Although hampered by a very limited amount of material, suggestive results have been secured. In addition to lysergic acid and ammonia,[2] phenylalanine has been obtained from it. Less success, however, was experienced in our attempts to obtain proline as the gold salt of its ester from the alkaline hydrolysis of ergotamine or after its reductive cleavage with sodium in butyl alcohol. However, in the latter case we have isolated in addition to α- and β-dihydrolysergol the picrate of the piperazine, $C_{14}H_{20}N_2$, corresponding with that obtained from ergotinine. There can be little doubt, therefore, that proline is also a constituent of ergotamine. This conclusion was supported by the strong pyrrol test given by the mixed amino-acid fraction obtained from the alkaloid after alkaline hydrolysis.

In another respect, however, we have noted a striking difference between ergotinine and ergotamine. By no method have we succeeded in detecting either isobutyryl formic acid as such, or its reduction product α-hydroxyisovaleric acid, as products of the cleavage of ergotamine.

Since the accepted formula for ergotamine is $C_{33}H_{35}O_5N_5$, which differs therefore from that of ergotinine by C_2H_4, the possibility was considered by us that in ergotamine and therefore also ergotaminine pyruvic acid occurs in place of the isobutyryl formic acid of ergotinine and ergotoxine. Our experience has given support to this suggestion. If ergotamine is heated a short while with dilute alcoholic alkali, the resulting solution gives a red color with nitroprusside similar to that given by pyruvic acid and which changes after addition of ammonium chloride through purple to blue. This reaction is not given by ergotinine under the same conditions. In addition, it has been possible to obtain in very small yield a phenylhydrazone from the acid fraction of the cleavage products of ergotamine, which gave the same melting point (189–190°) as the phenylhydrazone of pyruvic acid. A mixture of the two showed no depression.

On pyrolysis of ergotamine and under conditions which with ergotinine gave isobutyryl formamide without difficulty, none of the latter substance was obtained from ergotamine. Other crystalline substances, however, were found in the sublimate which are now under investigation.

It is suggested that while ergotinine and ergotoxine are derivatives of lysergic acid, isobutyryl formic acid, proline and phenylalanine, in ergotamine and therefore ergotaminine isobutyryl formic acid is replaced by pyruvic acid.

Lysergic acid has probably a biogenetic relationship to tryptophane and isobutyryl formic and pyruvic acids to valine (hydroxyvaline?) and alanine (serine?), respectively.

We are attempting to confirm these findings by further investigations.

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[2] This is in agreement with the isolation of ergine from this alkaloid by Smith and Timmis (*Jour. Chem. Soc.*, 1932: 1543).

ASCORBIC ACID (VITAMIN C) AND PHOTOGRAPHIC DEVELOPING ACTION

UNTIL recently, knowledge of the chemistry of vitamin C was limited to assumptions drawn from the behavior of antiscorbutic concentrates. The experiments of the early investigators were reviewed by McCollum and Simmonds[1] in 1929 and by Sherman and Smith[2] in 1931. The evidence indicated that vitamin C was a reducing substance which was highly susceptible to oxidation in alkaline solution but comparatively stable in acid and which gave some of the reactions of polyphenols.

These properties so strongly reminded me of the photographic developing agents that, in 1931, I prepared an antiscorbutic concentrate from decitrated lemon juice, made it alkaline and tested it for developing action. It produced faint blackening on light-struck photographic emulsion. Thus encouraged, I reversed the procedure, testing numerous developing agents for antiscorbutic action. Needless to say, this attempted short cut to the identification of vitamin C was unsuccessful; still the developing action of the lemon juice concentrate remained to be explained. Following the recent isolation and synthesis of vitamin C (*l*-ascorbic acid),[3] I have employed the commercial product in a resumption of the photographic experiments.

Ascorbic acid, dissolved in water with sodium sulphite (preservative) and sodium carbonate (accelerator) in the usual proportions of a developing solution, is a rapid developer which produces a black image and considerable fog. It is unusually sensitive to bromide (restrainer). As little as 20 mgm of potassium bromide per liter of solution markedly restrains fog, considerably slows development, requires longer exposure and changes the color of the image from black to brown. The developing action is illustrated by experiments with Formula 1, prepared by dissolving the chemicals in the order indicated. This solution, in a stoppered bottle, remains usable for about a week.

[1] E. V. McCollum and N. Simmonds, "The Newer Knowledge of Nutrition," 4th ed., New York, Macmillan, 1929.

