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QUANTITATIVE ANALYSIS OF ANTIFEEDANT TERPENOIDS OF COTTON CULTIVATED IN UZBEKISTAN

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Increasing the resistance of agricultural crops to insects is an ecologically safe method for decreasing harvest losses related to damage from insect pests and is a very important area of genetic selection studies.

It was shown earlier that cotton varieties with high contents of the dimeric sesquiterpenoid gossypol, which is toxic for a broad spectrum of insect pests, were more resistant to them [1, 2]. Other aldehyde terpenoids related to gossypol may also cause insect-resistance. These include hemigossypolone [5,8-dihydro-2,3-dihydroxy-6-methyl-4-(1-isopropyl)-5,8-dioxo-1-naphthaldehyde, HGQ] and its methyl ether (mHGQ) and their Diels—Alder condensation products with the volatile monoterpenes myrcene and β-ocimene, so-called heliocides (anthraquinon-1-aldehydes) [3, 4], which occur primarily in unripe cotton bolls and leaves. Their level correlated better than that of gossypol with cotton insect resistance. It was also shown that these compounds exhibit an antifeedant effect [5, 6].

Because various cotton varieties exhibit different resistances to insects, the resistance may be related to the heliocide levels in cotton leaves or bolls during their ripening. It is well known from the literature that cotton varieties of the species *Gossipium hirsutum* with the usual amount of pigment glands contain gossypol, hemigossypolone, and group H heliocides derived from it. The contents of heliocides H_1 and H_4 increased three times in resistant varieties rich in glands [7]. Cotton species *G. barbadense* L. contains mainly methylated analogs of the terpenoids (including group B heliocides) that are less toxic to insects. As a rule, heliocides H_2 and H_3 occur in wild specimens of *G. hirsutum*; B_2 and B_3, in second-generation *G. hirsutum* × *G. barbadense* interspecies hybrids [8, 9]. Based on these data, it can be assumed that group B heliocides will dominate in varieties with parent genotypes of *G. barbadense*; group H, in varieties issuing from *G. hirsutum.*

Thus, the goal of the present study was to determine the contents of antifeedant terpenoids in various cotton varieties cultivated in Uzbekistan as related to the original species and the insect resistance determined from the amount of damaged bolls.

We performed qualitative and quantitative analyses of individual heliocides H and B, their biosynthetic precursors (HGQ/mHGQ), and gossypol G in 2-3-day bolls of eight regionalized cotton varieties in Uzbekistan using a specially developed HPLC method. The method consisted of the simultaneous determination of this series of antifeedant terpenoid aldehydes in cotton-boll extracts.

The analysis was carried out using an 1100 liquid chromatograph (Agilent Technologies Inc. USA) equipped with a 4-gradient pump and variable wavelength detector (VWD) over a Discovery HS C18 column (4.6 × 75 mm, Sigma Aldrich/Supelco, USA) using a gradient of CH_3CN in aqueous H_3PO_4 (0.1%) at pH 2.5 (55–95%) with UV detection of the effluents at 272 nm [10]. Standard terpenoid aldehydes were supplied by Dr. R. Stipanovic (USDA/ARS Southern Plains Agricultural Research Center, College Station, TX, USA). Table 1 presents retention times (RT) of the studied terpenoids under the given conditions.

Pure terpenoids were isolated from unripe cotton bolls of variety Termez-31 using a modified literature method [11] and then purified by HPLC in order to obtain preparative amounts of them that were required to calibrate the quantitative method. Table 1 presents also the results of the chromatographic analysis.

