SUMMARY

A new plant growth regulator — 3,5-dihydroxy-2-octanoylphenylacetic acid, a seed germination inhibitor — has been isolated from the culture filtrate of a phytopathogenic fungus of the genus Phoma.

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INFLUENCE OF ADDITIONS OF ANTHRAQUINONE ON THE ALKALINE HYDROLYSIS OF COTTON-PLANT LIGNIN

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The action of catalytic amounts of anthraquinone on the alkaline hydrolysis of the stems and dioxane lignin of the cotton plant of the ssp. mexicanium has been investigated. It has been established that this leads to a substantial increase in the yield of low-molecular-weight hydrolysis products. Analysis of the monomeric fractions of the hydrolysis products by the GLC method has shown the presence in them of large amounts of substances with a p-coumaryl structure. This, and also the low level of syringyl derivatives, may be caused by the demethoxylation of the lignin under the conditions described.

The addition of catalytic amounts of anthraquinone (AQ) in the akaline digestion of wood leads to an appreciable increase in the rate of delignification through an increase in the breakdown of the β-ethers of units with free phenolic hydroxy groups [1, 2]. The mechanism of the cleavage with the participation of AQ of β-OH ether bonds between guaiacyl structural units forming the lignin of conifer wood has been studied in detail with the aid of experiments on model compounds [3]. The action of AQ on the lignin of the wood of broad-leaved trees, which also includes syringyl units, has not been studied.

We have investigated the influence of small additions of AQ on the alkaline hydrolysis of the stems and the dioxane lignin (DLA) of the cotton plant ssp. mexicanium. The DLA contained about 0.5% of carbohydrates the presence of which is necessary for the inclusion of AQ in the redox cycle [4] and which makes it effective in catalytic amounts.

Hydrolysis was performed in 8% NaOH solution in a nitrogen atmosphere at various temperatures with various amounts of AQ, and also without it. To facilitate the identification of the low-molecular-weight products formed, the reaction mixture was reduced with Raney nickel. After acidification to pH 7-8 the monomeric fraction of the hydrolysis products was extracted with ether, and the residual low-temperature-weight substances were extracted with ethyl acetate at pH 2.

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The yield of low-molecular-weight lignin degradation products as the result of the alkaline hydrolysis of the stems of the cotton plant ssp. mexicanium was (% on the amount of Komarov lignin):

	Temperature 100°C				Temperature 160°C			
	without AQ	+0.05% AQ	+0.1% AQ	+0.2% AQ	without AQ	+0.05% AQ	+0.1% AQ	+0.2 % AQ
pH 8	2.4	5.1	3.2	3.2	4.5	6.3	7.6	6.3
pH 2	3.9	4.8	4.0	3.8	5.1	4.3	10.0	6.8
Total	6.3	9.9	7.2	7.0	9.6	10,5	17.6	13.1

As can be seen from the figures given, in all cases the addition of AQ led to an increase in the total yield of low-molecular-weight lignin hydrolysis products with rises in the yields of both the ether and the ethyl acetate extracts. At a reaction temperature of 100°C the maximum yield (9.9%) was observed with the addition of 0.5% of AQ on the weight of the plant. In the experiments performed in an autoclave at 160°C, the greatest increase in yield was achieved by the addition of 0.1% of AQ (17.6%).

The composition of the ethyl acetate extracts was investigated with the aid of gel chromatography on Sephadex LH-20 (solvent: methanol—water (9:1)). It must be mentioned that in the presence of AQ some shift of the maximum of the molecular-weight distribution curve in the direction of higher molecular weights was observed, which indicates an increase in the proportion of hydrolysis products with higher molecular weights, this being particularly appreciable when the reaction was performed at 160°C (Fig. 1).

The monomeric fractions of the cotton -plant lignin hydrolysis products were investigated by gas—liquid chromatography. The qualitative composition and quantitative amounts of the monomeric phenols in the ethereal extracts were as follows (% on the Komorov lignin):

