TECHNICAL PAPERS

Confirmatory Analysis of the "Lost" Italian Varnish

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The old Italian violin makers such as Stradivari, the Guarneris, and the Amatis applied a varnish on their instruments that has not been equaled for beauty, transparency, and permanence. Unfortunately, they did not leave to posterity any record concerning its composition.

In a previous paper (*2*) confirmatory evidence of the rediscovery of the "lost" Italian varnish was presented from the results of spectrographic and microchemical analyses. However, all of the 10 specimens available for analysis at that time were brown in color. Subsequently, a good specimen of a brown-red varnish from a Francesco Ruggieri cello (1691) was obtained through the courtesy of Otto Lang, of St. Louis County, Missouri. As the red-colored varnishes of the old Italian violin makers were highly characteristic and as it has not been possible heretofore to produce red varnishes of similar transparency and permanence, spectrographic and microchemical analyses of this specimen should be informative.

Microchemical analysis. The theory was recently advanced by the writer (*1*) that the red color of the old Italian varnish was due to the presence of madder, which was the most important dyestuff known in those eras. A test for this coloring agent was developed, using varnishes containing madder (*1*). The presence of madder in the varnish from the Ruggieri cello was indicated by this test.

The behavior of this varnish upon solution in dilute alkali followed by precipitation with dilute acetic acid suggested the presence of resinous and/or fatty acids.

Spectrographic analysis. The Ruggieri specimen displayed the presence of a colored outer varnish and a yellow subvarnish, a combination frequently employed by the old Italian violin makers. As it was possible to separate the strata cleanly, spectrographic analyses were made of each layer. Shaw reported the following results for the two analyses: brown-red outer varnish—large amount of Ca, small amount of Si, Cu, Al, K and Mg, and trace amount of Na, Mn, and Fe; yellow subvarnish—large amount of Ca, small amount of Si, Cu, Al, K, Mg, Na, Mn, and Fe, and trace amount of Pb, Sn, and Ni.

The presence of calcium alone in relatively large amounts and of madder in a brown-red old Italian varnish is highly significant. It had been previously shown (*1*) that varnish films of madder-calcium rosinate are brown-red in color. Both analysis and synthesis have supplied some confirmatory evidence of the rediscovery of the "lost" Italian varnish.

The similarity of the analysis of the brown-red outer varnish to that of the subvarnish is also noteworthy. This would indicate that the subvarnish was converted to the color varnish by the addition of the coloring agents in madder, which is easily accomplished.

The other elements revealed by the spectrographic analyses may be due to the use of wood ashes, which the ancients could have employed to "harden" rosin and make it more suitable for varnish-making.

It was at first reported (*1*) that, if raw linseed oil is used with madder-calcium rosinate, the color is destroyed. However, by pretreating the oil, applying the varnish in thin films, and exposing these at once to light, the color becomes permanent. A brown-red varnish composed of alizarine-calcium rosinate and linseed oil, with turpentine as the solvent, has been prepared that possesses the desired depth of color, transparency, and permanence in its dried and aged films.

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[1] The cooperation of Otto Lang in supplying the specimen of varnish and of Everett J. Shaw in making the spectrographic analyses is gratefully acknowledged.

An Experimental and Theoretical Approach to the Mechanism of Cocaine Action[1]

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The mathematical theories of excitation developed by Hill (*5*) and others regard the rate of development of the excitatory process under the stimulating electrode to be of great importance. A certain group of blocking agents, including cocaine, act without appreciably altering the "resting" state of polarization of nerve (*1, 2*), and these appear to reduce permeability (cf. *6*). In view of these considerations an hypothesis has been set up with the postulate that the rate of transport of potassium from within to outside the fibers (e.g. under the cathode on "make") is a controlling factor in stimulation. On this basis, cocaine and related compounds would be expected to act by reducing membrane permeability to potassium. The following is a summary of some of the experiments which have been designed to test for such permeability

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[1] A preliminary account of these results was presented at the 32nd Annual Meeting of the Federation of American Societies for Experimental Biology. This work was aided by a grant from the American Philosophical Society.

changes in the sciatic nerve and sartorius muscle of *Rana pipiens*.