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TABLE 1. Quantitative Determination of Several Antifeedant Terpenoids in Cotton Bolls and Their Retention Times for HPLC Analysis

Variety	Terpenoid content, μg/g dry boll tissue (± 5%)							
	HGQ	mHGQ	G	H_4	H_1	$H_2 + H_3$	B_4	B_1
Termez-31	709.5	586.9	6.0	1005	1796	–	806.4	1245
Zharkurgan	316.3	13.2	2.3	379.2	850.1	7.6	16.8	25.6
C6524	340.5	25.5	2.0	310.2	706.2	3.5	24.0	37.5
Omad	95.4	3.8	1.5	239.7	525.5	195.0	23.2	27.3
Bukhara-6	139.3	7.2	1.6	187.4	462.9	282.5	4.4	6.8
Sultan	188.8	32.9	4.0	140.2	353.4	6.2	15.3	28.9
C2510	48.0	6.0	3.2	79.9	240.6	111.6	5.2	10.0
C8284	46.6	6.4	0.96	42.6	115.7	79.4	12.9	13.3
Retention time, min	4.453	7.538	11.246	14.193	14.427	14.935	18.142	18.479

HGQ, hemigossypolone; mHGQ, hemigossypolone 6-methyl ether; G, gossypol; H_1–H_4, B_1, B_4, heliocides.

A comparison of the studied varieties and the spectra of terpenoids contained in them indicates that variety Termez-31, which is a hybrid of two *G. barbadense* varieties (6608B and Termez-11), had the highest contents of heliocides B_1 and B_4. However, variety Zharkurgan with a complicated interspecies origin [F_4(F_1 *G. thurberi* × *G. raimondii*) × *G. hirsutum* L.] contained mainly group H heliocides. Two of these varieties had the maximum contents of both groups of heliocides of all those represented. Recent field observations noted the high resistance of these varieties to cotton bollworm *Heliothis armigera* Hb.

Susceptible varieties C2510 and C8284 had the lowest total contents of these antifeedant terpenoids. Therefore, they were damaged to a greater extent by the insect pests.

Thus, a relationship was found between the contents of several terpenoids and the insect resistance of cotton with various species origins. The quantitative contents in the parent pairs of both individual antifeedant terpenoids and their overall total contents should be considered in creating new insect-resistant cotton varieties. The selection should be directed at increasing the contents of these compounds in the hybrids.

REFERENCES

1. G. T. Bottger, E. T. Sheehan, and M. J. Lukefahr, *J. Econ. Entomol.*, **57**, 283 (1964).
2. J. N. Jenkins, F. G. Maxwell, and H. N. Lafever, *J. Econ. Entomol.*, **59**, 352 (1966).
3. R. D. Stipanovic, in: R. J. Petroski and S. P. McCormick (eds.), *Secondary-Metabolite Biosynthesis and Metabolism*, Plenum Press, New York (1992), pp. 319-328.
4. A. A. Bell, R. D. Stipanovic, D. H. O'Brien, and P. A. Fryxell, *Phytochemistry*, **17**, 1297 (1978).
5. H. J. Williams, R. D. Stipanovic, L. A. Smith, S. B. Vinson, P. O. Darnell, R. Montandon, D. L. Begin, G. W. Elzen, H. Gunasena, and A. A. Bell, *Rev. Latinoam. Quim.*, **18**, 119 (1987).
6. P. A. Hedin, W. L. Parrott, and J. N. Jenkins, *J. Econ. Entomol.*, **85**, No. 2, 359 (1992).
7. A. A. Bell and R. D. Stipanovic, in: *Proc. of the Beltwide Cotton Production Res. Conferences*, Las Vegas, NV, USA, Jan. 5-7, 1976, p. 52.
8. R. D. Stipanovic, A. A. Bell, and M. J. Lukefahr, in: *ACS Symposium Series, Host Plant Resistance to Pests*, American Chemical Society, Washington, D.C. (1977), **62**, p. 197.
9. A. A. Bell and R. S. Stipanovic, in: *Proc. of the Beltwide Cotton Production Res. Conferences*, Atlanta, GA, USA, Jan. 10-12, 1977; National Cotton Council, Memphis, TN (1977), p. 244.
10. V. V. Uzbekov, in: *Program and Abstracts of Papers of a Conference of Young Scientists Dedicated to the Memory of Acad. S. Yu. Yunusov* [in Russian], Tashkent, ICPS, Mar. 17, 2011, p. 27.
11. R. D. Stipanovic, A. A. Bell, D. H. O'Brien, and M. J. Lukefahr, *Phytochemistry*, **17**, 151 (1978).