[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Effect of Aqueous Sulfuric Acid on Reducing Sugars. VI. Formation of Insoluble Polymers from the Compounds Produced by the Action of Acid on the Aldopentoses[1,2]

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The formation of polymeric substances by the action of sulfuric acid on the compounds produced by the action of aqueous sulfuric acid on the aldopentoses was studied. It was found that the ultraviolet absorption spectrum of aqueous sulfuric acid solutions of mixtures of furfural, crotonaldehyde, acetaldehyde, and formaldehyde at concentrations approximating those produced by the action of aqueous sulfuric acid on an aldopentose, decreased without any changes in the shape of the ultraviolet absorption curve. This finding is in agreement with a previous suggestion that the steady state which is attained when an aldopentose is treated with aqueous acid follows as a consequence of the removal (as insoluble polymeric materials) of a certain proportion of the compounds formed by the action of acid on the aldopentose.

Individual and mixtures of the above aldehydes were treated with aqueous sulfuric acid for various intervals of time and the unreacted aldehydes recovered as 2,4-dinitrophenylhydrazones. Chromatographic studies indicated that although only furfural or crotonaldehyde will form insoluble polymeric material when treated singly with aqueous acid, all four aldehydes are incorporated into the polymeric material that is obtained when mixtures of the four aldehydes are treated with acid.

In previous communications[3] it was shown that the ultraviolet absorption spectrum that develops when an aldose is treated with aqueous sulfuric acid is due to the formation of certain specific aldehydic compounds. The aldopentoses form furfural, crotonaldehyde, acetaldehyde, and formaldehyde.[3] The ultraviolet absorption spectrum of a solution of an aldose in aqueous acid indicated that after an interval of time a steady state was reached. The characteristics of this steady state depended on the concentration and configuration of the aldose, the concentration of the acid and the temperature.

To account for the observed steady state, it was suggested that the aldehydes which were responsible for the ultraviolet absorption spectrum polymerized under the action of acid and gave rise to the insoluble materials (humins) that are observed when an aldose is treated with aqueous acid. (It is not impossible that compounds with little or no ultraviolet absorption characteristics enter into the composition of the polymeric product.) The humins, obtained by the action of acid on an aldopentose should, in all probability therefore, be the same as the product obtained by the action of acid on the aldehydes derived from the aldopentose. Infrared studies[4] indicated that this was essentially true. First, infrared spectra and elemental analyses demonstrated that so far as could be determined, each of the aldopentoses yielded the same insoluble polymer irrespective of the concentration of acid. Second, comparisons of the polymer obtained from the aldopentoses with the polymers obtained from the mixtures of furfural, crotonaldehyde, acetaldehyde and from furfural and crotonaldehyde alone indicated that the product obtained from a mixture of all four compounds most closely resembled that obtained from the aldopentoses.

If the formation of an apparent steady state (as measured by the ultraviolet absorption spectrum) depends on the polymerization of the aldehydes responsible for the ultraviolet absorption, it is also necessary, since the shape of the ultraviolet absorption curve changes little if any with time, that these aldehydes polymerize in such a way as to maintain the observed shape of the ultraviolet absorption curve. In order to do this, the aldehydes would need to polymerize or otherwise disappear from solution in such a way that the ultraviolet absorbance curves obtained over a period of time would be the reverse of those obtained when the aldehydes are formed from the aldopentose. Only in such a situation could the increase in absorbance, due to the formation of aldehydic compounds from the pentose, be balanced by the loss of the same compounds by polymerization and at the same time not show a change in the absorption curves. It was considered of interest to investigate this point.

Acetaldehyde has a negligible ultraviolet absorption compared to furfural or crotonaldehyde[5] and formaldehyde shows no absorption in the region 277 mμ to 220 mμ,[6] hence it was not readily possible to follow the incorporation of these two aldehydes into the polymeric material by ultraviolet absorption analyses. Accordingly at intervals the polymer which formed in acid solution was removed by

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[1] Published with permission of the Bureau of Ordnance, Navy Department. The opinions and conclusions are those of the authors.

[2] Presented in part at the 130th meeting of the American Chemical Society, Atlantic City, N. J., September 1956.

