Phytochemistry, 1977, Vol. 16, pp 729–733. Pergamon Press. Printed in England.

ABSOLUTE CONFIGURATION OF HETEROXANTHIN AND DIADINOXANTHIN*

Richard Buchecker† and Synnøve Liaaen-Jensen

Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Dedicated to Dr. Harold H. Strain

(*Received* 27 *September* 1976)

Key Word Index—Xanthophyceae; Dinophyceae; Bacillariophyceae; Haptophyceae; algal carotenoids; absolute configuration: heteroxanthin ((3*S*,5*S*,6*S*,3′*R*)-7′,8′-didehydro-5,6-dihydro-β,β-carotene-3,5,6,3′-tetrol), diadinoxanthin ((3*S*,5*R*,6*S*,3′*R*)-5,6-epoxy-7′,8′-didehydro-5,6-dihydro-β,β-carotene-3,3′-diol): *Trollius europaeus* minor carotenoids (3*S*,5*S*,6*S*,3′*S*,5′*R*,6′*R*)-6,7-didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,5,6,3′,5′-pentol and its 5*R* epimer: presumed artefacts.

Abstract—The absolute configurations of heteroxanthin ((3*S*,5*S*,6*S*,3′*R*)-7′,8′-didehydro-5,6-dihydro-β,β-carotene-3,5,3′,6′-tetrol) *ex Euglena gracilis* and of diadinoxanthin ((3*S*,5*R*,6*S*,3′*R*)-5,6-epoxy-7′,8′-didehydro-5,6-dihydro-β,β-carotene-3,3′-diol) from the same source have been established by chemical reactions, hydrogen bonding studies, ^{1}H NMR and CD. Two previously unknown carotenoids (artefacts?) from *Trollius europaeus*, assigned the structures (3*S*,5*S*,6*S*,3′*S*,5′*R*,6′*R*)-6,7-didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,5,6,3′,5′-pentol and its 5*R* epimer, served as useful models.

INTRODUCTION

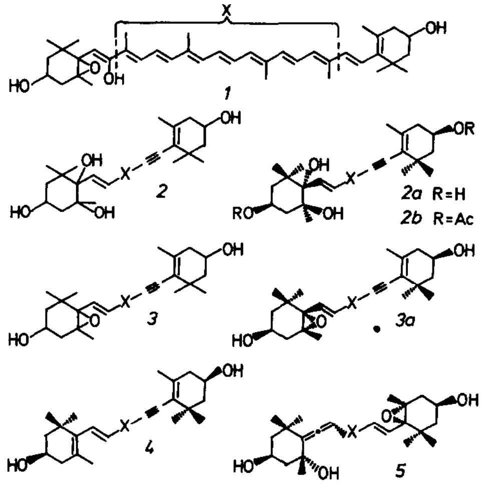
Heteroxanthin was first isolated from *Vaucheria sessilis* and *Botrydium granulatum* [1]. One year later Strain *et al.* [2] named the new pigment heteroxanthin (from Heterokontae) and established the molecular formula $C_{40}H_{56}O_4$. For this carotenoid, also present in *Tribonema aeguale* [3], the alternative structures **1**[4] (Scheme 1, unstable enol) and the spectroscopically documented **2** [5, 6] have been suggested.

Later heteroxanthin was isolated from *Euglena gracilis* [7], where it occurs together with diadinoxanthin (**3**, major carotenoid) [7] diatoxanthin (**4**) [3, 8, 9] and neoxanthin (**5**) [10].

So far heteroxanthin appears to be a characteristic carotenoid of the Xanthophyceae [11], and is also encountered in Euglenophyceae [7].

Diadinoxanthin, first isolated by Strain *et al.* [12] from dinoflagellates, is an acetylenic, epoxidic carotenoid obtained from Dinophyceae [13, 14], Bacillariophyceae [7, 12], Haptophyceae [15], Xanthophyceae [11] and Euglenophyceae [7]. It has been assigned the constitution **3** from spectroscopic and chemical data [7].

We now present evidence for the absolute configurations of heteroxanthin (**2a**) and diadinoxanthin (**3a**).



Scheme 1.