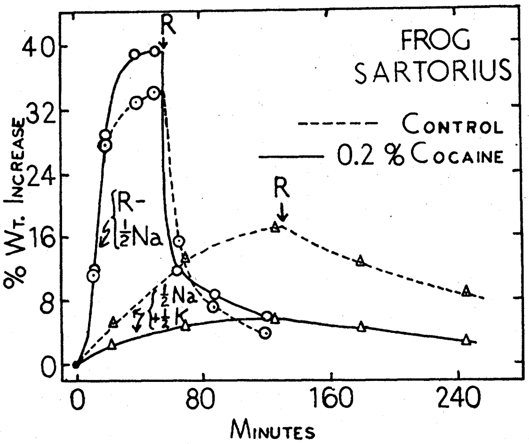

FIG. 1. The increase of weight, relative to that in Ringer after 2 hrs soaking with or without cocaine present, measured from the moment of change of the Na content of the medium. R indicates a return to normal Na levels. The lower curves are the averages of 6 paired muscles; the upper, of 3 paired preparations. Each pair behaved as indicated.

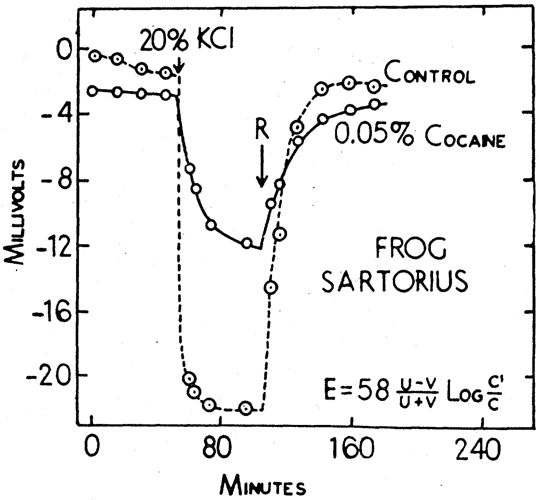

FIG. 2. The potential of the tibial end of paired sartorii, after a 2-hr preliminary soaking in Ringer with or without cocaine, relative to the central region used as a reference. The potassium solution, applied to the tibial region, was of the "replacement" variety. Similar results were obtained with KCl present in excess.

The permeability of muscle to anions as well as K will cause this tissue to swell in solutions in which Na is replaced by K (*3*); the rate of weight increase which occurs in such K-replacement media has been successfully employed in measuring relative permeabilities (*4*). Fig. 1 illustrates that when half of the Na in Ringer's solution is replaced with K, the weight increase which normally occurs is considerably reduced by 0.2% cocaine —a concentration which does not abolish the response to electrical stimulation. Water movement itself is not affected appreciably, as demonstrated by the swelling in a ½ × Ringer's solution. Under these conditions, therefore, cocaine reduces KCl penetrability.

In Fig. 1 it is apparent that KCl diffusion is still incomplete after 2 hrs; nevertheless, the maximum lowering of potential, produced at the tibial end by application of Ringer's solution with one-fifth of its Na replaced with K, is attained in 10–20 min. (Fig. 2). Obviously, this cannot be considered a Donnan equilibrium potential drop, inasmuch as the system is far from equilibrium. Rather, the conditions justify the application of the equation for a diffusion potential, such as that given in Fig. 2, where E is the change in potential; U, the mobility of potassium; V, the mobility of chloride; C′, the KCl concentration applied; and C, that previously existing in the Ringer. Short-circuiting by the extracellular space and the swelling of fibers limit the significance of the absolute potential changes obtained. However, from the diffusion equation it may be predicted that if the mobility of K relative to Cl is reduced, the effectiveness of K in lowering the potential will be correspondingly affected. The action of cocaine shown in Fig. 2 is typical of all 6 experiments which were performed and therefore supports the view that K penetrability is reduced by the anesthetic.

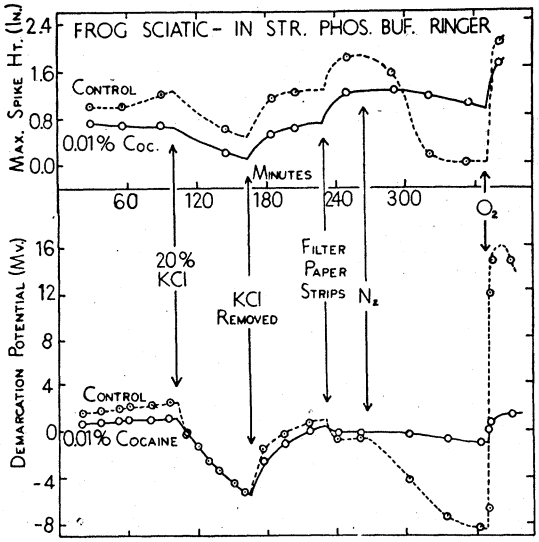

FIG. 3. The effect of localized anoxia and application of KCl (replacing an osmotically equivalent amount of NaCl from Ringer) on (A) the maximum spike height, given in inches of deflection of the cathode-ray beam, and (B) the demarcation potential relative to another region of the nerve kept in Ringer and oxygen for reference. As usual, the nerves are from the same animal and were soaked for 2 hrs in Ringer, with or without cocaine present, prior to the experimental run in the moist chamber. "Filter paper strips" indicates the elevation of the nerves on these as electrical conductors to facilitate gas exchange. In this experiment calcium was lacking from the medium to enhance the anoxic decline of potential.