[3] F. A. H. Rice and Lawrence Fishbein, *J. Am. Chem. Soc.*, **78**, 1005 (1956); **78**, 3731 (1956).

[4] F. A. H. Rice, *J. Org. Chem.*, **23**, 465 (1958).

[5] G. Mackinney and Odette Temmer, *J. Am. Chem. Soc.*, **70**, 3586 (1948).

[6] J. E. Purvis, *J. Chem. Soc.*, **127**, 9 (1925).

filtration and the filtrate treated with a solution of 2,4-dinitrophenylhydrazine in 2*N*-hydrochloric acid. The resulting hydrazones were separated by chromatography on a 3:1 (by weight) silicic acid[7]–Celite[8] mixture, identified, and weighed.

RESULTS AND DISCUSSION

Fig. 1 shows how the ultraviolet absorption of a solution of crotonaldehyde, furfural, acetaldehyde, and formaldehyde in 4*N* sulfuric acid solution decreases over a period of 30 hr. at 100°. The relative concentration of the aldehydes was approximately the same as that obtained from the treatment of an aldopentose with sulfuric acid. It will be seen that the series of curves are the reverse of those obtained from the aldopentose.[3] Since the aldopentoses, when they are treated with aqueous acid continuously form the above aldehydes it might be expected that, after a period of time depending on the rate at which the aldehydes are formed, they would show a steady state condition. The characteristics of this steady state would thus depend on the configuration of the aldopentose which apparently (other conditions being the same) determines the rate at which the aldehydes are formed.

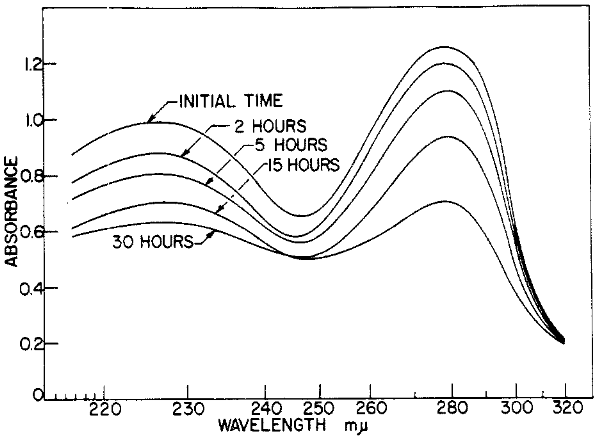

Fig. 1. Ultraviolet absorbance of mixtures of furfural (0.096 g.), crotonaldehyde (0.007 g.), acetaldehyde (0.0044 g.), and formaldehyde (0.003 g.) in one liter of aqueous sulfuric acid, after periods up to 30 hr. Temperature: 100°; concentration of acid: 4*N*

The effect of aqueous acid on furfural alone (Fig. 2) is shown for comparison. It should be noted that[3] the ratio of the absorption maxima is not the same as that shown by the aldopentoses.

In Fig. 3 the absorption maxima of the four aldehydes in 4 *N* sulfuric acid at 100° is plotted against the time. Again it will be seen that the curves are the reverse of those obtained from an aldopentose.[3] Fig. 4 shows the effect of the concentration of acid on the rate of disappearance of the ultraviolet

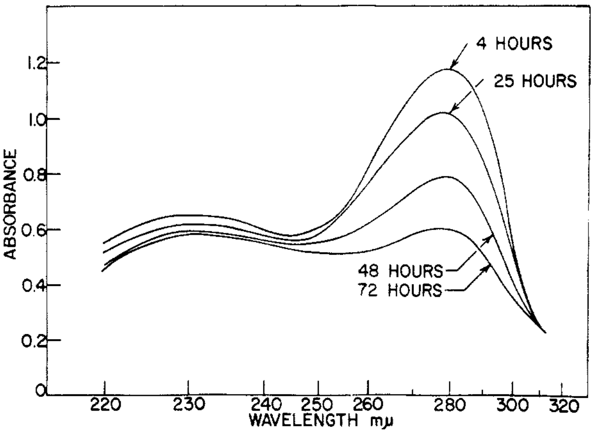

Fig. 2. Ultraviolet absorbance of furfural (0.096 g.) in one liter of 4*N* sulfuric acid at intervals up to 72 hr. Temperature: 100°

