described the scales of *Albula,* showing that they have much in common with those of *Amia,* and are very different from those of *Elops.* The Albulidæ are evidently much nearer to the Cycloganoidei than are the Elopidæ, and if these two families stand side by side in the system, it must be understood that they are nevertheless quite far apart in fact. The striking feature of the scales in which *Albula* resembles *Amia* is the entirely longitudinal (instead of transverse) arrangement of the basal circuli, which in fact should be called *fibrillæ.* In *Amia* the nucleus is subapical, and the broad nuclear area is rugulose or covered with fine labyrinthiform markings. All this is seen in the living *Amia calva,* but even more beautifully in the Miocene *Amia scutata* Cope, scales of which I obtained at Florissant last month. Cope states that the scales of *A. scutata* are larger than those of *A. calva,* but I find them to be practically of the same size, with very strong longitudinal fibrillæ, fraying out basally, and a most beautiful and intricate labyrinthiform sculpture in the broad nuclear area. This labyrinthiform condition of the nuclear area is not uncommon among the lower groups of teleosteans in the stricter sense, and is variably developed in *Elops.* In the characinid *Prochilodus rubrotæniatus* Schomb. the transition from the rugose or labyrinthiform nuclear area to the regularly circulate type is curiously shown, the area becoming multinucleate, with several small "islands" surrounded by circuli. *Albula vulpes* has large subquadrate scales, with about three basal radii, leading to deep emarginations of the base, which therein departs markedly from *Amia* and resembles the normal condition of many higher Teleosts. The subapical region is rugulose, very much as in *Amia,* but the true nucleus, just below it, is surrounded by fine regular circuli. It is in this small central region, above the nucleus, that *Albula* has genuinely transverse (concentric) circuli. It is also to be remarked that the basal circuli are all beaded in *Albula,* whereby they differ from *Amia,* but agree with the Osteoglossidæ.

Strong new interest in the Albulidæ has been aroused by the description of a new genus by Mr. Henry W. Fowler in *Proc. Acad. Nat. Sci. Philadelphia,* LXII. (1911), p. 651. This very interesting fish, *Dixonina nemoptera,* was found mixed with specimens of *Albula* from Santo Domingo, collected long ago by Gabb. Fowler writes of the scales that they are "cycoid, inner edges mostly crimped, outer or exposed edges thin or membranous and ragged, marked submarginally with a concurrent vertical ridge or striation, the true edge of the scale." I am greatly indebted to Dr. D. S. Jordan for an opportunity to study a couple of scales of *Dixonina nemoptera,* taken from the original type. They are about 8.5 mm. broad and long, and in structure agree perfectly with those of *Albula.* The nucleus with its concentric circuli, the beaded longitudinal basal circuli, the three basal radii and three basal emarginations, etc., are all the same. The dermal pigment spots also agree. In some ways this exact correspondence is rather disappointing, but it shows the conservative nature of the scale-pattern, and rather emphasizes its value as diagnostic not merely of the genus *Albula,* but of the group to which it belongs.

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THE SIGNIFICANCE OF LEAD ARSENATE COMPOSITION

The control of a large class of the insect pests of growing crops depends on the use of arsenical sprays, and the commercial importance of such spraying has assumed very large proportions in recent years. Two factors determine the limits to which such methods may be carried with success. The first factor is the amount, character and timing of the applications necessary to control the insect. The second factor is the degree of toleration for the spraying treatments which the crop in question may possess. It is with the latter part of the problem that the following discussion is concerned.

Arsenic may injure plants quite as seriously as animal tissue, and the efforts of investigators have been directed towards preventing the absorption of the arsenical by the sprayed plants. It is assumed that solid bodies can not penetrate the epidermis of healthy plants, but the absorption of liquids is known to take place. Nothing has developed to show that the first premise is unsound, and the question may well be asked, why have many of the arsenical compounds designated as insoluble by chemists, proved to be injurious when applied as sprays? The most obvious answer is found in the supposition that these compounds are not insoluble under the conditions of the application.

Solubility implies a solvent, and the most universally present solvent found in nature is water. Chemists base their estimates on solubility in pure water, and on the results of comparatively short exposures to this solvent. On the other hand, natural water may not be pure, and under some climatic conditions the exposure of spray deposits, on plants, to the action of natural water may be very prolonged.

