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A REVIEW OF INFORMATION ON ANABASINE

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INTRODUCTION

Anabesine is a liquid alkaloid which closely resembles nicotine in its physical, chemical, pharmacological, and insecticidal properties. It is soluble in water in all proportions and is less volatile than nicotine. Anabesine has the molecular formula $C_{10}H_{14}N_2$ and the following structural formula:

ANABESINE

NICOTINE

The structural formula of nicotine is shown for comparison, and it is evident that no other possible pyridyl-piperidine so closely resembles nicotine as does anabesine, which chemically is beta-pyridyl-alpha-piperidine.

The principal physical constants of anabesine are as follows:

Anabesine is a colorless, somewhat viscous liquid which turns brown on standing in contact with air. It is very stable, appreciably basic in reaction, and forms salts in typical alkaloidal fashion.

The odor of anabesine resembles that of nicotine but is less intense.

Solubility: Soluble in water in all proportions. Nicotine is soluble in water in all proportions only below 60° . Anabesine is also soluble in all organic solvents.

Specific gravity: 20/20 1.0481 (Nelson, 85)

Boiling point: 280.9° at 760 mm. (Nelson, 85)

Refractive index: $\frac{20}{D}$ 1.5443 (Nelson, 85)

Optical rotation: $[\alpha]_{\frac{20}{D}} -59.66$ (Nelson, 85)

On long standing at room temperature, or in 3 to 5 days when heated in a sealed tube at 200°, anabesine auto-racemizes with a corresponding drop in rotation.

Vapor pressure: $\log P_{m.m.} = 7.2423 - 2416.14 T_K^{-1}$ (Nelson, 85).

At 100° the vapor pressure is 6 mm. of mercury.

Anabesine is the only alkaloid that was synthesized before it was found in nature. Its synthesis from pyridine was effected by C. R. Smith (133) in 1929 and was fully described by him (134) in 1931. Because of its close resemblance to nicotine, Smith called synthetic anabesine neonicotine.

The Russian chemist Orekhov (90) in 1929 reported the isolation of the natural alkaloid from a weed belonging to the sugar beet family (Chenopodiaceae). This weed, called Anabasis aphylla, is indigenous to the steppes of the Caspian region, Turkestan, and Transcaucasia. Because of this source the alkaloid was called anabesine. In 1935 Smith (138) found anabesine in an American weed belonging to the Solanaceae, namely Nicotiana glauca R. Grah., known in the Southwestern States as tree tobacco.

Anabesine is of interest to the entomologist because it is a potent insecticide. When sprayed upon certain species of aphids it is reported to be four or five times as toxic as nicotine.

The purpose of this review is to call attention to the promising results that have been obtained with anabesine in combating certain insects and to stimulate the American production of this alkaloid so that it may again be commercially available in this country.

Anabesine is reported as being manufactured by the Staatlichen Alkaloid Fabrik zu Tschimkent (Kasakhstan), U. S. S. R., which is represented in this country by the Amtorg Trading Corporation of New York. Since 1936, however, anabesine has not been obtainable in the United States.

THE CHEMISTRY OF ANABESINE

Orekhov (90) in 1929 was the first to report the isolation of anabesine from Anabasis aphylla. From this subshrub, Orekhov extracted, with ammoniacal alcohol, a mixture of alkaloids. The chief of these, called anabesine, was purified. It is a yellowish oil, distillable in vacuo, soluble in water, and entrainable by steam. Orekhov reported the physical constants to be: Boiling point 145-146° at 15 mm.; specific gravity 20/0, = 1.044; optical rotation, $[\alpha]_D^{20} = -47^{\circ}21'$.

The physical constants reported by Nelson (85) in 1934 and given on pages 2 and 3 of this publication are believed to be more nearly accurate than those reported by Orekhov.

Analyses indicated the formula $C_{10}H_{14}N_2$. It formed a picrate, $C_{10}H_{14}N_2 \cdot 2C_6H_2(OH)(NO_2)_3$, melting point 205-207°, and a picrolonate, melting point 235-237°. Silicotungstic acid gave a white amorphous precipitate with even very dilute solutions of the base.

Orekhov and Menshikov (98) in 1931 published the first of a series of papers on the alkaloids of Anabasis aphylla L.

Percolation of the dried plant with 2 percent of ammonia in 95-percent alcohol, evaporation to dryness, extraction with 10-percent hydrochloric acid, precipitation with 50-percent sodium hydroxide, extraction with ether, drying with potassium carbonate, and evaporation yielded 2.33 percent of a thick oil, separated by vacuum distillation (12 mm. pressure) into 85 percent of a fraction boiling at 136-8.5° and 15 percent around 200°. The lower-boiling fraction could be separated by benzoylation, by the action of nitric acid, or by vacuum distillation into a tertiary amine, $C_{10}H_{14}NO$, having all the properties of the lupinine obtained from *Lupinus luteus*, and a secondary amine, $C_{10}H_{14}N_2$, designated anabasine, which with potassium permanganate gave nicotinic acid in good yield, and on dehydrogenation, either by heating with silver acetate or by refluxing with zinc dust, lost 6 hydrogen atoms, forming a bipyridyl, boiling point 293-4° (picrate, melting point 151-2°), thought to be identical with the alpha, beta-bipyridyl of Skraup and Vortmann, boiling point 295-6° (picrate, melting point 149.5°). Anabasine is, therefore, very probably alpha-piperidyl-beta-pyridine, which, however, is certainly different from Pictet's nicotine for which he suggested the same structure.

Anabasine, prepared from the benzoyl derivative (m. 82-83) and hydrochloric acid (d. 1.19) in sealed tubes at 100° was reported to have the following properties: b_{760}^{20} 276°, d_{20}^{20} 1.0455, n_D^{20} 1.5430, α_D^{20} -82.20°. Anabasine reacts strongly alkaline, is quite difficultly volatile with steam, stable for hours towards potassium permanganate in sulphuric acid; the hydrochloride salt immediately deliquesces in the air, and is dextrorotary.

The chemistry of anabasine has been studied by the Russian chemists Orekhov and associates (79, 80, 81, 82, 88, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106), Katznel'son and associates (47, 48, 49, 50, 53, 54, 55, 56), and Menshikov (78); and by the German chemists Ehrenstein (22) and Wenusch (158, 159); and the reader is referred to their publications for detailed information on this subject.

Other alkaloids of Anabasis aphylla

Orekhov and Menshikov (99) in 1931 reported isolating additional alkaloids from Anabasis aphylla, called aphylline and aphyllidine. In 1937 Orekhov (95) proposed a structure for aphyllidine, $C_{15}H_{22}N_2O$, melting point 112-15°, α_D^{25} 6.5, and also for aphylline, $C_{15}H_{24}N_2O$, melting point 162-4°, α_D^{25} 54.5, which is the corresponding saturated compound.

Synthesis of Anabasine

Anabasine was synthesized before it was found in nature, a reversal

of the usual order in the chemistry of alkaloids. The synthetic product was first made by Smith (133) in 1929 and described in 1931. From its resemblance to nicotine it was called neonicotine. By the reaction of pyridine, metallic sodium, and oxygen a mixture of compounds was formed from which neonicotine (beta-pyridyl-alpha-piperidine) was isolated.

In 1936 Späth and Mamoli (149) announced a new synthesis of dl-anabasine which consisted in refluxing N-benzoyl piperidone with ethyl nicotinate and dry sodium ethoxide in benzene, evaporating in vacuo, and heating with strong hydrochloric acid under pressure at 130°.

In 1937 Späth and Keszler (145) resolved dl-anabasine into the active components by means of the 6,6'-dinitro-2,2'-diphenic acids.

Infra-red absorption spectra of anabasine

O'Byrne (89) in 1933 reported on the infra-red absorption spectra of certain alkaloids, including anabasine. The absorption curves and wave lengths of absorption bands measured between 1.00 microns and 12.00 microns by means of constant-deviation spectrometers with rock-salt and fluorite prisms are given for alpha-beta-bipyridyl, anabasine, neonicotine, methyl-anabasine, nicotine, and other alkaloids. The C-H, C-H, C-H₂ and C₆H₆ bands are present. Natural anabasine and neonicotine show small differences in absorption.

Anabasine bentonite

Smith (137) in 1934 reported on the base exchange reactions of bentonite and salts of organic bases.

The reaction between bentonite and salts of organic bases is principally one of base exchange. Bentonite enters into base exchange with a definite chemical equivalent of organic bases where saturation can be reached. In the one sample of bentonite used 1 gram combined with 6.2 to 6.4 cc. of 0.1 N organic base. When saturation is approached with most bases, flocculation is produced. Flocculation indicates that a reaction has taken place with partial or complete saturation of the silicate. Saturation is promoted by the insolubility of the silicate complex and by removal of the inorganic salts by washing.

Anabasine reacting in two different concentrations showed an absorption close to that of nicotine. Nicotine bentonite has proved of great value in combating codling moth larvae, and anabasine bentonite is worthy of testing for the same purpose.

THE DETERMINATION OF ANABASINE

Wenusch and Bilowitzki (158) in 1934 published methods for the determination of anabasine. Anabasine can be quantitatively steam-distilled from an alkaline solution of commercial anabasine-sulfate, a nonvolatile base remaining in the residue. The distilled base can be further purified as the salt of picric acid, but even after several crystallizations from water and from alcohol, it gives no definite melting point. For the determination, add to 100 cc. of distillate 5 cc.

of 1:4 hydrochloric acid and 5 cc. of 12-percent silicotungstic acid and, after 12 hours, collect the precipitate in a Gooch crucible and dry at 120°. The weight of precipitate $\times 0.1001$ = grams of anabasine. However, in order to avoid any admixture which would give a similar precipitate, acidify slightly the 100 cc. of distillate with acetic acid and add 50 cc. of saturated picric acid solution. After 12 hours filter through a Gooch crucible and dry to constant weight at 65°. On account of the solubility of the salt, the weight of the precipitate $\times 0.29$ = grams of anabasine. Finally, a third quantitative procedure is offered by precipitation with picrolonic acid, as described before, and drying of the salt at 70°. The weight $\times 0.234$ gives very good results. By this procedure it is possible to obtain anabasine picrolonate even in concentrations which no longer yield any precipitates with nicotine.

Known solutions of purified anabasine were analyzed with these reagents. The results obtained with the different reagents were as follows: (1) 12-percent silicotungstic acid solution, precipitate dried at 120° C. (assuming precipitate of $12\text{WO}_3 \cdot \text{SiO}_2 \cdot 2\text{C}_{10}\text{H}_{14}\text{N}_2 \cdot 2\text{H}_2\text{O}$), found 0.0088 gram anabasine (in 100 cc.), theoretical 0.0090 gram; (2) cold-saturated aqueous picric acid solution, precipitate dried at 65° C. (using theoretical factor 0.258), found 0.0080 gram (in 150 cc.), theoretical 0.0090 gram; (3) cold-saturated aqueous picrolonic acid, precipitate dried at 70° C. (using theoretical factor 0.234), found 0.0292, 0.0143, 0.0072, and 0.003 gram (in 200 cc.), theoretical 0.0287, 0.0143, 0.0072, and 0.003 gram.

