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PLANT POLYSACCHARIDES.
VI. DETECTION OF A NATIVELY ACETYLATED MANNAN IN *Ungernia* BULBS BY IR SPECTROSCOPY

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IR spectroscopy has been used to detect a mannan in Ungernia *bulbs. The mannan was determined qualitatively and quantitatively directly in a preparation of ground bulbs, avoiding the process of extracting the polysaccharide.*

It has been reported previously that mannans from the bulbs of wild plants of the *Ungernia* genus (fam. Amaryllidaceae) are of interest as a source of mannose from domestic raw material. A method has been proposed for obtaining *D*-mannose and mannan [1, 2]. The mannose is used for the demands of chemistry, microbiology, and medicine, and the mannan as a drug [3-5].

The method for the chemical analysis of *Ungernia* bulbs [1] includes the laborious stage of isolating and purifying the polysaccharide. At the same time, in the processing of the bulbs on a semiindustrial or factory scale the task unavoidably arises of purifying a large number of batches of plant material gathered at different times from different sites.

The aim of the present investigation was a study of the possibility of the rapid detection of mannan directly in plant bulbs without the lengthy process of isolating the polysaccharide, and this has been achieved by an IR-spectroscopic method.

We studied the IR spectra of : (I) — the mannan; (II) — the mannan peracetate; (III) — a deacetylated analog of the mannan; and seven samples of flour of bulbs *of Ungernia, Narcissus,* and *Sternbergia:* (IV) — *U. oligostroma*; (V) — *U. sewerzowii*; (VI) — *U. spiralis*; (VII) — *U. trisphaera*: (VIII) — *U. victoris*; (IX) — *N. tazetta*; and (X) — *S. lutea.* A comparison was made of the characteristic frequencies in the 700-970 cm^{-1} region, corresponding to the out-of-plane vibrations of the $C-H$ bonds of pyranose rings. Analysis of the IR-spectral characteristics showed the presence in spectra of the samples investigated (I-IX) of two characteristic absorption bands, at 810 ± 5 cm^{-1} and 865 ± 5 cm^{-1} (Fig. 1), which were absent from the spectrum of a glucan (X) (see Table 1). It is known from literature sources that a maximum in the 810 cm^{-1} region characterizes the presence of β-*D*-mannopyranose, and an absorption band at 870 cm^{-1} corresponds to the deformation vibrations of the equatorial C_2-H bond in mannose [6].

Thus, the presence of the above-mentioned absorption bands makes it possible to assign the substances under study to the mannose-containing polysaccharides with the β-1-4 type of bond.

For the quantitative determination of the $O-Ac$ groups we chose as the analytical absorption band that with a maximum at 1742 cm^{-1}, corresponding to the stretching vibrations of the ester carbonyl in mannan peracetate (II), the position of which changes little (±5 cm^{-1}) with an increase in the number of acetyl groups.

A linear dependence of the optical density D ($\ln I_0/I$) on the concentration C confirmed the absence of an influence of the surrounding atoms and groups (Fig. 2). The equation of the straight line for the peracetate of the native mannan derived by the method of least squares has the form $D = 0.86 \cdot C + 0.90$. The reproducibility of a series of measurements is indicated by the standard deviations $S_D = D \pm 0.016$ and $S_C = C \pm 0.014$. The results (see Table 1) show that the content of OAc groups in the natively acetylated mannan was 17%, while in powdered *Ungernia* bulbs it did not exceed 6%.

Particular interest is presented by a comparison of the IR spectra in the 700-800 cm^{-1} region, corresponding to the out-of-plane vibrations of the C-H bonds of the pyranose rings of highly substituted acetates [7] and of the natively acetylated

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TABLE 1. Characteristic Absorption Bands in the 700-970 cm^{-1} Region of the IR Spectra of Polysaccharides I-X and their O−Ac Group Contents

Sample No.	δ_{C-H}, cm^{-1}	C, %
I	777*, 811, 871, 965	17
II	777, 958	–
III	813, 872	–
IV	813, 865, 930	5.0
V	816, 867, 927	3.0
VI	816, 868, 926	3.7
VII	816, 867, 929	5.9
VIII	813, 863, 927	4.0
IX	816, 867, 927	–
X	862, 928	4.8

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*Very weak intensity of the absorption band.

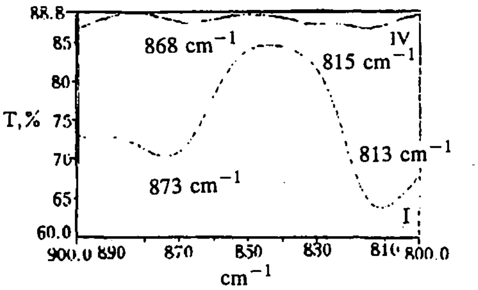

Fig. 1. IR spectra in the 800-900 cm^{-1} region: *I*) native acetylated mannan; *IV*) *U. oligostroma*.

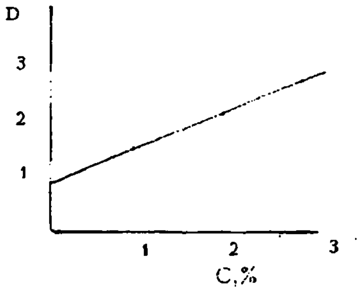

Fig. 2. Graph of the linear dependence of the optical density on the concentration for mannan peracetate (ν_{max} 1742 cm^{-1}).

mannan (I) and its peracetate (II) and of polysaccharides (IV-VIII). Analysis has shown that the intensity of the strong absorption band found at 777 cm^{-1} in the peracetate of the native mannan with the maximum content of OAc groups was appreciably lower in the natively acetylated mannan (I) containing about 20% of OAc groups, while this band had disappeared completely in polysaccharides (IV-VIII) containing not more than 10% of OAc groups. This experimental fact makes possible a relative quantitative determination of the OAc group content both in *Ungernia* raw material and in isolated mannans.

Thus, the possibility has been shown of using an IR-spectroscopic method for the qualitative and quantitative determination of mannans in *Ungernia* raw material.

EXPERIMENTAL

For the isolation of the polysaccharides and their derivatives (peracetates and deacetates), see [8].

The IR spectra of the samples were taken on a Perkin-Elmer system 2000 Fourier IR spectrometer in plates molded with KBr.

The concentrations of the samples investigated were 1, 1.5, 2, 2.5, and 3%.

The percentage contents of OAc groups were determined from the relation $C = (D$ of the sample$)/(D$ of peracetate (II)$) \times 100\%$, the correlation coefficient r being 0.97. Standard deviations: $S_D = D \pm 0.016$ and $S_C = C \pm 0.014$.

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