RESULTS AND DISCUSSION

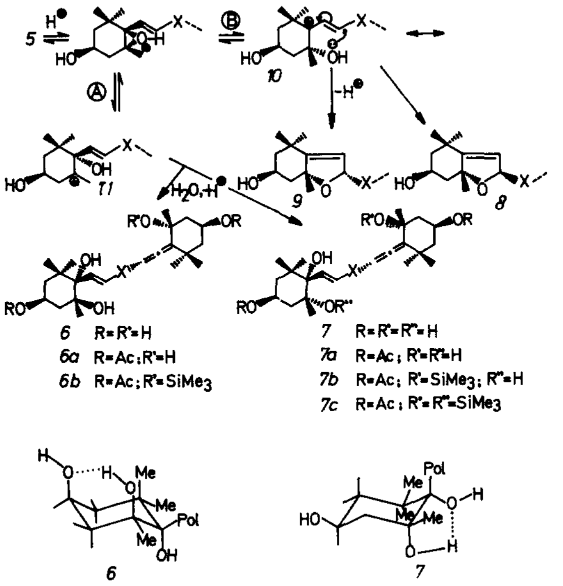
Minor carotenoids from Trollius europaeus.

Two epimeric pentols, **6** and **7**, in the present work isolated as minor constituents from a sample of trolliflor (=neoxanthin, **5** [16] *ex Trollius europaeus* served as useful model substances for the stereochemical assignment of heteroxanthin (**2a**).

The structural elucidation of these pentols (**6** and **7**) will therefore be treated first. They exhibited the same

---

* No 19 in the series 'Algal Carotenoids'. No 18 (1976) *Phytochemistry* **15**, 1015; † Present address: Organisch-chemisches Institut der Universität Zürich, Rämistrasse 76, CH-8001 Zürich, Schweiz.



Scheme 2.

electronic spectrum as neoxanthin (**5**) and characteristic allenic absorption in IR, but were more strongly adsorbed than neoxanthin (**5**); **6** being most strongly retained. Mass spectroscopy revealed similar MS of **6** and **7** with molecular ions consistent with $C_{40}H_{58}O_5$. Both provided diacetates (**6a** and **7a**) on standard acetylation and diacetate monotrimethylsilyl ethers (**6b**, **7b**) on silylation. However, only the silyl ether **7b** could be further silylated to a ditrimethylsilyl ether **7c**, even under forcing conditions. Another difference between the tetrols **6** and **7** was observed in the MS: **7** lost readily three moles of water, whereas **6** only exhibited two prominent losses of water. The same trend was seen in the MS of the corresponding diacetates **7a** and **6a**; only **7a** showed a prominent loss of water. As shown below, these differences can be accounted for by stereochemical differences.

Partial synthesis of the pentols **6** and **7** (ratio 3:1) was obtained in low yield from neoxanthin (**5**) on treatment with hydrogen chloride or sulphuric acid in aqueous medium. The main products of this reaction were the C-8 epimeric furanoxides, the neochromes **8** and **9**, consistent with the mechanism given in Scheme 2. In non-aqueous medium furanoxides are usually formed in quantitative yield via the tertiary, allylic, resonance-stabilized carbonium ion (**10**). Also the tertiary, non-allylic, less stable carbonium ion **11** may be formed, but in the absence of a nucleophile reversion to the epoxide, **5** is likely. However, with water present the two epimeric triol rings (**6** and **7**) should result with chirality at C-6 unchanged. Since the pentols **6** and **7** under the same aqueous, acidic conditions provided no furanoxides, subsequent racemization at C-6 via the carbonium ion **10** may be disregarded. The semisynthetic pentols **6** and **7** could not be differentiated from the corresponding tetrols *ex Trollius europaeus* either chromatographically, chemically or spectroscopically.

Regarding their configuration at C-5, assignments followed from hydrogen bonding studies in the near IR (Table 1). According to Kuhn [17, 18] H-bridges in cyclohexanediols of the size 30–40 cm^{-1} are characteristic of 1,2-*cis*-glycols, whereas 1,3-*cis*-glycols show stronger H-bridges (75 cm^{-1} or even stronger [19] for higher substituted cyclohexanols). For the minor semi-synthetic product, assigned configuration **7**, its diacetate **7a** and the diacetate 5-′trimethylsilyl ether (**7b**), characteristic 1,2-*cis*-glycol H-bonding was observed. For product **6** and its derivatives **6a** and **6b** the considerably stronger H-bonding ($\Delta\nu = ca\ 150\,\text{cm}^{-1}$) is compatible with 1,3-*cis*-glycol arrangement; see preferred conformations in Scheme 2.

