The Poisonous Effect Exerted on Living Plants by Phenols.

By

Rodney H. True, Ph. D., and Carl G. Hunkel, B. S.[1])

(Conclud.)

If the introduction of this radicle into the phenol molecule increases its toxic effect to so considerable an extent, the question arises concerning its effect when introduced into other compounds.

By replacing one H of the benzene ring with an NO_2 group, we have nitrobenzene, a compound differing from the nitrophenols just studied by having none of its H hydrogens replaced by the OH group. In nitrobenzene, consequently, we can have no $\overset{+}{H}$ ions. Since the introduction of OH groups does not materially affect the toxicity of a compound dissociating but slightly, as resorcinol, we may compare the toxic effect of nitrobenzene with that of the nitrophenols which do not dissociate; i. e., when no H ions are present. This is realized when Na OH is added to the nitrophenols.

Nitrobenzene, $C_6H_5NO_2$.

Table XXXVI.

Begun Mar. 2, 8 : 25 P. M.

Gram-mol. per liter.	Length Mar. 3. 3 : 15 P. M.	Length Mar. 5. 3 : 30 P. M.	Condition.
1/1600	15,0 mm	14,5 mm	Dead.
	19,0 „	21,0 „	„ (?)
	16,5 „	17,0 „	„
	18,0 „	18,0 „	„
1/3200	15,5 „	15,5 „	„
	18,0 „	21,0 „	Alive.
	17,0 „	19,0 „	„
	17,0 „	20,0 „	„
1/6400	17,0 „	26,0 „	„
	15,0 „	20,0 „	„
	18,5 „	23,0 „	„
	18,0 „	23,0 „	„

A comparison of Tables XXXIII and XXXVI shows that the toxic value of para-nitrophenol + 1 Na OH is found to be somewhat greater than that of nitrobenzene, the latter, however, being still strongly poisonous. Its toxic action is about equal to that of ortho-nitrophenol + 1 Na OH (Table XXX).

Returning to the phenol compounds, we may ask, in view of the destructive results seen to follow the introduction of one NO_2 group into the phenol molecule, what may be the effect of the presence of a larger number of these groups. Unfortunately, dinitrophenol, $C_6H_3(OH)(NO_2)_2$, was not available, picric acid, trinitrophenol, only being at hand.

Trinitrophenol (Picric Acid) $C_6H_2 (OH) (NO_2) (NO_2) (NO_2) = 1 : 2 : 4 : 6$.

Table XXXVII.

Begun Dec. 8, 4 : 00 P. M.

Gram-mol. per liter.	Length Dec. 9. 11 : 40 A. M.	Condition, Dec. 10.
1/3200	16,5 mm	Dead.
	17,5 "	"
1/6400	26,0 "	Alive.
	22,0 "	Dead.
1/12800	36,0 "	Alive.
	30,0 "	"

Tables XXXVIII.

Sodium picrate.

Begun Jan. 24, 4 : 00 P. M.

Gram-mol. per liter.	Length Jan. 25. 11 : 00 A. M.	Length Jan. 26.	Condition.
1/400	15,0 mm	—	Dead. translucent.
	15,0 "	—	"
	16,5 "	—	"
	15,5 "	—	"
1/800	15,5 "	15,5 mm	Dead.
	16,0 "	26,0 "	Alive.
	15,5 "	15,5 "	Dead.
	17,0 "	29,0 "	Alive.
1/1600	15,5 "	—	Dead.
	14,5 "	—	"
	19,5 "	30,0 "	Alive.
	16,0 "	24,0 "	"

Picric acid, trinitrophenol, contains three NO_2 groups, and should the multiplication of these groups increase the toxic action in proportion, this compound should be decidedly more poisonous than the mono-nitrophenols. A comparison of Tables XXIX, XXXII and XXXVI shows that this is not the case.

Ostwald[1]) has shown that trinitrophenol behaves much like the strong acids. Solutions of one gram-molecule in 1024 liters are almost completely dissociated, and we should expect it to follow the rule of these substances. According to Table XXXVI, we see that it behaves toward lupines in a manner similar to that of a completely dissociated monobasic acid.[2]) Its toxic value agrees with that found for HCl and HNO_3, 1/6400. The toxic action appears, however, to be due in part only to H ions, the anion seeming also to possess poisonous properties. This appears on comparing the toxic value of the acid with that of its sodium compound. The toxic action of the anion is seen by comparing the concentrations of sodium picrate and sodium chloride first allowing growth. The toxic value of sodium picrate is 1/800,

---

[1]) Ostwald, Journ. für prakt. Chemie. XXXII. p. 354.

