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## ELECTROHYDRAULIC EFFECT IN WATER-PLANT HETERODISPERSE SYSTEMS.

### I. COMPOSITIONS OF THE SOLID RESIDUE AND THE AQUEOUS PHASE

G. N. Dalimova, V. G. Gorokhova,  
L. N. Petrushchenko, N. A. Koshilev,  
L. B. Dem'yanovich, N. V. Lebedev,  
A. A. Shishko, V. A. Babkin,  
and Kh. A. Abduazimov

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The electrohydraulic (EH) treatment of water-plant heterodisperse systems leads to the partial degradation of the main components of the plant materials: lignin, cellulose, and carbohydrates. The presence of p-hydroxyphenyl and guaiacyl structures has been established on the basis of the results of the GLC analysis of the ether-extracted phenolic products of plant materials subjected to EH treatment. It has been shown that part of the carbohydrates passes into the aqueous phase in the form of free monosaccharides: pentoses and hexoses.

Electrohydraulic shock (EHS) - a high-voltage spark discharge in a liquid at a potential difference between the electrodes of 10-100 kV with a current amplitude of 1-50 mA - is capable of causing mechanochemical reactions with the participation of the components of the medium [1, 2]. The discharge is accompanied by the appearance of a branched system of streamers, the generation of powerful shocks and acoustic effects, and other phenomena, leading to the activation of the heterodisperse system in the interelectrode space.

There is only a little information in the literature on the practical application of this effect [2-4]. EHS cannot be included among purely mechanical effects: it is a multi-factorial physicochemical process in which shock waves having a hydrostatic pressure of  $10^2$ - $10^3$  MPa, plasma with a temperature of  $10^4$  K, a pulsed electric field, and x-radiation and luminous and thermal radiation all participate.

Hitherto, many physicochemical aspects of electrohydraulic processes have remained little studied. Having in view the highly promising possibilities of the electrohydraulic effect (EHE) in both the theoretical and the applied respects, we have investigated water-plant heterodisperse systems subjected to treatment by the EHE with the aim of elucidating

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Institute of Chemistry of Plant Substances of Uzbekistan Academy of Sciences, Tashkent. Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk. Siberian Institute of Terrestrial Magnetism, the Ionosphere, and the Propagation of Radio Waves, Siberian Branch, Russian Academy of Sciences, Irkutsk. Translated from *Khimiya Prirodnykh Soedinenii*, No. 6, pp. 707-711, November-December, 1992. Original article submitted March 10, 1992.

TABLE 1. Results of the EH Treatment of Plant Materials at E = 500 J (% of the total weight of the plant)

Sample	No. of EHSs	Solid residue	Suspended particles	Ether-extractable substances				Ether-insoluble substances	
				phenols	PAs	FAs	neutral substances	nonhydrolyzable residue	carbohydrates
1. Stems of a 108-F cotton plant	50	82,8	1,8	0,70	0,04	0,50	0,08	2,18	2,85
2. "	100	75,0	0,6	0,10	0,24	0,50	0,05	0,97	2,27
3. Stems of a Mexican cotton plant	50	82,85	0,6	0,96	0,07	0,10	0,06	3,45	2,05
4. "	100	90,0	0,5	0,01	0,1	0,11	0,02	0,59	4,25
5. Kenaf chaff	50	89,5	0,47	0,04	0,07	0,02	0,3	0,27	1,40
6. "	100	85,5	0,53	0,32	0,07	0,07	0,62	0,18	0,38

†PAs - phenolic acids; FAs - fatty acids.

the applicability of this process for the treatment of plant materials and studying the chemical compositions of the aqueous and solid phases. As the objects of investigation we chose cotton-plant stems and kenaf chaff - lignocellulose wastes of the agricultural industry of Uzbekistan.

The main results of the separation of the components (according to the scheme given in the Experimental part) of water-plant heterodisperse systems subjected to treatment by the EHE are given in Table 1. After EH treatment the amount of the initial plant material had diminished by 10-25%. The appreciable loss of plant material and, at the same time, the decidedly small amount of ether-extractable and ether-insoluble substances (EESs and EISs) can be explained in the following way. During the EH treatment a degradation of low-molecular-mass EISs and carbohydrates to form gaseous products probably takes place; these were not determined in the present study. A decrease in the amount of EISs with an increase in the number of EHSs and an increase in the yield of gaseous products have been observed in an investigation of the compositions of the products of the solid phase and of the aqueous phase in heterodisperse systems of hydrolysis and plant wastes subjected to EHE treatment [3, 4].

