# DRACOCEPHALOSIDE – A NEW FLAVONOID GLYCOSIDE FROM DRACOCEPHALUM THUMIFLORUM L.

V. I. Litvinenko and T. A. Sergienko

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The thymeflower dragonhead (Dracocephalum thymiflorum L.), which belongs to the family Labiatae, is an annual-biennial herbaceous plant which is widely distributed on the territory of the Soviet Union [1].

The dragonheads are of considerable interest for the national economy as good fodder-providing, honey-yielding, and essential-oil-bearing plants [2, 3]; however, their chemical composition has been studied extremely inadequately.

In the present paper we describe a chemical investigation of the flavonoid composition of thymeflower dragonhead collected in a pine wood near Kharkov*.

The plant was extracted with 50% methanol. The extract was evaporated to an aqueous residue, and the flavonoids were purified and separated on a column of polyamide sorbent. One of the flavonoids isolated in this way proved to be a new glycoside of luteolin and has been called dracocephaloside.

TABLE 1

Comparative characteristics of dracocephaloside.

| Properties | Dracocephaloside | Luteolin-5-glucoside (galuteolin) [4] | Luteolin-7 glucoside [5] | Luteolin-4 glucoside [4] |
|---|---|---|---|---|
| Mp, C | 243-245 | 280 | 255-258 | 177-178 |
| [a]D | –103.0°(c 0.33, pyridine-methanol-water, 1:1:1) | – | –100°(c 0.5, pyridine-methanol 1:1) | – |
| $\lambda_{max}$, mμ (UV region) | 256, 268, 350 | – | 255, 264, 350 | 255, 334 |
| Formula | $C_{21}H_{20}O_{11}$ | $C_{21}H_{20}O_{11}$ | $C_{21}H_{20}O_{11}$ | $C_{21}H_{20}O_{11}$ |
| Mol. wt. | 448.0 | 448.0 | 448.0 | 448.0 |
| $R_f$ value in 15% $CH_3COOH$ | 0.20-0.22 | – | 0.20-0.22 | – |
| *BAW (4:1:2) | 0.53-0.55 | – | 0.53-0.55 | 0.51 |
| Qualitative reactions | | | | |
| Bryant's cyanidin reaction [6] | Orange coloration (in water) | – | Orange coloration (in water) | – |
| With ammoniacal silver nitrate [7] | Negative | – | Positive | Negative |
| With lead acetate [8] | Negative | Yellow precipitate | Yellow precipitate | Negative |
| With ferric chloride | Green coloration | Negative | Green coloration | Green coloration |

*Translator's note: probably butanol-acetic acid-water.

We have compared the physicochemical properties of the glycosides investigated with those of known monoglucosides of luteolin (Table 1). From this it can be stated that dracocephaloside is a monoglucoside with free hydroxy groups in the 5- and 4'- positions. The hydroxy group in the 4' position is probably free, since a 4' glucoside should exhibit hypsochromy to 334 mμ in the UV spectrum. On the other hand, the negative reactions with an ammoniacal solution of silver nitrate [7] and with lead acetate make it possible to assume that one of the o-hydroxy groups in ring B is

*The species of the plant was determined by candidate of biological sciences I. G. Zoz (KhNIKhFI) [Kharkov Chemical and Pharmaceutical Research Institute].

substituted. In order to determine the position of the carbohydrate substituent and of the free hydroxy groups more accurately, we have carried out a spectroscopic investigation in the UV region using ionizing and complex-forming reagents [9] (Table 2).

As is evident from Table 2, the following free hydroxy groups are present in the glycoside and the aglycone: in the 7- position (from the bathochromic displacement of the long-wave band by 25 mμ under the influence of sodium acetate), in the 5- position (from the bathochromy with aluminum chloride), and in the 4'- position (from the bathochromy with sodium ethoxide). However, the presence in the UV spectrum of the glycoside and the aglycone (alcoholic solution) of two maxima in band II serves as an indication of the presence of substituents in the 3'- and 4'- positions [9]. Thus, the data obtained confirm the assumption of the existence in the glycoside of free phenolic groups in the 5-, 7-, and 4'- positions and a carbohydrate substituent in the 3'- position.

TABLE 2

Spectroscopic characteristics of dracocephaloside and its aglycone.

| Medium | Dracocephaloside $\lambda_{max}$, mμ | | | | Aglycone $\lambda_{max}$, mμ | | | |
|---|---|---|---|---|---|---|---|---|
| | Band I | Displacement of band I | Band II | Displacement of band II | Band I | Displacement of band I | Band II | Displacement of band II |
| $10^{-5}$ M solution in absolute ethanol | 350 | – | 268(256) | – | 350 | – | 267(253) | – |
| Same + sodium acetate | 375 | 25 | 260 | −8 | 375 | 25 | 270 | 3 |
| Same + boric acid and sodium acetate | 375 | 25 | 260 | −8 | 375 | 25 | 261 | −6 |
| Same + sodium ethoxide | 390 | 40 | 270 | +2 | 410 | 60 | 271 | 4 |
| Same + aluminum chloride | 410 | 60 | 270 | +2 | 410 | 60 | 270 | 3 |

Acidic and enzymatic hydrolysis of the glycoside gave luteolin and D-glucose. Enzymatic splitting of the glycoside with an amylolytic enzyme preparation from the mould Aspergillus oryzae [10], and also a comparison of the molecular rotation with that of phenyl glucosides give grounds for assuming that the D-glucose is present in the glucoside in the pyranose form and is linked to the aglycone by a β-glycosidic bond. The aglycone is identical with luteolin on the basis of its physicochemical properties, its chromatographic behavior, and a comparison of the IR spectra.

Consequently, dracocephaloside is 5,7,3',4'-tetrahydroxyflavone-3'-β-D-glucopyranoside.

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Kharkov Chemical and Pharmaceutical Research Institute

Kharkov Pharmaceutical Institute