QUANTITATIVE DETERMINATION OF CINEOL

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The most valuable component of eucalyptus preparations is cineol. The method of analysis recommended by the Xth edition of the State Pharmacopoeia [1] for the new material proposes for it the determination of the amount of essential oil by distillation, and for the essential oil the determination of the amount of cineol from the volume of oil that has undergone a complex-forming reaction with resorcinol [1], while for the tincture in the IXth edition of the State Pharmacopoeia [2] only a qualitative reaction for tanning substances is given. In addition to the volumetric method for the determination of cineol, there is also a gravimetric method in which the weight of the cineol–resorcinol complex formed is determined. The results of the gravimetric method fluctuate because of the inconstancy of the composition of the complex.

These methods for analyzing cineol are complex and laborious and do not permit the quantitative determination of cineol in the raw material and in tincture of eucalyptus. Consequently, it appeared of interest to develop a method for the analysis of cineol in the raw material and in eucalyptus preparations that is free from these defects. As such we have used an IR spectroscopic method. The quantitative determination of cineol in the pure form by this method was performed as in a published paper [5], but in this no method for the quantitative determination of cineol in the raw material and in eucalyptus preparations was developed.

An analysis of the IR spectra of cineol and the essential oil of eucalyptus showed that the absorption maxima of cineol appear distinctly in the essential oil. This provides the possibility of determining cineol qualitatively and quantitatively without its preliminary isolation.

The experiments were performed on a IKS-14A instrument in special nondismountable cells with a layer thickness of 1.03 mm; the pure solvent was placed in the comparison cell. The analytical absorption band was the band at 990 cm^{-1}.

To check absorption in this band by other components of the essential oil and of extracts, the cineol was eliminated from a hexane solution of the essential oil and from hexane extracts from the leaves and tinctures (repeatedly, by the resorcinol method). Then the IR spectra of the residues of the essential oil and of the extract from the tinctures and leaves were recorded. The absence from these of the maximum at 990 cm^{-1} showed that the other components of the essential oil and the extracts do not absorb in the region investigated.

In order to perform the analysis of cineol, it was necessary to dissolve it in an organic solvent. The best proved to be hexane, which dissolves extremely little water, does not mix with 70% ethanol, and has a low boiling point (68.95°C). These properties of hexane enabled it to be used both as a solvent and as an extractant.

As a result of the experiment it was established that the optical density of cineol at 990 cm^{-1} obeys the Bouguer–Lambert–Beer law in the range of concentrations from 0.03 to 0.8%. The amount of cineol can be determined by means of a calibration graph.

The results obtained have enabled the following method to be put forward:

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TABLE 1. Results of the Quantitative Determination of Cineol by Several Methods in Comparison with the IR Method Developed

Material analyzed	Method of analysis					
	resorcinol (gravimetric)		resorcinol (volumetric – pharmacopoeial)		IR method	
	x_i	metrological characteristics	x_i	metrological characteristics	x_i	metrological characteristics
Leaves	—	—	—	—	1,33	$\bar{x} = 1,30$
					1,28	$S^2 = 0,56 \cdot 10^{-3}$
					1,32	$S_{\bar{x}} = 0,9661 \cdot 10^{-2}$
					1,27	$E_{0.95} = 0,03$
					1,29	$A = \pm 0,75\%$
					1,31	
Essential oil	94,2	$\bar{x} = 93,17$	88,00	$\bar{x} = 87,22$	87,0	$\bar{x} = 86,57$
	93,1	$S^2 = 3,095$	86,00	$S^2 = 0,7837$	86,0	$S^2 = 0,4067$
	91,8	$S_{\bar{x}} = 0,7182$	86,67	$S_{\bar{x}} = 0,3610$	86,0	$S_{\bar{x}} = 0.2604$
	92,5	$E_{0,95} = 1,85$	88,00	$E_{0,95} = 0,93$	87,4	$E_{0.95} = 0,67$
	91,3	$A = \pm 0,77\%$	86,67	$A = \pm 0,41\%$	86,0	$A = \pm 0,30\%$
	96,1		88,00		87,0	
Tincture	—	—	—	—	0,0428	$\bar{x} = 0,432 \cdot 10^{-1}$
					0,0437	$S^2 = 0,1456 \cdot 10^{-5}$
					0,0418	$S_{\bar{x}} = 0,493 \cdot 10^{-3}$
					0,0453	$E_{0,95} = 0,13 \cdot 10^{-2}$
					0,0425	$A = \pm 1,06\%$
					0,0433	

Note: The resorcinol (gravimetric) method gives a high result.

1. For the quantitative determination of cineol in the essential oil, a weighed amount of the oil is dissolved in hexane to a concentration of about 0.8%, and the optical density at 990 cm^{-1} is found.

2. The quantitative determination of cineol in a tincture is performed in the same way: 40 ml of the tincture is extracted twice with 10 ml of hexane in a separating funnel for 5 min, and the optical density of the extract at 990 cm^{-1} is determined.

3. The quantitative determination of cineol in the raw material is performed by the equilibrium method [4]: a weighed sample of the raw material ground to a powder is covered with hexane in a ratio of 1:5 and is extracted with constant stirring for 3 h. Then 20 ml of the extract is filtered off, and its optical density at 990 cm^{-1} is determined.

A comparative evaluation of the methods for the quantitative determination of cineol has shown that the method is fairly accurate, the deviation of the values found from the values obtained by an independent method amounting to 0.65% (Table 1).

SUMMARY

1. A method for the quantitative determination of cineol in the raw material and in eucalyptus preparations by IR spectroscopy has been developed.

2. The method possesses high accuracy and is reliable and specific.

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