The infrared spectrum of the isolated pigment exhibited bands at 3450 (hydroxyl) and 1662 cm.$^{-1}$ (conjugated carbonyl). The visible spectrum (Figure 1) of reticulataxanthin indicated a decaenone chromophore similar to that of capsanthin (IV)[3-5] and citranaxanthin (V).[6]

The n.m.r. spectrum revealed a singlet at τ 7.72 which can be assigned to an end-of-chain methyl group α to a carbonyl group. Additionally, no signal could be detected in the τ 0.3–0.6 region characteristic of aldehydic protons with α,β-unsaturation.[7] The doublet at τ 2.50 (J = 16 c.p.s.) indicated that the double bond to which the vinyl proton β to the carbonyl is attached has the *trans* configuration.[8,9]

On treatment with aqueous alcoholic potassium hydroxide reticulataxanthin underwent a retroaldol cleavage to yield acetone and a compound identical with β-citraurin (III).[10,11]

On the basis of results described above, reticulataxanthin can be represented by structure II, but not I. This compound is a 3-hydroxy derivative of citranaxanthin.

Experimental[12,13]

Isolation of Reticulataxanthin.—The fruit of *Minneola tangor* was collected in Riverside, Calif., in Feb. 1964, when in the most highly pigmented stage. The peel (7 kg.) was separated from the endocarp and extracted with methanol. The methanol extract, covered with nitrogen, was then saponified overnight at room temperature. The nonsaponifiable mixture was transferred to ether, washed free of alkali, and evaporated to dryness *in vacuo*. The residue was taken up in methanol, and the pigment mixture was partitioned between 99% methanol and petroleum ether (b.p. 30–60°). Chromatography of the hypophase on a column of magnesium oxide–Hyflo Supercel (1:2 w./w.) isolated the ketone. Crystallization from peroxide-free ether–petroleum ether afforded 160 mg. of the pure ketone: m.p. 171–172°; infrared bands at 3450 (hydroxyl), 1662 (conjugated carbonyl), 1550, 1440, 1380, 1260, 1180, 1020, 970, 890, and 822 cm.$^{-1}$; λ_{max} in petroleum ether 463 and 490 mμ; n.m.r. signals[14] at τ 2.50 (J = 16 c.p.s.), 7.72, 8.02 (in-chain olefinic methyl group), 8.25 (methyl group on C=C in the cyclohexene ring), and 8.92 (*gem*-dimethyl group).

Anal. Calcd. for $C_{33}H_{44}O_2$: C, 83.82; H, 9.41. Found: C, 83.6; H, 9.45.

The oxime, prepared in the usual manner, had m.p. 202–203°. The substance was identical by chromatographic (on both magnesium oxide and deactivated alumina) and visible spectral criteria with reticulataxanthin kindly furnished by Dr. A. L. Curl.

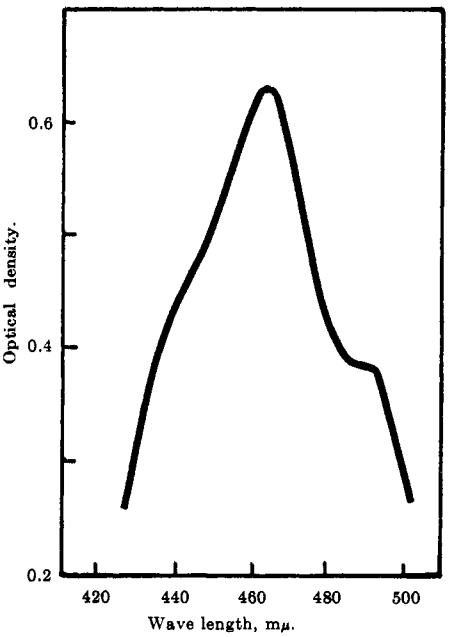

Figure 1.—Visible spectrum of reticulataxanthin in petroleum ether.

Alkali Cleavage of Reticulataxanthin.—A solution of 50 mg. of reticulataxanthin in 10 ml. of ethanol and 0.5 ml. of 1 N potassium hydroxide was heated at 55–65° with vigorous stirring in a stream of nitrogen for 20 min., and the distillate was collected in a receiver containing a solution of 2,4-dinitrophenylhydrazine in ethanol. The precipitate was recrystallized from ethanol to yield the 2,4-dinitrophenylhydrazone of acetone, m.p. 125–126° (melting point of an authentic sample 125°). Admixture of authentic sample did not depress the melting point.