Katz (52) in 1937 reported that anabasine sulfate and nicotine sulfate have many reactions in common. Sokolow (141) has shown that hydrofluosilicic acid is an excellent reagent for precipitating anabasine fluosilicate in the presence of nicotine, and it is now shown that if an ethereal solution of nicotine is mixed with an equal volume of ethereal iodine solution a precipitate of $\text{C}_{10}\text{H}_{14}\text{N}_2\text{I}_2 \cdot \text{HI}$ is formed, whereas anabasine does not give a similar precipitate.

Burkat (15) in 1937 described qualitative reactions of anabasine with picric acid, phosphomolybdic acid, and mercuric chloride. For a quantitative determination, the alkaloid is distilled from sodium hydroxide and sodium chloride into standard acid and back titrated.

Zerbey, Orinick, and Willard (162) in 1937 reported comparative tests of anabasine and its related compounds, its purification, and some physical constants. Anabasine is a colorless or pale-yellow liquid when pure, miscible with water in all proportions, and, like nicotine, it darkens on standing. An attempt was made to prepare pure anabasine from its sulfate by treating with 20-percent sodium hydroxide, allowing to stand overnight, and extracting the oil layer with ether. The oil thus obtained contained all the alkaloids. It was distilled under reduced pressure and separated into 21 fractions. Determinations of the density by the micro-pycnometer method, of the optical rotation with 5-percent solutions in alcohol, and of the refractive index with an Abbe refractometer were made on fractions 2, 5, 8, 11, 16, and 19. Since the values were different with each fraction tested, it was impossible to tell which one corresponded to pure anabasine, but it is probable that $n_D^{20} = 1.536\text{--}1.538$, $D_4^{20} = 1.046\text{--}1.048$, and $[\alpha]_D^{25} = -76.2$ to 79.10 . A table is given showing the behavior of anabasine and the related

alkaloids nicotine, lupinine, collidine, and lutidine toward gold chloride, mercuric chloride, Kraut's reagent, Wagner's reagent, Mayer's reagent, picric acid, barium nitrate, chloroplatinic acid, silicotungstic acid, phosphoantimonic acid, phosphomolybdic acid, cadmium iodide, potassium iodide + hydrogen peroxide, cobalt thiocyanate, and Millon's reagent. A table is also given showing the behavior of the different fractions toward most of these reagents and potassium chromate in addition. The most distinctive test is that with gold chloride; the crystals produced are quite different from those formed with nicotine.

Sokolov (142) in 1937 claimed priority for some of these tests.

OCCURENCE OF ANABASINE

In addition to Anabasis aphylla, the following plants have been found to yield anabesine:

Nicotiana tabacum (Späth and Keszler, 147, in 1937).

Nicotiana glauca (Smith, 138, in 1935, and Khmura, 57, 58, in 1937 and 1938).

Smith (138) reported that Nicotiana glauca roots contain about 1 percent of anabesine; it also occurs in the dried leaves. Not more than a trace of nicotine is present. Anabesine was isolated by digestion with warm 1-percent hydrochloric acid, filtration, making alkaline, and extracting with ethyl ether.

Khmura (57) in 1937 write that Nicotiana glauca may become of commercial importance because it contains 0.74 percent of anabesine, 7.16 percent of citric acid, and 7.90 percent of malic acid. The citric acid is concentrated mainly in the lower leaves, while anabesine is found mainly in the young upper leaves. The amount of anabesine extracted with chloroform exceeds that extracted by petroleum ether by 100 percent. A considerable amount of anabesine is present in the stalks and roots.

In 1933 Khmura (58) published additional information on the alkaloid of Nicotiana glauca.

Anabesine was extracted from the plant with 3-percent alcoholic ammonia solution. After distillation of the alcohol and solution of the residue in 5-percent hydrochloric acid, the alkaloid was set free by alkalization of the solution, and extracted with ether. The yield was 24.4 grams of pure alkaloid per 7.5 kilograms of plant (=0.32 percent).

Stanley (150) in 1924 described Nicotiana glauca Grah. as a glabrous shrub or small tree, 18 feet high or less. A native of Argentina and Uruguay, it has become thoroughly naturalized in some parts of North America. In the United States it is found from western Texas to southern California; in Mexico, from Sonora to Tamaulipas and Oaxaca. Its common names are as follows:

arbol de tabaco	lengua de buey	tabaco cimarron
buena moza	marihuana	tabacon
coneton	Marquiana	tabaquillo
Don Juan	mostaza montes	tacote
gigante	palo virgen	tepozan extranjero
gretana	palo virgin	tronadora
hierba del gigante	tabaco amarillo	virginio

This plant is abundant in some parts of Mexico. It is reputed to be very poisonous. The leaves are often applied as poultices to relieve pain, especially headache.

An interesting report on Nicotiana glauca, growing in the lower Rio Grande Valley of Texas and Mexico, was submitted by Bibby and Higdon (11) of the Bureau of Entomology and Plant Quarantine in January 1940. The plant is known by several common names, including the following: Arbol de tabaco, lengua de vaca, lingua de buey, mostazo monte, quebradora, sacred mustard, tabaco amarillo, tabaco cimarron, tabaquillo, tree tobacco, and tronadora.

Nicotiana glauca grows on well-drained sandy waste land along or near irrigation canals and usually in colonies. It is a fast growing plant; one tree 4 inches in diameter and 25 feet tall was only 18 months old. Sprouts from stumps apparently make an extremely rapid and succulent growth, bearing leaves much larger than those on the older plants.

In January 1940 temperatures as low as 29° F. were recorded at Brownsville, Tex., but apparently only young seedlings and young sprouts were injured by the freeze. In fact, many older plants bore fresh blooms, apparently uninjured.

Bibby and Higdon were informed by Ing. Tomas Leal Moreno of the Mexican Department of Agriculture that some Mexicans believe that plants of Nicotiana glauca will rid premises of fleas.

It is concluded that Nicotiana glauca could be grown commercially in the lower Rio Grande Valley.

Clayton and Foster (17) in 1940 reported on disease resistance in the genus Nicotiana. N. glauca (n=12) is immune from black root rot (Thielaviopsis basicola) and highly resistant to mosaic, root knot (Heterodera marioni), and wildfire (Bacterium tabacum). Smith's allopolyploid (N. tabacum + N. glauca, n=36) shows resistance to root knot and root rot.

Schmuck (128) in 1937 reported on the chemical composition of alkaloids in inter-species hybridization of plants of the genus Nicotiana. N. glauca contains anabasine; N. sylvestris and N. rusbyi probably contain nornicotine; and N. tabacum, alata, rustica and langsdorffii contain nicotine. The alkaloids from plants of the first generation of hybrids (N. tabacum x N. glauca) consisted of anabasine only, and the content of this was always considerably higher than in the original parent plant (N. glauca).

The hybrid plants of the third, fourth, and fifth generations contained either anabasine or nicotine as well as a mixture of nicotine with anabasine, but in such mixtures of the anabasine predominated. The complex hybrids (makhorka x glauca x tobacco) invariably contained anabasine or a mixture of anabasine and nicotine. No new alkaloids were found in any hybrids. As a rule the first-generation hybrid contains only one alkaloid, typical of one of the parents; in the following generation splitting occurs and plants appear bearing mixtures of the alkaloids as well as plants containing only one or the other of the parental alkaloids.

Späth and Mesztler (148) in 1937 reported that a minute quantity of levo-N¹ methylanabasine (picrate melting point 237-8°) was isolated from 1,800 grams of crude nicotine obtained from tobacco.

Zukov (165) in 1939 reported on the inheritance of nicotine and anabasine in interspecific hybrids Nicotiana rustica L. x N. glauca Grah. N. rustica contains nicotine only and N. glauca contains anabasine only. Commercial production of anabasine is based on the wild-growing half-shrub Anabasis aphylla; in the youngest parts of this plant is contained up to 2.53 percent of anabasine. The demand for anabasine cannot be wholly satisfied owing to the low proportion of it in A. aphylla and to limited production. Breeding a new form rich in anabasine is, therefore, not only of theoretical, but also of practical interest. Of 105 hybrids studied, 41 contained only anabasine, 40 only nicotine, and 24 both alkaloids. All the anabasine-bearing plants morphologically belonged to typical makhorka and were self-fertile. The anabasine content varied in these plants from 0.67 to 2.03 percent. The analysis of leaves was conducted on unpruned plants. By means of pruning and other agrotechnical treatment this percentage may be increased several times. As much as 6.61 percent of anabasine was found in the leaves of one of the unpruned hybrids.

Kostoff (62) in 1939 reported on the nicotine and citric acid content in the progeny of the allo-polyloid hybrid N. rustica L. x N. glauca Grah. Kostoff was of the opinion that this allo-polyloid as well as the backcrosses and other hybrids between N. rustica and N. glauca may answer the demands of industry for anabasine if breeding work with these plants be done on a somewhat larger scale. Some of the allo-polyloid segregates, on the other hand, grow very rapidly and give a very large amount of green mass, provided suitable environmental conditions are secured for their growth.

Allo-polyloid Nicotiana rustica-glauca is a plant interesting from an agricultural point of view, because it segregates forms with larger amounts of anabasine (1.986, 1.449, 1.395 percent, etc.) than the parental species N. glauca which, when grown under the same environmental conditions, contained 0.837 percent. At the same time the offspring contain a relatively large amount of citric acid. Further generations of some of the offspring should give the possibility to select forms with larger content of anabasine and citric acid. The populations produced from the backcrosses can be used for the same purpose. It should also be mentioned here that anabasine content can be increased about three times after decapitation, as the analysis by Zukov showed.

Carl von Linne (70) in 1753 was the first to describe Anabasis aphylla. It occurs on the shores of the Caspian sea. In 1797 he described 4 additional species of this genus.

Bogdanov-Kat'kov (12) in 1933 reported that Anabasis aphylla (family Chenopodiaceae) grows abundantly in the lower Volga region, southern Ural, and especially Kazakstan. The amount of anabasine contained in the plant depends on the stage of development; a sharp decline occurs during the flowering period and as the seeds mature, the maximum being found during the vegetative period before and after flowering. The raw material is, therefore, collected from the first of June till mid-October, but not during the time of flowering. The maximum quantity of the alkaloid (2.53 percent) is found in the small green twigs; the thick green branches contain 0.37 percent, and the old woody ones only 0.17 percent. The best method of collection is to remove small twigs at the level of the branching of the main stem; in this way it is possible to obtain a second crop of twigs 50 to 60 days after the first harvest.

Goryainov, Goryainova, and Koblova (38) in 1935 analyzed different parts of Anabasis aphylla and found the maximum quantity of alkaloids (1.84 to 2.63 percent) in the small green twigs, whereas the thick green branches contained 0.26 to 0.41 percent. Anabasine was easily extracted from ground plant material with water. At 20° C. material containing 2.98 percent of the alkaloids yielded 2.2 percent in 7 hours and 2.7 percent in 48 hours when added to water at the rate of 30 pounds per 100 imperial gallons. Heating or acidifying the water accelerated the extraction; at 70 to 80° all the alkaloids passed into the water, and in acidified cold water 2.7 percent was liberated in 7 hours.

