

## COMPARISON OF THE AMINO-ACID COMPOSITIONS OF *Artemisia gmelinii* AND *A. absinthium*

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Amino acids are highly active with respect to pharmacology and important physiological components of organisms [1, 2]. Half of the 20 proteinogenic human amino acids are obtained from plants. Therefore, studies of the amino-acid complexes of medicinal plants represent an important stage of pharmacognostic research.

Individual groups of biologically active compounds (BACs, polyphenolic compounds including flavonoids, terpenoids, etc.) from *A. gmelinii* herb were reported [3–7]. However, information about the amino-acid composition of this plant was missing. The pharmacopoeial *Artemisia* species in Kazakhstan are *A. absinthium* L., *A. leucodes* Schrenk., and *A. glabella* Kar. et Kir. [8]. Therefore, the study of unofficial *Artemisia* species (including *A. gmelinii* Weber ex Stechm.), which is broadly distributed in Kazakhstan [9] and has the sufficient raw-material base required to expand the pharmacopoeial medicinal species, makes the work promising and relevant.

Medicinal plant raw material of both *Artemisia* species was collected in Turgan Gorge, Enbekshikazakh District, Almaty Oblast, in May–June 2014 during the start of flowering.

The amino-acid compositions of the herbs of *A. gmelinii* and *A. absinthium* were compared at the Magarach National Institute of Grapes and Wine (Republic of Crimea). Free amino acids in a weighed portion (100 mg) of raw material were determined by adding HCl solution (0.1 M) containing  $\beta$ -mercaptoethanol (0.2%) and irradiating in an ultrasonic bath for 2 h at 50°C. Total free and bound amino acids were determined and hydrolytic cleavage was performed by adding HCl (6 M) containing  $\beta$ -mercaptoethanol (0.4%) to a weighed portion (10 mg) of raw material and irradiating in an ultrasonic bath for 24 h at 110°C.

Free and bound amino acids in the experimental samples were determined on an Agilent Technologies Model 1100 chromatograph equipped with a G1379A flow-through vacuum degasser, a G13111A low-pressure quaternary gradient pump, a G1313A autosampler, a G13116A thermostatted column compartment, and a G1316A Agilent diode-array detector. The chromatography used a Zorbax-XDB-C18 column (4.6  $\times$  50 mm) packed with octadecylsilyl absorbent (1.8  $\mu$ m) and a protective precolumn. The mobile phase used NaOAc solution (0.05 M) adjusted to pH 6.5 with AcOH solution (10 or 20 g/L) with added THF (30 g/L) and NaOAc solution (0.1 M) and MeCN in a 23:22 ratio adjusted to pH 6.5 with NaOAc solution (10 or 20 g/L). The mobile phase flow rate was 1.5–2 mL/min. The eluent working pressure was 220–275 kPa. The column was thermostatted at 50°C. The sample volume was 2  $\mu$ L. UV detection was made on a scale of 1.0 with scan time 0.5 s and detection wavelength 265 nm.

Table 1 presents the amino-acid compositions of the herbs of the studied *Artemisia* species. Studies of the free amino acids in the samples of *A. gmelinii* and *A. absinthium* identified 22 and 20 ones, respectively, of which 9 were essential. An investigation of the total amino-acid contents in *A. gmelinii* detected 20 amino acids; in *A. absinthium*, 19, of which 9 were essential.

Proline was the dominant free amino acid in both studied *Artemisia* samples. Table 1 shows that the content of total free amino acids in *A. absinthium* herb was 1775.1 mg/100 g; in *A. gmelinii*, 2158.9 mg/100 g.