In the solid residue (residual plant material) we determined the amounts of lignin, cellulose, and readily- and difficulty-hydrolyzable polysaccharides (RHPSs and DHPSSs, Table 2). With an increase in the number of EHSs the amounts of lignin, cellulose, and readily-hydrolyzable polysaccharides decreased. This shows the degradative nature of the electrohydraulic process. In the main, the amount of DHPSSs in the solid residue decreased, but this rule was true for only two samples: the stems of a Mexican variety of cotton plant and kenaf chaff. In the case of the cotton plant of the 108-F variety, an increase in the amount of DHPSSs was observed. The breakdown of the cellulose and hemicelluloses (of which the RHPSs and the DHPSSs, respectively, consist) of the plant residue treated with an electrohydraulic shock had a complex nature. The rates of conversion of the polysaccharides of the stems of the different varieties into the water-soluble state during acid hydrolysis were probably different.

The aqueous solutions obtained after the EH treatment of the water-plant heterodisperse systems had a pH value of 4-7, and the total yield of water-soluble products was 0.74-6.68%, of which the EISs made up 0.16-1.32% of the total weight of the plant material. By fractional extraction with diethyl ether from the aqueous phase at various pH values we isolated fractions of phenolic and neutral substances, and of phenolic carboxylic acids and fatty acids (i.e., ether-extractable substances). GLC showed the presence of p-hydroxyphenyl and guaiacyl structures in the fractions of phenolic substances from all the samples. The following compounds were identified: phenol, p-hydroxyphenylpropan-3-ol, guaiacol, vanillyl alcohol, propiovanillone, guaiacylethane, guaiacylpropane, guaiacylpropan-3-ol, and  $\beta$ -hydroxypropiovanillone.

From the aqueous phases after the separation of the EISs we isolated the carbohydrate fractions the yields of which are given in Table 1. Monosugars were identified by PC and GLC: xylose, glucose, and galactose.

Thus, during EH treatment the polysaccharides present in the plant undergo degradation, and some of them pass into the aqueous phase in the form of free monosaccharides.

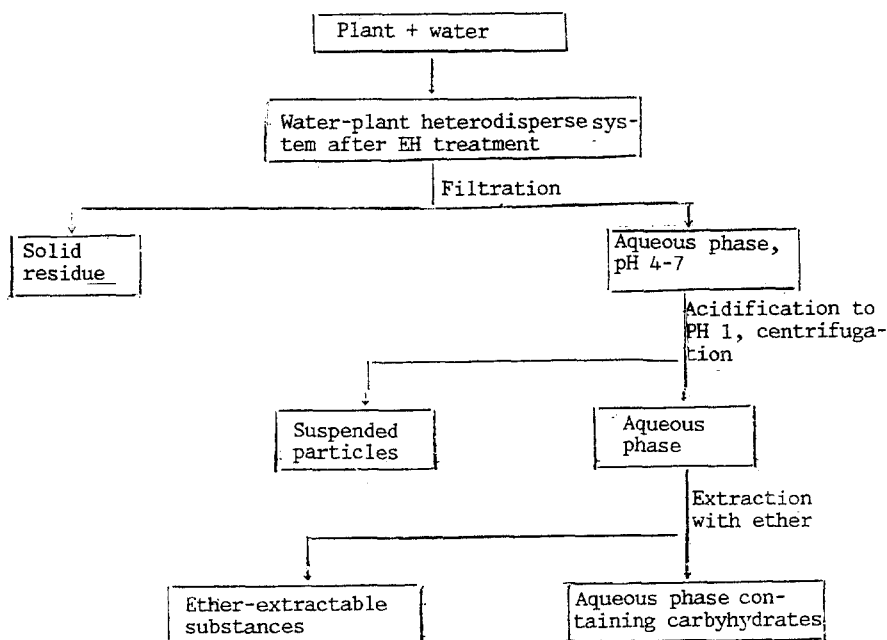
TABLE 2. Compositions of Plant Materials Subjected to EH Treatment at E = 500 Jm, %