[2]) Kahlenberg and True, Bot. Gaz. XXII. p. 92.

that of sodium chloride about 1/4. Plainly, therefore, the anion has very strong toxic properties towards lupines.

When the hydrogen of the OH group is replaced by CH_3, we obtain from phenol, anisol, from pyrocatechol, the monomethyl ether, guaiacol.

Anisol, $C_6H_5OCH_3$.

Table XXXIX.

Begun May 29, 4 : 45 P. M.

Gram-mol. per liter.	Length May 20. 2 : 35 P. M.	Length May 21.	Condition.
1/200	15,0 mm	14,5 mm	Dead.
	15,5 „	15,0 „	„
	15,0 „	15,0 „	„
	14,5 „	14,5 „	„
1/400	16,5 „	19,5 „	Alive.
	15,0 „	14,5 „	Dead.
	16,0 „	17,0 „	Alive. (?)
	18,5 „	25,0 „	„
1/800	15,0 „	14,5 „	Dead.
	15,0 „	18,0 „	Alive.
	15,5 „	17,5 „	„
	18,0 „	35,0 „	„

From this table, it appears that the toxic action of phenol is approximately the same as that of its methylether, anisol, about one gram-molecule in four hundred liters first permitting growth. Filaments of Spirogyra placed in solutions of this substance were found after nearly twenty hours to survive first in a concentration of about one gram-molecule in three hundred liters, a some what weaker solution than the corresponding concentration of phenol producing the same results. In cells of Spirogyra killed in an anisol solution (1/200 gram-molecule per liter) the chlorophyll loses its spiral form and collects in one or more round masses, but the protoplast does not shrink away markedly from the cell wall.

Guaiacol, $C_6H_4(OCH_3)(OH) = 1:2$.

Table XL.

Begun May 19, 4 : 30 P. M.

Gram-mol. per liter.	Length May 20. 2 : 30 P. M.	Length May 22. 3 : 30 P. M.	Condition.
1/400	15,0 mm	14,5 mm	Dead.
	15,0 „	14,5 „	„
	14,5 „	14,0 „	„
	16,0 „	18,0 „	„
1/800	22,0 „	42,0 „	Alive.
	20,0 „	28,0 „	„
	22,0 „	46,0 „	„
	17,0 „	18,0 „	„ (?)
1/1600	20,5 „	45,0 „	„
	15,0 „	15,0 „	Dead.
	16,0 „	20,0 „	Alive.
	17,0 „	20,0 „	„

From the accompanying table, guaiacol is an active poison to lupines, the most concentrated solution allowing growth being that containing 1/800 gram-molecule per liter, being, therefore, more strongly toxic than anisol. It will be observed that here, as in the case of anisol, the ether has the same toxic value as the phenol from which it may be regarded as derived by replacing the H of an OH group with the CH_3 group.

Spirogyra filaments give results differing somewhat from those obtained with the lupines. As in the case of anisol, the alga is more tolerant toward the compound than are the lupines, the first solution in which majority of the filaments survived being 1/150 to 1/200 gram-molecule per liter. This is a stronger solution than the alga was able to withstand in the case of anisol, thus reversing the relative positions in the scale of toxicity as seen for the lupines.

Salicylic acid, C_6H_4 (OH) (COOH) = 1 : 2, is both an acid and a phenol in its constitution, but the acid characteristics give it its most pronounced properties. The toxic value of salicylic acid has been determined by Kahlenberg and True.[1] The concentration first permitting lupines to survive was found in a solution containing 1/6400 gram-molecule per liter, the boundary observed, generally, for mono-basic acids undergoing complete dissociation. Ostwald[2] has shown that at the much stronger concentration of one gram-molecule in 1024 liters this acid dissociates 62,80 per cent. A materially greater degree of dissociation might be expected in the dilutions here used.

Ortho-oxy benzoic acid, salicylic acid, C_6H_4 (OH) (COOH) = 1 : 2. Boundary-concentration, 1/6400 gram-molecule per liter.

Table XLI.

Sodium salicylate.

Begun May 21, 5 : 25 P. M.

Gram-mol. per liter.	Length May 22. 3 : 30 P. M.	Length May 24. 3 : 00 P. M.	Condition.
1/100	16,0 mm	20,5 mm	Alive.
	15,0 „	15,0 „	Dead.
	16,5 „	18,0 „	Alive.
	15,5	15,0 „	Dead.
1/200	15,5 „	15,0 „	„
	16,5 „	20,0 „	Alive.
	15,5 „	20,0 „	„
	16,0 „	35,5 „	„

---

[1] Kahlenberg and True. Bot. Gaz. XXII. p. 120. and MSS. results not yet published.

