INFLUENCE OF SOME DEFOLIANTS ON THE GOSSYPOL PIGMENTS OF COTTON SEEDS

I. P. Nazarova, N. T. Ul'chenko,
N. K. Yuldasheva, A. I. Glushenkova,
and A. A. Umarov

UDC 547.972

The influence of a number of defoliants on the gossypol pigments of cotton seeds of variety S-4880 has been studied. It was established that the qualitative compositions of the pigments of the defoliant-treated plants and of the control plants were identical. However, their quantitative composition in seeds treated with defoliants having a severe action had changed substantially: they contained larger amounts of the bound forms of gossypol than in the variants with defoliants having a mild action.

The machine harvesting of cotton raw material became possible only thanks to defoliants, which ensure not only the preharvesting elimination of the leaves but also an acceleration of the development of the bolls. At the present time, the cotton production of the Republic is experiencing an acute need of effective defoliants of low toxicity. The demands for newly created preparations are rising continuously both in the technical and economic respect and in the ecological and toxicological respect.

Great attention has always been devoted to the study of the influence defoliants on the cotton harvest and quality. There is a fairly large amount of information in the literature on the influence of various preparations on the technological properties of the fiber, the oil content of the seeds, and their sowing properties [1-3]. However, the changes that defoliants cause in the amount and composition of the gossypol pigments of cotton seeds have not been studied. Nevertheless, these indicators are of great importance on the use of cotton seeds as a raw material for food and fodder purposes and for the industrial isolation of gossypol as an independent product.

We have, for the first time, determined the amounts of gossypol in the seeds of three varieties of cotton plants — 108-F, S-6524, and C-4880 — that had been treated with defoliants and compositions containing them created in the Defoliant Intersector Scientific and Technical Center.

Table 1 gives figures from which it can be seen that when the cotton plant varieties 108-F and S-6524 were treated with identical doses of defoliants, a tendency was observed to some rise in the oil content, although within the permissible limits of experimental error (0.3-0.6%). The increase in the weight of a thousand seeds was accompanied by an increase in the oil content as compared with the control. The amount of gossypol in the treated seeds was close to that of the control. For variety S-4880, the greatest increase in the oil content (0.5%) was observed on treatment with the defoliants ziëd, tsitodef, dropp, and a mixture of dropp and butylcaptax. So far as concerns the defoliants magnesium chloride and a mixture of butylcaptax with magnesium chloride, here marked decreases in the weight of 1000 seeds (by 6-15.8 g), in their oil content (by 2.0-2.5%) and in the level of free gossypol (by 0.15-0.17%), in comparison with the control, were observed. This may be due to the severe action of these defoliants.

The treatment of cotton plants of the varieties 108 F and S-4880 with the defoliant ziëd was accompanied by some simultaneous increase in the oil content and in the amount of free gossypol by 0.19-0.22%. A determination of the total amount of gossypol in the seeds of variety F-4880 showed that practically all the gossypol in them was present in the free state. The isolation and analysis of the gossypol pigments was performed on seeds of a cot-

Institute of Chemistry of Plant Substances, Uzbekistan Academy of Sciences, Tashkent.
Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 208-212, March-April, 1993. Original article submitted September 28, 1992.

0009-3130/93/2902-0169$12.50

TABLE 1. Characteristics of Cotton Seeds Treated with Defoliants

Defoliant	Variety of cotton plant									
	108-F			S-6524			S-4880			
	weight of 1000 seeds, g	oil content,* %	free gossypol, %	weight of 1000 seeds, g	oil content * %	free gossypol, %	weight of 1000 seeds, g	oil content,* %	Gossypol content, %	
									free	total
1. Control	110,7	21,3	0,96	112,8	21,9	1,00	105,3	19,5	0,90	0,93
2. Gemetrel	113 1	21,6	0,82	117,4	22,3	0,93	105,2	19,7	0,97	0,95
3. Butylcaptax + magnesium chlorate	117,9	21,9	0,87	118,7	22,4	0,84	99,3	17,7	0,73	0,74
4. Zied	114,7	21,9	1,18	—	—	—	111,1	20,0	1,09	1,06
5. Dropp + butylcaptax	117,4	21,8	0,86	122,4	22,5	0,88	109,3	20,1	0,98	0,95
6. Khaet	115,9	21,7	0,90	117,6	22,3	1,01	108,3	19,5	0 85	0,87
7. Tsitodef	117,9	21.9	1,09	121,4	22 4	1,06	111,0	20,0	0,91	0,90
8. Atoll	112,2	21,7	0,95	—	—	—	103 0	19,5	0,98	0,97
9. Dropp	114,7	21,8	0,91	122,3	22,5	1,11	110,5	20,0	0,97	0,95
10. Magnesium chlorate	113,9	21,6	0,85	—	—	—	89,5	17,5	0,75	0,73

*On the absolutely dry weight.