A writer under the initials G. K-L (46) in April 1937 wrote that, according to Balachowsky, Anabasis pretioides from French North Africa contains no anabasine.

Frein (111) in 1938 reported on the alkaloids in different species of Anabasis. Alkaloids were found in samples of Anabasis aphylla, A. eugeniace, A. truncata, A. eriopoda, A. salsa, and A. ramosissima. The alkaloid content varied within the same species according to the origin of the sample, e.g., from 4.31 to 1.29 percent in A. aphylla, and from 0.014 to 1.15 percent in A. salsa (considered alkaloid-free).

Ilyin (43) in 1938 reported on the possibilities of growing Anabasis aphylla.

Of all the various species of Chenopodiaceae, only Anabasis aphylla contains anabasine. A large factory situated near Chimket, U. S. S. R., is solely devoted to the production of anabasine. Anabasis aphylla is usually found growing wild in the semiarid regions, although the nature of the soil does not play an important part. Cultivation should take place during the first part of the summer, in order that the roots of the young plants may reach the moist subsoil. The seeds are preferable to seedlings. Harvesting very near to the surface of the soil is recommended, because the plant, as a rule, assumes the shape of a bush. The harvest from one plantation yielded approximately 5,000 kilograms of fresh, green, raw material.

THE PHARMACOLOGY OF ANABASINE

The pharmacology of anabesine was first studied by Haag (40), who reported his findings in 1933. The lethal dose of anabesine for guinea pigs (subcutaneous) is 22 milligrams per kilogram, compared with 26 milligrams per kilogram for nicotine. Toxic symptoms from the two alkaloids are similar, anabesine being somewhat less exciting and more depressing. Anabesine is readily absorbed from the skin and is detoxified in the liver. It appears more toxic than nicotine to guinea pigs and rabbits, but nicotine is somewhat the more active on frogs and earthworms.

Gersdorff (34) in 1933 compared the toxicity of nicotine and anabesine to goldfish.

As compared with rotenone, solutions of nicotine and anabesine become toxic at relatively high concentrations. The theoretical thresholds of toxicity for the three compounds against fishes from the same group, are 0.012, 8.0, and 9.5 milligrams per liter, respectively. The relatively low toxicities of the two alkaloids are also reflected in a comparison of the rates of increase of the theoretical velocity of fatality with increase in concentration. These rates, in the same order, are 90, 5.6, and 5.2 cc. per milligram per minute. Thus rotenone is 15 to 20 times as toxic as the two alkaloids. However, if the survival time alone is considered in comparison at the regions of constant velocity of toxicity, where the time periods are in the same order, about 130, 20, and 22 minutes, the two alkaloids have a toxicity 6 to 7 times as great as rotenone. Anabesine is slightly less toxic than nicotine throughout the range of concentrations used.

Sarguine (121) in 1933 and again (122) in 1934 also published on the pharmacology of anabesine. This alkaloid is very similar to nicotine in its action on animals. It changes the blood pressure and affects the intestines and uterus the same way as nicotine, and its general effects show that it can hardly be used in therapy.

The other alkaloids of *Anabasis aphylla*, aphyllidine and aphylline, proved to be of negligible pharmacological activity. Methyl anabesine proved to be much less active than anabesine.

Anichkov (4) in 1935 reported that anabesine is vaso-constrictor on the rabbit's ear, the effect being two-thirds as strong as that of nicotine.

Baruishnikov (9) in 1936 reported that the action of anabesine sulfate on the animal organism is similar to that of nicotine.

Filosofov (24) in 1936 published a study of the effect of alkaloids on yeast. Experiments with nicotine and anabesine sulfate showed that large quantities of these substances slow up fermentation, while small quantities have a stimulating effect and produce normal yeast.

Anichkov (5) in 1937 compared the action of cytisine, conine, and other poisons on the carotid sinus with that of nicotine, anabesine, and other compounds.

Leont'ev (68) in 1936 reported on the pharmacology of anabesine-protein compounds. Anabesine when injected with protein (from peas or soybean) is almost nontoxic for the common laboratory animals. The symptoms of intoxication with anabesine are analogous to those of nicotine, which are as follows: Increased irritability, lack of coordination, shivers, clonic convulsions, and nervous depression. The death of the animal is, as a result, caused by disturbances in the respiratory process. The protein acid obtained from soya beans, combined in equal proportion with the alkaloid, resulted in an anabesine product which had no harmful effects on warm-blooded or cold-blooded animals. Experiments revealed that the resistance of tested animals to anabesine was in the following increasing order: Guinea pigs, white mice, fish, white rats, birds, frogs.

Studies were reported in 1937 by Rotman (119) of the effect of anabesine on the gaseous exchange in insects, by Tarascva (152) on the effect of anabesine on the activity of the heart in insects, and by Ivanova (45) on the permeability to anabesine of the integument of insects. These papers are reviewed in the section of this paper dealing with the use of anabesine as an insecticide.

Mednikyan (77) in 1938 reported the results of comparative studies of the effect of certain ganglionic poisons on respiration. The intravenous injection of 0.04-0.05 milligram of nicotine, or 0.15-0.18 milligram of anabesine per kilogram of body weight, gives rise to practically equal values for the excitation of respiration.

THE USE OF ANABESINE AS AN INSECTICIDE

1930

Tests with anabesine as an insecticide were first made with the synthetic, optically inactive form called neonicotine and were reported by Smith, Richardson, and Snephard (140) in October 1930. Twenty-five bipyridyl derivatives and related compounds not previously reported were prepared and examined as contact insecticides. These included a number of isomeric bipyridyls, bipiperidyls, and pyridyl piperidines. Neonicotine (beta-pyridyl-alpha-piperidine) was the most toxic of these compounds, comparing closely with nicotine, to which it is chemically similar. Alpha-pyridyl-beta-piperidine stood next in toxicity to neonicotine of the compounds investigated. In general, the compounds with the alpha-beta and beta-alpha groupings lead in toxicity over compounds with rings located in other positions. Solutions or emulsions of each compound plus 0.3 percent of sodium fish oil soap or 1 percent of saponin were tested by spraying on Aphis rumicis L. on dwarf nasturtium plants.

1931

Nagel (84) in 1931 reported tests with an aqueous solution of dipyrri-dyl sulfate containing 40 percent of the dipyrri-dyls, and also with an emulsion containing 80 percent of dipyrri-dyls, upon larvae of the Mediter-ranean flour moth (Ephestia kuehniella Zell.). The more concentrated dipyrri-dyl preparation exceeded nicotine sulfate (40 percent) in toxicity, which was probably due to the presence of some neonicotine in the mixture.

1932

Austin, Jary, and Martin (7) in 1932 reported that when a commercial preparation of anabasine sulfate, guaranteed to contain 35 percent of anabasine, was diluted 1:5,600 (=1:16,000 anabasine), the insecticidal efficiency against hop aphids, Phorodon humuli (Schr.), was equal to if not greater than that of nicotine at the same weight concentration. Sodium oleate or sulphite lye was used as a spreader.

Zalkind (161) in 1932 studied the effect of anabasine sulfate upon the beet louse, Aphis fabae. Tests were carried out in the fields, on second-year beet plants, the flower stalks of which were entirely covered with colonies of the beet louse; and in laboratories, using Koch cups where young as well as grown-up specimens of beet lice had been put on sugar beet leaves. A 35-percent solution of anabasine sulfate was tested at concentrations in water of 0.01 percent to 4 percent. Zalkind con-cluded:

1. As a contact insecticide for the beet louse, anabasine sulfate is not inferior to the best contact insecticides known.
2. A 0.05-percent concentration of anabasine in water is the mini-mum dose producing 90 percent of mortality of the louse on second-year plants. This concentration destroys all the young lice; only grown-up females survive.
3. A complete destruction of young as well as of grown-up lice on second-year plants was attained by a 0.1-percent anabasine concentration abundantly moistened.
4. A 0.5-percent concentration of the anabasine solution produces a very prompt destruction of the louse.

For practical use Zalkind advised a 0.3-percent concentration of the anabasine solution (equivalent to 0.1 percent of actual anabasine).

1933

Craig and Richardson (18) in 1933 reported the results of studies of the relative toxicity (expressed as the concentration that killed 50 percent in 24 hours) of 11 alpha-substituted N-methylpyrrolidine com-pounds to Aphis rumicis L. The compounds were made up with 0.25 percent of sodium oleate and applied as a fine spray to the wingless adults.

There was a correlation between the relative toxicity and the basicity (dissociation constants) of the compounds, the former decreasing as the latter increased. The causes of this are discussed. The toxicity of most of the compounds to goldfish, tadpoles, and lupin seedlings are included for comparison. The laevo-nicotine was considerably more toxic to aphids than the optically inactive mixture (dl-nicotine) and also more toxic than anabasine.

Campbell, Sullivan, and Smith (16) in 1933 compared the relative toxicity of nicotine, anabasine, methyl anabasine, and lupinine for culicine mosquito larvae. The anabasine, methyl anabasine, and lupinine were prepared from a commercial insecticide labeled "anabasine sulfate, 40 percent." Based on the concentration required to kill 50 percent of a population of larvae culicine mosquitoes, *Culex pipiens*, *C. territans*, and *C. quinquefasciatus*, in 8 hours at 29.3° C. [84.74° F.], the relative toxicity of the four alkaloids is as follows: nicotine 100, anabasine 38, methyl anabasine 21, and lupinine 5 (?). According to the unpublished observation of other workers, nicotine and anabasine may be equally effective against aphids. Nicotine and anabasine are much less toxic than rotenone against mosquito larvae and houseflies.

Carman and Townsend (32) in 1933 reported on the seasonal life history of the white apple leafhopper, *Typhlocyba pomaria* McAtee, and experiments in its control in Connecticut. Extensive field counts made in apple orchards in Connecticut in 1932 showed that the first nymphs appeared early in May, hatching being complete about the middle of June. In experiments on the summer brood, sprays of nicotine sulfate and soap had some residual effect in killing eggs within the leaves, or nymphs after hatching and feeding on sprayed foliage. Many more nymphs hatched from unsprayed branches than from those sprayed with 1 percent oil and 1:600 nicotine sulfate. The addition of 3 pounds of soap to a spray of 1 pint of nicotine sulfate in 100 gallons of water showed no significant difference in field counts. Spraying should be directed against the lower surfaces of the leaves. Anabasine sulfate killed as many nymphs as did nicotine sulfate when used at the same dilution in small field experiments.

Carman (27) in 1933 reported greenhouse tests which showed commercial anabasine sulfate to be about 5 times as toxic for *Aphis rumicis* as nicotine sulfate. Under greenhouse conditions commercial anabasine sulfate gave a good clean-up of *Myzus persicae* (Sulz.) at 1:1000 without spreader. *Aphis spiraeicola* Patch on spirea bushes were killed at 1:1600, and anabasine sulfate was equal to nicotine sulfate against nymphs of *Typhlocyba pomaria* McAtee on apple trees. No foliage injury was caused by anabasine sulfate.