Table 1. Near-IR absorption (cm^{-1}) measured in tetrachlorethylene of selected carotenoids

Compound	Free OH Sec.	Free OH Tert.	H-bonded OH	Δν
Neoxanthin (**5**)	3617	3603		
Neoxanthin (**5**) diacetate		3604		
Pentol **7**	3616	3603	3565	51 and 38
Diacetate **7a**		3608	3571	37
Diacetate 5′-silyl ether **7b**		3610	3571	39
Pentol **6**	3616	3603	*ca* 3460	156 and 143
Diacetate **6a**		3608	*ca* 3460	148
Diacetate 5′-silyl ether **6b**		3615	*ca* 3460	155
Heteroxanthin (**2a**)		3610	*ca* 3460	150
Heteroxanthin diacetate (**2b**)		3610	*ca* 3460	150

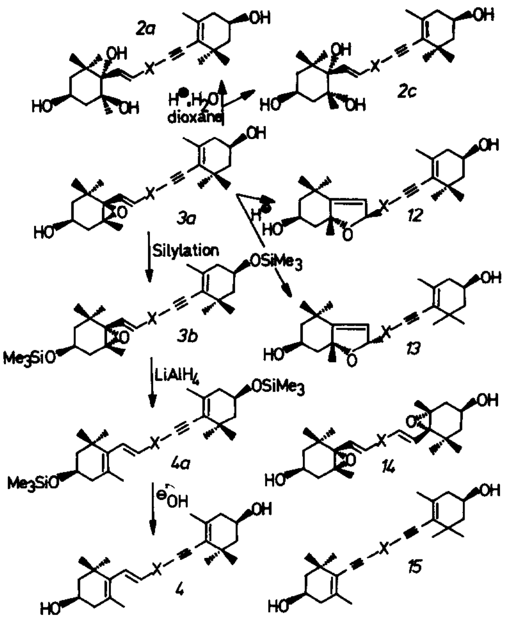
The strong 1,3 H-bonding in the pentol **6** and its derivatives is considered the reason why the diacetate 5′-trimethylsilyl ether (**6b**) cannot be silylated, in contrast to the epimer **7b**. The configuration dependent fragmentations on electron impact are noteworthy, as is the stronger adsorbance of the 1,3-*cis*-glycol **6** relative to the 1,2-*cis*-glycol **7**.

Since both C-5 epimeric tetrols, **6** and **7**, were isolated from *Trollius europaeus*, their non-enzymatic origin via a C-5 carbonium ion (**11**) is likely. Consequently, we desist from claiming them to be new naturally occurring carotenoids. However, their usefulness for configurational assignment of heteroxanthin (**2a**) is apparent.

Diadinoxanthin

In the carotenoid series it is known that 5,6-epoxides may be converted to the corresponding 5-ene by $LiAlH_4$ under forcing conditions [20]. Attempts to convert diadinoxanthin (**3**) *ex Euglena gracilis* [7] to diatoxanthin (**4**) or its enantiomer by treatment with $LiAlH_4$ failed. However, after protection of the hydroxy functions by silylation to **3b** the ditrimethylsilyl ether (**4a**) of diatoxanthin (**4**) was obtained in 33% yield, Scheme 3. The product (**4a**) exhibited the same R_f-value, electronic spectrum and MS as the ditrimethylsilyl ether prepared from authentic diatoxanthin (**4**) *ex Prymnesium parvum* [15]. Agreement in CD properties was only obtained after hydrolysis to free diatoxanthin (**4**) and separation into pure all-*trans* and 9′-*cis* [21] isomers, *cf*, Fig. 1. The opposite Cotton effect of the all-*trans* and 9′-*cis* isomers is consistent with previous findings for *cis*-carotenoids [9, 22, 23].

From the above conversion of diadinoxanthin (**3**) to diatoxanthin (**4**) of known 3*R*,3′*R*-configuration it may be concluded that diadinoxanthin (**3**) and diatoxanthin (**4**) have the same chirality at 3,3′.



Scheme 3.

A *trans* relationship between the 3-hydroxy function and the epoxy group in diadinoxanthin (3) followed from ^{1}H-NMR properties of the C-8 epimeric diadinochromes (**12** and **13**) prepared by acid treatment of diadinoxanthin (**3**). Goodfellow *et al.* [24] have shown that for 3-hydroxy-5,8-furanoxides there are characteristic shift differences for the surrounding methyl groups for the 3,5-*cis* and 3,5-*trans* isomers. From the data compiled in Table 2 *trans* configuration between the 3-hydroxy and epoxy group in diadinoxanthin may be concluded.