Frog nerve differs from muscle in its negligible permeability to anions, as indicated by potential (*7*) and osmotic (*10*) experiments. In terms of the diffusion equation discussed above, when V is very small, a change in U will have no effect on E until U approaches V. This provides an explanation for the failure of cocaine up to 0.2% to produce a consistent reduction in the effectiveness of applied KCl in lowering the potential (Fig. 3).

For frog nerve evidence has been presented that the rise of resting potential in 5% CO_2–O_2 and its decline during anoxia are due to the uptake and release of K by the fibers, the associated changes in the K concentration of the extracellular spaces being the immediate major cause of the potential changes under these conditions (*8, 9*). A reduced permeability to K therefore would be indicated by a decrease in the magnitude of the potential changes in both cases. This has been observed under a variety of experimental conditions and with the lowest cocaine concentration employed (viz., 0.0005%).[2] Fig. 3, typical of a number of such experiments, is particularly instructive, inasmuch as it demonstrates not only that cocaine delays the decline of potential of a section of nerve rendered anoxic, but that the prevention of this depolarization is a sufficient condition for the maintenance of functional activity as judged from the maximum attainable spike heights observed at the stimulating electrode.

An examination of substances which resemble cocaine by virtue of a "stabilizing" action, e.g. procaine (*1, 11*), sulfanilamide and thiophene-2-sulfonamide (*8, 9*), recalls that Wilbrandt (*12*) employed similar basic compounds to reduce and reverse the negative charge normally present on collodion membranes. Such a mechanism of action appears attractive, inasmuch as chemical potentials obtained with nerve and muscle indicate that these and probably most animal cells have negatively charged surfaces (*6*). Some unpublished observations indicating that *p*-aminobenzoic acid enhances the ability of sulfanilamide to counteract the anoxic decline of the resting potential in frog nerve are readily explained on this basis.

These experiments therefore support the view that cocaine, at properly controlled concentrations, reduces the permeability of frog nerve and muscle to potassium. On this basis another tool is at hand for the analysis of the role of ionic movement in highly transitory phenomena. Thus, observations which have already been made of its action on the time constant of the excitatory process (Hill's "k," which is related to chronaxie) and on the afterpotentials in nerve suggest ionic transport under these conditions. These results and others, which cannot be included in this brief report, will be presented in greater detail subsequently.

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[2] In a recently published monograph (*Stud. Rockefeller Inst.*, 1947, **131**, 117), Lorente de Nó concludes that the reduced anoxic decline of potential in cocaine is due to a lowered respiratory rate, although Sherif (*J. Pharm. exp. Therap.*, 1930, **38**, 11) has shown that these concentrations of cocaine have no effect on respiration.

Loss of Radioactivity From Barium Carbonate Samples[1]

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Several investigators have reported observations which lead them to conclude that barium carbonate samples containing C^{14} can lose rapidly rather significant fractions of their activity by exchange with atmospheric carbon dioxide through the agency of moisture. In many experiments it is desirable to store counting samples for possible checking after weeks or months, and any rapid loss of activity by exchange or any other process would make such a practice hazardous in so far as experimental accuracy is involved; other consequences of rapid exchange loss are legion and need not be detailed here.

Two current papers report the results of purposeful investigations of this exchange phenomenon. One of these (*2*) deals only with exchange loss when solutions of sodium bicarbonate (pH 8.8) are evaporated to dryness in a variety of atmospheres. It was observed that even the small concentration of carbon dioxide in laboratory air caused losses as high as 60% in a single evaporation.

Most C^{14} radioactivity determinations of solid samples are made on barium carbonate, and it is to be expected that this solid can lose activity by exchange with carbon dioxide, through carbonic acid and its ions, though the rate of this exchange should be inappreciable in the absence of water. Though several estimates have been made as to the rate of loss of activity from precipitates of barium carbonate, only one paper has been published which contains the results of experimentation designed to explore the problem (*1*).

In that study, thick deposits of barium carbonate were prepared by filtering a slurry of freshly precipitated solid through a retentive filter paper; the samples were dried by drawing air through the filter after washing the mass with acetone and ether. All samples used in the investigation were of "infinite thickness" with regard to the C^{14} beta radiations. Several samples thus prepared were subjected to atmospheres of (1) moist carbon dioxide,

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