NATURAL INHIBITORS OF THE GROWTH OF THE COTTON PLANT

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UDC 547.9+543.51

The aim of the present work was to isolate substances possessing inhibitory activity and formed in the period of accumulation of the cotton harvest. The best known inhibitor is abscisic acid (ABA) [1], which has been isolated, for example, from yellowed leaves of sycamore [1] and the fruit of the cotton plant [2]. The amount of inhibitory substances in the organs of the plant corresponds to a level of the order of 10^{-5}-10^{-6} %, in view of which the most acceptable methods for their detection are variants of combinations of chromatography and gas spectrometry. The separation was carried out by TLC on Silufol UV 254 in the isopropanol—ammonia—water (10 : 1 : 1) system. The individual zones distinguished by their color in UV light were eluted with ether or methanol. The eluates showed inhibitory activity in the test on wheat coleoptiles.

The active zones were investigated by fractionated direct introduction of the dried eluates into a MKh-1301 high-resolution gas spectrometer. Extracts of leaves of two varieties of cotton plant — Tashkent-1 and Listopadnyi-1 — collected on September 10, 1981, were studied by this method in order to establish possible differences and reveal substances responsible for the earlier time of leaf fall of one of the varieties.

In an eluate of the active zone of the variety Tashkent-1 we detected a compound with a molecular mass of 414, composition $C_{29}H_{50}O$, corresponding to sterols. The distribution of the intensities of the peaks in the region of high mass numbers did not correspond to the most common plant sterol — β-sitosterol; the highest intensity was possessed by the peak of the ion $(M - H_2O)^+$ with m/z 396, and a somewhat lower intensity by the peak of the ion $M - OH)^+$ with m/z 397. This nature of the spectrum could be a consequence of the presence of a heavy substituent at C-3 of the steroid skeleton. However, the metastable defocusing spectrum of the ion with m/z 396 showed a single origin — an ion with m/z 414. It remained to be assumed that the small difference an intensities was caused, for example, by a double bond in a position different from that in β-sitosterol, promoting the intensified splitting out of a molecule of water and a hydroxy radical. Furthermore, in the spectrum of this eluate ions with m/z 192 and 177 were detected the compositions and relative intensities of which coincided with those of an authentic sample of the coumarin scopoletin, and also a compound with the composition $C_{12}H_{20}O_3$ (M^+ 212), splitting out under electron impact a molecule of water with the formation of an ion with m/z 194. A molecule of this composition can arise from carotenoids of the type of violaxanthin — a probable precursor of ABA [3].

The mass spectrum of the eluate of the active zone of the variety Listopadnyi-1- taken under similar conditions (50 eV) was considerably poorer than the first spectrum. The heights of the peaks of the ions with m/z 414, 397, and 396 here were smaller. To determine the molecular peaks of the components, the mass spectra were obtained at a reduced electron energy of 12 eV. In sum, two new compounds were detected with molecular masses of 314 and 300 and the compositions $C_{21}H_{30}O_2$ and $C_{20}H_{28}O_2$. In addition to M^+, the fragments $(M - CH_3)^+$ with m/z 299 and 285, the heights of the peaks of which were approximately twice those of the molecular ions were determined.

According to Enzell and Ryhage [4], such a feature of the spectra is characteristic for diterpenes with a podocarpin skeleton and, in particular, for the derivative totarol isolated from *Juniperus conferta* [5].

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 120-121, January-February, 1983. Original article submitted June 30, 1982.

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OXIDATION OF BENZIMIDAZOLES TO BENZIMIDAZOLONES

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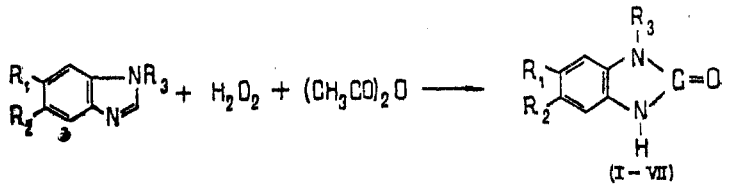
UDC 547.783.5.07:542.951.541.67

Two main methods of obtaining benzimidazolones are known: by the reaction of o-phenylenediames with urea or with phosgene [1, 2], but it is impossible to obtain certain benzimidazolones (for example, (III) and (VI), below) by these methods. This is due to the fact that not all substituted o-phenylenediamines are stable compounds and their use is accompanied by side reaction with the formation of azine dyes which leads to a marked decrease in the yield of the benzimidazolone derivative [3].

The aim of our work was to obtain substituted benzimidazolones by the oxidation of the corresponding benzimidazoles, since physiologically active compounds have been found among them [4, 5].

The oxidation reaction was carried out with hydrogen peroxide in acetic anhydride under conditions similar to those described by Sawlewicz [6] with our own simplifications in the isolation of the reaction products.



(I – VII)

Compound	R_1	R_2	R_3	Yield, %	mp, deg C (literature figures in parentheses)
I. Benzimidazolone	H	H	H	57	304–305 (305–306)
II. 5-Methylbenzimidazolone (III)	CH_3	H	H	41	291–292 (292)
III. 5-Methoxybenzimidazolone	CH_3O	H	H	23	218–219
IV. 5-Chlorobenzimidazolone	Cl	H	H	36	270–271 (269–270)
V. 5-Nitrobenzimidazolone	NO_2	H	H	22	305–306(306)
VI. 5,6-Dimethylbenzimidazolone	CH_3	CH_3	H	36	210-211
VII. 1-Methylbenzimidazolone	H	H	CH_3	35	191–192(191-192)

The optimum yields of reaction products were obtained by the action of one mole of the appropriate benzimidazole of 24 ml of 30% hydrogen peroxide in 80 ml of acetic anhydride. The reactions took place exothermically. After the reaction mixture had cooled, it was made weakly alkaline with 5 N NaOH and was then boiled for 1 h. After cooling, the reaction mixture was acidified with 4 N HCl and the resulting precipitate of benzimidazolone was filtered off, the unchanged benzimidazole being isolated from the acid filtrate by alkalinization. The benzimidazolones obtained were recrystallized from aqueous ethanol.

The benzimidazolones obtained were identified by mixed melting points with authentic samples obtained by a method described previously [1] and from their IR spectra. The IR spectra of compound (III) and (VI) each showed an absorption band at 1660-1680 cm^{-1} that is characteristic for C=O of a benzimidazolone ring.

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 0009-3130/83/1901-0124$07.50