Bogdanov-Kat'kov (12) in 1933 wrote that as an insecticide the commercial solution of anabasine sulfate containing 36 to 40 percent of anabasine may be used as a spray at a concentration of 0.03 percent with the addition of 0.4 percent of soft soap or naphthene soap. For orchard spraying, etc., the soap may be omitted and the anabasine sulfate combined at the same rate with water containing 0.08 percent of fine freshly slaked lime or with lime sulfur (1:60); it is not effective if used alone.

It may also be employed as a dust with a carrier such as lime or with calcium arsenate, at rates of from 5:95 to 15:85. The dust is prepared by spraying the solution uniformly over the carrier to obtain different concentrations of spray or dust. If the solution contains less than 36-40 percent of the alkaloid, the quantities are increased accordingly.

The present high cost of anabasine preparations makes their extensive use prohibitive, and further work should be carried out to determine the minimum effective dosages. Tables are given showing the amount of spray or dust necessary to treat a given area of orchard, vineyard, or cultivated field at a temperature of 15-20° C. [59-68° F.] The toxicity of anabasine increases at higher temperatures, and this permits of a decrease in dosage.

1934

Harman (41) in 1934 reported experiments which had been made during 1933 in three apple orchards in western New York with five cover sprays of various materials against Carpocapsa pomonella (L.), which was so abundant that 100 percent of the fruit was infested when cover sprays were omitted.

In a badly infested orchard of the King variety the following results were obtained:

Treatment, materials used per 100 gallons	Stings, percent	Worms, percent	Total injury, percent
Lead arsenate 3 pounds	60	13	73
Nicotine-oil	29	14	43
First cover, lead arsenate 3 pounds			
Remaining sprays, nicotine sulfate 1 pint, oil 3 quarts			
Anabasine-oil	19	50	69
First cover, lead arsenate 3 pounds			
Remaining sprays, anabasine sulfate 1 pint, oil 3 quarts			
Check, no treatment	0	99	99

Skalov (131) in 1934 reported on the application of anabasine sulfate as an insecticide for tobacco plants in the U. S. S. R. A solution of 20 grams of anabasine sulfate in 10 liters of water, when sprayed on tobacco plants, killed all Myzus persicae (Sulz.) organisms in 48 hours; a solution containing 10 grams of anabasine sulfate and 100 grams of green soap in 10 liters of water required only 24 hours. Lower concentrations of anabasine sulfate were insufficient in combating the insect. The appearance and the taste of the finished goods prepared from tobacco treated in the above manner were normal.

Garman (28) in 1934 reported studies on the control of the white apple leafhopper, Typhlocyba pomaria McAtee, in Connecticut. This insect was unusually abundant on apple in 1929-1930. Anabasine sulfate 1:800 without soap caused a reduction of 98.5 percent of second-generation nymphs. Nicotine sulfate similarly tested caused reductions of 89.4, 90.1, and 96.1 percent.

Garman (29) in 1934 reported tests of ten proprietary insecticides against Aphis rumicis L. on nasturtium leaves in greenhouses. None was as effective as nicotine sulfate or anabasine sulfate. At a dilution of 1:3200 with the addition of soap, anabasine sulfate was superior to nicotine sulfate. Apparently neither insecticide deteriorated with keeping. Pure anabasine gave better control than pure nicotine alkaloid, both in water alone and with pure soap. When 1 quart of either sulfate was used with 4 pounds of soap flakes in 200 gallons of water against Anuraphis roseus (Baker) on apple, anabasine sulfate was slightly more toxic to aphids than were actually covered with spray. In other trials both materials gave good control at 1:800 with soap, and favorable results were obtained by combining anabasine sulfate with lime-sulfur, Anabasine sulfate (1:1000) with 1 part of bead soap almost completely exterminated Myzus persicae (Sulz.) on peach seedlings. Tests on eggs of the oriental fruit moth, Grapholitha molesta (Busck), show that anabasine sulfate has no value as an ovicide, and it is apparently not a stomach poison.

Fleming and Baker (25) in 1934 reported on the effectiveness of several stomach poisons against the Japanese beetle, Popillia japonica Newm., when determined under controlled conditions. In each test 1000 beetles were confined in 5 cages without food (so that their mortality could be subtracted from that of the poisoned ones to allow for the repellent action of the insecticide on some individuals), 1000 with plants sprayed with commercial acid lead arsenate (8 pounds to 100 gallons, which proved slightly more effective than higher dosages), and 1000 with plants sprayed with the material to be tested. The efficiency of 8 pounds of lead arsenate being reckoned as 1, the values of 1, 2, 4, and 6 pounds were respectively 0.4, 0.7, 0.84 and 0.9. The spray was applied 24 hours before the beetles fed, and half the leaves were washed with the equivalent of 1 inch of rain, which reduced the efficiency of the standard 8-pound spray to 0.61. The efficiencies of nicotine and anabasine sulfate as dusts (5 percent absorbed on bentonite) was 0.22 and 0.03 respectively.

1935

Vavilov and Mukhitdinova (157) in 1935 published a report on the substitution of lime for soap in solutions of anabasine sulfate. In the U. S. S. R. anabasine sulfate is largely used as an insecticide, soft soap or sometimes lime being added to the spray. The authors consider that the great variations in the concentrations of anabasine sulfate required are probably due to differences in the hardness of water employed. The soap serves to liberate the free alkaloid; but when the water is hard, much of the soap reacts with the calcium and magnesium salts present, so that the harder the water, the less toxic

is the solution of anabesine sulfate with the same amount of soap. In the Crimea in 1934, solutions of 0.1 percent of anabesine sulfate were tested on Myzus (Myzoides) persicae (Sulz.) The aphids were immersed by a method already described, but to wet them evenly the test tubes were slowly rotated round their perpendicular axes, first in one direction and then in the other. Each test lasted 2 minutes, after which the aphids were kept at 25° C. [77° F.] and 70-75 percent relative humidity for 24 hours, and the dead and living individuals were counted. Distilled water was used in the control. The solutions were prepared with distilled water and water taken from a well and a river, the degrees (German) of hardness of which were 9.8 and 16.6, respectively, and were applied alone or with the addition of 0.1 percent of soap or 0.2 percent of lime. Then anabesine sulfate was used alone, the mortality percentages were 19.15, 47.56, and 60.2 in distilled, well, and river water respectively. With soap, the corresponding figures were 98.91, 88.04, and 94.68; and with lime, 53.06, 63.54, and 82.95. The author considers that alkaline earths in the hard waters liberated part of the alkaloid and that the toxicity of the hard-water solutions was decreased by the addition of soap because it softened the water. To determine the best proportion of lime in sprays prepared with the well water, it was added at the rate of 0.2-0.8 percent to 0.1 percent of anabesine sulfate. The highest mortality (74.47 percent) was obtained with 0.3 percent of lime.

Ginsburg, Schmitt, and Granett (35) in 1935 reported on the comparative toxicity of anabesine and nicotine sulfates to insects. In preliminary work in 1931, 0.1 percent of anabesine sulfate applied as a contact spray killed 100 percent of honeybees in 24 hours. Only 10 percent died in the same period when fed on honey containing 0.2 percent of anabesine sulfate.

In 1934, in laboratory tests with sprays of anabesine and nicotine sulfate with 0.2 percent of coconut oil soap as wetting agent, each at a dilution of 1:2400 gave over 90 percent mortality of Aphis pomi Deg. and Aphis rumicis L. At half or a quarter of this strength anabesine sulfate was decidedly more toxic than nicotine sulfate; at 1:4800 it killed over 90 percent of both aphids. Macrosiphum rosae (L.) was more resistant to both sprays, but anabesine sulfate was in all cases more efficient. The wetting agent used alone killed 14, 21, and 13 percent of the three aphids, respectively. In greenhouse tests with a dilution of 1:2400 against aphids on chrysanthemums, both insecticides killed 100 percent of Macrosiphum (Macrosiphoniella) sanborni (Gill.), but anabesine sulfate killed 87.1 to 87.8 percent of Rhopalosiphum rufomaculatum (Wilson), and nicotine sulfate killed only 32.1 to 28.8 percent.

When applied as a stomach poison to Bombyx mori L., at dilutions of 1:400, nicotine sulfate killed 100 percent in 2 days and anabesine sulfate 30 percent in 3 days. At 1:800 they killed 95 and 15 percent respectively in 3 days. The neutral wetting agent used (0.1 percent of Arescap) killed none. When adults of Melanoplus femur-rubrum (Deg.) were fed on tomato plants sprayed with dilutions of 1:800 and 1:400 with 0.1 percent of Arescap, nicotine sulfate killed 80 and 90 percent and anabesine sulfate 40 and 60 percent. Arescap alone killed 15 percent.

The New Jersey State Agricultural Experiment Station (87) in its annual report for 1935, reported that, because of frequent inquiries from growers as well as manufacturing concerns on the value of anabasine sulfate, a study was made of the insecticidal properties of anabasine sulfate as compared with nicotine sulfate. The results of Ginsburg et al. (35) are summarized.

Savchenko and Holkrzhitzkaya (126) in 1935 reported on the insecticidal properties of nicotine sulphite in comparison with some other nicotine preparations.

A detailed account is given of investigations in the Ukraine in 1932-1933 on the toxicity to insects of solutions of nicotine sulphite (the nicotine salt of sulphurous acid, which was first prepared in 1932). In laboratory tests various aphids, the larvae of Hyponomeuta padellus malinellus Zell. and of the bug Pyrrhocoris apterus (L.) were immersed for 5 minutes in the various solutions by a method similar to that of Shepard and Richardson. The nicotine sulphite proved more toxic than nicotine sulfate, nicotine chloride, nicotine naphthenate, or anabasine sulfate. The effect of nicotine sulphite on the aphids varied with the different species and forms; the wingless females of the summer generations were the most resistant species, 100 percent mortality of the larvae requiring a 0.105 percent concentration of 40 percent nicotine sulphite, as compared with 0.040 and 0.053 percent concentrations for larvae of Aphis sambuci L. and A. fabae Scop., respectively. The mean lethal concentration for the various species of aphids treated was 0.031 percent of actual nicotine in the form of the sulphite as compared with 0.05 percent of chemically pure nicotine. In field tests, which were made against Aphis fabae on beet, a mortality of 96.98 percent was obtained only with a 0.23-0.25 percent concentration of 40 percent nicotine sulphite.

Special experiments confirmed the higher toxicity of nicotine salts as compared with pure nicotine at equivalent concentrations, and did not support the conclusions of de Ong and Shepard and Richardson, whose work is critically reviewed. The mean percentages of mortality of aphids treated with different nicotine salts and anabasine sulphite were 98 and 91, respectively, as compared with 77 and 85 for pure nicotine and anabasine. At concentrations equivalent by weight, however, nicotine or anabasine produced a slightly higher mortality than the salts.

The high toxicity of nicotine sulphite solutions may be explained by the complex action of the nicotine and of sulfur dioxide liberated during hydrolysis, and by such physical properties as high viscosity and low surface tension. The effect of these factors on the toxicity of the various nicotine and anabasine preparations is discussed, and the correlation is shown in graphs and formulas. It was found that with the increase in the toxicity of the preparation, the curve of viscosity showed a pronounced tendency to rise, whereas that of the surface tension dropped.

