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## Wissenschaftliche Originalmittheilungen.\*)

The Poisonous Effect Exerted on Living Plants by Phenols.

By

Rodney H. True, Ph. D., and Carl G. Hunkel, B. S.<sup>1)</sup>

(Continued.)

According to Bader's results, pyrocatechol is almost entirely undissociated in watery solution, this conclusion being doubtless reached by a study of fresh solutions. When fresh, the solution of this phenol is colorless or practically so; on standing, however, it assumes a color which gradually darkens until a rather deep brown is seen, depending for its deepness on the strength of the solution. It was desired to avoid using the solutions after they

\*) Für den Inhalt der Originalartikel sind die Herren Verfasser allein verantwortlich.

Red.

had thus changed color, but since this change takes place with considerable rapidity, it was found impossible to entirely avoid it. Solutions freshly prepared were used immediately and were kept away from the light and air as much as was practicable, and the results obtained under such conditions were accepted as being in a general way reliable. As is shown in Table IV, this substance has more strongly toxic action toward the lupines than phenol. *Spirogyra* filaments placed for about eighteen hours in a solution of pyrocatechol, 1/800 gram-molecule per liter, were found to be dead and the color blackened. The protoplast was found to be somewhat shrunken away from the wall, and numerous conspicuous granules<sup>1)</sup> were seen in the cytoplasm. In stronger solutions, the spiral form of the chlorophyll band was fairly well preserved, the protoplast was not noticeably shrunken away from the cell walls. The conspicuous granules were numerous in all cases seen, the solutions used varying in strength between 1/50 and 1/800 gram-molecules per liter. It seems certain that old solutions of dark color are more strongly toxic than fresh solutions. It is not at all unlikely in view of the conduct of its isomer, hydroquinone, to be discussed later, that oxidation products may contribute largely to the toxic properties of these solutions. The action of ions in the fresh solutions seems improbable, the undissociated molecule producing the action seen.

Resorcinol,  $C_6H_4(OH) = 1 : 3$ .

Table VI.

Gram. mol. per liter.	Begun May 24, 3 : 00 P. M.		Condition.
	Length May 25. 5 : 00 P. M.	Length May 27. 3 : 00 P. M.	
1/200	20,5 mm	32,5 mm	Alive.
	18,5 "	25,0 "	"
	19,5 "	27,0 "	"
	18,5 "	22,5 "	"

Table VII.

Gram mol. per liter.	Resorcinol + 1 NaOH. Begun Jan. 28, 3 : 25 P. M.		Condition.
	Length Jan. 29. 2 : 00 P. M.	Length Jan. 30.	
1/200	18,5 mm	25,0 mm	Alive.
	15,0 "	—	Dead.
	17,0 "	—	"
	15,0 "	16,0 "	"
1/400	22,5 "	30,5 "	Alive.
	15,0 "	15,0 "	Dead.
	15,0 "	15,0 "	"
	22,0 "	28,0 "	Alive.
1/800	19,5 "	23,0 "	"
	18,0 "	30,0 "	"
	30,5 "	45,0 "	"
	22,5 "	32,0 "	"

<sup>1)</sup> Loew, *Natürliches System der Giftwirkungen*, p. 150. Also Klemm, P., *Desorganisationserscheinungen der Zelle*. (*Jahrbücher für wissenschaftliche Botanik*. XXVIII. 1895. p. 46.)

Table VIII.

Electrical Conductivity of Resorcinol (Bader).

V.	$\mu v$	100 K.
8,52	0,09	0,00000082
17,04	0,16	0,00000110
34,08	0,30	0,00000220
68,16	2,14	0,00005400
$\mu_{\infty} = 356$		K = ?

Resorcinol is seen by Bader's table (Table VIII.) to behave like phenol and pyrocatechol as regards dissociation, the electrical conductivity being but slight. It is seen, however, to be less poisonous than the ortho compound, their respective toxic values being, for pyrocatechol 1/800, for resorcinol 1/200. The latter substance seemed to be more stable in solution than pyrocatechol. Probably we have in the toxic value here given, 1/200, the effect of the undissociated resorcinol without any considerable increase coming from oxidation products. The stability of this solution was further rendered probable by the fact that *Spirogyra* filaments were exposed for two days to a solution containing 1 gram-molecule per 200 liters and were found to be uninjured as far as appearance and capability for prompt plasmolysis were concerned. It seems probable that for the alga this concentration is considerably weaker than the limit concentration.

This difference may possibly be explained in one of several ways. The addition of a second or third negative element or group into the benzene ring is known to affect the capacity for reaction of the first. In this case the change would be in large measure qualitative. On the other hand the change may be quantitative, due to the addition of  $\bar{O}H$  ions added in the form of the sodium hydroxide. Possibly both factors come into consideration.

Hydroquinone,  $C_6H_4(OH)(OH) = 1 : 4$ .

Table IX.

Begun May 2, 4 : 00 P. M.