The nonvolatile portion was extracted from the reaction mixture with peroxide-free ether and chromatographed on a column of magnesium oxide–Hyflo Supercel (1:2 w./w.). Pure β-citraurin (III) was isolated and crystallized from peroxide-free ether and petroleum ether, m.p. 145–146° (lit.[9] m.p. 147°). The oxime had m.p. 188–189° (lit.[10] m.p. 188°). Only about 0.1 mg. of β-citraurin, isolated from tangerine peel, was available for comparison. By chromatographic and visible spectral criteria the nonvolatile product obtained from the retroaldol cleavage of reticulataxanthin was identical with natural β-citraurin.

Acknowledgment.—The authors are grateful to Dr. David Dreyer of this laboratory for his helpful discussion and assistance in the n.m.r. analysis and to Dr. Walter Reuther and Mr. Ed Nauer of the University of California at Riverside for the fruit collections.

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(12) All melting point determinations were carried out in evacuated capillary tubes on a Electrothermal melting point apparatus and are uncorrected. Visible spectra were measured with a Cary Model 14 spectrophotometer. Infrared spectra were recorded in KBr disks on Perkin-Elmer Models 137 and 521 spectrophotometers. The n.m.r. spectra were determined in carbon tetrachloride–deuteriochloroform on a Varian A-60 n.m.r. spectrometer with tetramethylsilane as an internal standard. Analyses were provided by L. M. White.
(13) Use of trade names of specific materials or equipment does not constitute a recommendation by the U. S. Department of Agriculture to the exclusion of others which may also be suitable.
(14) Relative areas of n.m.r. peaks were consistent with assignments.

Formation of N-Methyl from Reduction of the N-Carbobenzoxy Group with Lithium Aluminum Hydride[1]

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It was anticipated that the $LiAlH_4$ reduction of the N-carbobenzoxy group, which consists of an adjacent

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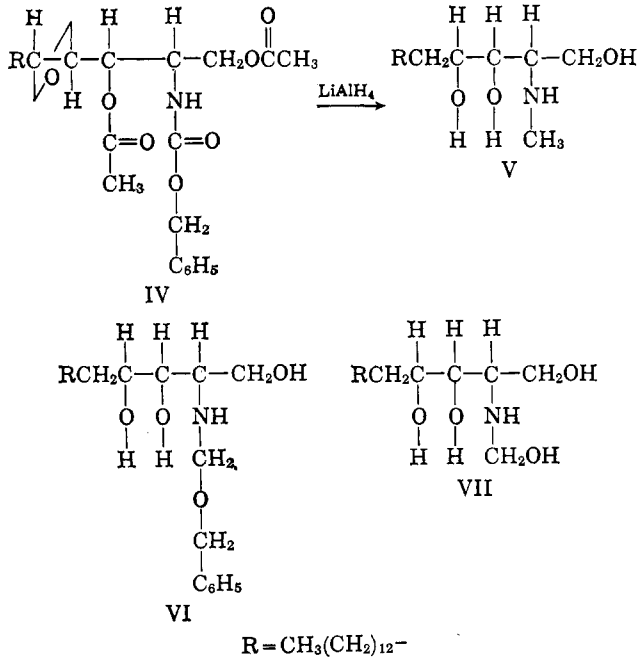

Figure 1.—The reduction of 4,5-*trans*-epoxy-1,3-diacetyl-N-carbobenzoxysphingosine (IV) with $LiAlH_4$ yields 1,3,4-trihydroxy-2-methylaminooctadecane (V); only the *erythro* diastereoisomer is shown. The anticipated N-substituents from the reduction of the carbobenzoxy group are represented in VI and VII. See text for details.