Substance	Temperature, 100°				Temperature, 160°			
	without AQ	0.05% AQ	0.1% AQ	0.2% AQ	without AQ	0.05% AQ	0.1% AQ	0.2% AQ
Phenyl	0,02	0.07	0.02	0.03	0,07	0,09	0,29	0.06
p-Hydroxyphenylethane	0,36	1.17	0.36	0,96	1,16	1,94	1.43	2.06
p-Hydroxyphenylpropane	0,47	1.09	0,36	0.60	0,92	1,08	1.17	1,32
Guaiacol	0.06	0,26	0.11	0.12	0.15	0,30	0,47	0,34
Guaiacylethane	0.51	0,86	0.54	0.22	0.48	0,60	1,40	0.39
Guaiacylpropane	0,22	0.38	0,20	0.09	0.27	0,50	0.73	0,44
1-Guaiacylethanol	0.01	—	0,04	—	0,17	0,14	0,20	0,10
1-Guaiacylpropan-1-ol	0,37	0.43	0.53	0,64	1,05	1.11	1,44	1,15
3-Guaiacylpropanol	0.10	0.33	0.69	0.36	—	—	—	—
Syringylpropane	0,28	0,42	0,26	0.13	0,18	0,23	0,25	0,26
Ratio								
p-coumaryl	0.67	1.03	0,35	1,11	1.01	1.17	0,68	1.36
guaiacyl	1	1	1	1	1	1	1	1
syringyl	0,22	0,18	0,12	0.09	0.08	0,08	0.06	0.10

Analysis of the ratio of the structural units showed that the total monomeric products from the alkaline hydrolysis of cotton-plant stems contained a very large amount of p-coumaryl derivatives, while, except in the experiments performed in the presence of 0.1% catalyst, additions of AQ appreciably increased their amount. Conversely, the proportion of syringyl derivatives was very small in comparison with their amount obtained in an investigation of the structure of the lignin of the cotton plant ssp. mexicanium performed previously [5]. It is obvious that under the conditions described a demethylation takes place which is promoted to some extent by the presence of the AQ. In this process, the syringyl series proved to be far more stable than the guaiacyl series. The partial demethoxylation of lignin and substances modeling it on heating with alkali has also been reported in the literature [6].

The alkaline hydrolysis of the dioxane lignin isolated from the ripe stems of the cotton plant of ssp. mexicanium [7] was accompanied by the following yields of low-molecular-weight degradation products (% on the DLA):

	Temperature 60°					Temperature 100°		Temperature 160°	
	without AQ	0.05% AQ	0.1% AQ	0.5% AQ	1% AQ	without AQ	0.1% AQ	without AQ	0,1% AQ
pH 8	12	12	22	20	16	14	34	15	12
pH 2	16	18	14	14	14	11	15	14	34
Total	28	30	36	34	30	25	49	29	46

It can be seen that the addition of AQ led to an appreciable increase in the yield of low-molecular-weight hydrolysis products, and a rise in the temperature intensified this effect. The highest yield of products was observed on the addition of 0.01% of AQ, and a

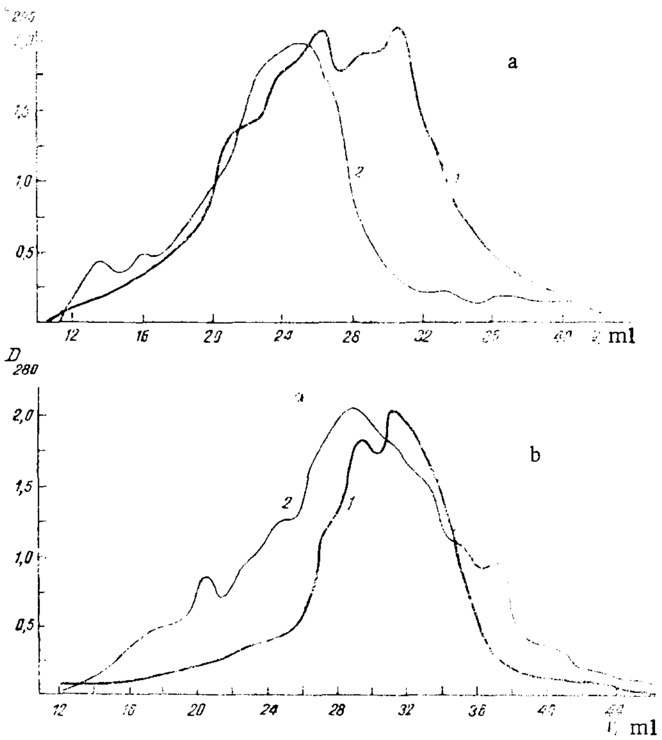

Fig. 1. Gel filtration curves of the total ethyl acetate extracts of the products of the alkaline hydrolysis of natural cotton-plant lignin: a) hydrolysis at 160°C; b) hydrolysis at 100°C; 1) control; 2) with the addition of 0.1% of AQ.

further increase in its amount led to a fall in yield. It is interesting that when the reaction was performed in an autoclave at 160°C the total increase in yield was achieved through the ethyl-acetate-extracted material, while at lower temperatures in the presence of 0.1% of catalyst a predominance of the proportion of the ether-extracted material was observed.