The absolute configuration of diadinoxanthin is therefore 3*S*, 5*R*,6*S*,3′*R* (**3a**), that is with one violaxanthin (**14**, Scheme 3) [9, 24] and one alloxanthin (**15**) [9] end group. The CD spectrum of diadinoxanthin (**3a**) is given in Fig. 1.

Heteroxanthin

Heteroxanthin (**2**), available from a previous study [7], was converted to the diacetate (**2b**, Scheme 1). Hydrogen bonding measurements (Table 1) were compatible with the 1,3 (actually 3,5)-*cis*-glycol arrangement in heteroxanthin (**2**). Consistent with 1,3 hydrogen bonding, and our previous experience [25] heteroxanthin diacetate (**2b**) could not be silylated. Other workers [5, 6] have claimed silylation of heteroxanthin diacetate, but no characterization of the trimethylsilyl ether has been published. Hydrogen bonding and silylation evidence clearly favour the same relative configuration of the triol ring as in the pentol **6** (Scheme 2).

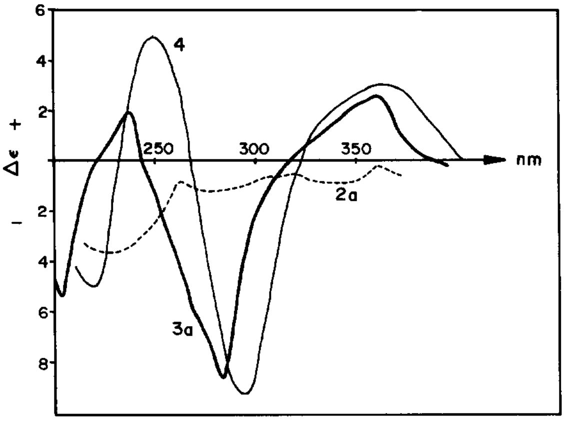


Fig. 1. CD spectra in EPA solution (diethyl ether–isopentane–ethanol 5:5:2) of all-*trans* diatoxanthin (**4**), diadinoxanthin (**3a**), and of heteroxanthin (**2a**).

Heteroxanthin (**2a**) and its C-5 epimer (**2c**) were prepared by partial synthesis from diadinoxanthin (**3a**) by treatment with aqueous acid, Scheme 3. From the mechanistic arguments already advanced (Scheme 2) both the semisynthetic epimers **2a** and **2c** consequently have the 3,6-*trans* relationship. Heteroxanthin (**2a**) thus prepared was more strongly adsorbed than its C-5 epimer **2c**, *cf* findings for **6** and **7**. The semi-synthetic heteroxanthin (**2a**) could not be silylated, whereas the C-5 epimer **2c** could. Semisynthetic heteroxanthin (**2a**) and its diacetate (**2b**) exhibited characteristic 1,3-*cis* glycol hydrogen bonding in the near-IR (Table 1). Furthermore semi-synthetic **2a** exhibited the same CD properties as natural heteroxanthin (Fig. 1). The Cotton effect of heteroxanthin is weak. However, the CD results exclude opposite chirality at C-3,3′ in diadinoxanthin (**3a**) and heteroxanthin (**2a**).

Biosynthetic considerations

The co-occurrence of diatoxanthin (**4**), diadinoxanthin (**3a**) and heteroxanthin (**2a**) and their structural relationship, including the stereochemical details here established (Scheme 1), suggest a close biosynthetic relationship.

EXPERIMENTAL

Materials and methods were as usually employed in our laboratory [26, 27]. Near-IR measurements were carried out with a Perkin Elmer Model 21 instrument with LiF optics in 1 cm quartz cuvettes: concn 1 mg/ml $C_2H_2Cl_4$ or less. CD spectra were recorded with a Roussel Jouan dicrographe.

(3S,5S,6S,3′S,5′R,6′R)-6,7-*Didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,5,6,3′,5′-pentol* (**6**). Comprised 1.5 mg (3%) of a

Table 2. Methyl signals (δ) associated with C-8 epimeric mixtures* of 3-hydroxy-5,8-furanoxides for 3,5-*trans* and 3,5-*cis* isomers according to Goodfellow *et al.* [24] and for diadinochrome (12 + 13)

	1-Me (eq.)		1-Me (ax.)		5-Me		9-Me	
3,5-*Trans* carotenoids [24]	1.15,	1.17	1.30,	1.32	1.58,	1.70†	1.69,	1.78
3,5-*Cis* carotenoids [24]	1.20,	1.21	1.14,	1.13	1.45,	1.46	1.74,	1.78
Diadinochrome (12 + 13)	1.14,	1.17	1.29,	1.31	1.62,	1.60	1.70	1.80

* Two signals for each methyl group due to C-8 epimeric mixture.

