- Bradbury, R. B., White, D. E., J. Chem. Soc., 3447 (1951).
- Bradbury, R. B., White, D. E., Vitam. Horm. (N.Y.) 12, 207 (1954).
- Braden, A. W. H., Southcott, W. H., Moule, G. R., Aust. J. Agric. Res. 15, 142 (1964).
- Chem. Eng. News 36(38), 49 (1958).
- Cheng, E., Story, C. D., Payne, L. C., Yoder, L., Burroughs, W., J. Anim. Sci. 12, 507 (1953).
- Curnow, D. H., Biochem. J. 58, 283 (1954).
- Edwards, R. H., Miller, R. E., de Fremery, D., Knuckles, B. E., Bickoff, E. M., Kohler, G. O., J. Agric. Food Chem. 23, 620 (1975)
- Ershoff, B. H., Proc. Soc. Exp. Biol. Med. 87, 134 (1954).
- Guggolz, J., Livingston, A. L., Bickoff, E. M., J. Agric. Food Chem. 9.330 (1961).
- Hanson, C. H., Loper, G. M., Kohler, G. O., Bickoff, E. M., Taylor, K. W., Kehr, W. R., Stanford, E. H., Dudley, J. W., Pedersen, M. W., Sorenson, E. L., Carnahan, H. L., U.S. Dept. Agric. Tech. Bull. No. 1333, 72 (1965).
- Knuckles, B. E., Bickoff, E. M., Kohler, G. O., J. Agric. Food Chem. 20, 1055 (1972).

- Knuckles, B. E., de Fremery, D., Bickoff, E. M., Kohler, G. O., J. Agric. Food Chem. 23, 209 (1975a).
- Knuckles, B. E., Miller, R. E., Bickoff, E. M., J. Assoc. Off. Anal. Chem. 58, 982 (1975b).
- Kohler, G. O., Bickoff, E. M., Spencer, R. R., Witt, S. C., Knuckles, B. E., Tech. Alfalfa Conf. Proc., 10th, ARS-74-46, 71 (1968). Loper, G. M., Crop Sci. 8, 104 (1968).
- Loper, G. M., Hanson, C. H., Crop Sci. 4, 480 (1964).
- Magee, A. C., J. Nutr. 80, 151 (1963).
- Miller, R. E., de Fremery, D., Bickoff, E. M., Kohler, G. O., J. Agric. Food Chem. 23, 1177 (1975).
- Story, C. D., Hale, W. H., Cheng, E. W., Burroughs, W., Proc. Iowa Acad. Sci. 64, 259 (1957).
- Stuthman, D. O., Bickoff, E. M., Davis, R. L., Stob, M., Crop Sci. 6, 333 (1966).

Wada, H., Yuhara, M., Jpn. J. Zootechnol. Sci. 35, 87 (1964).

Wong, E., Flux, D. S., J. Endocrin. 24, 341 (1962).

Received for review May 24, 1976. Accepted July 26, 1976.

## A Compendium of Inorganic Substances Used in European Pest Control before 1850

Allan E. Smith\* and Diane M. Secov

A list of 24 inorganic chemicals used in European agriculture up to 1850 for pest control is given, together with descriptions of their recorded usage from classical times. Attempts have been made to assess their possible efficacy.

The use of pesticides is sometimes considered to have dated from the latter half of the nineteenth century. However, a survey of the classical literature (Smith and Secoy, 1975) has shown that there were frequent references to chemicals and natural products which appear to have been used for the control of plant disease and for killing unwanted plants and animals. As a result of further research into contemporary writings, a compendium of inorganic chemicals used for pest control in European agriculture from earliest recorded times until the middle of the nineteenth century is now presented with attempts to assess their possible success.

#### ALUM

Reference is made to the use of alum as a fly repellant in the "Geoponika" (13, 12), compiled by Cassianus Bassus in the sixth or seventh century A.D., and also by Hill (1586, p 68). The insects were reputedly driven away from places where the compound had been sprinkled. Hill further maintained that flies would not touch plants which had been sprinkled with a mixture of alum, origanum, and milk.

From the eighteenth century onward alum became a common additive for seed steeps used for the prevention of smut diseases and as such was recommended by Mortimer (1721, p 84), Hale (1756, p 364), Duhamel du Monceau (1762, p 94), and Somerville (1800). An unknown contributer signing himself P.H. (The Farmer's Magazine (Edinburgh), 1801) held that alum dissolved in tobacco liquor would kill caterpillars on gooseberry bushes.

Alum is now defined as hydrated potassium aluminum sulfate, but in the past the term was also generally given to other double sulfates containing aluminum. Alum is an astringent and could have acted as an insect repellant by changing the flavor of plants. The high osmotic pressure of a concentrated solution of alum or alum in tobacco solution could have an effect on soft-bodied forms.

#### ANTIMONY

A recipe of unknown authorship in The Farmer's Magazine (1778) called for 1 oz of cantharides and 1 oz of crude antimony to be powdered together and added to 0.5 lb of currants and 1 pint of oatmeal. This poisoned bait was to be placed near rats' nests together with a supply of water for the rats to drink after eating the mixture.

According to Taylor (1957, p 147), before the nineteenth century the word "antimony" was correctly applied only to the black mineral stibnite (the trisulfide). As a rat poison the above concoction should have been effective although the cantharides may have proved more toxic than the antimony.

## ARSENICAL COMPOUNDS

Sandarach (or realgar) and orpiment (or auripigmentum) are sulfides of arsenic and were known and used by classical agriculturists. Arsenical compounds and "arsenic" (the oxide of the metal) have been in continuous use from early times as a poison to kill pests and vermin. Thus, the burning of arsenical sulfides to kill scorpions was referred to in the "Geoponika" (13, 9). The twelfth century Arab writer Ibn-Al-Awam (1864, Vol. 2, p 338) and Speed (1659, p 176) wrote that birds could be killed using baits treated with arsenical poisons. Worlidge (1669, p 194) and Ellis

Agriculture Canada, Research Station, Regina, Saskatchewan, S4P 3A2, Canada (A.E.S.), and the Biology Department, University of Regina, Regina, Saskatchewan, S4S 0A2, Canada (D.M.S.).

