trated ammonium hydroxide. The bomb is then closed and heated at 107–109° for twelve hours, cooled, and the reaction mixture transferred to a desiccator and evaporated. The non-volatile product, 21.2 g., m. p. 114–122°, contains 80.5% of nicotinamide,[6] the remainder being nicotinic acid.[7] The yield of amide is 72.66%. After two recrystallizations from ethyl acetate, the amide melts at 129–130°, and the mixed melting point with pure nicotinamide shows no depression.

Anal. Calcd. for $C_6H_6ON_2$: C, 59.01; H, 4.95; N, 22.94. Found:[8] C, 58.97, 59.06; H, 4.9, 5.11; N, 22.80, 22.82.

The amide may, however, be extracted directly in the reaction mixture in very pure condition by ethyl acetate. Using this procedure, we have obtained a product containing 98.93% of amide and melting at 129–130°.

Addition of sodium hydroxide to the reaction mixture results in markedly speeding up the reaction, with an increased production of nicotinic acid and a corresponding decrease in the yield of amide.

Hydrogen peroxide (3.5 moles in 30% solution) added to the ammonium hydroxide (2 moles) and nitrile (1 mole) shortens the reaction time and gives increased yields (94 and 96%). The product, however, contains more nicotinic acid and melts over a wide range of temperature.

Hydrogen peroxide (3.5 moles in 30% solution), sodium hydroxide (0.3 mole), and the nitrile (1 mole) heated for six hours at 50° gives yields of 89 and 93%. The product is discolored and is less easily purified than the product obtained by the use of ammonia alone.

The observation that ammonium hydroxide may hydrolyze nitriles to the corresponding amide without the use of hydrogen peroxide may make it possible to obtain amides from nitriles oxidized or polymerized by the peroxide.

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(6) C. F. Krewson, *Am. J. Pharm.*, **115**, 122–125 (1943).

(7) The evaporation of solutions of nicotinic acid in ammonia results in dissociation of any ammonium nicotinate present and leaves a residue of nicotinic acid free from ammonia.

(8) C and H determined by D. M. Mortimore; N by C. L. Ogg.

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The Stereochemistry of Coördination Number Eight. Isomers for the Trigonal Prism with Symmetry C_2^v

BY LOUIS E. MARCHI

In a previous paper[1] four likely configurations for compounds of elements exhibiting coördination number eight were considered. In the light of one referee's comments about the radius ratio the trigonal prism considered in that paper seems to be a very unlikely configuration for coördination number eight.[2] The trigonal prism with two extra bonds along the normals to two of the rectangular faces and with symmetry C_2^v, Fig. 1, previously suggested by Hoard and Nordsieck, and Kimball,[3] is now considered.

The possible isomers for all classes containing only monodentate groups are given in Table I.

For the bidentate groups the same restrictions were imposed as with the other configurations. The isomer numbers for the limited number of classes containing bidentate groups, which were considered, are given in Table II. (The classes 2AB 4C, 3AB 2C and 4AB have not been considered because a preliminary study of these classes has shown that the isomer count is probably greater than for the corresponding classes in the other configurations).

TABLE I

ISOMERS FOR MONODENTATE GROUPS

	Configuration, *T*	Optically active	Optically inactive	Total
8a	M	0	1	1
7ab	M	2	2	4
6a2b	M	12	4	16
6abc	M	26	2	28
5a3b	M	22	6	28
5a2bc		78	6	84
5abcd		168	0	168
4a4b	M	32	6	38
4a3bc		134	6	140
4a2b2c		204	12	216
4a2bcd		414	6	420
4abcde		840	0	840
3a3b2c		268	12	280
3a2bcd		560	0	560
3a2b3cd		828	12	840
3a2bcde		1,680	0	1,680
3abcdef		3,360	0	3,360
2a2b2c2d		1,252	22	1,274
2a2b2cde		2,508	12	2,520
2a2bcdef		5,040	0	5,040
2abcdefg		10,080	0	10,080
abcdefgh		20,160	0	20,160

M indicates that the isomer count was also determined by the construction of models and it was found in agreement with the number obtained by the use of Lunn and Senior's method.[4]

TABLE II

SPECIAL CLASSES OF BIDENTATE GROUPS

AA6b	6	3	9
AB6c	16	1	17
2AA4b	38	6	42
3AA2b	50	5	55
4AA	10	1	11

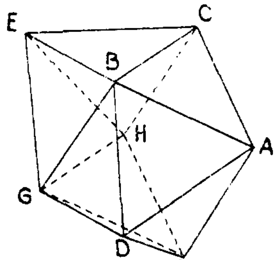

Fig. 1.—The trigonal prism is outlined by ABCFGH; D and E are the two extra bonds.

It is apparent that the number of isomers for class 4AA of this trigonal prism and of the dodecahedron, is exactly the same. Consequently

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(1) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, THIS JOURNAL, **65**, 329 (1943).

(2) L. E. Marchi, W. C. Fernelius and J. P. McReynolds, *ibid.*, ref. 5 d.

(3) Marchi, Fernelius and McReynolds, *ibid.*, ref. 5.

(4) Lunn and Senior, *J. Phys. Chem.*, **33**, 1027 (1929).

the conclusions arrived at for the resolution of the $[\mathrm{Co(C_2O_4)_3}]$[6] ion must be altered to include this trigonal prism as well. It is obvious also that it is not possible to distinguish between these two configurations on the basis of chemical methods alone.

(6) Marsh and McReynolds, This Journal, **65**, 333 (1943).