Klokov (60) in 1935 reported tests against the hessian fly, Phytophaga destructor (Say) (Mayetiola destructor (Say)) on wheat in the Ukraine and the Crimea.

Experiments with dusts and sprays designed to kill the eggs and young larvae were carried out on autumn- and spring-sown wheat in pots or field plots, and the results were estimated by comparison with untreated plants. Soap was added to all sprays as a spreader. The following were the percentage controls obtained with the more effective insecticides, the figures in parentheses showing the percentage concentration of the latter in the sprays or dusts: 74.3-99.2 with anabesine sulfate (0.1 spray); 60.6-94.1 with nicotine sulfate (0.1-0.15 spray); 80-86 with sodium fluoride (0.75-0.8 spray); 91.8 and 96.6 with anabesine sulfate (2.5 and 5 dust, respectively); 92.4-94.1 with anthracene (10 dust with lime). The rate of the application per acre depends on the size of the plants; about 40 gallons of spray or 20 pounds of dust is sufficient for sprouting wheat. Two applications should be made during the period of mass oviposition of the fly, with an interval of 4 to 7 days.

Goryainov, Goryainova, and Koblova (38) in 1935 gave an account of tests of the toxicity to leaf aphids, etc., of preparations from plants that produce alkaloids, chiefly Anabasis aphylla. The technique of testing the insecticidal value of dusts and solutions prepared from such plants is described. The solutions were tested as dips and sprays. The toxicity to aphids of alkaloids other than anabesine present in Anabasis aphylla (aphylline, aphyllidine, and lupinine) was negligible. A water extract of anabesine was as toxic to aphids as a solution of anabesine sulfate when the alkaloid contents were about the same. Solutions of anabesine sulfate were not very effective against aphids when used alone, but were rendered effective by the addition of soap, or cheaper materials, including petroleum acids and residue from the manufacture of viscose.

In tests with 5-percent anabesine sulfate dust with a number of carriers, 100 percent mortality of aphids was obtained on the day of the application of dusts mixed with silica gel, carbonates, chalk, or limestone. Special experiments showed that dusts prepared with carbonates killed the aphids in 10 to 12 minutes, whereas when other carriers were used the insects remained active after an hour. Further tests showed that the effectiveness of inert carriers, such as tripoli or loess dust, can be raised by the addition of at least 15 percent of carbonates, such as sodium carbonate, all the aphids being killed on the day of the application. Dusts of anabesine sulfate were as effective as the standard nicotine dusts, 100 percent mortality being obtained in 10 minutes at 16° to 17° C. [60.8° to 62.6° F.]. An anabesine dust (named "Aning") that was as effective as dry anabesine sulfate and is easier to prepare was made by wetting 2 parts of finely ground plant material with 1 part of water containing 1 percent sulfuric acid, and after 5 to 6 hours mixing it with 4 parts of a carrier, such as limestone powder or equal parts of limestone powder and loess dust.

The 7-hour water extract of anabesine sulfate (30 grams per liter), containing 0.06 percent of alkaloids, gave 90 percent mortality of Aulacarium pelargi. The 24-hour extract (anabesine sulfate 0.07 percent) gave 100 percent mortality. The deficiency of water extract, however, is the fact that it must be used fresh, as it becomes mouldy if left standing.

Howard, Brannon, and Mason (42) in 1935 reported on insecticides tested for the control of the Mexican bean beetle. Nicotine dusts containing 2 percent of nicotine in a bentonite-sulfur carrier and nicotine-bentonite-sulfur sprays at the rate of 1 pint of nicotine sulfate and 3 pounds of bentonite-sulfur to 50 gallons of water gave very poor results and indicated that these mixtures are not satisfactory stomach poisons for the control of the Mexican bean beetle. Anabasine sulfate was used under both laboratory and field conditions in Ohio during 1933. At a dilution of 1 part in 100 parts of water the control was poor and there was moderate injury to bean foliage. Such unfavorable results were obtained that the use of the material was discontinued.

Garman (31) in 1935 reported that nicotine and anabasine sulfate (1:800) gave efficient control of the white apple leafhopper, Typhlocyba pomaria McAtee, in field tests without the addition of soap. Anabasine sulfate is equal to nicotine sulfate in effectiveness.

Garman (30) in 1935 also reported on the toxicity of pure anabasine and pure nicotine for Aphis rumicis. On nasturtium leaves under controlled conditions, anabasine was superior in every case. It gave as high a kill as nicotine at 3 or 4 times the strength. Only mature wingless agamic females were counted in each experiment. Chemically pure sodium oleate (1:100) was used as a spreader.

Kovaleva (63) in 1935 reported on the chemical control of the codling moth in the U. S. S. R. Two applications of a spray of paris green, bordeaux mixture, and anabasine sulfate reduced the percentage of injured fruit to 5.5. In tests on a small scale linseed-oil emulsion containing 2 percent of anabasine sulfate killed 18 percent of the eggs.

Mizerova (83) in 1935 reported on the chemical control of the apple sucker, Psylla mali Schm., in central Russia. The most satisfactory ovicide in the laboratory was lime-sulfur (7 percent), which killed 76.7 percent of the eggs. In orchard experiments, however, the only sprays that showed any promise were two 4-percent mineral oil emulsions, and the percentages of dead eggs on trees sprayed with them were only 40.4 and 23.1, as compared with 10.7 on unsprayed trees. One application in the orchard of a spray of 0.1, 0.3, or 0.4 percent of anabasine sulfate with 0.4 percent of soft soap and 0.75 percent of lime-sulfur killed 75.4 percent of the young nymphs and 42 percent of the older ones, the difference in strength of the anabasine sulfate having no effect on the rate of mortality. A second spray did not further reduce the infestation enough to justify its cost. One application of 0.75-percent lime-sulfur killed 79.8 percent of the young nymphs and 69.9 percent of the older ones. Of insecticides used against the adults, a dust of anabasine sulfate (5 percent) and a spray of nicotine sulfate (0.3 percent with soft soap) were the most effective.

Pavlov (107) in 1935 reported a test of carriers of local importance in the manufacture of anabasine dusts. These tests were designed to find suitable carriers for anabasine sulfate dust that are available in large quantities in the black soil zone of the U. S. S. R. The anabasine sulfate used contained 28 percent of the alkaloid. In experiments against

the cabbage aphid, Brevicoryne brassicae (L.), the best results were 96.8 percent mortality in 3 days with a 4-percent dust in combination with a highly alkaline white clay and 95.7 with a 7-percent dust in combination with lime. The rate of application was 90 pounds per acre. In tests against the apple aphid, Aphis pomi Deg., all the aphids were killed in 3 days after the application of a 4-percent dust, with wood ash as the carrier, at the rate of 10 grams to a 4- or 5-year old tree. A 2-percent dust with wood ash or white clay killed 98.8 and 98.0 percent, respectively. In experiments against the apple moth, Hyponomeuta padellus malinellus Zell., 91.4 percent of the larvae of the fourth and fifth instars were killed in the field and 100 percent in the laboratory within 5 days by a 7- and 4-percent dust, respectively, mixed with white clay and applied at the rate of 3.5 ounces to an 8-year old tree. Dust mixed with wood ash came next in effectiveness. Special experiments with Aphis pomi showed that anabesine sulfate maintained its effectiveness for 24 to 28 hours after application, apparently irrespective of the carrier used.

The comparatively strong action of anabesine dust upon aphids transferred to leaves dusted with it may be explained by a considerable fumigating action. However, the experiments conducted indicate that spraying is more effective.

Sorogozhskaya (144) in 1935 reported field experiments against the sawfly Caliroa limacina Retz. on cherry trees in the Department of Voronezh, U. S. S. R., in 1934. The sprays were applied on the 5th or 6th of August when most of the larvae were hatching, on the 19th of August when they were in the second and third instars, and on the 2nd of September when they were full fed. Anabesine sulfate, 0.05 and 0.1 percent, and nicotine sulfate, 0.1 percent, with soft soap, 0.4 percent, acted more quickly than paris green, 0.1 percent, with lime, 0.2 percent. The best time for spraying is when the young larvae hatch.

Lisitzuina (71) in 1935 reported that in the Russian Union the weevils Stenocarus fuliginosus Mshl. and Ceutorhynchus macula-alba Hbst. cause severe damage to poppies, which are an important crop. Observations on them were, therefore, carried out in 1933 and 1934 in the Department of Voronezh. In laboratory experiments with insecticides, dusts of anabesine sulfate (1:20), lime being the carrier used, gave 100 percent mortality of the weevils on the third day after the treatment. Sprays of anabesine sulfate and soap were less effective. Of all the insecticides tested, only calcium arsenite scorched the plants.

Krafter (64) in 1935 reported on the comparative toxicity of soaps in connection with their chemical composition and some physical and chemical properties. An account is given of laboratory experiments carried out in 1933 in Russia on the toxicity to insects of various liquid soaps. The acidity of the fatty acids extracted from vegetable oils, dolphin blubber, colophony, and naphthene was determined, and neutral sodium, potassium, and ammonium soaps were prepared from them. Alkaloid soaps were also prepared by substituting nicotine and anabesine for the alkali. The tests were made on adults of Brevicoryne brassicae (L.) and a temperature of 21-24° C. [69.8-75.2° F.] was maintained.

In each experiment 50 aphids placed in a Petri dish lined with flannel were sprayed with 1 cc. of the tested solution. Control aphids were sprayed with distilled water. The insects were then transferred to glass tumblers with fresh cabbage leaves at the bottom, and the percentage of mortality after 48 hours was calculated.

It was found that the sodium soaps were more toxic in all concentrations than the potassium soaps, and the ammonium soaps were the least effective. The alkaloid soaps were much more toxic than the alkali soaps, 100 percent mortality being obtained in all cases with soaps containing 0.25 percent of any of the fatty acids and 0.14 percent of the alkaloid. At low concentrations the anabasine soaps were more effective than the corresponding nicotine soaps, probably because the latter are transformed into the molecularly dispersed dispersal condition and lose their colloidal properties sooner. Solutions of pure nicotine and anabasine and of their sulfates were considerably less toxic than the soaps with the same content of the alkaloid in the solutions.

1936

Daniel and Cox (19) in 1936 reported on control of the oriental fruit moth, Grapholitha molesta (Busck), in quince plantings in western New York. Tests were made with anabasine sulfate 1:800, also anabasine sulfate 1:800 + Volck oil 1:50, but it was little better than nicotine and less readily available.

Sinel'nikova (130) in 1936 reported that in tests under field conditions of a number of insecticides against the woolly aphid, Eriosoma lanigerum (Hausm.), on apple in Central Asia, various sprays containing anabasine, tobacco extract, or kerosene emulsion gave 90 to 98 percent mortality. The most effective consisted of 8 ounces of 36-percent anabasine sulfate and 3 pounds of soap or Petrov's "Contact" in 100 gallons of water. If the aphids are abundant and infest the smallest twigs, the quantity of the spray used should be at least 11 gallons to each tree 16 to 20 feet high.

