hydrolysis of compound (II) under the reaction conditions. It is obvious that the low yield of (IV) on the interaction of equimolar amounts of (II) and (Ia) (~5%) and of (II) and (Ib) (~30%) is a consequence of the parallel hydrolysis of (II). At the same time, the considerable difference in the yields of (IV) show a higher reactivity of (Ib) than of (Ia).

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CHROMATO-MASS SPECTROMETRIC IDENTIFICATION OF FOUR 12,13-EPOXYTRICHOTHEC-9-EN-8-ONES IN A SAMPLE OF FUSARIUM-INFECTED GRAIN

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The first report on the identification of two 12,13-epoxytrichothec-9-en-8-ones – the 3,4,7,15-tetrahydroxy derivative (nivalenol) and 4-deoxynivalenol – in a sample of barley was made in Japan in 1977 [1]. The combined presence of 4-deoxynivalenol and its 15-acetyl derivative in samples of Fusarium-infected maize has been described recently [2]. In the present paper we report the identification of 4-deoxynivalenol and its 3-acetyl and 15-acetyl derivatives and of 4,7-dideoxynivalenol from the results of TLC and the chromato-mass spectrometry of the trimethylsilyl (TMS) derivatives under the conditions of chemical ionization by positive and negative ions (CIPI, CINI) in an extract of a sample of Fusarium-infected wheat.

A sample of flour (200 g) was extracted with 600 ml of acetonitrile–water (5:1) in a mixer for 10 min. The extract was filtered through a column containing 10 g of a mixture of activated carbon and Celite and 10 g of neutral alumina. The filtrate was evaporated to dryness, the residue was dissolved in water, and the solution was passed through a PRE SEP C18 column (Czechoslovakia). A methanol–water (1:1) eluate from the column was evaporated to dryness in vacuum, the residue was dissolved in 5 ml of ethyl acetate, the solution was filtered through a layer of anhydrous sodium sulfate, and the product was analyzed by TLC on Silufol in comparison with authentic samples of natural 12,13-epoxytrichotec-9-en-8-ones. The substances were detected from their blue fluorescence in UV light (366 nm) after separate treatment of the plates with 10% solutions of H_2SO_4 and $AlCl_3$ in ethanol and heated at 92°C for 1 and 10 min, respectively.

TLC with chloroform–methanol (7:1) as the mobile phase revealed the presence in the eluate, together with 4-deoxynivalenol (I), R_f 0.26, of 4,7-dideoxynivalenol (II) with the same mobility as (I) but giving a characteristic blue fluorescence after treatment with acid and heating. In ethyl acetate–hexane (3:1) as the mobile phase, the substances of the eluate were found to have the same R_f values as 4-deoxynivalenol 3-acetate (III) (R_f 0.26) and 4-deoxynivalenol 15-acetate (IV) (R_f 0.15).

The dry residue from the filtrate was treated with 50 μl of TBT silylation mixture (USA), and after 20 min at 60°C the reaction mixture was analyzed on a Finnigan MAT 4615 chromato-mass spectrometer (0.32 mm × 45 m capillary column, 25 μm of OV-351) in the isothermal regime at 220°C with the recording of mass spectra in the CIPI and CINI regimes, the reagent gas being ammonia (0.7 mm Hg) and the ionizing voltage 70 V.

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The identification of the TMS ethers of (I-IV) in the CIPI regime from their characteristic ions with m/z 513 $(M + H)^+$ and 530 $(M + NH_4)^+$ for TMS-(I), 425 $(M + H)^+$ and 442 $(M + NH_4)^+$ for TMS-(II), and 483 $(M + H)^+$ and 500 $(M + NH_4)^+$ for TMS-(III) and TMS(IV), and in the CINI regime from the ions with m/z 297 and 215, 424, and 209, 482, and 267 for the TMS ethers of (I-IV) also confirmed the presence of these compounds in the sample. The complete mass spectra of the TMS ethers of the compounds of the natural sample were identical with the spectra of the TMS ethers of authentic substances with respect to m/z values and intensities of all the characteristic fragments.

The simultaneous presence of four compounds of this group in natural samples of Fusarium-infected grain has not been reported previously.

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