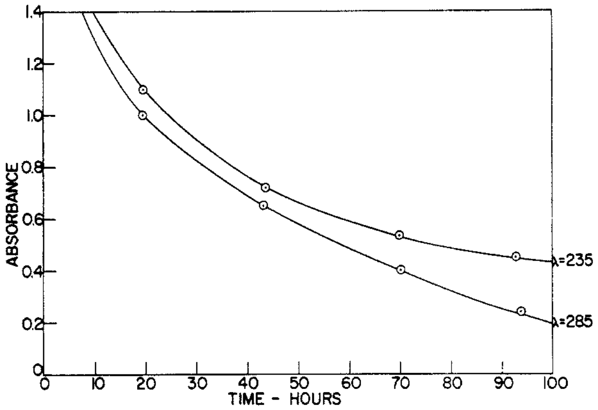

Fig. 3. Absorbance of mixture of furfural (0.096 g.), crotonaldehyde (0.007 g.), acetaldehyde (0.0044 g.), and formaldehyde (0.003 g.) in one liter of 4*N* aqueous sulfuric acid. Absorbance at maxima 284 mμ and 235 mμ shown over a period of 100 hr.

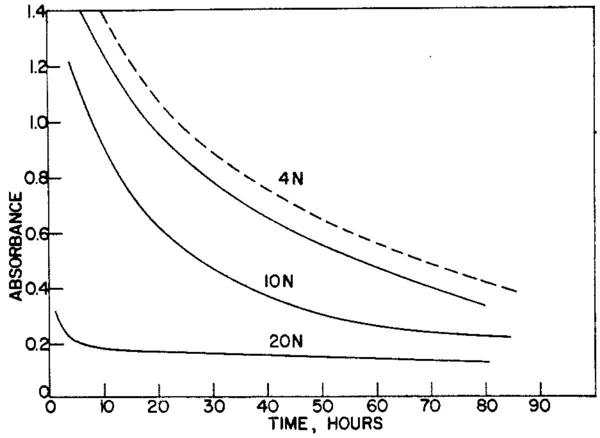

Fig. 4. Effect of the concentration of acid on the rate of disappearance of the ultraviolet absorption of mixtures of furfural (0.096 g.), crotonaldehyde (0.007 g.), acetaldehyde (0.0044 g.), and formaldehyde (0.003 g.) in one liter of aqueous sulfuric acid. Concentration of aqueous sulfuric acid as indicated. Dotted line shows furfural alone for comparison

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(7) Reagent grade, obtained from Merck & Co., Inc., Rahway, N. J.

(8) Number 535, obtained from the Johns Mansville Co., New York, N. Y.

TABLE I

WEIGHT OF POLYMER AND ALDEHYDES RECOVERED AFTER TREATMENT OF A MIXTURE OF FURFURAL (75 MG.), CROTONALDEHYDE (50 MG.), ACETALDEHYDE (15 MG.), AND FORMALDEHYDE (15 MG.) WITH 100 ML. OF 5N SULFURIC ACID

Time, Hr.	Weight of Polymer, Mg.	Weight of Mixed Hydrazones, Mg.	Weight (Mg.) of 2,4-Dinitrophenylhydrazones of			
			Furfural	$CH_3CH{=}CHCHO$	CH_3CHO	HCHO
0	5	530				
1	8	523				
2	16	510	200	125	75	75
4	23	465				
8	40	434	120	120	40	40
24	103	190				
48	110	130				
120	147	40	24	4.5	2.0	1.7

spectra. Again the experimental data are consistent with our suggestion that certain aldehydes with ultraviolet absorption characteristics are formed by the action of sulfuric acid on the aldopentoses and that these aldehydes polymerize to form insoluble polymeric materials and thus, after a period of time, give rise to the observed steady state. The steady state would be reached when the rate of formation of the aldehydes (which is determined by the configuration of the aldopentose, the temperature, and the concentration of acid) equals the rate at which the aldehydes polymerize (which is determined by the temperature and the concentration of the acid).