The gel-chromatographic analysis of the ethyl-acetate-extracted material showed an increase on the proportion of substance with high molecular weights in the case of experiments performed in the presence of the catalyst, and, as in the alkaline digestion of cotton-plant stems, this appeared to the greatest extent at 160°C (Fig. 2).

The results of a GLC analysis of the monomeric fractions of the products from the hydrolysis of the DLA of the cotton plant ssp. mexicanium are given below (yield, % on the DLA):

Substance	Temperature 60°C					Temperature 100°C		Temperature 160°C	
	without AQ	0.05% AQ	0.1% AQ	0.5% AQ	1% AQ	without AQ	0.1% AQ	without AQ	0.1% AQ
Phenol	0,08	0,13	0.02	0.07	0.07	0,06	0.30	—	0.22
p-Hydroxyphenylethane	0.24	4,37	3,68	2,77	4.78	1.48	11.12	4.48	3.61
p-Hydroxyphenylpropane	2,95	3,74	6,44	3,56	4,35	1.62	9.89	3.36	0.79
Guaiacol	0,08	0,09	0,04	0.11	0.07	—	0.24	—	0.36
Guaiacylethane	1,09	0.27	0,12	3,34	0,46	0.34	1,36	1.28	3.68
Guaiacylpropane	1,20	0,70	1,54	2,40	1,23	2.86	1,37	1.53	1,98
Vanillin	0,53	—	0.48	0,70	0,50	—	—	—	—
1-Guaiacylethanol	—	—	—	—	—	0.71	0.99	0.48	—
1-Guaiacylpropanol	2,30	0.77	3,04	4.60	2,76	5.14	3.71	2,64	0.64
Syringylpropane	0,26	0,52	0.52	1.17	0.30	1.15	1,50	1,22	0.66
Ratio									
p-coumaryl	0.63	4,50	1,94	0,57	1,71	0.35	2.78	1,32	0,69
guaiacyl	1	1	1	1	1	1	1	1	1
syringyl	0.05	0,56	0.10	0,10	0,06	0,13	0.20	0.20	0.10

As in the alkaline digestion of the cotton-plant stems, in the case of the hydrolysis of the DLA the monomeric fraction of the hydrolysis products contained a large amount of p-coumaryl structural units and the amount of syringyl units was again considerably smaller than that found previously [5].

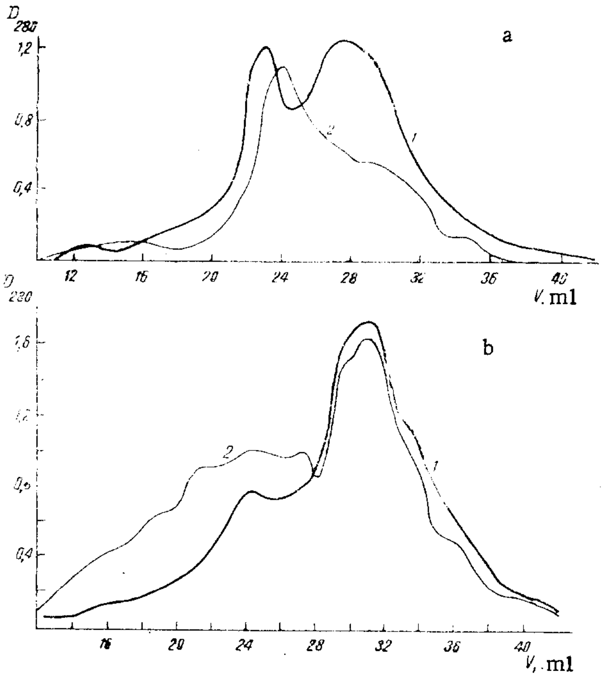

Fig. 2. Gel-filtration curves of the ethyl-acetate-extracted products of alkaline hydrolysis of cotton-plant dioxane lignin: arbitrary symbols the same as in Fig. 1.