amide–ester, would give rise to the N-benzyloxymethyl group (Figure 1, VI) or N-methylol group (Figure 1, VII), or a mixture of these substituents. However, after treatment with $LiAlH_4$ of 4,5-*trans*-epoxy-1,3-diacetyl-N-carbobenzoxysphingosine (Figure 1, IV), an intermediate prepared during the chemical synthesis of phytosphingosine from sphingosine,[2] the N-carbobenzoxy group was reduced to N-methyl (Figure 1, V), and the epoxide ring was opened exclusively at the least substituted carbon atom (C-5) to give the more highly substituted alcohol.[3] Although each of the diastereoisomers of 1,3,4-trihydroxy-2-methylaminooctadecane gave a positive ninhydrin reaction, a test characteristic for primary amines, the presence of the N-methyl substituent was confirmed by N-methyl, active hydrogen, and oxygen determinations. Similarly, the $LiAlH_4$ reduction of N-carbobenzoxysphingosine yielded the corresponding N-methyl compound which, also, gave a positive ninhydrin test. After hydrogenation of this compound to the dihydro form, the test was negative. Additional proof that the secondary amine gave a positive ninhydrin reaction was provided by N-ethylsphingosine which was prepared by the $LiAlH_4$ reduction of triacetylsphingosine. This compound, too, gave a negative ninhydrin test after hydrogenation to the dihydro derivative. The hydride reduction of the N-carbobenzoxy group may be of value in the preparation of monomethylamines in those instances where other functional groups in the molecule are not affected by the reductant.

Experimental

N-Methylsphingosine (I).—To 2.0 g. of N-carbobenzoxysphingosine, prepared as previously described,[4] in 50 ml. of cold dry ether was added 700 mg. of $LiAlH_4$. After the initial reaction subsided, the mixture was refluxed 4 hr. and then was treated successively with 50 ml. of methanol, 100 ml. of 2.5 *N* NaOH, and with three 150-ml. portions of ether–ethyl acetate (1:1). The combined organic layers were washed with water until neutral, filtered, and concentrated. The dried residue was crystallized from petroleum ether (b.p. 60–70°); m.p. 62–65°; yield 1.1 g.; ninhydrin reaction in 95% ethanol, positive; λ_{max} 570 mμ.

Anal. Calcd. for $C_{19}H_{39}NO_2$ (313.3): C, 72.77; H, 12.55; O, 10.22; NCH_3, 9.27; active H, 0.97. Found: C, 72.47; H, 12.66; O, 10.12; NCH_3, 9.02; active H, 0.93.

The infrared absorption bands in chloroform are 3450 (m), 3000 (s), 1470 (s), 1235 (m), 1098 (w), 1055 (s), and 980 cm.$^{-1}$ (m).

N-Methyldihydrosphingosine (II).—Compound I, 500 mg., was reduced over 100 mg. of platinum oxide in 200 ml. of ethanol at room temperature until the uptake of hydrogen ceased. The reaction mixture was filtered and the filtrate, after the addition of an equal volume of water and 1 ml. of 5 *N* NaOH, was treated with several portions of ether. The combined and washed ether layers were concentrated and the dried residue was crystallized from petroleum ether (b.p. 60–70°); m.p. 79–81°; yield 460 mg.; ninhydrin reaction, negative.

Anal. Calcd. for $C_{19}H_{41}NO_2$ (315.3): C, 72.31; H, 13.11; active H, 0.96. Found: C, 72.19; H, 13.22; active H, 1.02.

The infrared absorption bands in chloroform are 3400 (m), 2950 (s), 1470 (s), 1210 (m), and 1050 cm.$^{-1}$(s).

N-Ethylsphingosine (III).—Triacetylsphingosine was prepared according to the procedure of Carter, *et al.*[5]; 2.0 g. of the derivative was treated with 500 mg. of $LiAlH_4$. The conditions of the reaction and the isolation and crystallization of the product were conducted in the same manner as that described for the preparation of compound I; m.p. 51–53°; yield 0.96 g.; ninhydrin reaction, positive; λ_{max} 570 mμ.

Anal. Calcd. for $C_{20}H_{41}NO_2$ (327.3); C, 73.33; H, 12.63. Found: C, 73.23; H, 12.57.

N-Ethyldihydrosphingosine.—Compound III, 200 mg., was reduced, and the product was isolated and crystallized in the same manner as that described for the preparation of compound II; m.p. 66–68°; yield 186 mg.; ninhydrin reaction, negative.

Anal. Calcd. for $C_{20}H_{43}NO_2$ (329.3): C, 72.88; H, 13.16. Found: C, 72.80; H, 13.11.

