-3, H-3'), 2.02 (m, H-4, H-4'), 7.39 (d, J = 11.0, H-6, H-6'), 6.19 (d, J = 16.0, H-7), 6.51 (dd, J₁ = 15.0, J₂ = 11.0, H-7'), 6.13 (d, J = 16.0, H-8), 6.66 (d, J = 15.0, H-8'), 6.16 (d, J = 11.0, H-10), 6.37 (d, J = 11.0, H-10'), 6.67 (dd, J₁ = 11.0, J₂ = 15.0, H-11), 6.63 (dd, J₁ = 11.0, J₂ = 15.0, H-11'), 6.36 (d, J = 15.0, H-12), 6.47 (d, J = 15.0, H-12'), 6.29 (d, J = 11.0, H-14), 6.32 (d, J = 11.0, H-14'), 6.67 (m, H-15), 6.65 (m, H-15'), 1.03 (s, H-16, H-16'), 1.02 (s, H-17, H-17'), 1.7 (s, H-18, H-18'), 1.98 (s, H-19), 2.01 (s, H-19'), 1.99 (s, H-20), 1.98 (s, H-20'). Mass spectrum (EI, 70 eV, *m/z*): 536 [M]⁺, C₄₀H₅₆ [2].

Phytol (6): [α]_D²³ +0.13° (*c* 0.4, CHCl₃). PMR (500 MHz, CDCl₃, δ , ppm, J/Hz): 5.40 (1H, t, J = 6.9), 4.13 (2H, d, J = 6.9), 1.96 (2H, t, J = 7.6), 1.63 (3H, s), 1.54-1.00 (19H, m), 0.87 (9H, d, J = 6.6), 0.84 (3H, d, J = 6.5). Mass spectrum (EI, 70 eV, *m/z*): 296 [M]⁺, C₂₀H₄₀O [3].

β -Sitosterol (7): mp 134-136°C, [α]_D²³ +11° (*c* 0.2, CHCl₃). PMR (500 MHz, CDCl₃, δ , ppm, J/Hz): 0.66 (3H, s, H-18), 5.30 (1H, br.s, H-6), 0.83 (3H, t, H-29), 0.88 (3H, d, J = 6.5, H-21), 0.82 (3H, d, J = 6.2, H-26), 0.84 (1H, t), 0.78 (3H, d, J = 6.2, H-27). Mass spectrum (EI, 70 eV, *m/z*): 414, C₂₉H₅₀O [4].

Hentriacontanol (8): mp 82-83°C. IR spectrum (KBr, ν , cm⁻¹): 3325, 3227, 1330, 1132, 1112, 1043, 1020. PMR (500 MHz, CDCl₃, δ , ppm, J/Hz): 0.70 (6H, t, 2 × CH₃), 1.04-1.2 (56H, br.s, 28 × CH₂), 3.40 (1H, m, CHOH). Mass spectrum (EI, 70 eV, *m/z*): 452, C₃₁H₆₄O [5].

4-Methoxygallic acid methyl ester (9): mp 120-122°C. IR spectrum (KBr, ν , cm⁻¹): 3389, 2958, 2846, 2516, 1710, 1598, 1508, 1435, 1375, 1257, 1161, 1063, 1002, 985, 867, 771, 755. PMR (500 MHz, CD₃OD, δ , ppm, J/Hz): 7.69 (2H, s, H-2, H-6), 4.00, 3.73 (6H, s, OCH₃). Mass spectrum (EI, 70 eV, *m/z*): 198, C₉H₁₀O₅ [6].

2-O-Galloyl-D-glucofuranose (10): mp 150-152°C. PMR (500 MHz, acetone:water-d₆, δ , ppm, J/Hz): Gal.: 7.12, 7.11 (2H, s); α -glucose: 5.31 (1H, d, J = 2.0, H-1'), 4.74 (1H, dd, J = 8.0 and 2.5, H-2'), 4.84 (1H, t, H-3'), from 4.8 to 3.6 (m, H-4', H-5', H-6'); β -glucose: 5.25 (1H, d, J = 6.0, H-1'), 5.12 (1H, t, J = 9.0, H-2'), 5.38 (1H, t, H-3'), from 4.8 to 3.6 (m, H-4', H-5', H-6'). ¹³C NMR (125.76 MHz, acetone:water-d₆): Gal.: 122.0 C-1, 104.30 C-2, 145.65 C-3 and C-5, 139.80 C-6, 109.90 C-7, 166.0 C=O; α -glucose: 93.50 C-1, 77.30 C-2, 72.68 C-3, 69.77 C-4, 65.00 C-5, 62.44 C-6; β -glucose: 97.76 C-1, 78.35 C-2, 74.16 C-3, 71.94 C-4, 67.43 C-5, 63.40 C-6, C₁₃H₁₄O₁₀. **Peracetate:** mp 140-142°C, [α]_D²² +63.8° (*c* 2.0, acetone) [7].