TABLE 2. Characteristics of Hexane Extracts of Cotton Seeds of Variety S-4880 That Had Been Treated with Defoliants

Defoliant	Yield of extract, % on the weight of the seeds	Amount of gossypol, %			Bound gossypol as % of the total	Acid No., mg KOH
		free	bound	total		
Control	20,0	0,71	0,27	0,98	27,3	4,7
Butylcaptax + magnesium chlorate	16,0	0,56	0,64	1,20	53,8	6,2
Magnesium chlorate	18,5	0,31	0,59	0,90	65,8	5,2
Zied	15,6	0,36	0,55	0,91	60,4	7,7
Atoll	16,6	0,80	0,26	1,06	24,5	6,4
Tsitodef	18,3	0,76	0,40	1,16	34,4	6,1
Dropp	18,5	0,71	0,37	1,08	34,2	5,3

TABLE 3. Fatty Acid Compositions of the Seed Oils from Cotton Plants of Variety S-4880 That Had Been Treated with Defoliants

Acid	Amounts of acid (% GLC) in seeds treated with defoliants						
	control	butyl-captax + magnesium chlorate	zied	magne-sium chlorate	atoll	tsitodef	dropp
$C_{14:0}$	1,1	1,0	0,6	0,9	0,7	0,8	0,7
$C_{16:0}$	27,4	21,4	24,0	26,6	23,2	22,3	23,1
$C_{16:1}$	1,5	2,4	1,5	1,1	0,8	0,6	1,0
$C_{18:0}$	1,8	5,4	2,5	1,7	2,1	2,0	2,1
$C_{18:1}$	16,5	19,6	15,9	16,2	17,4	17,7	16,6
$C_{18:2}$	51,7	50,2	55,5	53,5	55,8	56,0	56,4

ton plant of variety S-4480, which readily undergoes the action of defoliants. We investigated the seeds of a control sample and of a sample that had been treated with powerful defoliants (butylcaptax + magnesium chloride, zied, magnesium chlorate, leading to severe withering of the leaves, and with gentle defoliants (atoll, tsitdef, dropp), with which the leaves are shed in the green state. The gossypol was extracted in the previously ground and hexane-defatted seeds. Table 2 gives some indices of the hexane extracts of the samples studied, which were obtained from 100 g of seeds. It can be seen that, on cold extraction with hexane, yields from the seeds that had been treated with defoliants were lower, and the acid numbers were higher than for the control. The oils of all the samples were found to contain not only free but also bound gossypol, and in the control and in the seeds that had been treated with mild defoliants the proportion of bound gossypol (% on the weight of the total) was considerably lower than for the oils from seeds that had been treated with powerful defoliants.

The fatty acid compositions of the seed oils (Table 3) were practically identical for all the samples studied. The gossypol pigments were extracted from the hexane-defatted seeds with chloroform.

In a determination of the balance of gossypol that had passed into the gossypol extract, it was found that this did not represent all the gossypol left in the defatted seeds. Apparently, during extraction with hexane some binding of the gossypol with substances of the seeds accompanying it takes place. To elucidate this circumstance we determined the amounts of free and total gossypol in the defatted seeds (Table 4). The figures obtained confirmed the conclusion that in the seeds of the defoliant-treated plants a considerable part of the gossypol was bound, while in the control sample only 13.8% had passed into the bound state. This fact may explain those difficulties which researchers have come up against recently in the industrial production of gossypol from cotton seeds that had been treated with defoliants.