(1742, p 187) mentioned the use of arsenic as a rat poison, while the "Geoponika" (13, 12), Hill (1586, p 68), de Bonnefons (1669, p 102), Worlidge (1669, p 199), Mortimer (1721, p 208), Hale (1756, p 707), and Speechly (1779, p 342) recorded its effectiveness for killing flies and other insects.

According to Buttress and Dennis (1947) arsenic (the oxide) was reported by Aucante in 1755 as being used in Germany for treating seed as a means of preserving them from disease. About the same time Hale (1756, p 372) mentioned that farmers in England added arsenic to their seed steeps for the control of smut diseases. Arsenic as a seed steep additive was similarly discussed by Mills (1763, p 403) and Duhamel du Monceau (1764, pp 292 ff). The latter described the earlier work of Tillet on control of the smut disease bunt (Tilletia sp.) indicating that Tillet had found arsenic satisfactory. The Abbé Tessier (1786) considered arsenic a dangerous additive and its use was eventually banned in France following deaths from high levels of arsenic in bread. The adding of arsenic to seed steeps in Britain was continued and mentioned by Andrews (1786), Young (1787), and Marshall (1788, pp 10 ff). Both Prevost (1807) and Young (1809, p 469) concluded that steeping seed in arsenic was successful against smut. Sinclair (1817, p 341) strongly objected to arsenic in steeps not only because of the danger to humans but because it killed game birds which ate the treated seed.

Pliny (17, 47) during the first century A.D. made reference to the use of a dusting of sandarach and ashes as a means of preventing grape rot, but no one else seems to have used arsenic for the treatment of such diseases until the latter half of the nineteenth century.

Arsenical compounds are very toxic and have fungicidal properties; therefore, the uses described should have proved successful.

### BITTERN

Bittern was a by-product of the early salt industry when salt was obtained by evaporation of sea water to the point where the sodium chloride crystallized out. These crystals were removed and the remaining solution, containing calcium and magnesium salts, was known as bittern. Worlidge (1683, p 36) maintained that bittern destroyed all vegetation and recommended its application for killing weeds in gravel paths and walks.

As a weed killer, bittern should have been as effective as any concentrated mineral solution.

#### CHALK (CALCIUM CARBONATE)

The Roman author Varro, during the first century B.C., advocated (1, 57) that in granaries the wheat be sprinkled with powdered chalk, seemingly as a pest deterrent. Both Palladius (1, 122), who wrote during the fourth century A.D., and Hill (1586, p 67) maintained that chalk sprinkled in rings around plants would protect them from ants. Hill also held that chalk bands applied to tree trunks would prevent pests from ascending. Ellis (1742, p 46) averred that thistles and many other weeds in his land could be eradicated by following deep plowing with chalking.

Although powdered chalk may have formed some sort of physical barrier to the ants it is likely that none of the above uses for chalk were effective.

### COBALT

Cobalt was described by the Abbe Tessier (1786) as a useless and dangerous addition to cereal seed steeps used for the control of smut. No indication was given as to the specific cobalt salt referred.

Cobalt salts have not been shown to have any fungicidal activity.

#### COPPER SULFATE (BLUESTONE, BLUE VITRIOL)

Copper sulfate seed treatments were first mentioned by Schulthess in 1761 (cf. Buttress and Dennis, 1947) as a preventative measure against smuts. However, not until the pioneering work of Prevost (1807) was it realized that bunt, or stinking smut (Tilletia sp.), of wheat was caused by infective spores which could be prevented from germinating and killed by exposure to minute traces of copper salts. Prevost also worked out a method for seed treatment with copper sulfate on a field scale. News of Prevost's discoveries was introduced into Britain by Sinclair (1817. pp 340 ff). According to Sinclair (1821, pp 81 ff) Hipkys seems to have been the first to try the treatment and comment favorably upon it after trials over several years. Sinclair noted (1821, pp 81 ff) that if the wheat were to be sown broadcast it should be treated with lime, whereas if it was to be drilled then the treated wheat was to be dried in the air. From the time of the publication of Prevost's work the use of copper sulfate for seed treatment against smut diseases in Europe seems to have been a general occurrence as references by Barclay (1821), 'Agricola" (1823), de Candolle (1832, p 1482), and Cutting (1840) imply. Cutting mentioned that after treatment of the grain with copper sulfate solution the liming stage normally recommended could be omitted since in his opinion calcium sulfate would be formed which was of little use

The phytotoxic effects of copper salts were demonstrated by de Saussure (1804, p 253) who showed that plants grown in copper sulfate solution died rapidly. Similarly, Phillips (1821) told of copper salts proving fatal to a young poplar tree. Barclay (1821) reported that by carefully adjusting the amount of copper sulfate in his steep he could selectively destroy the germinating properties of the seeds of the weeds pabble (*Agrostema githago*) and vetch (*Vicia sativa*) without unduly affecting the germinating quality of the wheat.

Copper sulfate seed treatments did prove effective against bunt and became widespread during the latter half of the ninteenth century. A serious objection to the use of bluestone was that excess copper could cause reduced germination of the wheat. This was overcome by steeping for a limited time followed by drying with lime. The lime not only converted the soluble copper salts into insoluble cupric hydroxide, thereby reducing the crop damage, but dried the grain for sowing.

A combination of copper sulfate and lime was recommended by Charles Morren in 1845 (cf. Johnson, 1935) as a means of protecting potatoes from the blight (*Phytophthera infestans*) but this was not tried and found successful until almost 40 years later. Copper sulfate solutions were discovered by Boucherie in 1838 (cf. Johnson, 1935) to be effective for the preservation of wood against various fungi.

