

other rare earth on the column as the material is eluted. It was also noted that in the cases tested the pH of the solution which comes from the column varies with the rare earth being eluted and differs by about 0.05 of a pH unit for adjacent rare earths. With binary mixtures of 50–50% neodymium–praseodymium and neodymium–samarium, it has been found possible to recover from 60 to 90% of each of the rare earths in such purity that the other rare earths could not be detected spectrophotometrically in these fractions.

Work is being continued and the details of this process will be presented in a paper soon to be submitted for publication.

CONTRIBUTION No. 29  
FROM THE INSTITUTE FOR  
ATOMIC RESEARCH AND  
THE DEPARTMENT OF  
CHEMISTRY, IOWA  
STATE COLLEGE  
AMES, IOWA

F. H. SPEDDING  
E. I. FULMER  
BUELL AYERS  
T. A. BUTLER  
JACK POWELL  
A. D. TRVEBAUGH  
ROBERT THOMPSON

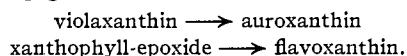
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#### LEAF XANTHOPHYLLS

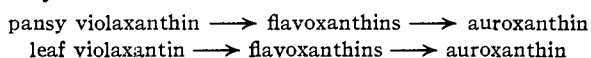
Sir:

Recently, a violaxanthin-like xanthophyll called xanthophyll-epoxide has been reported as a new leaf pigment.<sup>1</sup> However, earlier observations indicate that this leaf xanthophyll is spectroscopically identical with violaxanthin, obtained originally from pansies (*Viola*).<sup>2</sup> Moreover, leaf violaxanthin and pansy violaxanthin are chromatographically identical in Tswett columns of magnesia or of sugar.<sup>3</sup>

Karrer and co-workers also claim that, in spite of other similarities, violaxanthin and leaf violaxanthin (their xanthophyll-epoxide) yield different pigments when treated with acids<sup>1</sup>



By contrast, I have found violaxanthin from the two sources to react with acids in the following way



Obviously, pansy violaxanthin and leaf violaxanthin are identical with respect to their reaction with acids. This xanthophyll, whether obtained from pansies or from leaves, should, therefore, be called violaxanthin, not xanthophyll-epoxide.

In spite of Karrer's assertions to the contrary,<sup>1</sup> numerous experiments confirm the complexity of the leaf pigment mixture. The leaves of some fifty plants, ranging from ferns to angiosperms, have yielded the following pigments: chlorophylls a and b (with traces of chlorophylls a' and b'), neoxanthin, zeaxanthin, violaxanthin,

(1) Karrer, Krause-Voith and Steinlin, *Helv. Chim. Acta*, **31**, 113 (1948).

(2) Kuhn, Winterstein and Lederer, *Z. physiol. Chem.*, **197**, 141 (1931).

(3) Strain, Manning and Hardin, *Biol. Bull.*, **86**, 169 (1944).

lutein, cryptoxanthin-like pigments and  $\beta$ -carotene =  $\alpha$ -carotene. In leaves of eleven species of cycads representing six genera, taraxanthin, identical with taraxanthin from dandelions, accompanies the pigments just enumerated. In most of these plants, lutein is the principal xanthophyll, violaxanthin is slightly less abundant, neoxanthin occurs in small amounts, and zeaxanthin and the cryptoxanthin-like pigments are present in very small proportions. Traces of flavoxanthins are sometimes found in the leaf extracts.

When the pigments of fresh leaves are extracted with methanol or acetone, transferred to petroleum ether, adsorbed in columns of powdered sugar, and washed with petroleum ether containing 0.5% propanol, the following sequence of adsorbed pigments is obtained: neoxanthin, violaxanthin, (flavoxanthins), chlorophyll b, (taraxanthin), lutein plus zeaxanthin<sup>4</sup> plus chlorophyll b', chlorophyll a, chlorophyll a', cryptoxanthin-like pigments and the non-adsorbed carotenes.