† The original value reported [24], 1.52, is in error according to repeated measurements of neochrome (**9** + **10**).

crystalline sample of trolliflor = neoxanthin (**5**) [16] *ex Trollius europaeus* form the collection of the late Prof. P. Karrer. **6** had $R_f = 0.32$ (circular Whatman Si gel paper, 35% Me_2CO in petrol = SG 81, 35% APE): UV $\lambda_{max}^{Me_2CO}$ nm: 418, 441 and 470; IR Table 1 and ν_{max}^{KBr} cm^{-1}: 3030 *w*, 2968 *s*, 2930 *s*, 2855 *m*, 1927 *w*, 1450 *m*, 1368 *m*, 1152 *m*, 1070 *w*, 1045 *w*, 962 *m*, 861 *w*, 816 *w*, 720 *w*; MS *m/e* (rel. int.): 618 (55, M), 600 (100, M–H_2O), 582 (22, M–H_2O–H_2O), 556 (2, M–H_2O–H_2O–16), 564 (4, M–3xH_2O), 526 (6, M–92), 508 (1, M–92–H_2O), 502 (3, M–80–H_2O–H_2O), 221 (31, homopyryllium), 181 (36, furyllium).

Diacetate **6a**. **6** (0.1 mg), submitted to standard acetylation [27], gave an intermediary acetate and a final diacetate (**6a**) with $R_f = 0.70$ (TLC kieselgel 60 F254, 40% APE) relative to $R_f = 0.10$ for **6** in the same system: UV $\lambda_{max}^{Et_2O}$ nm: 418, 439 and 468; IR Table 1; MS *m/e* (rel. int.): 702 (50, M), 684 (100, M–H_2O), 642 (3, M–HAc), 624 (50, M–HAc–H_2O), 662 (6, M–80), 610 (7, M–92), 263 (33, homopyryllium). 223 (42, furyllium).

Diacetate monotrimethylsilyl ether **6b**. **6a** (0.05 mg) was completely silylated under standard conditions [27] after 3 hr. **6b** had $R_f = 0.22$ (SG 81, 6% APE) relative to $R_f = 0$ for **6a** in the same system; UV λ_{max} as **6a**; IR Table 1; MS *m/e* (rel. int.): 774 (100, M), 756 (2, M–18), 714 (4, M–HAc), 684 (97, M–Me_3-SiOH), 682 (9, M–92), 624 (19, M–Me_3SiOH–HAc), 263 (29, homopyryllium), 223 (31, furyllium). Attempts to silylate **6b** further with longer reaction periods and higher temp. (50°) gave no new products.

(3S,5R,6S,3′S,5′R,6′R)-6,7-Didehydro-5,6,5′,6′-tetrahydro-β,β-carotene-3,5,6,3′,5′-pentol (**7**). Comprised 0.18 mg (4%) of the trolliflor sample. **7** had $R_f = 0.38$ (SG 81, 35% APE), UV $\lambda_{max}^{Me_2CO}$ nm: 419, 441 and 470; IR Table 1 and ν_{max}^{KBr} cm^{-1}: 3030 *w*, 2960 *m*, 2930 *s*, 2860 *s*, 1930 *w*, 1660 *w*, 1460 *m*, 1380 *m*, 1160 *w*, 1070 *m*, 1045 *m*, 970 *m*, 895 *w*, 820 *w*, 725 *w*; MS *m/e* (rel. int.): 618 (15, M), 600 (47, M–H_2O), 582 (53, M–H_2O–H_2O), 566 (30, M–H_2O–H_2O–16), 564 (26, M–3xH_2O), 526 (38, M–92), 502 (23, M–80–H_2O–H_2O), 221 (99, homopyryllium), 181 (100, furyllium).

Diacetate **7a**. Standard acetylation of **7** (0.1 mg) provided one intermediary monoacetate and a final diacetate **7a** with $R_f = 0.89$ (TLC kieselgel 60 F254, 40% APE) relative to $R_f = 0.14$ for **7** in the same system; UV $\lambda_{max}^{Et_2O}$ nm: 417, 439 and 468; IR Table 1; MS *m/e* (rel. int.): 702 (34, M), 684 (100, M–H_2O), 668 (12, M–H_2O–16), 666 (23, M–2xH_2O), 624 (28, M–HAc–H_2O), 622 (18, M–80), 610 (5, M–92), 606 (8, M–HAc–2xH_2O), 604 (6, M–80–H_2O), 586 (11, M–80–2xH_2O), 263 (32, homopyryllium), 223 (3, furyllium).