### GAS LIME

Gas lime was hydrated lime that had been used for purifying coal gas and was thus impregnated with ammonia, hydrogen sulfide, and other impurities. Applications were recommended by both Sinclair (1832, pp 132 ff) and Yates (1841) to turnip crops prior to germination as a control against the ravages of the "fly" (*Phyllotreta* sp., probably). The effects seem to have been rather unsuccessful (Sinclair, 1832, pp 132 ff).

## GLAUBER'S SALT (SODIUM SULFATE)

Glauber's salt was used by Mathieu de Dombasle (cf. Large, 1962, p 80) in France during the early part of the nineteenth century as a cereal seed treatment in conjunction with lime (q.v.) for the control of the smut disease bunt (*Tilletia* sp.). The grain was watered with an 8%solution of Glauber's salt and dried with lime before sowing. Large records that the treatment was effective.

Sodium sulfate in the presence of lime would give rise to insoluble calcium sulfate and alkaline sodium hydroxide by double decomposition. The French scientist Prevost (1807) was the first to show that growth of bunt spores is inhibited in acid or alkaline solutions, which probably accounted for the success of "The Absolute Preservative of Mathieu de Dombasle".

## IRON AND IRON SALTS (FERROUS SULFATE)

The suggested use of iron or iron salts to kill mice and rats was mentioned several times in the "Geoponika" (13, 4), by Estienne and Liebault (1600, p 400) and by Markham (1631, p 94). Iron salts were reported as being bad for rue, savory, mint, or basil by Pliny (19, 57) during the first century A.D., and Hale (1759, p 16) cited instances of poor crop yields in the vicinity of soils and waters containing iron deposits. In *Loudon's Gardeners Magazine* (1826) a writer noted that in France copperas (ferrous sulfate) was considered to be so poisonous to plants that weeds could be killed by mowing them with a scythe whose blade had been sharpened on a stone dipped in ferrous sulfate solution. The French scientist de Candolle (1832, p 1482) also mentioned this curious practice.

Copperas, also known as vitriol or green vitriol, was commonly added to cereal seed steeps for the control of smut after the middle of the eighteenth century; this use was mentioned by Hale (1756, p 364), Duhamel du Monceau (1762, p 94), Varley (1770, p 179), and many others. The steeping of cereal grain in copperas-containing steeps was also considered by Hale (1756, p 705) to discourage worms from attacking the germinating seed. An author under the pseudonym of "A Real Farmer" (1768, p 50) did not advocate the addition of copperas to seed steeps since he maintained that it destroyed the germination of the grain. However, this writer did recommend that it be mixed with soot (or with sulfur, lime, salt, and wormwood) and sprinkled over young wheat as a means of protecting the young plants from attack by worms (1768, p 57).

An attempt seems to have been made by Hobbs (1841) to use copperas-treated poles placed round hop plants to keep insects from infesting the plants.

The use of iron salts to kill rodents is perhaps of magical origin and has not been shown to have any efficacy. As a deterrent against worms and insects copperas was probably ineffective. Ferrous sulfate is a herbicide and it is possible that as such it was successfully used in France (though not in the mode described above) prior to 1826. Iron salts do have some slight fungicidal activity and Prevost (1807) noted that iron sulfate in large amounts did inhibit the germination of bunt spores. If large quantities of copperas had been used in seed steeps then germination of the cereals would have been affected as noted by "A Real Farmer".

## LIME (CALCIUM HYDROXIDE, SLAKED LIME)

Lime has been used continuously since the late 1500's as a general chemical for killing insects and soft-bodied invertebrates such as slugs, snails, etc. The lime was either sprinkled around the plants to be protected, or the crops and pests were dusted with it. In many cases the lime was mixed with sulfur, ashes, soot, or water for added effect. Authors recommending these uses for lime include Mascal (1569, p 65), Heresbach (1586, p 43), Markham (1631, pp 88 ff), Speed (1659, pp 98 ff), Bonnefons (1669, p 101), Worlidge (1669, p 197), Mortimer (1721, p 206), Hale (1756, p 704), Jacob (1783), Forsyth (1802, pp 250 ff), Menzies (1808), Williams (1830), and J.M. (*The British Farmer's Magazine*, 1842). The use of lime as a wash or paint for trees to destroy pests harboured in the bark was described by Tench (1799), Wedgwood (1822), and Huddlestone (1826). For the control of many greenhouse pests without harming plant foliage N.T. (*Loudon's Gardeners Magazine*, 1830) recommended a boiled mixture of sulfur, soap, tobacco, and lime.

Seeds were sprinkled with lime, often together with other ingredients, to prevent birds and other predators from eating them. The principle seems to have been more one of repellance than anything else and was advocated by Markham (1631, pp 88 ff), Hartlib (1651, p 16), and Speed (1659, pp 98 ff) among others.

Perhaps the main use of lime from 1600 was for protection against smut diseases and specifically bunt (Tilletia sp.). The cereal seeds were generally steeped in brine solutions at which time the light (and often diseased) seeds floated and were skimmed off and discarded. The remaining seed was dried by applications of slaked lime or quick lime (q.v.). Often other additives were included in the steeping solution, many of which are mentioned elsewhere in this paper. The practice of brining and liming was discussed by all the major agricultural writers and carried out until the middle of the nineteenth century when it gradually died out. The work of Tillet, Tessier, and Prevost (cf. Prevost, 1807) in France during the last half of the eighteenth century showed that bunt of wheat was caused by infection and that lime and other alkaline treatments would lessen the infections. Prevost (1807) also showed that copper sulfate (q.v.) was much more effective for the control of bunt. For a detailed history of seed steeping in England and the use of lime in seed steeps, reference should be made to the review article by Buttress and Dennis (1947).