1,2-Dichloroethane, formerly employed for the resolution of leaf xanthophylls by adsorption,<sup>5</sup> decomposes easily, especially in the presence of moisture, yielding hydrochloric acid. Unless special precautions are observed, the action of this acid on the leaf xanthophylls dissolved in dichloroethane may decrease the amount of violaxanthin and increase the amounts of flavoxanthins and isolutein.<sup>5</sup>

All these facts confirm the identity of violaxanthin from leaves and from pansies. They indicate that flavoxanthins can be converted into auroxanthin. They illustrate the complexity and the lability of the leaf xanthophylls. They point to precautions to be observed in the handling of leaf xanthophylls, and they illustrate problems in nomenclature arising from the use of different names for a single substance.

(4) Strain, *This Journal*, **70**, 588 (1948).

(5) Strain, "Leaf Xanthophylls," Carnegie Inst. Wash., Publ. 490, Washington 1938.

CARNEGIE INSTITUTION OF WASHINGTON  
DIVISION OF PLANT BIOLOGY  
STANFORD, CALIFORNIA

HAROLD H. STRAIN

RECEIVED MARCH 29, 1948

#### A SYNTHESIS OF STREPTIDINE

Sir:

There has been reported<sup>1</sup> the synthesis of hexaacetylstreptamine from D-glucosamine by a method which establishes its configuration, and that of streptidine, as all-*trans*. We wish to record herein the conversion of hexaacetylstreptamine to streptidine sulfate monohydrate, thus completing the synthesis of the latter from D-glucosamine. Hexaacetylstreptamine was saponified with aqueous sodium hydroxide under reflux and the product was crystallized as the sulfate. The

(1) M. L. Wolfrom and S. M. Olin, *Abstracts of Papers*, 113th Meeting, Am. Chem. Soc., Chicago, Illinois, April 19–23, p. 5Q (1948).

resultant streptomycin sulfate<sup>2-4</sup> was characterized by its X-ray powder diffraction diagram, which was identical with that of an authentic specimen obtained from streptomycin. Streptomycin sulfate was treated with the stoichiometric amount of barium hydroxide and the resultant aqueous solution of the free base was heated at 70–80° for forty-eight hours with an equivalent amount (added in portions) of S-methylthiopseudourea sulfate.<sup>5</sup> A crystalline reaction product was ob-

(2) H. E. Carter, R. K. Clark, Jr., S. R. Dickman, Y. H. Loo, J. S. Meek, P. S. Skell, W. A. Strong, J. T. Alberi, Q. R. Bartz, S. B. Binkley, H. M. Crooks, Jr., I. R. Hooper and M. C. Rebstock, *Science*, **103**, 53 (1946).

(3) J. Fried, G. A. Boyack and O. Wintersteiner, *J. Biol. Chem.*, **162**, 391 (1946).

(4) R. L. Peck, C. E. Hoffhine, Jr., Elizabeth W. Peel, R. P. Graber, F. W. Holly, R. Mozingo and K. Folkers, *THIS JOURNAL*, **66**, 776 (1946).

(5) B. Rathke, *Ber.*, **14**, 1774 (1881); R. Phillips and H. T. Clarke, *THIS JOURNAL*, **45**, 1755 (1923).

tained which, when triturated with dilute ammonium hydroxide, yielded streptidine sulfate monohydrate,<sup>2,3,6,7</sup> identified by its X-ray powder diffraction diagram,<sup>8</sup> nitrogen analysis (calcd., 22.2%; found, 22.1) and octaacetyl derivative<sup>7</sup> (m. p. 259–261°, unchanged on admixture with an authentic specimen prepared from streptomycin).

DEPARTMENT OF CHEMISTRY  
THE OHIO STATE UNIVERSITY  
COLUMBUS, OHIO

M. L. WOLFROM  
W. J. POLGLASE<sup>9</sup>

RECEIVED MARCH 19, 1948

(6) N. G. Brink, F. A. Kuehl, Jr., and K. Folkers, *Science*, **102**, 506 (1945).

