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FLAVANES FROM *Limonium gmelinii*. II.

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In continuation of research on polyphenols from roots of *Limonium gmelinii* [1], fractional extraction and adsorption-distribution chromatrography isolated pure compounds **1-4** that were identified as flavan-3-ols. Compounds **1-3** were isolated for the first time from this species. Compound **4** has not been previously described in the flavane literature.

Dried, ground, and previously defatted raw material was extracted exhaustively with aqueous ethanol (50%). The resulting extract was concentrated in vacuo and worked up successively with ethylacetate and *n*-butanol. Repeated chromatography of the ethylacetate fraction over polyamide using gradient elution by acetone and acetone:water mixtures isolated **1-4**.

(+)-Gallocatechin (1), amorphous substance, $C_{15}H_{14}O_7$, $[\alpha]_D^{24}$ +15° (*c* 0.3, ethanol). The peracetyl derivative of **1** was colorless needles, mp 142-143°C, $[\alpha]_D^{24}$ +30° (*c* 0.5, acetone).

PMR spectrum of hexaacetyl-(+)-gallocatechin (100 MHz, $CDCl_3$, δ, ppm, J/Hz): 1.86 (3H, s, aliph. OAc), 2.2 (15H, s, phenol. OAc), 6.79 ($J_{6,8}$ = 2.2, H-6), 6.87 ($J_{8,6}$ = 2.2, H-8), 7.3 (s, H-2′, H-6′), 5.05 ($J_{2,3}$ = 8, H-2), 5.78 (m, H-3), 2.6-2.9 (q, $J_{3,4eq}$ = 8, H-4_{eq}, $J_{3,4ax}$ = 10, H-4_{ax}).

^{13}C NMR of **1** (acetone-d_6—D_2O, 500 MHz, δ, ppm): 82.0 (C-2), 72.8 (C-3), 28.5 (C-4), 95.8 (C-8), 96.6 (C-6), 156.7 (C-5), 157.1 (C-7), 157.4 (C-9), 101.1 (C-10), 131.3 (C-1′), 109.0 (C-2′, C-6′), 133.4 (C-4′), 145.6 (C-3′, C-5′) [2, 3].

(-)-Epigallocatechin (2), amorphous substance, $C_{15}H_{14}O_7$, $[\alpha]_D^{25}$ -57° (*c* 0.2, ethanol). The peracetyl derivative of **2** was an amorphous substance, $[\alpha]_D^{25}$ -19.5° (*c* 0.25, acetone).

PMR spectrum of hexaacetyl-(-)-epigallocatechin ($CDCl_3$, 100 MHz, δ, ppm, J/Hz): 1.86 (3H, s, aliph. OAc), 2.3 (15H, s, phenol. OAc), 6.51 ($J_{6,8}$ = 1.5, H-6), 6.7 ($J_{8,6}$ = 1.5, H-8), 7.3 (s, H-2′, H-6′), 5.0 (s, H-2), 5.36 (br.s, H-3), 2.92 (2H, br.s, H-4).

^{13}C NMR of **2** (acetone-d_6—D_2O, 500 MHz, δ, ppm): 78.6 (C-2), 67.2 (C-3), 28.8 (C-4), 155.9 (C-5), 96.6 (C-6), 157.1 (C-7), 96.2 (C-8), 157.5 (C-9), 100.0 (C-10), 131.3 (C-1′), 107.3 (C-2′, C-6′), 146.1 (C-3′, C-5′), 132.9 (C-4′) [2-4].

(-)-Epigallocatechin-3-*O*-gallate (3), amorphous substance, $C_{22}H_{18}O_8$, $[\alpha]_D^{25}$ -182° (*c* 0.4, ethanol).

PMR spectrum of octaacetyl-(-)-epigallocatechin-3-*O*-gallate (100 MHz, $CDCl_3$, δ, ppm, J/Hz): 2.2 (30H, s, phenol. OAc), 6.53 ($J_{6,8}$ = 2, H-6), 6.7 ($J_{8,6}$ = 2, H-8), 7.3 (2H, s, H-2′, H-6′), 5.1 (s, H-2), 5.4 (br.s, H-3), 2.92 (2H, br.s, H-4), 7.2 (2H, gallic acid H-2″ and H-6″).

^{13}C NMR of **3** (acetone-d_6—D_2O, 500 MHz, δ, ppm): 77.4 (C-2), 69.4 (C-3), 27.8 (C-4), 155.8 (C-5), 96.9 (C-6), 157.0 (C-7), 96.3 (C-8), 157.6 (C-9), 101.0 (C-10), 131.3 (C-1′), 106.6 (C-2′, C-6′), 145.2 (C-3′, C-5′), 133.4 (C-4′); gallyl group: 120.0 (C-1″), 110.1 (C-2″, C-6″), 145.6 (C-3″, C-5″), 138.9 (C-4″), 164.5 (–COO) [2-4].

3,5,7,3′,4′,6′-Hexahydroxyflavane (4), amorphous substance, $[\alpha]_D^{20}$ -35.2° (*c* 0.2, ethanol).

The PMR spectrum of the peracetyl derivative of **4** contained signals for five aromatic (δ 2.0 ppm) and one aliphatic (δ 1.89 ppm) acetyls. A 1H doublet with SSCC 1.5 Hz was assigned to the H-6 (δ 6.51 ppm) and H-8 (δ 6.67 ppm) protons of a phloroglucinol ring. The H-2 and H-3 protons of the heterocycle resonated as singlets at δ 4.98 and 5.29 ppm, respectively, consistent with the 2,3-*cis*-configuration at C-2 and C-3 [3]. Signals of the two H-2′ and H-5′ protons of the side phenyl ring were found in the range 6.91-7.12 ppm.

^{13}C NMR spectrum of **4** (acetone-d_6—D_2O, 500 MHz, δ, ppm): 78.5 (C-2), 66.1 (C-3), 28.2 (C-4), 155.3 (C-5), 96.8 (C-6), 156.0 (C-7), 95.0 (C-8), 157.2 (C-9), 99.5 (C-10), 131.5 (C-1′), 115.5 (C-2′), 145.0 (C-3′), 146.5 (C-4′), 112.5 (C-5′), 146.1 (C-6′).

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The ^{13}C NMR spectrum of **4** lacked signals for C atoms characteristic of pyrogallyl-type oxidation. The 2,3-*cis*-configuration for C-2 and C-3 was confirmed by resonance for C-2 at δ 78.5 ppm [5]. Mass spectrum (EI, 70 eV, *m/z*): 318 $[M]^+$, $C_{15}H_{14}O_7$.

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