It is very important to note that the last implied condition, that of prolonged exposure of the spray deposit to moisture, is one which prevails to a great extent in the Pajaro Valley, California. This valley is situated near the coast, about one hundred miles south of San Francisco, and opens out onto the ocean. The apple orchards of the locality have exhibited a remarkable susceptibility to arsenical injury, and to such an extent as to seriously interfere with effective control of the codling moth by the use of arsenic compounds. The industry is a large one, as the production has averaged over three thousand cars annually for the last ten years. An industry of such proportions was deserving of considerable attention from those delegated to foster the horticultural interests of the state, and the university experiment station has properly responded to the demand.

Field and laboratory work was commenced in the spring of 1903, and the author became connected with the investigation in the fall of that year. Since that date the work has gone on continuously, and largely under the writer's supervision.

That the results have been satisfactory, is reflected by the methods of spraying and materials used by the growers at the present time. The influence of this investigation is also apparent in the orchard practise of the entire Pacific coast and many of the interior states, but comparatively little publication has been done. Now that the attention of many investigators is being attracted to arsenical injury and kindred problems it appears that the results of our work should be properly published. With this end in view, the author has recently issued a circular entitled "Foliage Testing of Arsenicals." In the present article it is intended to cover in more detail the purely chemical considerations.

To continue with water solubility; the climatic conditions of the Pajaro Valley are peculiar in that there is a large amount of fog and dew moisture through the spring and summer months. The foliage of the trees becomes wet early in the evening and remains so during the night and well into the following morning. This condition may continue without interruption for a period of several weeks. The dew and fog moisture may at times be abundant enough to drip liberally from the trees, but more often it is nearly all retained on the foliage where it evaporates during the following forenoon. Such conditions are evidently ideal for dissolving substances on the leaves, and for the absorption of the solutions by the plant tissues. As contrasted with rains which wash dissolved substances entirely away, the above-described conditions are much more trying, and partly explain why apple foliage in the eastern states has been so little subject to arsenical injury.

With regard to the action of substances in solution in the water used to suspend arsenical compounds, when applied as a spray, Haywood and McDonnell[1] and others have shown that chlorides, carbonates and sulphates render the arsenic oxide in certain varieties of arsenate of lead more soluble and increase the danger of foliage injury. On the other hand, we have found that distilled water does not

[1] U. S. Dept. of Agr., Bureau of Chemistry, Bul. 131, p. 46.

eliminate the injury, but may prolong the time required for it to take place. Also, arsenicals of several types, applied as dust sprays (without water), have produced injury under our climatic conditions. At the same time and under the same conditions arsenicals have been applied that produced no injury or a very small amount. Such variation from perfect foliage neutrality to serious injury was found in a series of arsenate of lead samples. The samples which produced no injury were found to still retain their non-injurious properties when mixed up for spraying in any of the various waters in common use in the locality. These waters vary from 40 to 150 parts per 100,000 of salts in solution; chlorides, carbonates and sulphates forming the bulk of the salts.

Thus, all degrees of injury were obtained when samples of that material commonly known as arsenate of lead were applied to foliage with the same water. Such results indicated a radical difference in the chemical properties of the various samples. Chemical authorities mention several plumbic arsenates, but consider them as being alike insoluble in water. However, "Handbuch der Anorganischen Chemie" (O. Dammer), Vol. 11, Part 2, pp. 565 and 566, states that pyro-arsenate ($Pb_2As_2O_7$) is soluble in ammonia while the ortho-arsenate [$Pb_3(AsO_4)_2$] is not. This brief statement requires interpretation and may be expanded as follows:[2] The acid arsenates are stable under acid conditions, but are transposed into the ortho-arsenate, the most stable compound, under neutral and alkalin conditions. This transposition involves the liberation of arsenic oxide or soluble arsenates. The significance is at once apparent. When arsenate of lead is applied as a spray it is subjected to neutral and alkalin conditions. This is especially true if the water used in spraying contains alkalies. That is, the conditions favorable to transposition of the acid arsenates into the ortho-compound obtain. As fast as the neutral waters of fogs, dews and rains wash away the liberated arsenic oxide, or when the latter is absorbed by the plant tissues themselves, the conditions are restored for more to be formed. The ultimate result is the complete transposition of the acid arsenates to the ortho-compound and the liberation of the excess arsenic oxide.