Diacetate 5,5′-di(*trimethylsilyl*) *ether* **7c**. **7b** (0.05 mg) was upon standard silylation (3 hr) nearly completely converted to **7b** with $R_f = 0.38$ (SG 81, 6% APE); UVλ_{max} as **7a**; IR Table 1; MS *m/e* (rel. int.): 774 (93, M), 756 (26, M–H_2O), 740 (9, M–H_2O–16), 714 (19, M–HAc), 684 (100, M–Me_3SiOH), 666 (18, M–Me_3-SiOH–H_2O), 640 (14, M–Me_3SiOH–H_2O–16), 624 (20, M–Me_3SiOH–HAc), 263 (44, homopyryllium), 223 (54, furyllium).

Diacetate 5,5′-di(trimethylsilyl) ether **7c**. **7b** (0.05 mg) was incompletely converted to **7c** after standard silylation for 40 hr; $R_f = 0.73$ (SG 81, 6% APE); λ_{max} as **7b**; MS *m/e* (rel. int.): 846 (100, M), 830 (22, M–16), 828 (16, M–H_2O), 756 (45, M–Me_3SiOH), 666 (18, M–2xMe_3SiOH), no homopyryllium or furyllium ions.

Neoxanthin = trolliflor. (**5**) [16] and its diacetate [16] and near-IR absorption as given in Table 1.

Partial synthesis of pentols **6** and **7** *from neoxanthin* (**5**). Treatments of **5** in aq., peroxide-free dioxane with HCl or H_2SO_4 gave **6** and **7** in relative ratios 2:5 to 1:3. At optimum conditions **5** (1.01 mg) in dioxane (8 ml, purified on Al_2O_3), H_2O (4 ml) and 0.001 N aq. H_2SO_4 (8 ml) were reacted for 3.5 hr followed by Et_2O extraction; pigment recovery 0.72 mg (71%). The reaction mixture contained neoxanthin (**5**, 6%), neochromes (**9** and **10**, 81%), pentol **6** (8%) and pentol **7** (3%).

Partially synthetic **6** and **7** had identical R_f (co-chromatography), λ_{max} and MS with the original samples. **6** was converted to the diacetate **6a** and the diacetate mono(trimethylsilyl ether) **6b**. **7** was converted to the diacetate **7a** and the diacetate ditrimethylsilyl ether **7c**. Chromatographically the derivatives of **6** and **7** corresponded to those prepared from **6** and **7** *ex Trollius europaeus*. Acid treatment of **6** and **7** under the above conditions gave no neochromes (**9**, **10**).

Diadinoxanthin (**3a**) *ex Euglena gracilis* was available from a previous study [7]; CD spectrum Fig 1. Treatment of **3a** with $LiAlH_4$ under various conditions gave only more polar products of shorter chromophore.

Diadinoxanthin ditrimethylsilyl ether **3b**. **3a** (3.5 mg) was converted by standard procedure [27] to **3b**; $R_f = 0.52$ (SG 81, 1% APE).

Conversion of **3b** *to diatoxanthin* (**4**). **3b** (3.5 mg) in dry Et_2O (10 ml) and $LiAlH_4$ (3 spatula tips) were refluxed at 80° for 30 min; pigment recovery after transfer to Et_2O 2.0 mg (58%). The reaction mixture contained **4a** (1.1 mg, 33%) and 4 more polar byproducts and little unreacted **3b**. Diatoxanthin ditrimethylsilyl ether **4a** had $R_f = 0.77$ (all-*trans*, $CaCO_3$ paper Schleicher & Schüll 290, 1% APE) and $R_f = 0.87$ (9-*cis*) and both isomers cochromatographed with an authentic sample prepared from **4**. **4a** *ex* **3b** had MS *m/e* (rel. int.).: 710 (M), 695 (5, M–15), 638 (2), 620 (3, M–Me_3SiOH), 618 (2, M–92), 604 (2, M–106), as found for **4a** *ex* **4**. **4a** (0.5 mg) *ex* **3b** was treated with 5% KOH in Et_2O–MeOH (1:1) for 4 hr, providing all-*trans* diatoxanthin (**4**, $R_f = 0.61$ SS290, 20% APE) and neo A ($R_f = 0.81$ same system). All-*trans* **4** after chromatography on a $CaCO_3$ column had UV $\lambda_{max}^{Et_2O}$ nm: 420, 448 and 472; CD (EPA) 374 ($\Delta\varepsilon = 0$), 343 (+3.0), 308 (0), 286 (−9.2), 265 (0), 250 (+4.8), 236 (0), 227 (−5.1) nm. Neo A had UV $\lambda_{max}^{Et_2O}$ nm: 427, 446 and 475 with *cis*-peak at 343 nm; CD (EPA) 378 (0), 341 (−6.8), 303 (0), 285 (+6.0), 265 (0), 245 (−9.8), 230 (0), 224 (+3.3) nm.