Forsyth (1802, pp 250 ff) boiled lime, sulfur, tobacco, and elder buds with water to make a preparation which he used to control mildew on plant foliage. Seemingly, the only reference to lime being used as a herbicide was by Brodie (1811) who remarked that heath and certain other plants could be killed by soil applications of lime.

The use of lime for killing insect and larvae pests should have been moderately successful if the treatments were carried out repeatedly. The treating of seeds with lime to deter birds may have been slightly effective. Used in conjunction with seed steeps some benefit against smut diseases must have been obtained as the work of Tillet, Tessier, and Prevost showed (cf. Large, 1962, pp 70 ff). Forsyth (1802) and N.T. (Loudon's Gardener's Magazine, 1830) in preparing their lime mixtures made a lime-sulfur compound which should have been both fungicidal and insecticidal. Although lime is not a herbicide, making the land more alkaline would suppress heath and other plants adapted to acidic soils.

## MERCURY (QUICKSILVER)

Estienne and Liebault (1600, p 400) advocated the mixing of mercury with meat as a rat poison. According to Bradley (1724, p 249) and Weston (1773, p 291) insects could be banished from fruit trees by inserting mercury into a hole drilled into the stem. A recipe involving the dissolving of quicksilver in boiling water followed by the addition of soft soap to the cool solution was given by Speechly (1779, pp 122 ff) as a drench for pineapple plants to destroy insect pests infesting them. Both Speechly (1779, pp 122 ff) and Abercrombie (1789, p 121) recommended that quicksilver be kept in glazed vessels at the bottom of the water cisterns in greenhouses since plants watered with this solution would be kept free of insects and their larvae.

Elemental mercury is considerably toxic and should have been useful as a rat poison in the manner described. The use detailed by Bradley and Weston would have been completely ineffectual although it is an interesting attempt at a systemic poison. Mercury is not soluble in water, but in the greenhouse cisterns soluble mercury salts may have been formed which could have proved toxic to insect pests.

## MERCURIC CHLORIDE (CORROSIVE SUBLIMATE)

Speed (1659, p 176) recorded that meat treated with sublimate was a means of poisoning rooks, crows, jackdaws, and magpies. Corrosive sublimate was later used as an additive to seed steeps for the control of smut in cereals. Prevost (1807) wrote that Tessier had successfully used corrosive sublimate for this purpose and agreed with his observations, concluding that anything which destroyed the germination of the bunt spores was a preventative of the infection. Prevost did not recommend its general use because of its toxity and expense. An aqueous solution of corrosive sublimate was used to kill insects in the wood and on the walls of greenhouses (Boothby, 1822), and was described as a preservative against wood rot and decay by de Candolle (1832, p 1482) and by an anonymous writer in "Baxter's Agricultural and Horticultural Annual" (1836, p 34). The latter author gives an account of this chemical's use in the early 1830's by the British Admiralty for preserving ship's timbers, together with an account of practical tests carried out in the fungus pit at Woolwich.

Since mercuric chloride is very toxic and a potent fungicide, the above uses should have proved effective.

## NITER (SALTPETER, POTASSIUM NITRATE)

Charles Cotton (1675, p 88) wrote that some gardeners sprinkled the branches and leaves of trees with a solution of saltpeter to kill caterpillars. Sinclair (1832, pp 71 ff) maintained that niter would destroy slugs. The other major use for saltpeter seems to have been as a seed steep. This was first advocated by Plat (1600, p D) as a means of increasing yields of cereal grains, but later cereal steeps were used almost exclusively for attempted control of smut diseases. Worlidge (1669, p 56) and Mortimer (1721, p 41) both mentioned the addition of saltpeter to seed steeps as did Hale (1756, p 373), Ellis (1750, p 24), Duhamel du Monceau (1762, p 94), Varley (1770, p 179), and many others.

For the control of fungal diseases the potassium nitrate would be of no use. For the killing of soft-bodied caterpillars and slugs, a strong aqueous solution applied directly to the animal should have been an effective desiccant.

### NITRIC ACID (AQUA FORTIS)

A curious preparation for preserving timber, ropes, cables, fishing nets, and ships' masts from attack by "worms" and from putrefaction was given by Evelyn (1664, p 70). The process involved the addition of *aqua fortis* to sulfur which was followed by distillation of the mixture to dryness. This was repeated two or three times when the remaining dark colored sulfur was dissolved in oil and applied to the infected materials, or materials to be preserved. Evelyn noted that this mixture as well as being a preservative for timber and cordage, etc., was "a wonderful *arcanum* for tinging wood".

The effectiveness of such treatments is unknown.

## NITRUM (NATRON, SODIUM CARBONATE)

Virgil (first century B.C.) wrote (1, 195) that prior to sowing many farmers treated their seeds by drenching them in nitrum and black oil lees (amurca). This operation was considered to result in an increased yield. Columella (first century A.D.) held (2, 10) that this treatment was also successful in reducing attack by weevils after the crops had reached maturity.

Roman nitrum was obtained from natural deposits in Egypt which still yield large quantities of the material. It consists of sodium carbonate with some bicarbonate, sulfate, and chloride (Taylor, 1957, p 128). The roll of amurca (the watery residue obtained as a by-product during the crushing of olives for their oil) in classical agriculture has already been discussed (Smith and Secoy, 1975).

The nitrum and amurca treatments may have resulted in some seed protection by acting as a pest repellant.