(7) R. L. Peck, R. P. Graber, A. Walti, Elizabeth W. Peel, C. E. Hoffhine, Jr., and K. Folkers, *THIS JOURNAL*, **68**, 29 (1946).

(8) I. R. Hooper, L. H. Klemm, W. J. Polglase and M. L. Wolfrom, *ibid.*, **69**, 1052 (1947).

(9) Bristol Laboratories Research Fellow of The Ohio State University Research Foundation (Project 224).

## NEW BOOKS

**Quantitative Organische Mikroanalyse.** Fifth Austrian Edition. By F. PREGL and H. ROTH. Springer-Verlag, Vienna, 1947. 317 pp. 80 Figs. 16 × 23.5 cm. Price \$7.40 (Swiss Francs 32.--).

F. Pregl's "Die quantitative organische Mikroanalyse" has had three original editions (1st, 1916, 2nd, 1922, and 3rd, 1929). Since Pregl's death on Dec. 13, 1930, two revisions by H. Roth have appeared: the first in 1935 and the second, or present fifth edition, in 1947.

Since neither the fourth nor the present fifth edition have been previously discussed in *THIS JOURNAL*, it was thought expedient to not only examine these two revisions but also compare them with the third and last original Pregl edition. This is being done in the table given herewith.

TABLE I

Chapters	Number of pages		
	3rd edition	4th edition	5th edition
Balances	14	16	14
Methods of elementary analysis	175	164	175
Carbon and hydrogen	69	66	59
Oxygen	...	...	11
Nitrogen (Dumas)	30	20	20
Nitrogen (Kjeldahl)	11	8	7
Halogen	21	28	25
Sulfur	15	12	19
Miscellaneous	28	26	28
Methods of structure analysis	29	86	78
Molecular weight determinations	15	24	16
Determ. of physical constants	2	25	20
Total	256	328	317

As can be seen from the table, the two revisions differ from the last and original Pregl edition chiefly by an enlargement in the structure analytical section. Thus, in this field, there have been added the well-known iodometric determination of O-, S- and N-alkyls by F. Vie-

boeck and C. Brecher and three methods by R. Kuhn and co-workers, such as a gasometric determination of active hydrogen, an oxidation procedure (acetic acid) and a method of ozonolysis (acetone). In the field of elementary analysis the additions involve iodometric methods for the determination of oxygen (J. Unterzaucher) and of sulfur (W. Zimmermann), a hydrogenation method for nitrogen (A. Lacourt) and an alkalimetric determination for chlorine and bromine (M. K. Zacherl).

The fifth edition differs from the fourth by the iodometric methods for the determination of oxygen (1940) and sulfur (1943) and the determination of nitrogen by hydrogenation (1940) cited above. On the other hand, the chapter on molecular weight determinations has been weakened by the omission of any and all ebullioscopic methods. The literature references are incomplete and none goes beyond 1943. There is no author index, nor does the book contain any log or nitrogen reduction tables. Use of ordinary balances in quantitative organic microanalysis is not mentioned.

In view of the foregoing, which at the same time might also be regarded as an indication of the progress of organic microchemistry in Central Europe for the last twelve years, the present edition appears to be rather a "Second Printing" of the fourth edition, or first revision. The bypassing of Pregl's original and still active laboratory at the University of Graz, Austria, his successor and original co-workers as co-authors appears inexcusable and is most unfortunate.

JOSEPH B. NIEDERL

**Violin Varnish.** A Plausible Re-creation of the Varnish Used by the Italian Violin Makers between the Years 1550 and 1750, A. D. By JOSEPH MICHELMAN. Published by Joseph Michelman, 5050 Oberlin Boulevard, Cincinnati, Ohio, 1946. 185 pp. 14 × 21 cm. Price, \$3.75.

The question of the varnishes used by the great Italian violin makers of the mid-sixteenth to the mid-eighteenth centuries has always provoked great curiosity and specula-