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[Contribution from the Carnegie Institution of Washington, Division of Plant Biology]

A Unique Polyene Pigment of the Marine Diatom *Navicula Torquatum*

By Harold H. Strain and Winston M. Manning

Among the pigments of the colonial pennate diatom *Navicula torquatum*, we have discovered a hitherto undescribed, yellow, polyene compound. This new pigment exhibits properties characteristic of the polyene hydrocarbons or carotenes. Isomerization reactions of this pigment indicate that its chromophoric polyene group occurs in the stable or *trans* form. Its spectral absorption properties resemble those of the violaxanthins and of neoxanthin[1]; hence, all these compounds probably contain similar chromophoric structures.

In *Navicula torquatum*, this new carotenoid comprises about one-fourth to one-third of the total carotenes. It was not found in several other diatoms nor in brown algae.

Experimental

Filamentous masses of the diatom *Navicula torquatum* were collected near Half Moon Bay, California, where they were found growing epiphytically on several species of large brown algae, the common kelps of the Pacific Coast. Pigments extracted from the diatoms with alcohol were transferred to petroleum ether and adsorbed upon a column prepared from a mixture of equal parts of Micron Brand magnesium oxide No. 2641 and heat-treated siliceous earth (Filter Aid 501).[1,2] Under these conditions, the new carotenoid formed a lemon-yellow band below the orange band of β-carotene. Between these two pigment zones there appeared a small yellow zone containing an isomer of the new carotenoid. Concentration of the elutriate from the lowest yellow band yielded golden-orange crystals of the new pigment.

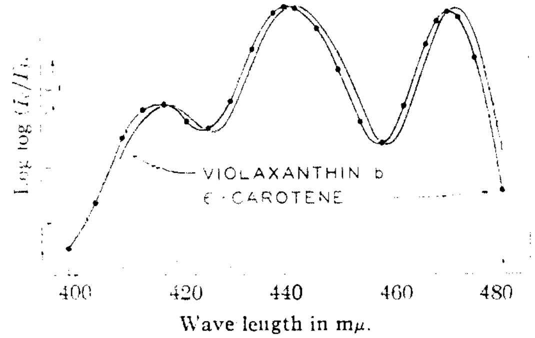

Fig. 1.—Characteristic spectral absorption curve of ε-carotene compared with that of violaxanthin b from leaves[1]; solvent, 95% ethanol.

The pigment from *Navicula* exhibited color reactions typical of polyene compounds. Crystals of this substance were turned deep blue by concentrated sulfuric acid. This acid removed the pigment from solution in chloroform and the acid layer became blue. A solution of the pigment in chloroform was also turned blue by antimony trichloride.

In respect to its solubility, adsorbability and chemical reactions, the pigment from *Navicula* behaved like a polyene hydrocarbon or carotene rather than like an ester or ether of a xanthophyll. It was but slightly soluble in methanol, yielding a pale yellow solution. It was more soluble in ethanol and quite soluble in ether and petroleum ether. Upon partition between petroleum ether and 95% methanol all but traces of the pigment dissolved in the petroleum ether layer. Treatment of the pigment with alcoholic potassium hydroxide did not alter its spectral properties, adsorbability or solubility. An ether solution of the pigment yielded no trace of blue color when treated for a week with an equal volume of concentrated hydrochloric acid. Mixed with α-carotene and adsorbed upon a column of magnesia from solution in petroleum ether, the polyene from *Navicula* formed the lower or least adsorbed band. It moved through the column about three times as fast as the α-carotene. This new pigment was not extractable from solution in petroleum ether with 85% phosphoric acid,[3] whereas all the xanthophylls and xanthophyll esters which were available for examination and which included cryptoxanthin and its *p*-nitrobenzoate were partially or wholly extractable.

When heated in *n*-propanol at 100° for three hours or when treated with iodine dissolved in petroleum ether containing pyridine, the new carotenoid yielded small quantities of a more adsorbed pigment. This product resembled the second yellow pigment observed in the extracts of the diatom. Spectral absorption curves of these pigment preparations exhibited maxima and minima which were less pronounced than those of the unheated pigment and which occurred about 5 mμ nearer the violet region of the spectrum. All these facts indicate that the new carotenoid is the stable isomer of a polyene hydrocarbon, probably a carotene, for which we suggest the provisional name ε-carotene.

When dissolved in the same solvents, the *Navicula* carotenoid exhibited spectral absorption maxima at wave lengths almost identical with those reported for violaxanthin b.[1, p. 73] Characteristic spectral absorption curves of these two pigments in ethanol, Fig. 1, are nearly identical in shape. They are also nearly identical in shape with the curve reported for neoxanthin,[1] although the latter is shifted about 4 mμ toward the violet region of the spectrum.

This unusual coincidence in shape of absorption curves which have absorption maxima at different wave lengths appears to be the exception rather than the rule among polyene compounds.[4] It has prompted us to compare the spectral absorption curves of the flavoxanthins of leaves[1] with the spectral curve of a "flavoxanthin-like" polyene pigment of carrots. To this end, the "flavoxanthin-like carotene," provisionally called ζ-carotene, was again prepared from carrots,[5] and its spectral absorption curve was determined in ethanol. Maxima and minima occurred at wave lengths about 22.5 mμ nearer the violet region of the spectrum than those of the flavoxanthins from leaves; yet the shapes of the curves were remarkably similar. An even closer correspondence in shape between the two curves was

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(1) H. H. Strain, "Leaf Xanthophylls," Carnegie Institution of Washington Publication No. 490, 1938.

(2) H. H. Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, Inc., New York, N. Y., 1942.

(3) Haagen-Smit, Jeffreys and Kirchner, *Ind. Eng. Chem., Anal. Ed.*, **15**, 179 (1943).

(4) Hausser, *Z. tech. Physik*, **15**, 10 (1934).

(5) Strain, *J. Biol. Chem.*, **127**, 191 (1939).