# POTASH (LYE, SALT OF TARTAR, POTASSIUM CARBONATE)

Both Markham (1631, p 95) and Hale (1756, p 705) mentioned that the sprinkling of "strong lye" on seed corn before sowing would protect it from attack by worms after planting. Worlidge (1669, p 197) and Mortimer (1721, p 206) held that worms could be killed by watering the ground with a lye solution prepared from ashes. Duhamel du Monceau (1762, pp 96 ff) in discussing wheat bunt referred to the work of Tillet on this disease, carried out in the early 1750's in France. Tillet had observed that steeping the seed grain in alkaline lyes afforded protection against bunt. However, this practice does not seem to have gained much favor, although Andrews (1786) and others advocated its use in seed steeps along with other ingredients. From the writings of Mills (1763, pp 391 and 417) it is learned that lyes were used to try to control rust diseases. The young plants were either watered with such solutions or strewn with woolen rags steeped in the lye. A lye of wood ash was used by Speechly (1779, p 168) to destroy Acarus sp. in greenhouses though Speechly warned that unless great care was exercised the plants could be damaged.

Potassium carbonate is alkaline and as such would have effects on worms, larvae, and small arthropods. As a seed steep against bunt, the lye should have been very effective since the alkali would inhibit germination of the disease spores (cf. Prevost, 1807). The effects for control of rust diseases would be minimal.

## QUICKLIME (UNSLAKED LIME, CALCIUM OXIDE)

Mention is made in the "Geoponika" (13, 15) that quicklime scattered over the floors of houses would kill fleas. Quicklime was sprinkled over plants by Worlidge (1700, p 225) to protect them from snails and worms, while Sinclair (1832, pp 71 ff) advocated its use against slugs and grubs. Williams (1830) applied lime to gooseberry bushes to kill caterpillars infesting them. Freshly slaked lime was held by Corbett (1835) to kill snails in gardens and turnip fields while J.M. (*The British Farmer's Magazine*, 1842) stated that hot slaked lime harrowed into cultivated land was an excellent means of destroying both snails and slugs. Against wheat "fly" Kirby (1844) recommended dusting the crop with powdered quicklime.

The practice of steeping cereal seed in brine followed by drying with lime (q.v. salt and lime) was used from the early seventeenth century as a method for controlling smut diseases in cereals. In addition Mortimer (1721, p 41), Tull (1743, p 66), Varley (1770, pp 179 ff), and many others advised unslaked lime for the drying of the wet grain after the steeping.

Quicklime should have been effective against flies, snails, slugs, and other crop pests. Used with seed steeping, quicklime, being alkaline, should have prevented germination of bunt spores (Prévost, 1807). Also, the addition of quicklime to the wet grain would have generated heat as the calcium oxide was being converted to the hydroxide. It is now known that heat is an effective method for killing rust and smut infections in cereal seed grains.

## SAL AMMONIAC (AMMONIUM CHLORIDE)

This compound, also known as Salt of Ammon, has been known since antiquity when it was prepared from camel's urine supposedly near the shrine of Jupiter Ammon. The "Geoponika" (13, 3), Hill (1586, p 74), and Estienne and Liebault (1600, p 399) all list the same curious use of mixing sal ammoniac with wheat to poison or drive away weasels. Mills (1763, p 391) referred to the work of Count Ginanni of Ravenna who earlier had written a treatise on the "distempers of corn in the blade"; Count Ginanni was reputed to be able to prevent "rust" by sprinkling the plants, before the ears were formed, with a solution of sal ammoniac in water mixed with alkaline substances.

Neither of these uses for sal ammoniac would have been effective.

## SALT (SODIUM CHLORIDE)

The harmful effects of salt on vegetation are referred to in writings from the early civilizations of the Mediterranean region as seen in Judges (IX, 45), Xenophon (20, 12), Virgil (2, 226), Pliny (31, 7), and Palladius (1, 9). In the late sixteenth century Plat (1594, p 43) recorded that salt sown with cereals would kill weeds and Markham (1620, pp 11 and 22) also urged this usage. During the latter part of the seventeenth century both Evelyn (1676, p 103) and Worlidge (1683, p 34) described its use for the killing of weeds in paths and gravel walks. An anonymous writer in a book written by a Private Society of Husbandmen and Planters (1733, p 48) wrote of salt being spread on winter fallow to destroy weeds and Holdich (1825, p 69) mentioned that it was being tried for the control of perennial weeds such as thistles.

Salt was also used as an insecticide from earliest times with references to this usage being given in the "Geoponika" (13, 1, 15). Salt solutions were suggested as a means of killing caterpillars by Mascal (1569, p 53) while Markham (1620, p 90) considered that salt would control ants. Other references to the use of salt against worms and caterpillars are to be found in the writings of Speed (1659, p 98), Mortimer (1721, p 206), Hitt (1757, pp 265 ff), Peters (1771, p 34), and Adam (1789, p 166).

Perhaps the major use of salt from the end of the sixteenth century until the early nineteenth century was as a seed steep for the control of smut diseases. The cereal seed was steeped in a strong brine solution, the grains which floated were skimmed off and discarded, while the heavy seed was removed and usually dried with lime (q.v.) and then sown. In many cases other substances were added to the brine in which the seed was steeped (cf. Buttress and Dennis, 1947).

The use of salt as a pesticide and seed steep has recently been reviewed in detail and the efficacies discussed (Smith and Secoy, 1976).

## SULFUR

One of the earliest references to sulfur is to be found in Homer's "Odyssey" (22, 493) where it appears to have been burned to avert the ill influence of the dead. Sulfur was known to the classical Roman agricultural writers Cato (95), Pliny (17, 47), and Palladius (1, 127, 129, 130, 133) who advocated its use for pest control either by burning the element (usually in combination with pitch and other evil smelling combustibles) or by adding the sulfur mixed with herbs, oil, or vinegar to the insect pests. The