Sample	No. of EHSs	Komarov lignin	Cellulose	RHPSs	DHPSs
1. Stems of a cotton plant of variety 108-F	50	26,02	28,30	12,28	22,32
2. "	50	22,83	26,40	9,47	30,60
3. "	100	21,90	25,52	10,18	42,48
4. Stems of a Mexican cotton plant	0	23,82	30,90	17,71	34,92
5. "	50	27,32	28,34	13,11	43,14
6. "	100	26,22	28,05	10,25	31,68
7. Kenaf chaff	0	26,70	39,13	7,41	46,91
8. "	50	25,75	38,34	6,75	45,36
9. "	100	24,72	36,34	5,24	28,04

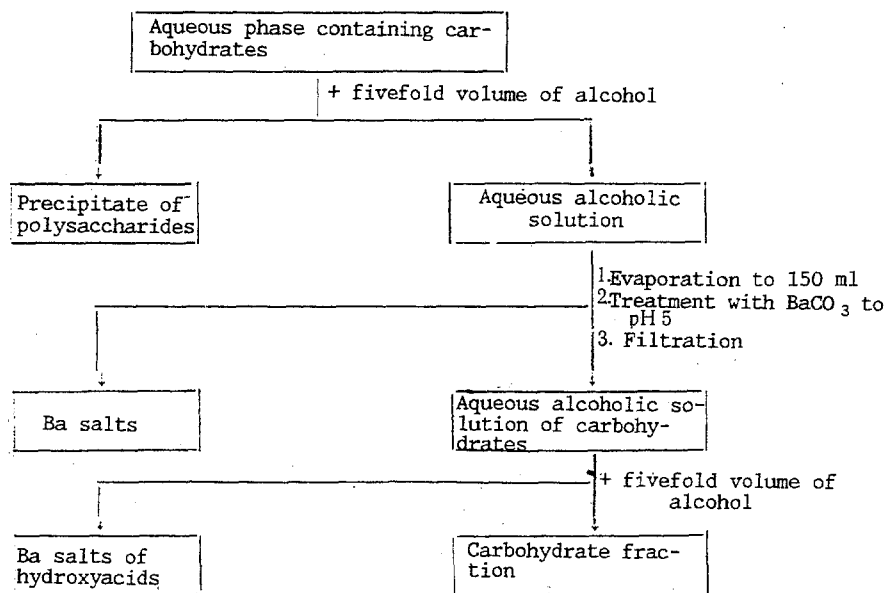
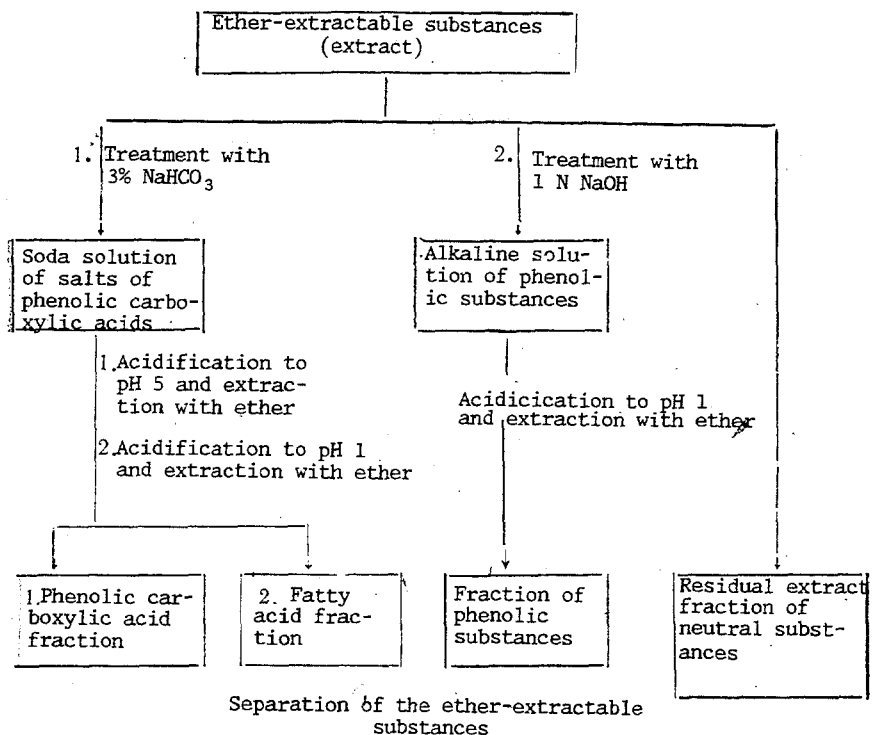
### EXPERIMENTAL