4,5-*trans*-Epoxy-1,3-diacetyl-N-carbobenzoxysphingosine (IV).—To 5.2 g. of 1,3-diacetyl-N-carbobenzoxysphingosine, prepared by the reaction of N-carbobenzoxysphingosine with acetic anhydride in pyridine,[6] in 20 ml. of chloroform was added 2.76 g. of perbenzoic acid in 100 ml. of benzene. After 24 hr. at room temperature in the dark, the reaction mixture was washed with 5% $NaHCO_3$ and with water until neutral. The solution was filtered, dried over Na_2SO_4, and concentrated. The product was crystallized from petroleum ether; m.p. 109–111°; yield 3.13 g.

Anal. Calcd. for $C_{30}H_{47}NO_7$ (533.6): C, 67.46; H, 8.88; N, 2.62. Found: C, 67.24; H, 8.85; N, 2.57.

The infrared absorption bands in chloroform are 3500 (w), 3000 (s), 1775 (s), 1520 (s), 1470 (m), 1375 (m), 1235 (s), and doublet 1055–1030 cm.$^{-1}$ (s).

***erythro*-1,3,4-Trihydroxy-2-methylaminooctadecane[7] (V).**—To compound IV, 1.0 g., in 50 ml. of cold dry ether was added 350 mg. of $LiAlH_4$. The conditions of the reaction and the isolation of the crude product were conducted in the same manner as that described for the preparation of compound I. The dried residue, after crystallization from ethanol–petroleum ether (1:20), melted at 134–136°; yield 220 mg.; ninhydrin reaction, positive; λ_{max} 575 mμ.

Anal. Calcd. for $C_{19}H_{41}NO_3$ (331.3): C, 68.81; H, 12.47; NCH_3, 8.76. Found: C, 68.47; H, 12.35; NCH_3, 8.57.

The infrared absorption bands (KBr disk) are 3470 (s), 3000 (s), 1480 (s), 1430 (m), 1355 (m), 1260 (w), 1240 (w), 1160

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(4) B. Weiss, *ibid.*, **79**, 5553 (1957).
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(6) B. Weiss, *Biochemistry*, **3**, 1288 (1964).
(7) The corresponding N-benzyl compounds, also, were resolved into their *erythro* (high melting) and *threo* (wax) forms; the former isomer yielded phytosphingosine after debenzylation over palladium. The melting point of the N-benzoyl derivative of the base agreed with that of the natural compound.[8]
(8) H. E. Carter, W. D. Celmer, W. E. M. Lands, K. L. Mueller, and H. H. Tomizawa, *J. Biol. Chem.*, **206**, 613 (1954).

(w), 1140 (w), 1125 (m), 1080 (s), 1060 (s), 1020 (w), 1010 (w), and 935 cm.$^{-1}$ (s).

A wax consisting mostly of the *threo* isomer was obtained after concentration of the ethanol–petroleum ether supernatant from the crystallization of compound V; yield 255 mg.; ninhydrin reaction, positive.

Analysis of Aldehydes.—Vapor phase chromatography[9] of the aldehydes obtained after periodate oxidation of N-methylsphingosine showed two peaks, the first at 10.25 min., hexadecanal (13% of the total aldehydes), and the second at 18.75 min., hexadecenal; the former peak arises from the presence of dihydrosphingosine in the original base preparation. N-Methyldihydrosphingosine under the same conditions gave one peak at 10.25 min. Only 1 major peak at 7.0 min., pentadecanal, was obtained from compound V; the wax from this preparation yielded a similar peak along with a minor one at 10.25 min.

The 2,4-dinitrophenylhydrazone of the aldehyde obtained from the periodate oxidation of compound V melted at 104–106°; this is in agreement with the melting point of the same derivative reported for pentadecanal.[8]

Anal. Calcd. for $C_{21}H_{34}N_4O_4$ (406.3): C, 62.03; H, 8.44. Found: C, 62.00; H, 8.30.

Acknowledgment.—The author is grateful to both Dr. Warren M. Sperry, in whose laboratory this work was done, and Dr. David Rittenberg for reading this manuscript. Thanks are due, also, to Mr. Richard L. Stiller for his competent technical assistance.