"Geoponika" (13, 7, 8, 10, 11, 14), the twelfth century Arab agricultural writer Ibn-Al-Awam (1864, Vol. 1, pp 591 ff), and the sixteenth century writers Hill (1586, pp 65 ff), Heresbach (1586, p 68), and Estienne and Liebault (1600, pp 399 ff) all mention the same agricultural uses of sulfur as given by the earlier Roman writers. From the seventeenth century on sulfur was used as a fumigant for killing insects and larvae on plants, fruit trees, and in greenhouses as witnessed by the writings of Speed (1659, p 170), Evelyn (1664, p 70), La Quintinie (1693, p 101), Mortimer (1721, p 207), Hale (1756, pp 372 and 706), A.S. (The Farmer's Magazine (Edinburgh), 1802), and "Cultivator Middlesexiensis" (1811), among others. From the late eighteenth century on there was a tendency to add tobacco with the sulfur being burned, and also to direct the smoke by judicious use of bellows. Sulfur was mixed with turnip seed prior to sowing to protect the young turnips from the ravages of the "fly" (probably Phyllotreta sp.) as described by Hale (1759, p 73), Ellis (1742, p 187), "A Real Farmer" (1768, p 55), and Sturgeon (1803). In many cases other additives such as ashes, lime, and oil of aniseed were also included with the sulfur. Against mites and other small arthropodous pests of the greenhouse, free sulfur was advocated by Weston (1773, p 291) and Speechly (1779, p 114). Speechly (1779, pp 165 ff), Salisbury (1820), and Kent (1822) all recommended that against mites a mixture of lime and sulfur be painted on the greenhouse flues so that the volatilizing sulfur would kill the pests. Sulfur and soap mixtures which sometimes contained other ingredients were mentioned by Speechly (1779, pp 165 ff), Nicol (1797, p 34), Robson (1822), and Burges (1826) as being effective against insect and larval pests.

The use of sulfur-containing preparations for the control of horticultural fungus diseases seems to have been first mentioned by Speechly (1779, pp 165 ff) who noted that a preparation containing sulfur, turpentine, and soap appeared to reduce mildew on peach and apricots. Later Forsyth (1802, pp 249 ff) used a lime-sulfur preparation (q.v. lime) to control mildew on fruit trees. Robertson (1824) described the successful control of peach mildew using a sulfur soap spray while Tucker (1847) utilized sulfur and lime water to cure *Oidium* mildews attacking his grape vines.

Sulfur has been in continual use from earliest recorded times until the present day and, since sulfur has both insecticidal and fungicidal properties, its use for those purposes, as described above (whether in solid form or as a fumigation), must have resulted in some benefits to agriculture.

# SULFURIC ACID (OIL OF VITRIOL, SPIRIT OF VITRIOL, OIL OF SULFUR)

Reference to sulfuric acid as an agricultural chemical was made by Jennings (1799), in describing his experiments on the control of smut in wheat. Jennings concluded that the infection could be destroyed by steeping his grain in "vitriolick acid" diluted 30 times with water. The Earl of Dundonald (1803, p 137) held that dilute vitriolic acid would destroy insects in land under cultivation, while Sinclair (1832, pp 71 ff) maintained that applications of sulfuric acid would probably kill slugs.

Since the work of Prevost (1807) showed that bunt spores would not germinate in acidic solutions, sulfuric acid seed treatments should have been effective. Sulfuric acid for the destruction of surface insects and slugs should also have proved successful.

## VERDIGRIS (COPPER ACETATE)

Verdigris was used as a component of cereal seed steeps for the control of bunt and smut diseases as mentioned by

The cupric ion is a potent fungicide so verdigris would have been effective in preventing germination of bunt spores infecting diseased seed wheat (q.v. copper sulfate). WATER

The Greek Theophrastus (fourth century B.C.) noted (4, 14) that rain at the right season seemed to prevent larvae from appearing on olive trees and this observation may have caused him to conclude that watering plants with rain water would destroy pests damaging the foliage (7, 5). Pliny maintained also (17, 37) that rain would prevent caterpillars and worms on fruit trees from breeding. In a similar vein, Mascal (1569, p 53) wrote that at blossom time trees could be protected from caterpillars by casting water or salt water every 2 or 3 days over the trees using primitive wooden or metal sprayers. Plattes (1656, p 62) urged that water should be squirted on hop plants using fire pumps so that the water fell like rain since this should protect them from mildew. Both Worlidge (1669, p 198) and Mortimer (1721, p 208) recommended dashing water on trees during dry spells to rid them of plant lice. The use of scalding water to kill ants in fields and gardens was mentioned by Markham (1620, p 90). Young (1836, pp 382 ff) referred to a farmer James Ellis, who, as a preventative against smut and other diseases, prepared his cereal seed for sowing by dipping it for 1 min in boiling water, and, after cooling it in cold water, mixed it with quicklime to dry.

Although water is not an insecticide or fungicide the uses described above indicate its usage for pest control. Applications of water may have had some effect in washing insects and larvae from trees and plants. Hot water against ants should have been effective also. The use of hot water as a seed steep in conjunction with quicklime (q.v.) must have been very effective against bunt, rust, and smut diseases since heat treatments are now known to be effective in destroying fungal spores and infections in seed grain.

## ACKNOWLEDGMENT

The authors wish to thank the Rothamsted Experimental Station, Harpenden, England, for the use of their library facilities and acknowledge the help rendered by T. Cawley and his library staff. The critical comments of P. Harris and J. R. Hay of the Canada Agriculture Research Station, Regina, are greatly appreciated.

## LITERATURE CITED

For the citations to the works of Columella, Pliny, Theophrastus, Varro, and the "Geoponika" the boldface type refers to the book number while the second number identifies the chapter. For the writings of Palladius the numbers are to the book and stanza, while for Homer and Virgil, the numbers indicate book and paragraphs, respectively. The works of Cato and Xenophon are not divided into books; thus the boldface type refers to the numbered sections. As these sections are very long in Xenophon's "Oeconomicus" the second number indicates the paragraph. In the case of many early works no publishers existed as such, and the books were privately printed. For the citations of references from nonclassical works the numbers are for year and page. References to journals are in accordance with normal procedure.