[2] Ostwald, W., Zeitschrift für physik. Chemie. Band II.

Table XLII.

Methyl salicylate.
Begun May 22, 4 : 25 P. M.

Gram-mol. per liter.	Length May 23. 2 : 30 P. M.	Length May 25. 4 : 00 P. M.	Condition.
1/800	15,0 mm	15,0 mm	Dead.
	15,0 „	15,0 „	„
	15,5 „	15,0 „	„
	15,5 „	15,0 „	„
1/1600	19,5 „	22,0 „	Alive.
	15,5 „	15,5 „	Dead.
	15,5 „	16,5 „	Alive.
	16,0 „	18,5 „	„

By replacing the acid hydrogen of salicylic acid with some harmless ion, we are able to obtain some idea of the intensity of the action of the anion, assuming relatively complete dissociation. The Na compound and methyl salicylate were studied in this connection and gave, as Tables XL and XLI show, quite different results. The low toxic value of the sodium salt would be expected, the hydrogen ions, found to constitute in general the markedly toxic agent in acids, being disposed of, practically harmless sodium appearing instead. The remaining toxic activity, a still appreciable quantity, is due to anions or to a possible residue of undissociated molecules or to both.

Methyl salicylate conducts itself somewhat differently. Its boundary-concentration is a much more strongly diluted solution than that of sodium salicylate. This greater toxicity is hardly to be attributed to the presence of the methyl group (CH_3). Probably hydrolytic dissociation takes place, forming methyl alcohol and salicylic acid. As is shown by the persistence of the characteristic odor, this hydrolytic splitting up is only partial. It would be expected that the salicylic acid thus split off would undergo electrolytic dissociation and a greater or less quantity of $\overset{+}{H}$ ions would appear in the solution, increasing proportionally its toxic action. It is probably, therefore, $\overset{+}{H}$ ions which render the solution of methyl salicylate so much more deadly than sodium salicylate.

In a recent work, Davenport[1]) states that „by replacing one of the H atoms of phenol by COOH (or carboxyl), thus producing salicylic acid, the poisonous qualities are reduced“. For the lupines and Spirogyra, this statement seems not to hold, as the following comparison of limit-concentrations shows. For lupines this limit is 1/6400 gram-molecule per liter of salicylic acid and 1/400 gram-molecule per liter of phenol; for Spirogyra the limit concentration for salicylic acid is about 1/2000

---

[1]) Davenport, C. B., Experimental Morphology. Vol. I. 1897. p. 19.

gram-molecule per liter, and 1/200 gram-molecule per liter of phenol.

Sumary of Results.

In order to facilitate a comparison of the toxic values of the substances studied, we bring together in the following table their names and the boundary concentrations found for *Lupinus albus*:

Substance.	Formula.	Boundary Concentration.
Mon-atomic Phenols.		
Benzophenol	C_6H_5OH	1/400 gram-mol. per liter.
Benzophenol + 1 Na OH		1/400 „ „
Benzophenol + 1 Na Cl		1/400 „ „
Benzophenol + 2 Na Cl		1/400 „ „
Benzophenol + 3 Na Cl		1/400—1/800 „
Di-atomic Phenols.		
Pyrocatechol	$C_6H_4(OH)(OH) = 1:2$	1/800 „ „
Resorcinol	$C_6H_4(OH)(OH) = 1:3$	1/200 „ „
Resorcinol + 1 Na OH		1/400 „ „
Resorcinol + 2 Na OH		1/800 „ „
Hydroquinone.	$C_6H_4(OH)(OH) = 1:4$	1/1600 „ „
Tri-atomic Phenols.		
Pyrogallol (fresh sol.)	$C_6H_3(OH)(OH)(OH) = 1:2:3$	1/1600 „ „
Pyrogallol (old sol.)		1/6400 „ „
Phloroglucin	$C_6H_3(OH)(OH)(OH) = 1:3:5$	1/400 „ „
Derivatives.		
Ortho-cresol	$C_6H_4(CH_3)(OH) = 1:2$	1/800 „ „
Ortho-cresol + 1 Na OH		1/400 „ „
Meta-cresol	$C_6H_4(CH_3)(OH) = 1:3$	1/800 „ „
Meta-cresol + 1 Na OH		1/400 „ „
Para-cresol	$C_6H_4(CH_3)(OH) = 1:4$	1/1600 „ „