2-O-Galloyl-3-O-(1-dehydrodigalloyl)-4,6-hexahydroxydiphenylglucofuranose (11): mp 202-203°C, [α]_D²² +120.3° (*c* 1.0, EtOH). UV spectrum (λ_{\max} , CH₃OH, nm): 272. IR spectrum (KBr, ν , cm⁻¹): 3200-3400, 1740, 1690, 1630, 1530, 1470, 1350. PMR (500 MHz, acetone:water-d₆, δ , ppm, J/Hz): HHDP: 7.02 and 7.05 (1H, s); DHDG: 7.22, 7.21, 6.60, 6.58 (1H, d, J = 2.0), 7.08 and 7.07 (1H, s); Gal.: 7.08 and 7.07 (2H, s); α -glucose: 4.89 (1H, dd, J₁ = 3.0 and J₂ = 6.0, H-2'), 5.24 (1H, t, J = 9.0, H-3'), from 4.2 to 3.5 (m, H-4', H-5', H-6'); β -glucose: 5.32 (1H, d, J = 6.0, H-1'), 5.03 (1H, t, J = 8.0, H-2'), 5.71 (1H, t, J = 9.0, H-2'), from 4.2 to 3.5 (m, H-4', H-5', H-6'). ¹³C NMR (125.76 MHz, acetone:water-d₆): Gal.: 120.03 C-1, 109.02 C-2, 109.11 C-6, 145.35 C-3, 139.16 C-4, 145.35 C-5, 163.23 C=O; DHDG: 120.39 C-1, 108.99 C-2, 146.65 C-3,

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139.29 C-4, 146.83 C-4', 108.94 C-8'', 138.78 C-4'', 139.49 C-5'', 142.14 C-6'', 142.39 C-7'', 109.21 C-8, 113.24 C-8', 166.57 COOH, 165.89 C=O; HHDP: 120.53 C-1, 106.39 C-2, 145.38 C-3, 137.84 C-4, 144.84 C-5, 113.09 C-6, 120.88 C-1', 106.62 C-2', 145.14 C-3', 136.39 C-4', 144.84 C-5', 113.09 C-6', 166.42 and 166.30 C=O; α -glucose: 89.67 C-1, 76.25 C-2, 72.84 C-3, 71.65 C-4, 68.40 C-5, 61.17 C-6; β -glucose: 94.69 C-1, 76.28 C-2, 73.01 C-3, 72.08 C-4, 68.63 C-5, 61.21 C-6. PMR (500 MHz, DMSO-d₆, δ , ppm, J/Hz): HHDP: 6.84, 6.88 (1H, s); DHDP: 7.01, 6.40 (1H, d, J = 2.0) and 6.90 (1H, s); Gal.: 6.90 and 6.94 (1H, s), 5.12 (1H, d, J = 2.0, H-1'); α -glucose: 4.65 (1H, d, J = 8.0, H-1); β -glucose: 4.8 (t, H-2), 5.50 (t, H-3), from 4.5 to 3.5 (H-4, H-5, H-6, H-6'), C₄₁H₃₀O₂₇ [8].

Total acid hydrolysis afforded **1-3**; partial, **1-3** and **10**. Glucose was identified in the hydrolysate. The attachment sites of gallic and dehydrodigallic acids were established by two-dimensional heteronuclear correlation spectroscopy HMBC.

The compounds obtained were also identified in the aerial part of *T. ramosissima*.

REFERENCES

1. N. A. Sultanova, Zh. A. Abilov, V. B. Omurkamzinova, and I. M. Chaudri, *Khim. Prir. Soedin.*, 80 (2002).
2. J. D. Connolly and R. A. Hill, *Dictionary of Terpenoids. Di and Higher Terpenoids*, Chapman and Hall, (1991), Vol. 2, p. 1422.
3. G. D. Brown, *Phytochemistry*, **36**, No. 6, 1553 (1994).
4. G. G. Zapesochnaya, V. A. Kurkin, E. V. Avdeeva, D. M. Popov, and M. V. Kopolokova, *Khim. Prir. Soedin.*, 55 (1992).
5. P. K. Agrawal, *Planta Med.*, **57**, 397 (1991).
6. M. A. Nawwar, A. M. Souleman, and S. Buddrus, *Tetrahedron Lett.*, **25**, No. 1, 49 (1984).
7. T. K. Chumbalov and T. N. Bikbulatova, *Khim. Prir. Soedin.*, 496 (1970).
8. M. A. Nawwar, S. A. Hussein, and S. Buddrus, *Phytochemistry*, **35**, No. 5, 1349 (1994).