Conversion of diadinoxanthin (**3**) *to heteroxanthin* (**2a**). **3** (6.9 mg) in peroxide-free dioxane (70 ml), H_2O (40 ml) and 0.001 N H_2SO_4 (30 ml) was kept for 4 hr, pigment recovery after Et_2O extraction and TLC (kieselgl, 40% APE) 56%. The reaction mixture contained diadinochrome (**12** plus **13**, 3.0 mg), heteroxanthin (**2a**, 0.56 mg) and the C-5 epimer (**2c**, 0.25 mg).

Semi-synthetic heteroxanthin (**2a**). $R_f = 0.44$ (SG 81, 35% APE), inseparable from natural heteroxanthin; UV $\lambda_{max}^{Et_2O}$ nm: 425, 446, 475; IR Table 1; MS *m/e* (rel. int.): 600 (100, M), 582 (15, M–18), 577 (12, M–23), 666 (4, M–16–18), 664 (4, M–18–18), 551 (6, M–49), 549 (6, M–51), 537 (3, M–63), 523 (5, M–77), 508 (4, M–92), 221 (36, homopyryllium), 181 (46, furyllium), identical with a previously recorded MS spectrum of natural heteroxanthin *ex Vaucheria* sp [25]; CD (EPA) 327 ($\Delta\varepsilon = -0.8$), 275 (−2.3), 241 (−1.9), 225 (−2.1) nm. Acetylation gave heteroxanthin diacetate (**2b**), $R_f = 0.13$ (SG 81, 6% APE), identical with **2b** *ex* natural heteroxanthin; IR Table 1. **2b** *ex* **3** provided no trimethylsilyl ether under conditions where **2c** was silylated.

Semi-synthetic 5-epimeric heteroxanthin (**2c**). $R_f = 0.54$ (SG 81, 35% APE); UV $\lambda_{max}^{Et_2O}$ nm: 423, 443 and 476; MS *m/e* (rel. int.): 600 (100, M), 582 (24, M–18), 566 (5, M–16–18), 551 (7, M–49), 537 (5, M–63), 523 (6, M–77), 508 (4, M–92), 221 (54, homopyryllium), 181 (96, furyllium). Acetylation provided a diacetate with $R_f = 0.16$ (SG 81, 6% APE). The diacetate was partly (*ca* 40%) converted to a monotrimethylsilyl ether upon standard silylation for 48 hr; $R_f = 0.62$ (SG 81 6% APE); MS *m/e*: 756 (M), 740 (M–16), 738 (M–18), 666 (M–90), 664 (M–92).

Diadinochrome (**12** + **13**) had $R_f = 0.73$ (SG 81, 35% APE), UV $\lambda_{max}^{Et_2O}$ nm: 408, 429 and 456; ^1H-NMR ($CDCl_3$): δ 1.14, 1.17, 1.29 and 1.31 (16, 17-Me), 1.14 and 1.20 (16′, 17′-Me), 1.62 and 1.70 (Me–18), *ca* 1.70 and 1.80 (Me–19), 1.97 (Me–19′, 20, 20′), *ca* 5.0–5.5 (H–7,8), *ca* 6.0–6.7 (olefinic H).

Heteroxanthin (**2a**). Available from a previous study [7] had $R_f = 0.44$ (SG 81, 35% APE); UV $\lambda_{max}^{Et_2O}$ nm; 423, 444 and 474.

Heteroxanthin diacetate (**2b**). Prepared by standard acetylation of **2a** had $R_f = 0.14$ (SG 81, 6% APE); λ_{max} as **2a**; IR Table 1. The diacetate (**2b**) provided no trimethylsilyl ether on standard silylation for 40 hr (room temp.) followed by 4 hr at 50°.