[2] H. C. Sherman and S. L. Smith, "The Vitamins," 2nd ed., New York, Chemical Catalog Company, 1931.

[3] L. J. Harris, *Ann. Rev. Biochem.*, 3: 264, 1934.

FORMULA 1 (FOR REDDISH BROWN TONES)

Distilled water	1000.0 cc
Sodium sulphite, anhydrous	12.5 gm
Sodium carbonate, anhydrous	12.5 "
Potassium bromide	0.1 "
l-Ascorbic acid	5.0 "

Prints of a landscape were made on representative "chloro-bromide" papers (Noko, Azo and Velox) and on one bromide paper (Eastman P.M.C.). The relative sensitivities of these emulsions, based on development in ordinary developers, were no guide to the exposures required of prints to be developed in vitamin C. Noko No. 0, the slowest of the papers, required twice its usual exposure. It gave prints with reddish black shadows and pinkish highlights. Azo No. 2, a slightly more sensitive paper, required 10 times its normal exposure. It gave copper-colored prints of good quality. Velox No. 2, a still more sensitive paper, required about 6 times its normal exposure. It gave brown prints of mediocre quality. The highly sensitive bromide emulsion of P.M.C. No. 2 developed so slowly, in spite of relatively long exposures, that chemical fog ruined the prints before density could be built up. The optimal period of development for each emulsion was 7 minutes at 23°. Fog became noticeable in 8 minutes, serious in 15 minutes. There was no stain. The images appeared orange or light brown when wet and darkened to their final color on drying.

In Formula 2, I replaced the sodium carbonate of Formula 1 by a stronger alkali, trisodium phosphate, and increased the amount of bromide. This solution should be used within one or two days.

FORMULA 2 (FOR BROWNISH BLACK TONES)

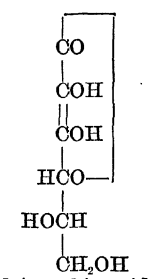
Distilled water	1000.0 cc
Sodium sulphite, anhydrous	12.5 gm
Trisodium phosphate, hydrous	40.0 "
Potassium bromide	0.5 "
l-Ascorbic acid	5.0 "

Prints were made on Azo No. 2 paper. The required exposure was 3 times the normal. The optimal period of development was 3 minutes at 23°; the fog limit, 4 minutes. There was no stain. In fresh solution the images were brownish black, of good quality. Older solutions gave increasingly brown tones.

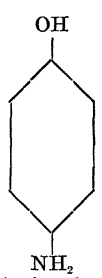
That the (photographic) reduction potential of vitamin C is low in comparison with other developers is indicated by the sensitiveness of ascorbic acid to the restraining action of bromide.[4] This low reducing energy and a comparatively high fogging power are doubtless related to the anomalous properties which Green[5] observed in his study of the potentials of this reversibly oxidizable substance.

The developing action of ascorbic acid is a fact of importance in the theory which relates developing function to molecular configuration. It should be recalled that not all reducing agents are developing agents. While innumerable organic compounds, including vitamin C, reduce silver nitrate, only a few have the power to reduce the latent image in silver halide emulsions. The classical studies of A. and L. Lumière[6,7] on the *fonction développatrice* showed that this special reducing ability is confined, except for a few inorganic substances, to benzene derivatives in which there are two hydroxyl or two amino, or one hydroxyl and one amino groups, in the ortho or para positions. A partial exception is found in some naphthalene compounds, but in general the Lumière rule has held for over 40 years.

Ascorbic acid, a sugar derivative, is an outstanding exception, as is shown by its formula in comparison with that of a typical developer within the rule. In all probability, it is but one of a series of exceptions.



l-Ascorbic acid



p-Aminophenol

Those who are interested in the chemistry of photography will want to investigate the developing action of the analogues, homologues and derivatives of ascorbic acid and the related reductones, especially since a considerable number of such compounds have been described in recent months.[3,8]

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[4] A. H. Nietz, "The Theory of Development," New York, Van Nostrand, 1922.

[5] D. E. Green, *Biochem. Jour.*, 27: 1044, 1933.

[6] A. Lumière and L. Lumière, *Bull. Soc. franc. Phot.*, ser. 2, 7: 310, 1891.

[7] A. Seyewetz, "Le Négatif en Photographie," 2nd ed., Paris, Doin, 1923.

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