The Chemical Components of Onion Vapors Responsible for Wound-healing Qualities

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THERE IS PROBABLY NO OTHER FOOD TO which is attached so much legendary history as is the case with the onion, although Pliny, the Naturalist, credits it with being the remedy for only 28 maladies—a moderate figure compared with the 87 for cabbage. Many of the legends have a bearing on physical health. Considering those dealing with evil spirits, the onion is involved even in mental health.

It requires but little observation to be aware of some strikingly peculiar chemical components in the onion. Their effect on the organs of the senses of smell and sight soon make this apparent. While man has been crying over onions since the beginning of history, like Mark Twain's weather, nothing has been done about it. It is surprising that the chemistry of onion vapors with such striking characteristics has been developed to such a slight degree.

In recent years facts have appeared indicating that certain onion constituents have notable physiological properties. That onion vapors possess bactericidal properties has been shown by Walker, Lindegren, and Bachmann (*6*). In a later publication, Ingersoll, Vollrath, Scott, and Lindegren (*2*) "provisionally identified acrolein or crotonaldehyde as the bactericides" in the vapors of both onion and garlic. From the data herewith presented it will be evident that this conclusion with respect to onions is incorrect.

In Russia, B. Tokin (*4*), over a period of 14 years, studied the bactericidal, phytoncidal, and protistocidal properties of over 150 plants. Onions and garlic were found to be most potent, with horse-radish, peppers, and radishes next in order. Onion and garlic were lethal to white staphylococci, typhus, and a number of other bacteria, and to all protozoa, the latter being killed by exposure to onion vapor for 1–3 minutes. Tokin found that the onion vapors killed protozoa even more promptly than bacteria and termed the vapors "phytoncides." He also found that by chewing raw onion 3–8 minutes, and sometimes for only 1 minute, the buccal lining usually became completely sterile. Tokin judged the onion phytoncides to be extremely volatile because onion paste ceased to give off bactericidal vapors after 10–15 minutes. As will be evident below, instability rather than volatility is the true explanation.

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Recently, Lucas and Hamner (*3*) demonstrated that the sodium salt of 2,4-dichlorophenoxyacetic acid became a much more potent herbicide when dissolved in onion juice diluted with 20–30 times as much water as when it was dissolved in water alone.

Inspired by such properties and impressed with the idea that ancient and traditional remedies should not be regarded as naive and absurd, Toroptsev and Filatova (*5*), of the Tomsk State University and the All-Union Institute of Experimental Medicine of the USSR, studied the effect of onion vapors on purulent inflammatory wounds. They placed the paste of one or two onions in a shallow dish the size of the wound and exposed the wound to the vapors for 10 minutes, usually in two 5-minute intervals, using the paste of fresh onion for each exposure. These investigations started with 25 patients, but for lack of onion (a striking commentary on war times) the number had to be reduced to 11. Of these, seven had amputations of the arm, one of the thigh, and three of the foot. In two of the patients the wounds were complicated with gangrene and in one with frostbite; the others were purulent and contained streptococci, white staphylococci, and other bacteria. All wounds showed distinct purulent inflammation, some with odor and edema of the soft tissue. Some patients complained of pain.

After the initial treatment all wounds became rose colored instead of gray, and there was no more complaint of pain. After the second treatment purulence subsided, odor disappeared, and regeneration was induced. Regeneration began to lag in a few cases after several days treatment, suggesting possible overexposure. Without minimizing the value of synthetic preparations to the practice of medicine and surgery, the Russian investigators take the position that the so-called phytoncides also have their place. The following study suggests to a chemist, however, that not the onion but the synthetic laboratory should be their source.

Onions were ground expeditiously in 800-gram quantities through a household meat and vegetable grinder and introduced into a 2-liter, round-bottomed flask with short neck. This was fitted with a Kjeldahl connecting bulb, which in turn was attached by a short, heavy rubber tubing to a flask imbedded in a salt-water-ice mixture to serve as a condensing receptacle. The bore of the tubing must be large in order not to impede distillation. After the whole system was pumped devoid of air by a

"high-vac" pump, the flask containing the onion was alternately submerged in water at 50° C. and lifted out to be vigorously shaken. This alternate shaking and periodic immersion is necessary. Unless it is properly performed, the distillate will contain the constituents to be described in far-reduced quantities. The idea is to introduce heat into the mass of onion as fast as the evaporation of the distillate takes it out and to avoid heating any part of the onion mass appreciably above room temperature, since by overheating the ingredients of the distillate sought are decomposed. It required about 6 minutes to grind the onion, introduce it into the flask, and evacuate the system, and 12 minutes more to obtain an amount of distillate equal to 15 per cent of the weight of the onions.