Gram mol. per liter.	Length May 3.		Length May 5.		Condition.
	3 : 10 P. M.		2 : 25 P. M.		
1/800	14,0	mm	14,0	mm	Dead.
	16,5	"	16,5	"	"
	16,5	"	18,0	"	"
	19,0	"	19,0	"	"
1/1600	18,0	"	28,0	"	Alive.
	15,0	"	14,5	"	Dead.
	26,0	"	51,0	"	Alive.
	14,5	"	14,5	"	Dead.
	17,0	"	17,5	"	Alive.
	23,0	"	61,0	"	"

Table X.

Electrical Conductivity of Hydroquinone (Bader).		
V.	$\mu\text{v}$	100 k.
11,6	0,15	0,0000016
23,2	0,26	0,0000024
46,4	0,58	0,0000059
92,8	1,94	0,0000260
$\mu\infty = 356.$		$K = ?$

Electrolytic dissociation can hardly play any important part in determining the toxic action of hydroquinone solutions. The solutions of this substance in the course of a very few hours turned to a dark cinnamon-brown. They were hardly to be regarded as solutions of hydroquinone in view of the ease with which this substance is oxidized.<sup>1)</sup> Fresh solutions were used and kept in the dark except when the lupines were under observation. Even then the solutions became strongly discolored. The toxic value of this discolored solution is 1/600 gram-molecule of the original hydroquinone per liter or perhaps even more dilute. The results here obtained could hardly be regarded as due to the phenol itself, and the toxic value of hydroquinone unchanged we do not know. A large number of experiments with *Spirogyra* were performed, and some very interesting results were obtained.<sup>2)</sup> It seemed that before color changes set in, hydroquinone solutions are not much more poisonous than phenol toward this alga. As, however, the color of the solution deepened, the poisonous action increased in intensity. Solutions were exposed to light and air in the hope of obtaining a stable solution. After several days, the action on *Spirogyra* was again tested with rather surprising results. The toxicity had increased to a great degree, and the first concentration in which a majority of the filaments of the alga were found to be able to respond to plasmolysing agents was 1/25600 gram-molecule calculated on the hydroquinone originally contained.

Some experiments conducted by Mr. W. D. Frost, Assistant in Bacteriology at the University of Wisconsin, and by Mr. Robert Gay, a student of the same institution, showed that this discolored solution had a strong antiseptic action, vegetative cells of *Staphylococcus pyogenes aureus* being in great part killed or rendered incapable of growth when exposed for thirty minutes to a solution containing 1/1500 gram-molecule of hydroquinone per liter. This phase of the action of this compound is now under study.

It was thought that possibly a like treatment of solutions of the stabler phenols might show somewhat analogous though perhaps less striking results. Accordingly, a solution of phenol

<sup>1)</sup> Schmidt, E., Ausführliches Pharmaceutisches Lehrbuch der Chemie. 3. Aufl. Band II. p. 942.

<sup>2)</sup> True, R. H., Algae and Antiseptics. (Pharm. Review. XV. 1897. p. 152.)

was similarly exposed to light and air and its toxic value again determined. No increase in its poisonous activity was to be seen.

Of the tri-atomic phenols, pyrogallol and phloroglucin were studied.

Pyrogallol,  $C_6H_3(OH)(OH)(OH) = 1:2:3$ .

Table XI.

Begun May 25, 6:00 P. M.

Gram-mol. per liter.	Length May 26. 2:25 P. M.	Length May 28. 3:25 P. M.	Condition.
1/800	16,5 mm	—	—
	16,5 "	16,5 mm	Dead.
	17,0 "	17,0 "	"
	16,0 "	16,0 "	"
1/1600	20,0 "	42,0 "	Alive.
	18,0 "	37,0 "	"
	18,5 "	36,0 "	"
	18,0 "	35,0 "	"

Table XII.

Pyrogallol (repeated).  
 Begun Dec. 3, 5:25 P. M.

Gram-mol. per liter.	Length Dec. 4. 9:45 A. M.	Length Dec. 5. 7:00 P. M.	Condition.
1/200	17,5 mm	—	Dead.
	16,5 "	—	"
1/400	22,0 "	—	"
	19,0 "	—	"
1/800	24,5 "	25,0 mm	"
	23,0 "	24,5 "	"

Table XIII.

Pyrogallol (repeated).  
 Begun Dec. 8, 3:00 P. M.

Gram-mol. per liter.	Length Dec. 9. 12:00 M.	Condition.
1/1600	15,5 mm	Dead.
	15,0 "	"
1/3200	21,0 "	"
	18,0 "	"
1/6400	25,0 "	Alive.
	24,0 "	"

Table XIV.

Electrical Conductivity of Pyrogallol (Bader).

V.	$\mu v$	100 k.
56	0,16	0,0000051
112	1,12	0,0000097
224	1,88	0,0000130
488	3,12	0,0000170

$\mu\infty = 355$ .

K = ?