Lesnikovskaya (69) in 1936 reported that a spray of anabasine sulfate applied three times against the San Jose scale, Aspidiotus perniciosus Comst., failed to give control, as it did not kill the more mature scales.

When a certain species of fruit aphid was sprayed with paris green, the mortality was 22.4 percent, and when the same insect was sprayed with anabasine sulfate, the mortality was 24.7 percent.

Garman and Townsend (33) in 1936 recorded the results of investigations carried out in Connecticut in 1932-34 on the bionomics and control of the white apple leafhopper, Typhlocyba pomaria McAtee, on apple. In 1935 there was very little difference in the percentage of nymphs killed on trees sprayed with nicotine sulfate (1:800) alone and those sprayed with nicotine sulfate and soap. Pyrethrum soaps have given satisfactory control in some tests, but in general both pyrethrum and derris or rotenone sprays have not been so efficient as nicotine sulfate

or anabasine sulfate. No spray or dust has proved satisfactory against the adults in the field. Among other insecticides for control of the white apple leafhopper, anabasine sulfate has proved equally if not more effective than nicotine sulfate at the same strength. This material was used by commercial growers in Connecticut in 1934 with good results but is now (1936) off the market and cannot be obtained.

Skalov, Skalova, and Meleberdinskii (132) in 1936 reported that "Insectitzin," a new contact poison made of tobacco tar, which is a by-product obtained in the preparation of nicotine, proved to be the most effective of the sprays tested for the control of Thrips tabaci. Used at concentrations of 0.5 or 0.25 percent with the addition of 0.5 percent of soft soap, it was considerably more toxic than anabasine sulfate applied at the same or even higher concentrations and caused no injury to the tobacco plants. In a 0.2 percent concentration with 0.3 percent of soft soap, anabasine was more effective than anabasine sulfate. Experiments carried out by Skalov and Meleberdinskii showed that insecticides against the thrips are most effective in control if applied at the beginning of the vegetative period when the thrips are least numerous. The best method is to make three applications 20, 27, and 37 days, respectively, after the planting of the tobacco.

Investigations by Skalov (131) showed that spraying with anabasine sulfate is very effective against Myzus persicae on tobacco, a concentration of only 0.2 percent killing almost all the aphids if both surfaces of the leaves were well covered by the spray. The addition of 1 percent of soft soap increased its effectiveness. The treatment did not injure the plants or affect the chemical composition or flavor of the tobacco from them.

Kremer and Kurichinskii (65) in 1936 stated that a carefully mixed dust of anabasine sulfate and finely ground slaked lime, called "Imagocide" and containing 5 to 10 percent of anabasine, has proved effective in destroying mosquitoes in houses, sheds, etc. It keeps well in corked bottles and is applied with a hand duster; contact with the smallest particle paralyzes and kills a mosquito in 1 to 2 minutes.

Kagenova-Kharnskaya (51) in 1936 reported that, in experiments in the Russian Far East, spraying with anabasine sulfate at concentrations of 0.1 and 0.2 percent gave 100 percent mortality of the cabbage aphid, Brevicoryne brassicae (L.), in 24 hours, and good results against Aphis gossypii Glov. on cucumbers in greenhouses were obtained even with a 0.05-percent concentration.

Fotaraya (110) in 1936 reported tests to control Aspidiotus destructor, which has 2 or 3 generations a year in the tea regions of the U. S. S. R. Sprays of 0.07 percent of anabasine sulfate and 0.05 percent of nicotine sulfate, each with the addition of dolphin-oil soap (1 pound to 12 gallons), gave 89.1 and 86.4 percent mortality, respectively, before scale formation.

Richardson, Craig, and Mansberry (112) in 1936 reported a study of the toxic action of nicotine, nornicotines, and anabasine upon Aphis rumicis.

Six nitrogen heterocyclic compounds, tested as sprays in 0.25-percent sodium oleate solution under standardized conditions, yielded the following toxic order when based upon median lethal concentrations: Anabesine > 1-beta-nicotine = dl-beta-nornicotine > dl-beta-nicotine > dl-alpha-nicotine = dl-alpha-nornicotine. The presence or absence of a methyl group on the pyrrolidine nitrogen of a pyridyl pyrrolidine is not essential for toxic action to Aphis rumicis. Compounds with linkage at the beta position of the pyridine nucleus are the most toxic in this series. The relation between the beta position and toxicity in these compounds may prove to be fairly general; it seems to hold for certain vertebrates and invertebrates. The dl-beta-nicotine is about half as toxic as natural nicotine, the laevo fraction probably containing most of the toxicity. Anabesine, the most toxic to aphids of the compounds reported here, is probably somewhat more toxic than its racemic form, neonicotine.

Bel'skii (10) in 1936 reported tests of baits of fermenting molasses in large shallow wooden basins which are extensively used in the Russian Union to catch the adults of Euxoa segetum Schiff. and other noctuids.

In some experiments a poison was added to the molasses, and it is concluded from the results that this should always be done if the containers used are of a type from which many of the moths can escape. Of the poisons used, sodium arsenite at a concentration of 0.05 percent retarded fermentation of the molasses, but sodium fluoride at less than 0.4 percent and anabesine sulfate and nicotine sulfate at any concentration tested did not hinder it. The relative efficiency of these poisons was not constant during the three years' tests; on the whole, sodium fluoride (0.25 percent) appeared to be the best, though in individual tests sodium arsenite (0.05 percent) and anabesine sulfate (1 percent) were superior to it. The attractiveness of the baits was increased by the addition of a few drops of amyl acetate. Devices that exposed the poisoned molasses by means of a wick did not prove so effective as the standard containers.

For the future experiments it is proposed to use anabesine and nicotine sulfates at a concentration of 0.5 percent.

Savchenko and Ratner (127) in 1936 reported laboratory experiments in Russia to compare the effectiveness against aphids of anabesine, its sulfate, naphthenate, and resinate, and of lupinine, which is obtainable in considerable quantities from Anabasis aphylla. The aphids used were Aphis fabae Scop. and Myzus persicae Sulz., and the rate of mortality produced by spraying with the various preparations are shown in tables; the percentages give the average for both species. In the first series of tests the anabesine and the salts were dissolved in water (with or without the addition of naphthene soap) at a concentration equivalent to 0.02 percent of the alkaloid. Lupinine was also tested at a higher concentration. When used without the soap, the most effective was anabesine naphthenate, which killed 79 percent of the aphids. If its efficiency is rated as 100, the relative efficiencies of the other sprays were anabesine sulfate 91, anabesine resinate 77, anabesine 58, and lupinine 3. When naphthene soap was used in the sprays, the highest kill (89 percent) was obtained with anabesine sulfate, and the relative

efficiencies were anabesine sulfate 100, anabesine naphthenate 98, anabesine 96, anabesine resinate 35, and lupinine 3. The relative decrease in the effectiveness of anabesine naphthenate when combined with naphthene soap was probably due to a decrease of the hydrolysis of the soap as the result of the presence in the spray of ions of naphthene acid from two sources (the soap and the anabesine naphthenate), so that the concentration of the free naphthene acid, which possesses an independent insecticidal action, was reduced. From these tests it is concluded that anabesine resinate and lupinine are unsuitable for use in insecticides.

Further tests on Myzus persicae, in which various concentrations of anabesine and anabesine sulfate were used with 0.4 percent of naphthene soap, and anabesine naphthenate was used alone, showed that the latter spray would be the cheapest, since even at a concentration of 0.03 percent it killed 96 percent of the aphids. The addition of mineral oil emulsions or of small quantities of "Contact" or pectin glue considerably increased the effectiveness for anabesine.

With a view to determining the factors on which the effectiveness of these preparations depends, the physico-chemical properties of the solutions were studied and are discussed in detail. It was found that the hydrogen-ion concentration exercises a considerable influence on the effectiveness of the spray, chiefly in the case of different solutions of the same preparation. With the addition of naphthene soap all the preparations acquired an alkaline reaction, whereas the addition of large quantities of "Contact" or pectin glue considerably increased the concentration of the hydrogen ions, which reduced the effectiveness of the spray. With a decrease of the surface tension and viscosity the effectiveness of the spray usually increased. There is a certain antagonism of action between surface tension on one side and viscosity and pH on the other. A high concentration of hydrogen ions and high viscosity usually neutralizes the effect of low surface tension. It appears that the bicyclic alkaloids are more toxic than the monocyclic ones. The insecticidal properties of alkaloids that are similar in structure depend on the elasticity and volatility of their vapors, but their toxicity is equally decreased when volatility is too high or too low. The comparative effectiveness of the water solutions of nicotine or anabesine and their salts also depends on the volatility of the vapors since, when applied as sprays, they act as fumigants. The volatile anabesine and nicotine rapidly form high concentrations but do not maintain them for long, whereas the corresponding salts evaporate slowly and keep up a definite concentration of vapors during a prolonged period, which explains their relatively greater effectiveness.

The authors suggest the use of the term "effectiveness" instead of "toxicity" to express the insecticidal value of alkaloids in sprays. Under these conditions the alkaloids and their salts possess equal potential toxicity, as the active principle of both is the alkaloid that penetrates into the body of the insect in a vaporous or gaseous state through the tracheal system. The insecticidal action, therefore, does not depend on the different toxicity of the preparations, but on the effect of the physical properties of the solutions on the rate of evaporation and penetration of the alkaloid into the tracheae.

Reference is made to investigations conducted by Dashkevitch in 1935 which indicated that anabesine was more toxic than lupinine to the larvae of mosquitoes of the Culex species.

Mason (76) in 1936 reported tests with anabesine sulfate (40 percent) to determine its toxicity to the squash bug, Anasa tristis (Deg.). He found that at a dilution of 1:100 anabesine sulfate killed a high percentage of squash bugs under both laboratory and field conditions. Under the latter conditions slight injury resulted to the margins of some of the squash leaves, but it was not serious. In combination with Fenetrol (sulfonated oxidized gas oil) 1:200 or pine oil 1:200, serious injury resulted to the young growing tips of the squash vines. The percentage of kill from anabesine sulfate 1:200 was unsatisfactory, and 1:400 gave practically no kill at all. Powdered soap, 1 pound to 50 gallons of water, in combination with anabesine sulfate, although tested only under laboratory conditions, increased the kill several percent.

1937

Richardson, Deonier, and Simanton (113) in 1937 found that 5 percent of anabesine sulfate in bentonite used as a dust in the field killed only 5 percent of chinch bugs (third and fourth instars). There was no injury to corn plants. [A mixture of anabesine sulfate and bentonite reacts to form a definite chemical compound, namely, anabesine bentonite, which is nonvolatile and insoluble in water. R. C. R.]