EXPERIMENTAL

Alkaline Hydrolysis of Cotton-Plant Stems in the Presence of Anthraquinone. The ground (0.25 mm) cotton-plant stems that has been extracted with ethanol—benzene (1:2) and with hot water (10-g portions) were treated with 100 ml of 8% NaOH and with AQ in amounts of 0.05, 0.1, and 0.2% on the weight of the plant, and the mixtures were boiled with stirring in an atmosphere of nitrogen for 4 h. In each case, the precipitate was separated by centrifugation and was washed with 8% NaOH (3 × 50 ml). The combined solutions were reduced with 20 g of Raney nickel in an atmosphere of nitrogen for 6 h. After decantation, the catalyst was washed by being boiled with 50 ml of 8% NaOH. Then the reaction mixture was acidified with dilute HCl (1:1) to pH 7-8 and with monomeric fraction of lignin hydrolysis products was extracted with ether (1 liter), after which it was acidified to pH 2 and the residual low-molecular-weight products were extracted with ethyl acetate (1 liter). When the experiments were performed in an autoclave at 160°C, the reaction mixture was first purged with nitrogen for 2 min. Heating to 160°C took 1 h, and the autoclave was kept at this temperature for 3 h. The subsequent working-up procedure was carried out as described for the experiments at 100°C. Control experiments were performed under the same conditions but in the absence of a catalyst.

Alkaline Hydrolysis of Cotton-Plant Dioxane Lignin in the Presence of Anthraquinone. AQ was added in amounts of 0.05, 0.1, 0.5, and 1% of the weight of the lignin to solutions containing 0.5 g of DLA in 20 ml of 8% NaOH. The reaction was performed in an atmosphere of nitrogen at 60, 100, and 160°C (autoclave) for 4 h. Then each reaction mixture was reduced by being boiled with 5 g of Raney nickel in an atmosphere of nitrogen. The solution was deanted off and the catalyst was washed by being boiled with 10 ml of 8% NaOH. The solution was acidified with dilute (1:1) HCl to pH 7-8 and the monomeric hydrolysis products were extracted with ether (1 liter), and then, after acidification to pH 2, the residual low-molecular-weight hydrolysis products were extracted with ethyl acetate (1 liter).

GLC Analysis of the Monomeric Hydrolysis Products. A Chrom-4 chromatograph was used with a flame-ionization detector and a 3.7 m × 3 mm stainless-steel column filled with 15% of Apiezon L on Chromaton N-AW-DMCS (0.100-0.125 mm). The thermostat temperature was 205°C and the rate of flow of the carrier gas (helium) was 40 ml/min. The products were identified from their retention times and by the addition of standard samples.

SUMMARY

1. The addition of anthraquinone leads to an appreciable increase in the yield of low-molecular-weight products of the alkaline hydrolysis of cotton-plant lignin.

2. The monomeric fractions of the hydrolysis products contain a high level of p-coumaryl structures and a very low level of syringyl structures, which may be due to the demethyoxylation of the lignin under the conditions described.

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INSECT PHEROMONES AND THEIR ANALOGS.

XII. SYNTHESIS OF THE ISOMERIC DEC-5-ENYL ACETATES – THE SEX PHEROMONES OF Anarsia lineatella AND Agrotis segetum

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A new route for the synthesis of dec-5E- and -5Z-enyl acetates – the sex pheromones of the peach-tree borer and of the turnip moth – is proposed which is based on the two-stage hydroxyethylation of hex-1-yne using 2-chloroethyl vinyl ethers and ethylene oxide.

The sex pheromones of the peach-twig borer (Anarsia lineatella) and the turnip moth (Agrotis segetum), which have been identified as dec-5E- and -5Z-enyl acetates, respectively, have been obtained previously by the use of the allyl rearrangement [1] or the Wittig reaction [2, 3] at the stage of constructing the alkene fragment.

We have developed a new scheme for the synthesis of these pheromones which is based on a two-stage hydroxyethylation, first with 2-chloroethyl vinyl ether (CEVE) and then with ethylene oxide. The starting material was hex-1-yne (I), the lithium derivative of which, under the action of CEVE gave oct-3-yn-1-ol (II), which was converted into 1-bromooct-3-yne (IV) via the tosylate (III). The lithium derivative of the bromide (IV) was converted into dec-5-yn-1-ol (V) by treatment with ethylene oxide. Reduction of the alkynol (V) with the aid of sodium in liquid ammonia or of 9-borabicyclo[3.3.1]nonane (BBN) took place with high selectivity and led to dec-5E-enol (VI) or dec-5Z-enol (VII), respectively, the acetylation of which gave the corresponding acetates (VIII) or (IX) – the desired pheromones (scheme).

It must be mentioned that the use of ethylene oxide in the first stage of hydroxyethylation substantially lowered the yield of the alcohol (II), while the hydroxyethylation of the bromide (IV) took place more smoothly with ethylene oxide. The stereochemical individuality of compounds (VIII) and (IX) was confirmed by capillary GLC. In the ^{13}C NMR spectra the signals of the allyl carbon atom of the acetate with the E configuration (VIII) were shifted downfield substantially as compared with the corresponding signals of the Z isomer (IX) [4].

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