At the time when these conclusions were reached we had the records of a large number of foliage tests with arsenate of lead samples. Checking these off showed that without exception those simple plumbic arsenates which produced no injury contained lead oxide and arsenic oxide in the correct proportions to produce the ortho-arsenate.

These results were obtained in 1906 and in the early part of 1907, and while the evidence was then sufficient to exclude practically all doubt, it was thought best to wait until several years of commercial spraying and supplementary experimental work should give incontestable grounds to announce the deductions as fully supported by experimental evidence.

To continue further with deductions which are probably correct. Some authors recognize pyro-arsenate ($Pb_2As_2O_7$) and others only hydrogen-arsenate ($PbHAsO_4$) as occurring in wet precipitates. Our results apparently show that both compounds may occur in commercial lead arsenate. Foliage tests show that pure hydrogen-arsenate behaves differently from mixtures containing considerable proportions of the ortho-arsenate. These mixtures of ortho and pyro are more rapidly injurious than the pure hydrogen-arsenate.

A chemical explanation of this fact is apparent. Lead-hydrogen-arsenate is $Pb_2As_2O_7$ to which one molecule of water has been added; that is, $Pb_2As_2O_7 + H_2O = (PbHAsO_4)_2$. In other words, $PbHAsO_4$ is a product of the hydrolysis of $Pb_2As_2O_7$. The H_2O may even be regarded as water of crystallization as the hydrogen-arsenate is crystalline rather than amorphous in structure. This rearrangement of the molecule gives opportunity for rapid transposition to the ortho-arsenate, and would

[2] The credit for this interpretation belongs to Mr. E. E. Luther, at that time (1906) an assistant in the laboratory at Watsonville. This discovery not only explained the injurious properties of certain types of lead arsenate, but also indicated the means by which such injury could be overcome.

explain the more rapid injury from samples containing unhydrolized pyro-arsenate.

The Ammonia Test.—The reaction between ammonia water and the acid arsenates of lead may be used to test the presence of these compounds in a sample.

A fair-sized sample (10 to 20 grams) is worked up in water (25 to 50 c.c.) and an equal volume of strong ammonia (26° B.) is added. This is digested with heat, agitated and finally brought to the boiling point. The sample is then allowed to cool and settle, and the clear solution decanted through a filter. The filtrate is boiled until the ammonia is nearly or all driven off. The remaining solution is then made distinctly acid with acetic acid, and a concentrated solution of lead acetate containing free acetic acid is added. Any arsenic acid which the filtrate may carry will then be precipitated in the form of acid arsenate of lead. With no precipitate forming at first, add the lead acetate solution to large excess and allow to stand. A preciptate may appear in a few minutes or an hour.

With this treatment pyro-arsenate, hydrogen-arsenate and mixtures of ortho and pyro give abundant white precipitates. In any case where the precipitate forms at once and can be designated as more than a trace, *i. e.*, renders the filtrate opaque, the sample will prove injurious under foliage test conditions, and will probably prove injurious in commercial spraying operations, especially where climatic conditions favor such injury. On the other hand, samples which show no ammonia test are practically free from foliage-injuring properties.

The ammonia reaction is complete and may be used for the quantitative determination of any arsenic oxide that may be present in excess of that required to form the ortho-compound.

Errors arising from Chemical Tests and Analysis.—It is not enough to know that the ratio of As_2O_5 to PbO is as 1 to 2.90 or more. The essential thing is whether all the PbO is combined with the As_2O_5. Chlorine and organic bodies may retain sufficient lead to materially affect the nature of the compound. In case the arsenic oxide content is slightly greater than it should be, and an estimable quantity of chlorine is present, the sample will certainly give an ammonia test and prove injurious to foliage under test conditions.

The true ortho samples will probably show an excess of lead oxide amounting to 1 to 4 per cent.

The ammonia test is positive except in rare cases where the uncombined lead is sufficient to take up the liberated arsenic oxide.

Water Solubility.—This subject has received much attention from chemists but as usually handled, does not indicate the true condition of the sample. Most arsenicals yield only a limited portion of their arsenic to a given amount of water, but may repeat this a very great number of times. As has already been shown, the liberation of arsenic oxide from the acid arsenates depends on transposition to ortho under neutral and alkalin conditions. However, the amount of arsenic acid taken up by a given volume of water can not exceed a very small quantity before the reaction of the solvent becomes acid and stops the transposition. As a matter of fact, such solutions are neutral or alkalin to litmus.