TABLE 4. Amounts of Gossypol in Defatted Cotton Seeds

Defoliant	Amount of gossypol, %			Bound gossypol as % on the total
	free	bound	total	
Control	0,81	0,13	0,94	13,8
Butylcaptax + magnesium chlorate	0,43	0,21	0,64	32,8
Zied	0,63	0,39	1,07	36,4
Magnesium chlorate	0,36	0,34	0,70	48,6
Atoll	0,86	0,15	1,01	14,9
Tsitodef	0,63	0,28	0,91	30,8
Dropp	0,79	0,24	1,03	23,3

TABLE 5. Characteristics of Chloroform Extracts of the Defatted Cotton Seeds

Defoliant	Yield of extract, %	Amount, %	
		free gossypol	gossypurpurin
Control	1,38	50,62	0,75
Butylcaptax + magnesium chlorate	0,92	32,55	1,09
Zied	1,00	43,75	1,15
Magnesium chlorate	0,85	33,20	0,90
Atoll	1,38	53,06	0,89
Tsitodef	1,26	39,62	0,82
Dropp	1,39	46,41	0,73

TABLE 6. Amounts of Gossypol after Extraction of the Defatted Seeds with Chloroform

Defoliant	Amount of gossypol, %			Amount of bound gossypol in the defatted seeds, %
	free	bound	total	
Control	0,10	0,13	0,23	0,13
Butylcaptax + magnesium chlorate	0,11	0,23	0,34	0,21
Zied	0,13	0,42	0,55	0,39
Magnesium chlorate	0,08	0,34	0,42	0,34
Atoll	0,09	0,18	0,27	0,15
Tsitodef	0,05	0,29	0,34	0,28
Dropp	0,08	0,25	0,33	0,24

In the defatted seeds that had been treated with mild defoliants, and also in the oil extracted from them, a considerably larger amount of gossypol (from 32.8 to 48.6%) was in the bound state than in seeds treated with the defoliants atoll, tsitodef, and dropp (from 14.4 to 30.8%).

On the extraction of the defatted seeds with chloroform, it was mainly free gossypol that passed into the extract (Table 5). Gossypurpurin was found in amounts of 0.75-1.15% of the yield of extract in the chloroform extracts of both the control and treated samples of seeds.

Figures for the amount of gossypol remaining in the seeds after defatting with hexane followed by extraction with the chloroform are given in Table 6. On extraction with chloroform, no further binding of the gossypol took place, and its amount remained at the level in the defatted seeds. It was established with the aid of analytical TLC that the qualitative compositions of the gossypol pigments in the control and in the treated samples were identical: gossypol, its methoxy derivatives, gossypurpurin, and gossypol transformation products not giving the qualitative reaction for an aldehyde group. In the quantitative respects, the extracts from the control samples contained considerably more free and less transformed gossypol than those from the seeds of plants that had been treated with defoliants.

EXPERIMENTAL

The objects of investigation were the seeds of cotton plants of the varieties 108-F (Tadzhikistan) and S-6524 (Namangan province) and of variety S-4880 grown in the Central Asian Institute for the Mechanization and Electrification of Agriculture. The plants were treated with the defoliants in September, 1989 when an average of 40-50% of the bolls on a bush were open. Sample bolls were taken on the 12th day after treatment with defoliants from the first positions with 5-6 sympodia.

The oil and moisture contents of the seeds were determined by standard methods [4]. The oil was extracted from the ground seeds by three treatments with hexane. Analytical TLC was conducted on Silufol in the solvent system benzene–methanol (4:1), and the spots were revealed with a 2% solution of $SbCl_3$ in chloroform.

The amounts of free and total gossypol were determined by the para-anisidine method [5]. The amount of gossypurpurin was calculated from the optical densities of chloroform solutions at 565 nm [6].

LITERATURE CITED

1. A. I. Imamaliev, Defoliants and Their Physiological Action on the Cotton Plant [in Russian], FAN, Tashkent (1969), p. 307.
2. T. S. Zakirov, The Chemical Defoliation and Desiccation of the Cotton Plant [in Russian], Tashkent, Uzbekistan (1968), p. 180.
3. A. A. Umarov, M. Khamidov, T. Van'yants, and I. Ishankulov, Khlopok, No. 4, 29 (1989).
4. Handbook on Methods of Investigation, Technical and Chemical Control, and the Accounting of Production in the Oils and Fats Industry [in Russian], Leningrad, Vol. II, (1965), p. 146.
5. A. L. Markman and V. P. Rzhekhin, Gossypol and Its Derivatives [in Russian], Pishchevaya Prom-st' (1965), p. 218.
6. Handbook on Methods of Investigation, Technical and Chemical Control, and the Accounting of Production in the Oils and Fats Industry [in Russian], Leningrad, Vol. IV, No. II (1974), p. 42.