The distillate was water clear, nitrogen free, and contained the lachrymal principle of the onion, as a tiny drop in the eye at once demonstrated unmistakably. There was only mild lachrymating effect if the eye was held against the mouth of the flask containing the distillate. This indicates that not the volatility of the lachrymal principle but the turgidity and succulence of the onion tissue, causing invisible droplets of onion juice to be dispersed, is the cause of man's weeping over onions. Whereas spooning a grapefruit may be said to deliver a macro squirt on one's tie, cutting an onion delivers a micro squirt in one's eye. The distillate had an onion odor but contained none of the essential oil to which the flavor of the onion is due; the residue retained its full onion flavor. In a short time the water-clear distillate began to take on a milky appearance and, if held until the succeeding day, the density of the milkiness was comparable to that of skimmed milk. By that time it had, however, lost every vestige of lachrymal effect or any irritation in the eye even though the distillate was stored in a closed container to prevent any escape.

Acid hastened the development of the milkiness; alkali inhibited it. Bromine almost instantaneously clears up the milkiness and produces sulfate. But if bromine is added promptly to the distillate before any milkiness develops, practically no sulfate is formed, even with heat and long standing in the presence of bromine, and the milkiness does not develop thereafter. If, after the milkiness fully develops, the distillate is again distilled under the same vacuum and temperature, the milkiness remains as a gummy residue for which no satisfactory organic solvent has been found, although bromine water momentarily clears it up with the formation of the usual quantity of sulfate.

In a typical experiment the clear distillate of five 800-gram batches of onion was collected in a tared flask from which it could be redistilled. After holding until polymerization was complete and redistilling under vacuum at low temperature there remained a residue weighing .108 gram. Upon treatment with bromine, 0.3400 gram of barium sulfate was obtained. This indicates slightly over 43 per cent of sulfur in the residue, representing the polymerized material. The sulfur content of thiopropionaldehyde and thioallylaldehyde is, respectively, 43.2 and 44.4 per cent.

Because of the unstability of this sulfur-bearing, lachrymating substance it is difficult to estimate its total quantity in onions, since loss is going on from the moment the onions are ground and during the distillation period. To arrive at an approximation, one 800-gram batch of onions was ground and subjected to distillation at once, while in the meantime enough onions for 5 additional batches were ground in the shortest time possible. From

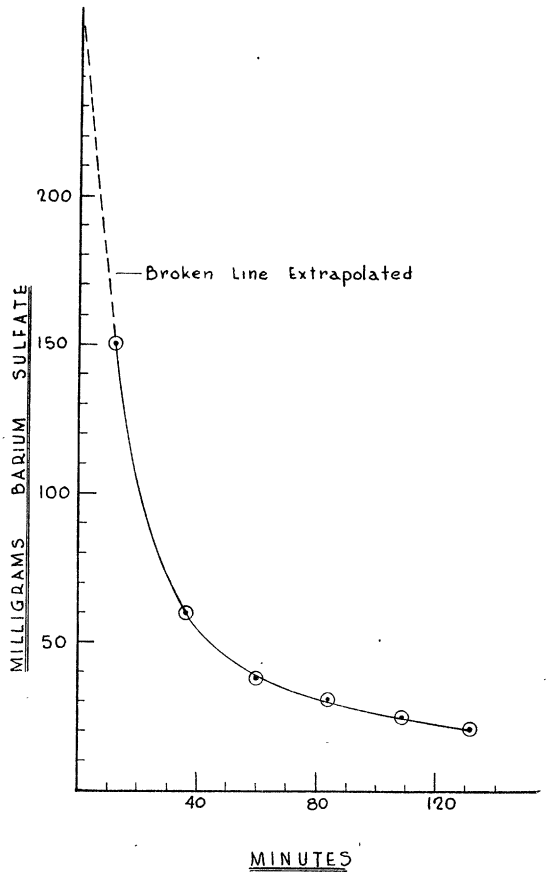

FIG. 1

these, at 24-minute intervals, an additional batch was subjected to distillation. By reckoning the time intervals from when the grinding in each case was half completed to when the distillation was half completed and plotting these against the barium sulfate obtained, Fig. 1 was constructed. By extrapolating this to zero time it is estimated that 800 grams of onion might yield 250 mg. of barium sulfate, which, calculated as thiopropionaldehyde, amounts to 100 mg./kilo. As indicated in the graph, prompt distillation yielded 150 mg. of barium sulfate. By using tubing with a larger bore between the flasks, 190 mg. were subsequently obtained.