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TABLE 1. Amino-Acid Contents of Individual *Artemisia* Species, mg/100 g

| Amino acid                              | <i>A. absinthium</i> |               | <i>A. gmelinii</i> |               |
|---|----------------------|---------------|--------------------|---------------|
|   | Free                 | Total content | Free               | Total content |
| Essential proteinogenic amino acids     |                      |               |                    |               |
| Val                                     | 64.4                 | 348.9         | 77.5               | 412.2         |
| Ile                                     | 35.5                 | 257.1         | 38.0               | 291.5         |
| Leu                                     | 43.7                 | 442.6         | 45.6               | 611.1         |
| Lys                                     | 36.8                 | 395.7         | 39.1               | 450.9         |
| Met                                     | 59.5                 | 125.1         | 61.6               | 137.1         |
| Thr                                     | 37.6                 | 383.3         | 41.6               | 495.8         |
| Phe                                     | 36.6                 | 326.0         | 39.0               | 384.3         |
| Arg                                     | 51.3                 | 595.0         | 53.4               | 677.4         |
| His                                     | 26.9                 | 200.7         | 49.9               | 270.0         |
| $\Sigma_{\text{ess aa}}$                | 392.3                | 3074.4        | 445.7              | 3730.3        |
| Non-essential proteinogenic amino acids |                      |               |                    |               |
| Gly                                     | 13.7                 | 373.3         | 16.8               | 580.3         |
| Ala                                     | 76.4                 | 505.7         | 83.5               | 708.3         |
| Ser                                     | 51.7                 | 418.3         | 63.2               | 502.5         |
| Asp                                     | 20.9                 | 904.8         | 53.3               | 1251.2        |
| Glu                                     | 20.3                 | 827.2         | 74.5               | 1372.6        |
| Asn                                     | 109.2                | —             | 193.2              | —             |
| Gln                                     | 9.3                  | —             | 12.3               | —             |
| Cys                                     | 2.9                  | 10.4          | 3.7                | 26.2          |
| Tyr                                     | 34.9                 | 293.0         | 52.4               | 339.9         |
| Pro                                     | 1033.8               | 1477.4        | 1112.8             | 1574.4        |
| $\Sigma_{\text{non aa}}$                | 1373.1               | 4810.1        | 1665.7             | 6355.4        |
| Non-proteinogenic amino acids           |                      |               |                    |               |
| GABA                                    | —                    | 51.5          | 28.9               | 84.3          |
| Hyp                                     | 9.7                  | 125.1         | 11.5               | 56.3          |
| Cystine                                 | —                    | —             | 7.1                | 112.2         |
| $\Sigma_{\text{nonp aa}}$               | 9.7                  | 176.6         | 47.5               | 252.8         |
| $\Sigma_{\text{aa}}$                    | 1775.1               | 8061.1        | 2158.9             | 10338.5       |

Amino acids such as asparagine and glutamine can undergo almost quantitative acid hydrolysis into aspartic and glutamic acid, respectively. Cystine under the same conditions can partially or completely decompose into cysteine and cysteic acid.

Thus, the sums of asparagine + aspartic acid and glutamine + glutamic acid should be used to calculate the contents. The sum of cystine and cysteine can also be used to calculate the content of bound amino acids. However, it should be considered that a cystine molecule decomposes into a cysteine and a cysteic acid molecules.

The dominant amino acids with respect to total contents in the studied *Artemisia* species were proline, aspartic acid (with asparagine), glutamic acid (with glutamine), and arginine.

The results suggested that both *Artemisia* species contained significant amounts of free and bound amino acids. However, their content in *A. gmelinii* was considerably greater than in *A. absinthium* (official species). In contrast to *A. absinthium* (20 amino acids), the herb of *A. gmelinii* contained 22 amino acids. GABA and cystine were found only in *A. gmelinii* herb. This allowed these amino acids to be considered distinguishing markers of *A. gmelinii* herb when mixed with *A. absinthium*.

The results showed that *A. gmelinii* herb had higher contents of free and bound amino acids than the official species *A. absinthium*. The herb of *A. gmelinii* contained marker compounds (GABA and cystine) that allowed *A. gmelinii* raw material to be distinguished when mixed with *A. absinthium*.

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