Kremer and Kuvichinskii (65) in 1937 reported laboratory and field tests in the Crimea of the effectiveness against mosquitoes and sand flies (Phlebotomus) of dusts of anabesine sulfate and finely ground slaked lime. The results of dusting mosquitoes in buildings in various localities at temperatures varying from 1 to 30° C. [33.8-86° F.] with dusts containing 10, 15, or 20 percent of anabesine sulfate are given in a table; the stronger dusts gave 100 percent mortality in all tests and the weakest one did so in 4 tests out of 7. It is emphasized that the dust must come in contact with the body of the insect. In hot weather the mosquitoes were paralyzed in 1 to 2 minutes and eventually all died, though a few of those dusted with the lowest concentration survived until the following day. The rapidity of action of the dust increased with the temperature. Dusting at the rate of 1 ounce to 2,000 cubic feet in inhabited houses and 1 ounce to 1,500 cubic feet in animal quarters was found sufficient to destroy all the mosquitoes, whereas 75 ounces of tobacco dust would be required to fumigate the same space. In tests in houses in Sebastopol, practically all sand flies were paralyzed almost instantaneously by 10 to 15 percent concentrations of the dust, and died in 5 to 10 minutes.

In the laboratory tests the mosquitoes were placed into cages protected with fine-mesh wire, and were dusted from outside from a distance of 1 to 1-1/2 meters with 10 percent anabadust. If the outside temperature was sufficiently high, the mosquitoes showed indications of poisoning in 1 to 2 minutes. They were unable to fly, fell on their backs; their legs and heads were contorted with spasms. In the majority of cases their abdomens became inflated like balloons, ready to burst.

Anabesine dusts are prepared by saturating the well-dried, sifted lime with the required quantity of anabesine sulfate, after which the moistened lime was mixed in a mixing apparatus. After 15 to 20 minutes of mixing, the preparation is slightly dried in the sun and placed in a tank protected from sun and moisture. Anabesine dust is preserved in large bottles made of dark glass, which are securely corked. If placed in paper containers or in open boxes, it loses its potency and, therefore, especially when the temperature is high, it is essential that the anabesine dust containers be hermetically closed. The control sprayings were made with a solution containing 0.3 percent of anabesine sulfate and 0.6 percent of lime.

Rumyantzev (120) in 1937 reported that of a number of dust insecticides tested against the hemp flea-beetle, Psylliodes attenuata Koch, on hemp in the Gor'kii Province of the U. S. S. R., sodium fluosilicate was the most effective and rapid in action. Calcium arsenate and anabesine dust were practically valueless.

Ivanova and Nemiritskii (44) in 1937 reported tests of insecticides for quarantine treatment of living plants against scale insects by submersion in toxic solutions.

In experiments in Leningrad and Sukhum on the control of coccids on nursery stock (chiefly citrus), infested branches were immersed in water solutions of various insecticides. Those tested were pure anabesine and nicotine; naphthenates of anabesine, nicotine, sodium, and potassium; sulfates of anabesine and nicotine; and soaps of anabesine, nicotine, or sodium prepared with fatty acids of dolphin blubber. None of the solutions caused complete mortality of the coccids, even with concentrations of up to 0.5 percent of the alkaloid and an exposure of 60 to 90 minutes, at an average temperature of 20° C. [68° F.]. Heating the solutions to 45° C. [113° F.] gave a mortality of up to 100 percent, but equal results are obtainable with hot water at 50° C. [122° F.]. Since, however, some plants do not survive exposure to hot water at 50° C., and as the alkaloid soaps proved to be considerably more effective than any of the other solutions tested, further investigations on their application at 40-45° C. [104-113° F.] are recommended.

The insecticidal properties of anabesine and nicotine (as pure alkaloids, naphthenates, sulfates, and dolphin oil soaps) were investigated on the imaginal stage of the following coccids: Chrysomphalus dictyospermi, Lepidosaphes gloverii, Pseudococcus gahani, P. maritimus, and P. adonidum. Not one of these preparations, even when taken in concentrations of 0.5 percent of alkaloid content in the average temperature of 20° to 25° C., produced a lethal effect on P. adonidum, when this insect was submerged for 40 to 60 minutes in the preparation. The mortality of C. dictyospermi reached, however, with some of the above preparations, nearly 100 percent.

Rotman (119) in 1937 studied the effect of anabesine on the gaseous exchange in insects. Larvae of Plethonus riversii Scop., after being dipped into a 0.5-percent solution of anabesine, or a 1-percent solution of anabesine sulfate (containing 40 percent anabesine), discharged liquid from the mouth and anus and became paralyzed in 2 to 15 minutes. The

rate of respiration of larvae dipped in anabasine sulfate first increased strongly, but soon returned to practically the normal level; no increase in the rate was observed in those dipped in basic anabasine. In about 1 to 3 hours paralysis of the older larvae passed and the normal respiration rate was restored; younger larvae remained paralyzed for 8 to 12 hours, and some died. It is concluded that the anabasine preparations probably act on the nervous and muscular systems and only in a secondary way on the respiratory system. Similar experiments with larvae of Pieris brassicae L. resulted in a slow decrease in the respiratory rate and a general sluggishness, and death often ensued during molts.

Savchenko (123) in 1937 reported on the determination of effective dosages of anabadusts [anabasine dusts] for the control of beet aphids. The results are given of laboratory tests against immature beet aphids of dusts of anabasine sulfate mixed in concentrations of 1 to 6 percent with various carriers. Their effectiveness was compared with that of "Aning" which gave 98.5 percent mortality. All the dusts were applied at a rate equivalent to 36 pounds per acre. A 4-percent dust prepared with freshly slaked lime was the most effective, giving 98.3 percent mortality. Dusts mixed with talc or kieselguhr were the least effective, and although a 4-percent dust prepared with magnesium carbonate gave 95.7 percent mortality, it did not adhere well and formed lumps.

Savchenko and Dzevaltovskaya (125) in 1937 reported the results of comparative tests on new activators for anabasine sulfate in combating the beet aphid.

In the Russian Union soft soap is usually added to sprays of anabasine sulphate to increase their effectiveness against aphids on beet. It is, however, expensive and can be used only with soft water. Other possible activators were, therefore, tested in the laboratory in 1935-36; they were applied in sprays containing 0.03 percent of anabasine sulfate to immature examples of Myzus persicae (Sulz.) on leaves of beet. At this concentration anabasine sulfate alone gave 37 percent mortality in 24 hours. Several of the activators proved to be satisfactory substitutes for soft soap; the best were three samples of sodium salts of naphthalene-sulfonic acids, since they increased the percentage of mortality of the aphids to 80 or more when used at a concentration of only 0.5 percent, dissolved easily, and could be used with hard water as well as soft.

The physico-chemical properties of the solutions were studied and are discussed. Practically all the organic activators (notably the sodium naphthalene-sulfonates) decreased the surface tension of the solution, which showed maximum effectiveness when the surface tension was rather less than half that of distilled water. An activator that gave an acid solution did not reduce its effect to any marked extent provided that the surface tension was sufficiently reduced. On the whole, viscous solutions were less effective than others, as they moved more slowly along the tracheae of the aphids.

A comparison of the mechanism of activation of anabasine sulfate with that of nicotine sulfate showed them to be identical. Carbonates of alkaline metals, which are known to increase the effectiveness of nicotine

sulfate, could, therefore, be used to activate anabesine sulfate; they do not scorch beet and so could be applied against beet aphids without preliminary tests.

Kevskii, Uspenskaya, and Shaposhnikova (86) in 1937 reported on a control program for the codling moth, (Cydia Carpocapsa pomonella (L.). in Russia. Nicotine sulfate and anabesine sulfate were ineffective when used alone, even if they were prepared as "fixed compounds" adsorbed on sulfur, but they increased the effectiveness of arsenical sprays to which they were added.

Pavlov (108) in 1937 reported on chemical methods for controlling the pea aphid in Russia. In field experiments against the pea aphid, Macrosiphum enobrychis Boy., on peas in the eastern part of the Province of Voronezh in 1935, no difference was observed in the effectiveness of dusts containing anabesine or nicotine. Complete mortality of the aphids was obtained on the fifth day after applying 5-percent dusts at the rate of 90 pounds per acre, but 3-percent dusts at the same rate or 7-percent dusts at 45 pounds per acre were much less effective. The cabbage aphid, Brevicoryne brassicae (L.), proved to be more susceptible, as 3-percent anabesine dust at the rate of 63 pounds per acre killed 90 percent of the aphids on seed cabbage, and a second application 8 days later killed the remainder.

Pivovarov and Guterman (109) in 1937 reported that in experiments in Voronezh, U. S. S. R., a dust of finely ground slaked lime impregnated with 5 to 10 percent of anabesine sulfate was found effective against hibernating mosquitoes, when applied at the rate of 5 ounces per 1,000 cubic feet. In the laboratory, at temperatures ranging from 39.2 to 24.8° F. and humidity of 59 to 91 percent, it gave 100 percent mortality of culicines taken from hibernation quarters in four tests and 99.15 percent in another. Some of the mosquitoes were not killed immediately but died in the course of 2 to 3 days as a result of paralysis of the motor centers. When the dust was applied with a hand duster in cellars in which mosquitoes were hibernating, it killed over 98 percent of Culex and 97.5 percent of Anopheles. As the dust acts only when in direct contact with a mosquito, it is essential for the carrier to be dry and for the apparatus to effect a good dispersion.

Tarasova (152) in 1937 reported a study of the effect of anabesine on the activity of the heart in insects. Larvae of Plethonus ribesii submerged in a 1-percent solution of anabesine sulfate survived for up to 6 hours, whereas they died in a 1-percent solution of sodium chloride in about 2 hours. The rate of pulsations of the dorsal vessel in the larvae submerged in the anabesine sulfate solution at first somewhat increased, but became normal in half an hour. When the solution was applied with a brush the larvae reacted immediately by strong movements and emission of fluid from the mouth and anus; in 7 to 10 minutes paralysis occurred, and the rate of pulsation of the dorsal vessel increased four times as compared with the normal rate. The paralysis continued for a few hours (up to 24), after which the larvae appeared to recover completely. The action of the poison on the pulsation was much less noticeable when the ventral nervous chain was cut, which suggests that anabesine sulfate

acts not directly on the circulatory system, but on the nervous and muscular systems. Experiments on the direct application of anabesine sulfate to the dorsal vessels of larvae of Pieris brassicae dissected alive showed that even concentrations as low as 0.00001 percent result in an immediate and final cessation of its pulsations. This suggests the possibility of using the dorsal vessels of these caterpillars as an indicator for anabesine sulfate. Incidentally, the experiments showed a characteristic difference in the rate of pulsation of larvae parasitized by Apanteles glomeratus L., in which it was 6 per minute, as against 29 in the normal caterpillars. Caterpillars fed on nasturtium leaves had an irregular pulsation rhythm. The action of anabesine sulfate on the dorsal vessel of Blatta orientalis L. was only temporary.

Ivanova (45) in 1937 reported a study of the permeability of the integument of insects with regard to anabesine. Experiments with dialysers prepared from the integuments of larvae of Pieris brassicae and Pteronix ribesii showed that the degree of penetration of fluids is variable and depends on such factors as food, season, parasitization, etc. The chitinous cuticle is penetrated very easily, but the hypodermal layer presents an effective barrier to penetration. Anabesine and anabesine sulfate facilitated penetration of fluids through the integuments, the rate of penetration increasing with the increase in the concentration of the poisons. It is suggested that anabesine acts by narcosis of the hypodermal cells.