Acknowledgements—We thank Dr. H. H. Strain, previously at Chemistry Division, Argonne National Laboratory, Ill. USA, for samples of heteroxanthin, diadinoxanthin and violaxanthin. CD spectra were kindly recorded by Mag. G. Borch, Chemistry Department A, Technical University of Denmark, Lyngby, Denmark. R.B. was supported by a postdoctorate fellowship from the Schweizerische Nationalfond.

REFERENCES

1. Kleinig, H. and Egger, K. (1967) *Z. Naturforsch.* **22B**, 868.
2. Strain, H. H., Svec, W. A., Aitzetmüller, K., Grandolfo, M. and Katz, J. J. (1968) *Phytochemistry* **7**, 1417.
3. Strain, H. H., Benton, F. L., Grandolfo, M. C., Aitzetmüller, K., Svec, W. A. and Katz, J. J. (1970) *Phytochemistry* **9**, 2561.
4. Nietsche, H. (1970) *Tetrahedron Letters*, 3345.
5. Strain, H. H., Aitzetmüller, K., Svec, W. A. and Katz, J. J. (1970) *Chem. Commun.* 876.
6. Nietsche, H. (1973) *Arch. Mikrobiol.* **90**, 151.
7. Aitzetmüller, K., Svec, W. A., Katz, J. J. and Strain, H. H. (1968) *Chem. Commun.* 32.
8. Mallams, A. K., Waight, E. S., Weedon, B. C. L., Chapman, D. J., Haxo, F. T., Goodwin, T. W. and Thomas, D. M. (1967) *Chem. Commun.* 301.
9. Bartlett, L., Klyne, W., Mose, W. P., Scopes, P. M., Galasko, G., Mallams, A. K., Weedon, B. C. L., Szabolcs, J. and Tóth, G. (1969) *J. Chem. Soc. C* 2527.
10. Cholnoky, L., Györgyfy, K., Rónai, A., Szabolcs, J., Tóth, G., Galasko, G., Mallams, A. K., Waight, E. S. and Weedon, B. C. L. (1969) *J. Chem. Soc. C* 1256.
11. Stransky, H. and Hager, A. (1970) *Arch. Mikrobiol.* 164.
12. Strain, H. H., Manning, W. H. and Hardin, G. (1944) *Biol. Bull.* **82**, 169.
13. Johansen, J. E., Svec, W. A., Liaaen-Jensen, S. and Haxo, F. T. (1974) *Phytochemistry* **13**, 2261.
14. Jeffrey, S. W., Sielicki, M. and Haxo, F. T. (1975) *J. Phycol.* **11**, 374.
15. Berger, R., Liaaen-Jensen, S., McAllister, V. and Guillard, R. R. L. *Biochem. Syst.* in press.
16. Buchecker, R., Liaaen-Jensen, S. and Eugster, C. H. (1975) *Phytochemistry* **14**, 797.
17. Kuhn, L. B. (1952) *J. Am. Chem. Soc.* **74**, 2492.
18. Kuhn, L. B. (1954) *J. Am. Chem. Soc.* **76**, 2954.
19. Kuhn, L. B. (1958) *J. Am. Chem. Soc.* **80**, 5950.
20. Liaaen-Jensen, S. (1971) in *Carotenoids* (Isler, O. ed.), Chpt. III. Birkhäuser, Basel.
21. Weedon, B. C. L. (1970) *Rev. Pure Appl. Chem. (Australia)* **20**, 51.
22. Moss, G. P., Szabolcs, J., Tóth, G. and Weedon, B. C. L. (1975) *Acta Chim. Acad. Sci. Hung.* **87**, 301.
23. Liaan-Jensen, S. (1976) *Pure and Appl. Chem.* **47**, 199.
24. Goodfellow, D., Moss, G. P., Szabolcs, J., Tóth, G. and Weedon, B. C. L. (1973) *Tetrahedron Letters*, 3925.
25. Norgård, S., Svec, W. A., Liaaen-Jensen, S., Jensen, A. and Guillard, R. R. L. (1974) *Biochem. Syst.* **2**, 7.
26. Kjøsen, H. and Liaaen-Jensen, S. (1972) *Acta Chem. Scand.* **26**, 4121.
27. Liaaen-Jensen, S. and Jensen, A. (1971) *Methods Enzymol.* **23**, 586.