The water solubility of arsenate of lead is readily shown in a qualitative way by digesting in water for a time (ten to twenty-four hours), decanting through a filter, acidifying the filtrate with acetic acid and then adding lead acetate solution as in the ammonia test. A white precipitate or turbidity indicates water-soluble arsenic oxide. This operation should be repeated a number of times to determine whether the amount of dissolved arsenic oxide remains a constant. With this method of treatment ortho- and acid-arsenate samples show a decided difference in behavior. Both arsenates may show about the same arsenic oxide content per unit volume of water for the first two or three washings. After that, however, the quantity of arsenic removed from the ortho sample will be very much reduced, but that from the acid sample will remain practically constant for a large number of washings. A device by which a constant stream of pure water could be run through the sample and collected for evaporation to a suitable volume would likely be the best method for determining relative water solubility.

Laboratory Preparation of Lead Ortho-arsenate.—Very few American chemists appear to have experimented with the ortho-arsenate of lead. Probably this is due to the fact that the formulas most often published do not produce this compound in the pure state, that is: unmixed with acid arsenates. True ortho-arsenate may be prepared as follows:

Solutions of lead acetate or nitrate and arsenic acid or ammonium, sodium or potassium arsenate containing the correct weights of the oxides (1 part of As_2O_5 to 2.90 PbO) are poured together. The water should be sufficient to dilute the precipitate so that it will not form too thick a mass. To this mixture ammonia is added to strong alkalinity. The mixture is digested with gentle heat for an hour or more, allowed to settle, and the clear liquid tested for arsenic oxide as described under the ammonia test. If a precipitate forms, a little more lead solution is added and the procedure repeated until no precipitate appears. It is well to wash the finished product and again treat with ammonia. If any arsenic oxide appears in the filtrate more lead solution should be added. Finally wash to the complete removal of water-soluble salts. In accordance with well-known principles of chemistry the retention of the arsenic oxide will not be complete until there is an excess of the precipitant, that is, lead oxide. For this reason true ortho samples will show less than the theoretical percentage of arsenic oxide (25.59 per cent.). With commercial samples, where allowance has to be made for impurities, this percentage is still further reduced.

It appears, then, that the federal insecticide and fungicide law rules out commercial ortho-arsenate of lead prepared on a 50-per-cent. water basis, by requiring 12.5 per cent. arsenic oxide. The manufacturers may still comply with the law by reducing the water percentage, but this is done at expense of easy remixing, so working a hardship on the consumer. It is my opinion that this clause in the act should be amended to read: "In the case of strictly ortho-arsenate of lead, the arsenic oxide content shall not be less than 11 per cent. or more than 12.5 per cent. on a 50-per-cent. water basis."

Further Discussion of Water.—Haywood, as already cited, has shown that chlorides, carbonates and sulphates may seriously increase arsenical injury from acid and pyro-ortho mixtures even when present in comparatively small amounts. Some recent results with these arsenates in commercial spraying apparently bear out such conclusions. The commercial ortho-arsenate usually contains enough excess lead oxide to offset these effects, but cases can be imagined where this compound might be partly decomposed. In such instances it is clearly possible to overcome the difficulty by treating the water with lead acetate. The addition of lead acetate until the water shows a reaction for soluble lead should give the desired result. The presence of small amounts of lead acetate will not prove injurious, and we have applied the carbonate and sulphate in very large quantities without producing the slightest injury. Lead acetate will completely overcome the effects of carbonates and sulphates and should greatly reduce the solvent action of chlorides.

Acknowledgments.—The investigations of which the features of this discussion form a part have had a wide scope and important contributions have been made by several people, among whom may be mentioned Professors C. W. Woodworth, W. T. Clarke, Geo. E. Colby and Mr. E. E. Luther.

W. H. VOLCK

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SOCIETIES AND ACADEMIES

THE WASHINGTON ACADEMY OF SCIENCES

THE Washington Academy of Sciences held its 71st meeting in the auditorium of the New National Museum on the evening of April 18, 1911. President F. W. Clarke presided.

Sir John Murray, of Scotland, gave a most interesting and beautifully illustrated lecture on "The Ocean."