Here, electrolytic dissociation can hardly be regarded as playing an important rôle in giving to fresh pyrogallol solutions their poisonous properties. The physiological results are seen to vary considerably as presented in Tables XI, XII and XIII. The length of time elapsing between the making of the solution and the time of using it is seen to exert a marked effect. The solution used immediately after preparation gives a toxic value of  $1/1600$ . The solution used in XII was fresh but was not diluted far enough to reach the limit. After standing five days, this same stock solution was again used, the toxic action having in the meantime increased, giving  $1/6400$  gram-molecule per liter as the first dilution in which the lupines survived. Table XII shows in addition an interesting phenomenon, indicating the progressive development of the poisonous activity of the solution on standing. In the dilution containing  $1/800$  gram-molecule of pyrogallol per liter, the radicles made during the first 17 hours spent in the solution a growth nearly normal for distilled water and ordinary temperature, viz. 9,5 mm and 8,0 mm respectively. In no other instance did the radicles succumb within the time limits here observed after making so great a growth. This can be understood when the chemical behavior of pyrogallol under circumstances similar to those here found is taken into account. Ph. de Clermont and P. Chautard<sup>1)</sup> find that pyrogallol is slowly oxydized in the air to purpurogallin, having the composition  $C_{20}H_{16}O_9$ , from which they prepared a sodium compound of the formula  $C_{20}H_{12}Na_4O_9$  and a barium compound,  $C_{20}H_{12}Ba_2O_9$ . Purpurogallin, therefore, seems to be an acid, but how many carboxyl and how many hydroxyl hydrogens the compound contains cannot well be even surmised from our present chemical knowledge of the substance. The great toxic effect of the decomposed solution would seem to indicate, however, that it contains at least one carboxyl group, which upon dissociation furnishes the strongly toxic  $H^+$  ion or ions.

The toxic value of a completely dissociated mono-basic acid, as HCl, is, according to Kahlenberg and True<sup>2)</sup>,  $1/6400$  for lupines. For other acids undergoing complete dissociation, the same value is found for every acid hydrogen atom, carboxyl hydrogen in the case of organic compounds, one-half this concentration for acids containing two acid hydrogen atoms undergoing complete dissociation, and for other acids in like ratio.

<sup>1)</sup> P. de Clermont and P. Chautard. (Berichte der deutschen chemischen Gesellschaft. Bd. XV. p. 1457.)

<sup>2)</sup> Kahlenberg and True. Bot. Gaz. XXII. 1896. p. 92.

Phloroglucin,  $C_6H_3(OH)(OH)(OH) = 1:3:5$ .  
 Table XV.

Begun May 1, 2:30 P. M.			
Gram-mol. per liter.	Length May 2, 2:35 P. M.	Length May 4, 2:00 P. M.	Condition.
1/200	16,0 mm	15,5 mm	Dead.
	14,5 "	14,0 "	"
	15,0 "	15,0 "	"
	15,0 "	14,5 "	"
	22,0 "	53,0 "	Alive.
1/400	15,5 "	15,0 "	Dead.
	16,0 "	19,0 "	Alive.
	21,5 "	50,0 "	"
	18,0 "	35,0 "	"

Phloroglucin is much more stable than the preceding compound and is much less poisonous. The toxic action is probably due to the undissociated compound.

Although, as we have seen in a number of cases, certain complications have prevented us from obtaining the toxic value for all of the above enumerated substances, some changing their nature so soon after the preparation that our results are questionably due to the substances named, in cases, still we may be permitted to draw some conclusions regarding the effect exerted by replacing hydrogens of the benzol ring by OH groups. Omitting the results obtained for pyrocatechol, hydroquinone and pyrogallol, these being manifestly not the effects produced by the unaltered compounds, we find remaining as stable substances one each of the mono-, di- and tri-atomic phenols, benzophenol,  $C_6H_5OH$ , with a toxic value of 1/400; resoreinol,  $C_6H_5(OH)(OH) 1:3$ , with a toxic value of 1/200, and phloroglucin,  $C_6H_3(OH)(OH)(OH) 1:3:5$ , with a toxic value of 1/400. From these examples, it thus appears that the increase in the number of OH groups replacing H in the benzol ring exerts no plain effect on the toxic action, neither a regular increase nor a regular decrease being found.

Loew<sup>1)</sup> reports that with the replacement of the H atoms of the benzol ring, the poisonous activity increases in direct proportion to the number of hydrogens replaced by OH groups.

A number of phenylic compounds, derivatives in the main, obtained by introducing various radicles into the foregoing phenols or their homologues were tested in the hope that we might be able to ascertain somewhat concerning the relation of molecular structure to physiological action for the plants under study.

By replacing one of the OH groups of a di-atomic phenol with a methyl group  $CH_3$ , we obtain the three isomeric cresol compounds. These substances were tested with reference to their action on the lupines.

(To be continued.)

<sup>1)</sup> Loew. Ueber Giftwirkung. (Archiv für die gesammte Physiologie. XL. 1887. p. 440. — Cited in Davenport's Experimental Morphology. New York 1897. p. 18.)

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