We investigated the stems of cotton plants of the 108-F variety and a Mexican variety. The plant raw material that had been comminuted, extracted with a mixture of alcohol and benzene (1:2), washed with hot water, and dried was used for EH treatment on a ÉGY-5S apparatus created in the Siberian Institute of Terrestrial Magnetism, the Ionosphere, and the Propagation of Radio Waves (Irkutsk) with series of from 50 to 100 EHSs having a previously accumulated energy of 500-1500 J in a single discharge. The amount of the initial plant material was 60-100 g, and the volume of water 1000-1100 ml.

The separation of the products of the EH treatment of water-plant heterodisperse systems was carried out by a method proposed by workers in the Irkutsk Institute of Organic Chemistry (see scheme).



Separation of the products of the EH treatment of water-plant hetero disperse systems



The amounts of Komarov lignin, cellulose, RHPSSs, and DHPSSs were determined by methods given in the literature [5]. The GLC analysis of the phenolic products was performed on a Chrom-41 instrument (Czechoslovakia). Conditions of separation: glass column 0.3 × 370.0 cm filled with Chromaton NAW impregnated with 15% of Apiezon L. Rate of flow of the carrier gas (helium) 40 ml/min; temperature of the sample 220°C and of the thermostat 205°C.

For the paper chromatography of the carbohydrate fraction we used FN-12 paper in the butanol-pyridine-water (6:4:3) system, with aniline hydrogen phthalate as the revealing agent. Carbohydrate derivatives in the form of aldonitrile acetates were obtained by the procedure described in [6]. GLC analysis was conducted on a Chrom-41 instrument. Stainless steel column, dimensions 0.3 × 200.0 cm, filled with 5% of XE-30 on Chromaton NAW (0.200-0.250 mm) at a rate of flow of the carrier gas (helium) of 60 ml/min and a column temperature of 230°C.

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## INSECT PHEROMONES AND THEIR ANALOGUES

## XLIII. CHIRAL PHEROMONES FROM (S)-(+)-3,7-DIMETHYLOCTA-1,6-DIENE

## 3. SYNTHESIS OF (4R)-4-METHYLNONAN-1-OL - SEX PHEROMONE OF

*Tenebrio molitor* AND ITS RACEMIC ANALOGUE

V. N. Odinkov, G. Yu. Ishmuratov,  
M. P. Yakovleva, O. V. Sokol'skaya,  
R. Ya. Kharisov, É. P. Serebryakov, and  
G. A. Tolstikov

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Starting from the readily available enantiomerically enriched (S)-(+)-3,7-dimethylocta-1,6-diene (ee  $\approx$  50%), we have synthesized (4R)-4-methylnonan-1-ol - the sex pheromone of the yellow mealworm beetle *Tenebrio molitor* L. A scheme for synthesizing the racemic analogue of the pheromone from 4-methyltetrahydropyran has been developed.

The sex pheromone of the yellow mealworm beetle *Tenebrio molitor* L, which has been identified as 4-methylnon-1-ol with the (R)-configuration (R-1) [1], has been synthesized previously from (R)-(+)-pulegone [1] and from monomethyl (3R)-3-methylglutarate [2]. Since the racemic alcohol (I) is also biologically active [3], its synthesis is of practical interest and has been performed from methyl oct-2-ynoate [2] and from 2-oxopentan-5-ol [3].

We have developed a new pathway to the synthesis of the pheromone R-1, starting from the readily accessible [4] (S)-(+)-3,7-dimethylocta-1,6-diene (dihydromyrcene, ee  $\approx$  50%) (II), which, as we have shown, is smoothly converted into  $\beta$ -(-)-citronellol (III) with the aid of the hydroalumination reaction [5]. Alcohol (III) was oxidized to the corresponding aldehyde (IV), the interaction of which with propylmagnesium bromide led to a high yield of (6S)-6,10-dimethylundec-9-en-4-ol (V); this was converted into the corresponding tosylate (VI), which, on reduction with zinc in the presence of NaI, gave the alkene (VII). Ozonolysis of the latter led to the desired pheromone R-1 with an overall yield of 21%, calculated on the initial (II).

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