Abercrombie, J., "The Hot-House Gardener", London, 1789. Adam, J., "Practical Essays on Agriculture", Vol. 2, London, 1789. "Agricola", The Farmer's Magazine (Edinburgh) 24, 433 (1823). Andrews, R., Annals of Agriculture 6, 173 (1786)

Barclay, J., The Farmer's Magazine (Edinburgh) 22, 411 (1821).

- "Baxter's Agricultural and Horticultural Annual", London, 1836. Boothby, B., Transactions of the Horticultural Society 3, 22 (1822)
- Bradley, R., "New Improvements of Gardening", 4th ed, London, 1724.
- The British Farmer's Magazine 6 (n.s.), 20 (1842).
- Brodie, P., Communications to the Board of Agriculture 7, 64 (1811).
- Burges, J., Loudon's Gardeners Magazine 1, 389 (1826).
- Buttress, F. A., Dennis, R. W. G., Agric. History 21, 93 (1947).
- Cato and Varro, "De Re Rustica", translated by W. D. Hooper and H. B. Ash, Loeb Classical Library, Wm. Heinemann Ltd., London, 1967.
- Columella, "De Re Rustica", Books 1-4, translated by H. B. Ash, Loeb Classical Library, Wm. Heinemann Ltd., London, 1960.
- Corbett, J., Transactions of the Horticultural Society 1, 77 (1835). Cotton, C., "The Planters Manual", London, 1675.
- "Cultivator Middlesexiensis", Agricultural Magazine 9, 269 (1811).
- Cutting, J. B., The British Farmer's Magazine 4 (n.s.), 106 (1840).
- de Bonnefons, N., "The French Gardiner", translated by John Evelyn, London, 1669.
- de Candolle, A. P. "Physiologie Végétale", Vol. 3, Paris, 1832.
- de Saussure, T., "Recherches Chimiques sur la Végétation", Paris, 1804.
- Duhamel du Monceau, H. L., "A Practical Treatise of Husbandry", 2nd ed, London, 1762.
- Duhamel du Monceau, H. L., "The Elements of Agriculture", Vol. 1, translated and revised by P. Miller, London, 1764.
- Dundonald, Earl of, "A Treatise, Shewing the Intimate Connection that Subsists Between Agriculture and Chemistry", London, 1803.
- Ellis, W., "The Modern Husbandman", London, 1742. Ellis, W., "The Farmer's Instructor", 2nd ed, London, 1750.
- Estienne, C., Liebault, J., "Maison Rustique" or "The Countrie Farme", translated by R. Surflet, London, 1600.
- Evelyn, J., "Sylva", London, 1664. Evelyn, J., "A Philosophical Discourse of Earth", London, 1676.
- The Farmer's Magazine (Edinburgh) 2, 144 (1801).
- The Farmer's Magazine (Edinburgh) 3, 19 (1802).
- The Farmer's Magazine and Useful Family Companion, Agricola Sylvan, Ed., 3, 100 (1778). Forsyth, W., "A Treatise on the Culture and Management of
- Fruit-Trees", London, 1802.
- "Geoponika" or "Agricultural Pursuits", translated from the Greek of Cassianus Bassus by T. Owen, London, 1805.
- Hale, T., "A Compleat Body of Husbandry", London, 1756. Hale, T., "A Continuation of the Compleat Body of Husbandry", London, 1759.
- Hartlib, S., "His Legacie", London, 1651.
- Heresbach, C., "The Foure Bookes of Husbandry of Conrad Heresbach", translated by B. Googe, London, 1586.

- Hill, T., "The Gardeners Labyrinth", London, 1586. Hitt, T., "A Treatise of Fruit-Trees", 2nd ed, London, 1757. Hobbs, J., The British Farmer's Magazine 5 (n.s.), 260 (1841).
- Holdich, B., "An Essay on the Weeds of Agriculture", G. Sinclair, Ed., 2nd ed, London, 1825.
- Homer, "The Odyssey", translated by R. Fitzgerald, Doubleday, New York, N.Y., 1961.
- Huddlestone, T., Loudon's Gardeners Magazine 1, 388 (1826).
- Ibn-Al-Awam, "Le Livre de l'Agriculture", 2 Vol., translated by J.-J. Clement-Mullet, Paris, 1864.
- Jacob, J., Letters and Papers on Agriculture, Planting, Etc. (Bath and West of England Society) 1, 227 (1783).
- Jennings, J., Letters and Papers on Agriculture, Planting, Etc. (Bath) 9, 97 (1799).
- Johnson, G. F., Agric. History 9, 67 (1935).
- Kent, W., Transactions of the Horticultural Society 3, 287 (1822).
- Kirby, The British Farmer's Magazine 8 (n.s.), 417 (1844).
- La Quintinie, J. De, "The Compleat Gard'ner", translated by J. Evelyn, London, 1693.
- Large, E. C., "The Advance of the Fungi", Dover Publications, New York, N.Y., 1962.
- Loudon's Gardeners Magazine 1, 444 (1826).
- Loudon's Gardeners Magazine 6, 403 (1830).
- Markham, G., "Farewell to Husbandry", London, 1620. Markham, G., "A Way to Get Wealth", London, 1631.