Table I shows the approximate weight of the polymeric material formed and the yield of mixed and individual 2,4-dinitrophenylhydrazones at several intervals of time. It will be seen that not only did the yield of mixed hydrazones decrease as the insoluble polymeric material increased, but as shown by the weights of chromatographically separated material, the concentration of all four aldehydes decreased and hence all four undoubtedly enter into the formation of the polymeric material.

When the aldehydes were individually treated with aqueous sulfuric acid it was found that neither formaldehyde or acetaldehyde formed any quantity of polymeric material and consequently the weight of 2,4-dinitrophenylhydrazones isolated from those aldehydes remained constant for at least 96 hr. On the other hand, furfural and crotonaldehyde formed considerable quantities of polymeric material with a consequent decrease in the quantities of the 2,4-dinitrophenylhydrazones isolated (Table II).

It would seem that although only furfural or crotonaldehyde will form polymeric material under the influence of aqueous sulfuric acid other aldehydes such as acetaldehyde and formaldehyde when present with either or both of these aldehydes will copolymerize and become incorporated into the resulting humin material. In this connection it is interesting to speculate, since it is at least possible that amines or aldehydes other than those derived from the sugar would copolymerize with the aldehydes derived from the sugar, that the copolymerization of such amines or aldehydes are an important factor of the well known browning reaction.

TABLE II

WEIGHT OF POLYMER AND ALDEHYDE (AS HYDRAZONE) RECOVERED AFTER TREATING FURFURAL (96 MG.) AND CROTONALDEHYDE (70 MG.) SEPARATELY WITH 5N SULFURIC ACID FOR PERIODS UP TO 96 HR.

	Furfural		Crotonaldehyde	
Time, Hr.	Weight polymer, mg.	Weight hydrazone, mg.	Weight polymer, mg.	Weight hydrazone, mg.
0	0	245	0	220
24	0	240	0	123
48	16	232	23	74
96	20	225	29	46

EXPERIMENTAL

The ultraviolet absorption spectra were taken at room temperature on a Beckman Model DU quartz recording spectrophotometer.

Materials. Furfural and crotonaldehyde were purified by distillation. Acetaldehyde was used in the form of paraldehyde and was redistilled. Formaldehyde was used in the form of trioxymethylene.

Procedure. Quantities of the aldehydes necessary to yield the desired concentrations were weighed and dissolved in a measured volume of aqueous sulfuric acid which had been previously standardized at the required concentration. Concentrations of acid of 2N, 4N, and 16N were studied. The temperature was either room temperature (23–25°) or the temperature of boiling water (referred to as 100°). Aliquots were withdrawn at intervals, cooled in ice and water when necessary, and either the ultraviolet absorption spectrum measured at room temperature or the mixture was filtered and the filtrate treated with 2,4-dinitrophenylhydrazine in 2N hydrochloric acid.[9] The insoluble 2,4-dinitrophenylhydrazones were weighed and chromatographed. The insoluble humins were dried at room temperature under a high vacuum and weighed (Table I and II).

Chromatography. The hydrazones were chromatographed after the manner of Roberts and Green.[10] A 3:1 (by weight) mixture of silicic acid[7]–Celite[8] was used as the absorbent. The zones were developed with a 3:2 (by volume) mixture of benzene-heptane containing 0.5% *tert*-butyl alcohol. The

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(9) O. L. Brady and G. V. Elsmie, *Analyst*, **51**, 77 (1926).

(10) J. D. Roberts and Charlotte Green, *Ind. Eng. Chem., Anal. Ed.*, **18**, 335 (1946).

material in the zones were eluted with ethanol, crystallized from ethanol, and identified[3,11] by melting point, mixed melting point ultraviolet and infrared analyses. On several occasions the purity of the zone was checked by a high vacuum sublimation.

INDIAN HEAD, MD.