Savchenko (124) in 1938 reported that nicotine sulfate is more potent than anabesine sulfate when tested upon beet flies. Under favorable meteorological conditions, and in the presence of soft or medium-hard water, and provided liquid soap is added to the solution, nicotine sulfate can be used at a concentration of 0.06 percent, and anabesine sulfate at 0.08 percent. If the water is hard or the weather is cool, the concentration of the solutions should be increased by 0.01 to 0.02 percent. Liquid soap can be replaced by sulfonates derived from petroleum and, in certain cases, even by sodium carbonate.

1938

Sugak (151) in 1938 reported that aphids on lupin, of which Aphis medicaginis Koch was the most common, were successfully controlled by spraying twice with soap solutions containing anabesine sulfate or nicotine sulfate.

Fulton and Howard (26) in 1938 tested anabesine sulfate with and without oils upon the squash bug, Anasa tristis (Deg.). Tested upon the squash bug, anabesine sulfate (40 percent) at 1:200 killed only 8 percent after 72 hours at 80° F. and 70 percent relative humidity. Under similar conditions nicotine sulfate at 1:100 killed 19 percent. The addition of 1 percent of certain oils (teaseed, corn, peanut, olive, petrolatum, and tung), emulsified with sodium lauryl sulfate, to anabesine sulfate or nicotine sulfate solutions greatly increased their toxicity to the squash bug. The mixtures of oil with nicotine sulfate 1:100 were more toxic than the mixtures with anabesine sulfate 1:200.

1940

Yothers and Griffin (160) in 1940 reported tests made with insecticides upon the woolly apple aphid, *Eriosoma lanigerum* (Hausm.), and the green apple aphid, *Aphis pomi* Deg., at Wenatchee, Wash., during 1931 to 1933.

The results of these tests indicate the following conclusions: Anabasin sulfate and nicotine sulfate are, at the greatest dilutions tested (1:4800), about equal in effectiveness against both the woolly and the green aphids. Each gave approximately 97 percent kill of the woolly aphid at the above dilution used with an alkylated naphthalene sulfonate as a wetting agent, inclusive of 58 percent killed by the latter alone. Somewhere between a dilution of 1:3200 and 1:4800 both anabasin sulfate and nicotine sulfate, even with the wetting agent doubled, begin to fall off from 100 percent kill of the woolly aphid. Somewhere between the same dilutions they also begin to fall off from 100 percent kill of the green aphid, with sodium oleate as a wetter, but with the wetter not increased at the greater dilution, as is the case with the woolly aphid. Against the green apple aphid nicotine and anabasin sulfate with accessory agents gave almost complete mortality up to dilutions of 1:3200, and the anabasin gave 95 percent kill at 1:4800.

PATENTS

Katznel'son and Kabachnik (53) in Russian patent 39,108, issued October 31, 1934, describe a process of making aminoanabasin by heating anabasin with amides of alkali metals in the presence of organic solvents. Efimov (21) in Russian patent 40,355, issued December 31, 1934, describes a process of making nicotine and anabasin sulphites by treating the alkaloids with sulphurous acid.

Dashkevich (20) in Russian patent 47,865, issued July 31, 1936, describes the preparation of salts of anabasin for use as insecticides. Anabasin is treated in a solution or directly with weak acids or their anhydrides, e.g., hydrogen sulphide or carbon dioxide, and the salts formed are separated from the solution.

Sokolov and Kretov (143) in Russian patent 51,137, issued May 31, 1937, describe the preparation of anabasin fluosilicate by treating a solution of anabasin or its sulfate consecutively with fluosilicic acid and ethyl alcohol or methyl alcohol.

Smith (139) in United States patent 2,033,856, issued March 10, 1936, applied for July 5, 1934, claims the method of preparing organic base-bentonite compounds, which comprises bringing together, in the presence of water, bentonite and organic bases of sufficient alkalinity to be titratable with mineral acids. Anabasin is mentioned as a base that reacts readily with bentonite.

McConnell (73), assignor to Tobacco By-Products and Chemical Corporation, in United States patent 2,071,171, issued February 16, 1937, applied for June 15, 1935, claims a fumigating package consisting of a hermetically sealed metallic receptacle having its vertical side wall scored

to provide knock-outs, and a fumigant within and only partly filling the receptacle, the fumigant consisting of a combustible material, an oxygen-supplying material, and a parasiticide material which will evolve a parasiticial vapor during fumigation. There are a number of such parasiticides, such as, for example, nicotine, anabasine, pyrethrum, derris, naphthalene, thiocyanates, and sulphur. A specific mixture contains about 67 percent of dry powdered tobacco, 14 percent of anhydrous nicotine of 98-percent purity, and 19 percent of sodium nitrate.

Markwood (74) in United States patent 2,123,248, issued July 12, 1938, applied for January 14, 1937, claims the substantially water-insoluble reaction products of peat with organic bases of the group consisting of arecoline, anabasine, codeine, ethylene diamine, and piperidine. These products are made by bringing together peat and the organic bases in the presence of water.

REVIEWS AND POPULAR ARTICLES ON ANABASINE

Smith (133), in the United States Department of Agriculture's Year-book of Agriculture, 1928 (published in 1929), called attention to neonicotine, a synthetic compound which is equivalent to nicotine in toxicity to certain insects.

The Oil, Paint and Drug Reporter (134) in April, 1930, called attention to Smith's paper on neonicotine which was presented at the Atlanta meeting of the American Chemical Society. The Review of Applied Entomology, Series A (134), abstracted this report and called neonicotine a powerful new insecticide equal and perhaps superior to nicotine itself. Smith's paper was later published in the Journal of the American Chemical Society (134).

Romanovich (117) in 1932 reviewed the literature on nicotine, neonicotine, and anabasine. The toxicity of Anabasis aphylla L. was known among the inhabitants of Central Asia many years before this property attracted the attention of the investigators at the Moscow Institute of Chemico-Pharmaceutical Investigations. The active principle, anabasine, in some specimens of the plant reaches 2 percent. The insecticidal properties of anabasine were investigated in 1930 at the All-Union Institute of Plant Protection. A. M. Illinsky at Leningrad and Z. N. Shirokova at Moscow, both specialists of this Institute, showed that the toxic properties of anabasine are not inferior to those of nicotine, and, consequently, it may be used with success as a contact insecticide.

An anonymous (1) writer in June 1932 reported in the Pharmazeutische Monatshefte of Vienna that anabasine is an alkaloid obtained from Anabasis aphylla growing wild in Turkestan. It is used as an insecticide and is sold by the Amtorg Trading Corporation of New York.

Knight (61) in 1933 wrote that the utilization of fruits and vegetables had been aided by chemical discoveries. From pyridine, a constituent of coal tar, a substitute of nicotine has been synthesized. This product, called neonicotine, has recently been found in a Russian weed and has become commercially available.

Roark (114) at the Fifth Pacific Science Congress, Canada, 1933, reported on recent developments in insecticide research. For many years efforts have been made to synthesize a compound that would have insecticidal properties similar to those of nicotine. The most promising of these is neonicotine, found by Smith, Richardson, and Shepard to compare favorably with nicotine in killing the bean aphid, *Aphis rumicis*. Recently Russian investigators have found neonicotine (called anabesine by them) in a weed of the sugar-beet family known as *Anabasis aphylla*. This plant contains about 2 percent total alkaloids, including anabesine, methyl anabesine, and lupinine. An extract of the *Anabasis* plant has recently been placed on the market under the name of anabesine sulphate.

In 1934 an anonymous (2) writer in Science Service called attention to anabesine as an insecticide.

"Anabesine is a double discovery. American chemists, striving to make something stronger than nicotine, synthesized a compound which they called 'neonicotine.' At the same time, Russian chemists extracted a most efficient insect poison from a common weed bearing the classic Greek name *Anabasis*, and called it anabesine. A comparison of the synthetic and the natural compounds showed them to be chemically identical.

"*Anabasis* is a genus of dry-land weeds common in North Africa, Asia Minor and parts of Russia. There are about fifty species, of which only one, *Anabasis aphyllum*, has been investigated as a source of insect poison. The plant is related to such common American weeds as lamb's quarter, tumbleweed and greasewood.

"While chemists and entomologists are looking into its usefulness as a source of aphid poison, botanists of the United States Department of Agriculture are undertaking tests to find whether it can be grown with profit in some of the warm, dry lands of the Southwest, which are similar to its native habitat."

The United States Department of Agriculture, Bureau of Chemistry and Soils (155), in its annual report for 1934 referred to the work of Nelson in determining the physical properties of anabesine.

The United States Department of Agriculture, Bureau of Entomology and Plant Quarantine (156), in its annual report for 1935 called attention to Smith's isolation of anabesine from *Nicotiana glauca* growing in the Southwestern States.

Robinson (116) in 1935 published a review of the literature for 1933-34 dealing with the chemical constitution of anabesine, and other alkaloids.

Orekhov (94) in 1936 reviewed recent alkaloidal investigations. The production of anabesine is organized at the Chimkentzsky plant located at Kazakhstan, U. S. S. R., where the raw material is found in great abundance.

Anabesine not only replaces nicotine for many purposes, but in some respects it is regarded as a better insecticide than nicotine. Contrary to expectations, the experimental work indicated that the introduction of a methyl group caused a sharp decline in the toxicity of anabesine.

Martin (75) in 1936 discussed compounds structurally related to nicotine, including anabesine, and speculated upon the reasons for their high insecticidal efficiency.

Roark (115) in 1936 reviewed work on anabesine published during 1934 and 1935 by Smith, Nelson, Ginsburg et al., and Garman.

An anonymous (3) writer in 1937 reported a talk before the Vegetable Growers Association of America by T. H. Parks of Ohio on new insect control measures. Reference is made to rotenone, pyrethrum, nicotine, and anabesine.

Shepard (129) in 1939 reviewed information on anabesine and compared its insecticidal action with that of nicotine, nornicotine, and related compounds.

SUMMARY

Tests to determine the insecticidal efficacy of anabesine and its salts have in most cases been carried out under such conditions that it is difficult to assign a quantitative value to the results. For that reason the compiler has not indicated the effectiveness of anabesine against each species of insect tested but has only listed the species with references to the publications describing the results of the tests.

In general, the published reports indicate the following:

Anabesine closely resembles nicotine in its physical, chemical, and insecticidal properties, but there are some important differences. Anabesine is less volatile than nicotine and, as might be expected, is less effective as a fumigant. As a contact insecticide, anabesine is equal to or even superior to nicotine, especially against aphids. Some experimenters have reported that anabesine is five times as toxic as nicotine when sprayed upon the bean aphid (*Aphis rumicis* L.). As a stomach poison to insects, anabesine appears distinctly inferior to nicotine in tests upon the larvae of the oriental fruit moth, red-legged grasshopper, Mexican bean beetle, Japanese beetle, honeybee, and the silkworm. Anabesine appears valueless against the eggs of insects.

It would seem, therefore, that anabesine is a valuable contact insecticide, especially for use against aphids; but that little can be expected from it as a fumigant, an ovicide, or a stomach poison.

However, tests of anabesine as an insecticide have been limited, and new uses for it may be found. It seems well worth while to test its suitability for the control of the pea aphid and other insects now combated with nicotine.

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