- Marshall, W., "The Rural Economy of Yorkshire", Vol. 2, London, 1788.
- Mascal, L., "A Booke of the Art and Maner, Howe to Plante and Graffe", London, 1569.
- Menzies, R., Communications to the Board of Agriculture 6, 162 (1808).
- Mills, J., "A New and Complete System of Practical Husbandry", Vol. 2, London, 1763.
- Mortimer, J., "The Whole Art of Husbandry", Vol. 1, 5th ed, Dublin, 1721.
- Nicol, W., "The Scotch Forcing Gardener", Edinburgh, 1797.
- Palladius, "On Husbondrie", B. Lodge, Ed., N. Trubner & Co., London, 1873.
- Peters, M., "The Rational Farmer", 2nd ed, London, 1771. Phillips, R., Thompson's Annals of Philosophy 2, 76 (1821).
- Plat, H., "The Jewell House of Art and Nature", London, 1594. Plat, H., "The New and Admirable Arte of Setting of Corne", London, 1600.
- Plattes, G., "Practical Husbandry Improved", London, 1656. Pliny, "Natural History", Books 17-19, translated by H. Rackham,
- Loeb Classical Library, Wm. Heinemann Ltd., London, 1971. Pliny, "Natural History", Books 28–32, Translated by W. H. S.
- Jones, Loeb Classical Library, Wm. Heinemann Ltd., London, 1963.
- Prévost, B., "Mémoir sur la cause immédiate de la carie ou charbon des bles", Paris, 1807, translated from the French by G. W. Keitt and issued by the American Phytopathological Society as "Phytopathological Classics", No. 6, Menasha, Wis., 1939.
- Private Society of Husbandmen and Planters, "The Practical Husbandman and Planter", Vol. 1, London, 1733.
- "Real Farmer", "The Modern Farmer's Guide", Vol. 2, Glasgow, 1768.
- Robertson, J., Transactions of the Horticultural Society 5, 175 (1824).
- Robson, M., Transactions of the Horticultural Society 4, 143 (1822).
- Salisbury, R. A., Transactions of the Horticultural Society 1, 261 (1820).
- Sinclair, Sir J., "Code of Agriculture", London, 1817.
- Sinclair, Sir J., "Appendix to Code of Agriculture", 3rd ed, London, 1821.

- Sinclair, Sir J., "Code of Agriculture", 5th ed, London, 1832.
- Smith, A. E., Secoy, D. M., J. Agric. Food Chem. 23, 1050 (1975).
- Smith, A. E., Secoy, D. M., Agric. History 50, 506 (1976).
- Somerville, J., Communications to the Board of Agriculture 2, 200 (1800).
- Speechly, W., "A Treatise on the Culture of the Pine-Apple and the Management of the Hot-House", York, 1779.
- Speed, A., "Adam out of Eden", London, 1659.
- Sturgeon, J., Annals of Agriculture **39**, 326 (1803). Taylor, F. S., "A History of Industrial Chemistry", Wm. Heinemann Ltd., London, 1957.
- Tench, J., Annals of Agriculture 32, 435 (1799).
- Tessier, The Abbe, Annals of Agriculture 6, 199 (1786).
- Theophrastus, "Enquiry into Plants", translated by A. F. Hort, Loeb Classical Library, Wm. Heinemann Ltd., London, 1968. Tucker, The Gardener's Journal, 212 (1847).
- Tull, J., "The Horse-Hoing Husbandry", 2nd ed, London, 1743.
- Varley, C., "A New System of Husbandry", Vol. 1, York, 1770.
- Virgil, "The Georgics", in "Eclogues, Georgics, Aeneid", translated by H. R. Fairclough, Loeb Classical Library, Wm. Heinemann Ltd., London, 1974.
- Wedgwood, J., Transactions of the Horticultural Society 3, 361 (1822).
- Weston, R., "Tracts on Practical Agriculture and Gardening", 2nd ed. London, 1773.
- Williams, R., Transactions of the Horticultural Society 7, 403 (1830).

- Worlidge, J., "Systema Agriculturae", London, 1669. Worlidge, J., "Systema Horti-culturae", London, 1683. Worlidge, J., "Systema Horti-culturae", 4th ed, London, 1700. Xenophon, "Oeconomicus" in "Memorabilia, Oeconomicus, Symposium and Apologia", translated by E. C. Marchant, Loeb Classical Library, Wm. Heinemann Ltd., London, 1968.
- Yates, J., The British Farmer's Magazine 5 (n.s.), 395 (1841). Young, A., Annals of Agriculture 8, 409 (1787).
- Young, A., "The Farmer's Calendar", 8th ed, London, 1809. Young, A., "The Farmer's Calendar", 20th ed, J. Middleton, Ed., London, 1836.

Received for review January 23, 1976. Accepted July 12, 1976.

## **Preparation and Insect Attractant Activity of Some Alkoxystyrene Derivatives**

Philip E. Shaw,\* James H. Tatum, Doris H. Miyashita, and Kiichi Ohinata

The synthesis of hydroxy- and alkoxystyrene derivatives was studied and 15 derivatives were prepared from inexpensive, naturally occurring reagents. These compounds were evaluated as fruit fly attractants in an outdoor olfactometer, and several were moderately attractive to male Mediterranean fruit flies. Others were moderately to strongly attractive to male oriental fruit flies. Several derivatives were moderately attractive to female Mediterranean fruit flies or melon flies, and 4-hydroxy-3-methoxystyrene benzoate was moderately attractive to both male and female melon flies. Effective female attractants are not available currently for these three insect pests.

Use of insect attractants to determine movement of insect populations and optimum time for insecticide application is important to proper crop management

(Beroza, 1972). Attractants also have been used with insecticides so that insects could be eradicated from an area with a minimum amount of insecticide (Steiner et al., 1965). The need for potent and longer lasting attractants continues, and, for many damaging insects, adequate attractants remain to be found.

Attractants have been studied extensively for Mediterranean (Ceratitis capitata) and oriental (Dacus dorsalis) fruit flies and melon flies (Dacus cucurbitae), three of the world's worst insect pests of fruit crops (Beroza, 1972). Powerful attractants for males of each of the three species are known, but no effective attractants have been

Citrus and Subtropical Products Laboratory, one of the laboratories of the Southern Region, U.S. Department of Agriculture, Agricultural Research Service, Winter Haven, Florida 33880 (P.E.S., J.H.T.) and Hawaiian Fruit Flies Laboratory, one of the laboratories of the Western Region, U.S. Department of Agriculture, Agricultural Research Service, Honolulu, Hawaii 96728 (D.H.M., K.O.).