These various reactions are interpreted to indicate that we are dealing with a thioaldehyde, the milkiness being the polymerized form. The fact that no sulfate is formed by bromine if added promptly after distillation and before polymerization is interpreted to indicate the reaction described by Douglass and Johnson (*1*), in which sulfonyl halide is formed from various thio-compounds. This meaningful reaction with bromine is the clue for future work toward the definite identification of this interesting thio-compound which apparently constitutes the lachrymal principle of the onion but which is not the essential oil that constitutes the onion flavor. It is suggested that it may be a step toward the synthesis by the onion of the essential oil. To our knowledge, no thioaldehyde has heretofore been demonstrated in nature. All are unstable, subject to ready polymerization.

From this low-temperature onion distillate obtained under vacuum the mononitro- and dinitro-phenyl hydrazones of propionaldehyde have been prepared and identified by melting points and analyses. The same quantity is obtained whether the preparation is made immediately after distilling, before any milkiness has developed, or after full milkiness has developed, or whether it is made from the clear distillate obtained by redistilling after full milkiness has developed, in which case the material causing the milkiness is left behind. If the phenylhydrazone preparation is made on the original clear distillate, a small amount of hydrogen sulfide is formed, which should theoretically occur if phenylhydrazine reacts with a thioaldehyde. The idea that thiopropionaldehyde is the lachrymal principle and that in the course of the development of the milkiness this is converted to propionaldehyde has not been disproved. But there seems no precedent for such a reaction. It seems more likely that the lachrymal principle is a sulfur compound present in addition to the propionaldehyde. The highly acid medium in which the nitrohydrazones are prepared would be expected to cause quick polymerization and thus prevent efficient reaction with the hydrazines.

In a typical experiment, the distillate from five 800-gram batches of onions amounted to 12 per cent of the weight of the onions and yielded 0.88 gram of dinitrophenyl hydrazone after crystallizing twice from alcohol. This is equivalent to .21 gram of propionaldehyde or 52 mg./kilo of onion.

It is thus apparent that there is a sound basis for some of the traditions bearing on health which the onion has acquired. It is conceivable that eating raw onions has a curative effect on sore throat resulting from colds. There is good reason for onion vapors having bactericidal and phytoncidal properties, and such vapors may be useful in healing wounds. But it is also apparent from the nature of the components of onion vapors that those compounds can be made available far more practically by synthetic chemical laboratories.

To control the fungus (*Urocystis cepulae*) responsible for smut in onions, formaldehyde is applied to the soil with onion seeds. The fact that this fungus no longer invades the seedling when it is several days old suggests that the seedling may protect itself by its own aldehyde. There is a tendency to ascribe any changes that take place in a broken or ruptured plant cell as being due to enzymic activity. But here we have a product removed from all contact with enzymes by distillation, yet undergoing profound chemical changes. It was recently announced that at Yale University 300 different chemical compounds have been obtained from the tuberculosis bacillus, which is a plant of but one cell. While the effect of enzymes is known to be profound, the imagination can easily picture many reactions between the numerous organic compounds that exist in organic materials such as food mixtures. The food chemist well knows that such reactions do occur spontaneously, unaided by enzymic catalysis, sometimes favorable, sometimes unfavorable. But he is still a long way from being able to control the media that contain such complex mixtures to direct the reactions according to his will.

Thus we have seen that propionaldehyde, which has been identified in the low-temperature vacuum distillate obtained from onions, is not the lachrymal principle in the onion. The lachrymal substance is concentrated in such a distillate, and the chemical reactions with it indicate a thioaldehyde. It is not so much the volatility of this substance that is responsible for the lachrymating effect of cutting an onion but the turgidity and succulence of the onion cell that disperses fine droplets of onion juice. Finally, if the components of onion vapors have a place in medicine and surgery, the organic chemist, not the onion, should supply them.

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