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[11] J. D. Roberts and Charlotte Green, *J. Am. Chem. Soc.*, **68**, 214 (1946); E. H. Brande and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

[CONTRIBUTION FROM THE ENTOMOLOGY RESEARCH DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Preparation of Some Substituted Derivatives of Sesamol. I. Synthesis of Halogenated Sesamol Esters

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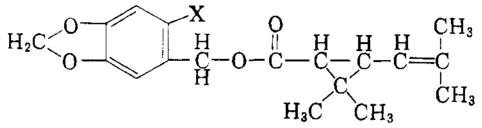
Following studies on two exceptionally active insecticidal substances, 6-chloropiperonyl chrysanthemumate and its bromo analog, a series of new halogenated sesamol (3,4-methylenedioxyphenol) esters having a structural resemblance to them have been synthesized. A method for the bromination of sesamol is described. Simultaneous addition of halogen to a double bond and substitution in the ring was obtained in the bromination of sesamyl chrysanthemumate.

6-Chloro- and 6-bromopiperonyl chrysanthemumates (I)[1] have shown marked insecticidal properties in preliminary tests against a wide variety of insects. In view of the considerable interest in these chrysanthemumates, the preparation of similar compounds was undertaken. VII, a halogenated sesamol derivative, was synthesized and found to be insecticidal. Since the literature discloses no previous syntheses of halogenated sesamol compounds, many such derivatives were prepared and tested, and those more closely related to the active esters (I) are reported here.

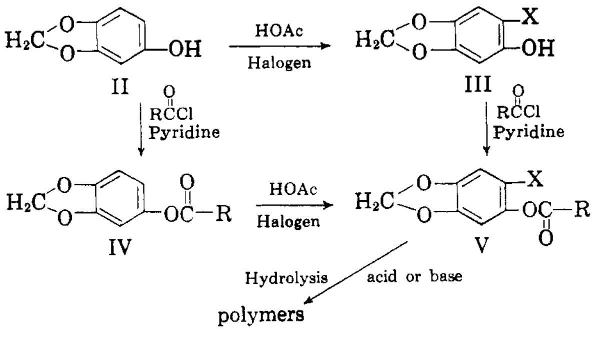


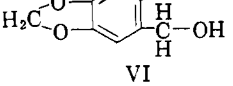
I, X = Br or Cl

Very little has been reported also on the chemistry of sesamol derivatives, although several methods of synthesizing the parent compound (II) have been described.[2,3] Haslam and Haworth presented the synthesis of sesamol *p*-toluenesulfonate[4] in 1955. A year later Beroza[3] reported the preparation of 66 sesamol ethers, esters, acetals, sulfonates, and urethans, some of which have outstanding properties as pyrethrin synergists.

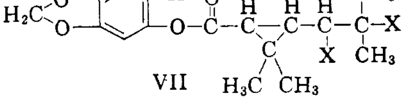
The 6-halopiperonyl alcohols (VI) were made by halogenation of piperonyl alcohol to give 6-halopiperonyl halide, acetylation of the halide, and then hydrolysis of the resultant acetate.[1,5] A similar halogenation of sesamol acetate (IV) gave V, but attempts to saponify it to give III yielded only polymeric substances. Polymer formation was avoided and the product (III) obtained in 90% yield by adding halogen to sesamol in glacial acetic acid below 10° and working up the mixture immediately.

The chrysanthemumoyl ester (IV, R = C_9H_{15}) was made from synthetic chrysanthemumoyl chloride which is a DL-*cis-trans* compound. The preparation of VII from IV (R = C_9H_{15}) involves the simultaneous addition of halogen to a double bond and substitution in the ring.





VI



VII

EXPERIMENTAL

3,4-Methylenedioxyphenyl acetate (IV, R = CH_3) was prepared as previously reported;[3] b.p. 144–145°/14 mm., n_D^{25} 1.5265; yield quantitative.

3,4-Methylenedioxyphenyl chyrsanthemumate (IV, R =

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[1] W. F. Barthel and B. H. Alexander, *J. Org. Chem.*, **23**, 1012–14 (1958).

[2] J. Boeseken, W. D. Cohen, and C. J. Kip, *Rec. trav. chim.*, **55**, 815 (1936).

[3] M. Beroza, *J. Agr. Food Chem.*, **4**, 49 (1956).

[4] E. Haslam and R. D. Haworth, *J. Chem. Soc.*, 827 (1955).

[5] R. G. Naik and T. S. Wheeler, *J. Chem. Soc.*, 1780 (1938).