PHOTOMETRIC DETERMINATION OF PHENOLS IN ESSENTIAL OILS

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A photometric procedure is described for determining terpene phenols in essential oils which is based on the formation of colored indophenols with p-quinone chloroimine in an alkaline medium. A comparative evaluation of the results obtained with those of the pharmacopoeial method shows the greater economy, sensitivity, and accuracy of the proposed procedure.

The use of essential oils in the national economy and medicine is presenting increased demands on their quality. To determine phenols in essential oils, the USSR State Pharmacopoeia adopts a method based on the dissolution of the phenols in sodium hydroxide and their determination from the decrease in the volume of the essential oil [2]. The method is simple in performance but has serious disadvantages – the time for a determination (90 min) and its low sensitivity (it requires 5 ml of essential oil). Plants containing from 0.1 to 1% of essential oil are investigated most frequently. In this case, for a single investigation it is necessary to treat from 0.5 to 5.0 kg of raw material, and in order to obtain statically reliable results from 3 to 30 kg of valuable plant raw material. In addition, the accuracy of the method depends on subjective factors (manual shaking) which increases the percentage of errors.

We have developed a more economical and accurate photometric method of determining phenols in an essential oil from medicinal plant raw material and have compared our results with those obtained by the pharmacopoeial method.

The basis of the photometric method was the capacity of phenols for forming colored indophenols with p-quinone chloroimine in an alkaline medium [6]. Since the main phenolic components of essential oils are thymol and its isomer carvacrol, which are very similar to one another in chemical, physical, and pharmacological properties, the method was developed with the use of a standard sample of thymol.

The investigation showed that in 0.1 N sodium hydroxide solution thymol forms a blue product with p-quinone chloroimine. Obedience to Beer's law is observed in the interval of concentrations of thymol of from 0.08 to 1.00 mg in 100 ml of solution undergoing photometry, which corresponds to thymol concentrations of from 20 to 250 μg in the sample being analyzed.

Subsequent investigations were performed on, for example, the essential oil obtained from the herb Thymus serphyllum L. (wild thyme) growing in the Zaporozh'e region (Nikolai-Pole gorge), Zaporozh'e Province.

TABLE 1. Results of the Quantitative Determination of Phenols in the Essential Oil of Wild Thyme by the Pharmacopoeial and the Photometric Method

Method of determination	Sample, mg	Phenols found, %	Metrological characteristics			
			$\bar{X}$	$S \cdot 10^{-1}$	$Sr \cdot 10^{-3}$	$\pm St$
Pharmacopoeial	5,0	72,0; 74,0; 74,0; 74,0; 76,0; 76,0	74,3	15,1	20,25	3,87
Photometric	0,10	72,97; 73,36; 74,14; 74,14; 74,53; 74,92	74,0	7,26	9,81	1,87

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As is well known, in wild thyme the terpene phenols thymol and carvacrol (the main pharmacologically active substances) are present in the essential oil in amounts from 1 to 70% [3-5]. Calculated to the amount in 10 μl of essential oil, this comes to 100-7000 μg of phenols, and, therefore, where necessary the essential oils must be diluted with ethanol to the optimum concentration.

To check the reliability of the results obtained, the phenols were determined in the same sample by the pharmacopoeial method. The results obtained were treated statistically in accordance with the demand of IUPAC [7] (Table 1).

As follows from Table 1, the results of the determination of phenols by the photometric method are reliable and correspond to those obtained by the pharmacopoeial method. Furthermore, the photometric method developed is distinguished by economy (it requires a 50 times smaller amount of essential oil), rapidity (the time of performing an analysis is shortened by a factor of 2-3), and accuracy of the result (the relative standard deviation does not exceed $9.81 \cdot 10^{-3}$).

EXPERIMENTAL

The essential oil was obtained by the steam distillation method according to the USSR State Pharmacopoeia, 11th edition [2], method 1.

The phenols content was determined in accordance with the method of the USSR State Pharmacopoeia, 10th edition [1].

The photometric determination of the phenols was performed by the following procedure: A 25-ml measuring flask was charged with 5 ml of ethanol, 10 μl of an ethanolic solution of thymol, and 5 ml of a 0.1% ethanol solution of p-quinone chloroimine and the mixture was made up to the mark with a 0.1 N solution of sodium hydroxide. A control experiment without thymol was performed in parallel. After mixing, the optical density of the solution was measured on a KFK-2 photoelectric colorimeter at a wavelength of 590 nm in a cell with a layer thickness of 5 mm against the background of the control experiment.

To study the intervals of concentrations of thymol within which Beer's law is obeyed, a series of 25-ml measuring flasks were charged with the samples to be analyzed containing from 10 to 320 μg of thymol with an interval of 40 μg and the further procedure was as described above.

The quantitative determination of the phenols in the essential oil was carried out with respect to a solution of a standard sample of thymol having a concentration of 160 μg in 10 μl.

The amount of phenols in the essential oil was calculated from the formula

$$C = \frac{D \cdot C_0 \cdot 25 \cdot V}{D_0 \cdot p \cdot V_1},$$

where D and D_0 are the optical densities of the test and the standard solutions, respectively; C_0 is the concentration of the standard thymol solution (0.00064 g in 100 ml of photometered solution); V and V_1 are the volumes of the dilutions of the essential oil and of that taken for analysis, respectively, ml; and p is the amount of essential oil taken for analysis, ml.

CONCLUSIONS

A procedure for the photometric determination of terpene phenols in essential oils has been developed that is highly sensitive, economical, and simple in performance.

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