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Low-Pressure Hydrogenation of Alkoxyanilines with Noble Metal Catalysts

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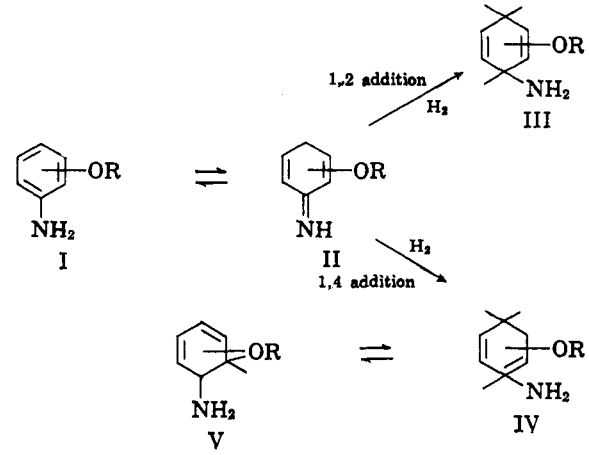
A study of the hydrogenation of nuclear-substituted anilines with ruthenium catalyst included work with some alkoxyanilines.[1] It was found that hydrogenolysis which occurred during conversion of the isomeric methoxyanilines decreased as the alkoxy group became larger. Smith and Thompson, investigating the reduction of mono-, di-, and trimethoxybenzenes, reported that temperature as well as catalyst was a factor in cleavage of the ether groups.[2]

We were interested in studying the effect of other noble metal catalysts under milder conditions than those used with ruthenium (90–100°, 70 atm.); we were particularly interested to see whether the methoxy- and ethoxycyclohexylamines could be produced in good yield.

From the results, rhodium appears to be the catalyst of choice for use under low-pressure conditions. Respectable yields of alkoxycyclohexylamines are obtained, hydrogenolysis is not extensive, and secondary amine formation, in most instances, is at a low level. Reaction time in neutral solvent is sometimes long, but when the reduction is run in the presence of an equivalent of acetic acid hydrogen uptake proceeds much more rapidly.[3] Steric effects, which are likely the cause of the longer reaction period for 2-alkoxyanilines, may also contribute to the lesser amounts of cyclohexylamine found in these reductions than in the conversion of the 4-substituted compounds. It is of interest that less cleavage is also noted when the 3-alkoxyanilines are hydrogenated.

CHART I



Hydrogenolysis probably occurs during an intermediate reduction stage.[1,2] We suggest that allyl-type ethers, which are susceptible to cleavage,[4] are formed as shown in Chart I. 1,2 addition of hydrogen to II (forming III) would yield an allyl ether only if the substituent is in the 4-position. On the other hand, 1,4 addition (forming IV) would yield an allyl ether for 3- and 4-substituted anilines, but not for 2-substituted compounds. Rearrangement of IV to V would make an allyl ether possible for even 2-substituted anilines. Since allyl-type intermediates are statistically favored with 4-alkoxy derivatives, more hydrogenolysis should result with such compounds if the proposed mechanism is correct. This is in accord with experimental findings when rhodium catalyst is used.

Palladium on carbon has some utility but also many drawbacks. No uptake of hydrogen took place in neutral solution or in alcohol containing acetic acid. Hydrogenation, however, did proceed in acetic acid solution, although considerable amounts of secondary amine were obtained and the reaction period was rather long unless a high catalyst ratio was used. Reduction with platinum oxide not only gave cyclohexylamine, but dicyclohexylamine as well as mono- and dialkoxydicyclohexylamines. The large amounts of secondary amine formation with these catalysts made it difficult to assess whether the position of the substituents had any effect on hydrogenolysis (see Table I).

Experimental[5]

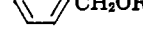
The following is an example of reduction with 5% rhodium on alumina.[6]

(1) M. Freifelder and G. R. Stone, *J. Org. Chem.*, **27**, 3568 (1962).

(2) H. A. Smith and R. G. Thompson, *Advan. Catalysis*, **9**, 727 (1957).

(3) M. Freifelder [*J. Org. Chem.*, **26**, 1835 (1961)] has reported on the promoter effect of certain acids on rhodium reductions where the end product is a strong base.

(4) Benzyl ethers, readily hydrogenolyzed catalytically to toluene and alcohols, can be viewed as allyl-type ethers.



(5) Microanalyses were carried out by Mr. O. F. Kolsto and his associates; infrared determinations were by Messrs. A. Kammer and W. Washburn.