Substance.	Formula	Boundary Concentration.		
Para-cresol + 1 NaOH		1/1600	gram-mol.	per liter
Carvacrol	$C_6H_3(CH_3)(OH)(C_3H_7) = 1 : 2 : 4$	1/3200	„	„
Carvacrol + 1 NaOH		1/3200	„	„
Thymol	$C_6H_3(CH_3)(OH)(C_3H_7) = 1 : 3 : 4$	1/3200	„	„
Thymol + 1 NaOH		1/3200	„	„
Ortho-nitrophenol	$C_6H_4(OH)(NO_2) = 1 : 2$	1/12500	„	„
Ortho-nitrophenol + 1 NaOH		1/3200	„	„
Para-nitrophenol	$C_6H_4(OH)(NO_2) = 1 : 4$	1/6400	„	„
Para-nitrophenol + 1 NaOH		1/6400	„	„
Tri-nitrophenol	$C_6H_2(OH)(NO_2)(NO_2)(NO_2) = 1 : 2 : 4 : 6$	1/3200	„	„
Tri-nitrophenol + 1 NaOH		1/800	„	„
Nitrobenzene	$C_6H_5NO_2$	1/3200	„	„
Anisol	$C_6H_5(OCH_3)$	1/400	„	„
Guaiacol	$C_6H_4(OCH_3)(OH) = 1 : 2$	1/800	„	„
Orcinol	$C_6H_3(CH_3)(OH)(OH) = 1 : 3 : 5$	1/400	„	„
Salicylic acid	$C_6H_4(OH)(COOH) = 1 : 2$	1/6400	„	„
Sodium salicylate		1/100—1/200		„
Methyl salicylate		1/1600	„	„

In reviewing the foregoing, we find, as far as our knowledge of the dissociation of the phenylic compounds permits us to draw conclusions, that, except in isolated instances, electrolytic dissociation plays but a very subordinate rôle in determining the toxic properties of the substances. Picric and salicylic acids strongly dissociate and become powerfully poisonous by virtue of the H ions, in great measure. Pyrogallol and probably methyl salicylate first undergo other molecular changes, after which their products dissociate electrolytically. Here the H ions may account for much of the toxic action. In the cresols and mono-nitrophenols, electrolytic dissociation seems to exert a pronounced influence. Some phenols are comparatively weak in their integrity, but quickly change to substances containing constituents even more fatal than

H ions. Pyrocatechol and especially hydroquinone are of this class.

Certain radicles seem to have specific properties when introduced into the molecule, modifiying the toxic value. The number of hydroxyl groups (OH) present seems to have little influence on the toxic action of the phenols, as in the series: benzophenol (1 OH), resorcinol (2 OH), and phloroglucin (3 OH). The introduction of the methyl group (CH_3) into the benzene nucleus increases the toxicity to a considerable, but rather variable, degree, as in the cresols, less plainly in orcinol. The introduction of the isopropyl group ($—CH[CH_3]_2$) into the cresols increases the toxic value of these substances, as carvacrol and thymol. The presence of one or more nitro groups (NO_2) increases the toxic action to a great degree; mono- and tri-nitrophenols. An increase in the number of the NO_2 groups present does not seem to increase the toxic action. When the H of an OH group is replaced by a (CH_3) group, little influence seems to be exerted on the toxic action, e. g., anisol and guaiacol. The carboxyl group (COOH) brings with it a degree of toxicity corresponding directly to the degree of dissociation and the number of H ions it affords; salicylic acid.

Nachträgliche Bemerkung

zu meinem Aufsatz in Nr. 9 dieses Bandes. p. 298: Das Leuchten des *Ceratium tripos* hat soeben J. Reinke (Wissenschaftliche Meeresuntersuchungen. Band III. 1898. p. 39—41) näher studirt. Dasselbe wird nicht durch Bakterien verursacht.

Prof. Dr. Ludwig-Greiz.

Instrumente, Präparations- und Conservations-Methoden etc.

Der Sudan III und seine Verwendung in der botanischen Mikrotechnik.

Von

Dr. Luigi Buscalioni

in Rom.

Der Farbstoff Sudan III wurde seit einiger Zeit in der medicinischen und zoologischen Mikrotechnik sehr empfohlen, um die Fette zu färben. Jedoch ist meines Wissens dieses Reagenz in der botanischen Mikrotechnik bis jetzt nicht angewendet worden. Ich habe daher damit Versuche angestellt. Aus meinen eingehenden

Zeitschrift/Journal: Botanisches Centralblatt

Jahr/Year: 1898

Band/Volume: 76

Autor(en)/Author(s): True Rodney H., Hunkel Carl G.

Artikel/Article: The Poisonous Effect Exerted on Living Plants by Phenols. (Conclud.) 391-398