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THE CARBOHYDRATE MOIETIES BOUND TO THE CAROTENOIDS MYXOL AND OSCILLOL AND THEIR CHEMOSYSTEMATIC APPLICATIONS*

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Key Word Index—*Oscillatoria agardhii*; Carotenoid glycosides; myxol; oscillol; α-chivonosides; α-3-*O*-methylfucosides.

Abstract—The sugar moiety bound to myxol in *Oscillatoria agardhii* was shown by ^{1}H NMR (400 MHz) experiments and glycoside hydrolysis to be α-linked chinovose, tentatively with the L-configuration. Direct comparison of 100 MHz ^{1}H NMR spectra of the acetates of myxol α-chinovoside and of oscillaxanthin *ex Arthrospira* sp. suggests the same sugar component in oscillaxanthin, and also in myxoxanthophyll from the latter source. The *O*-methyl methylpentoside bound to myxol in *O. bornetii* f. *tenuis* was identified by ^{1}H NMR as α-linked 3-*O*-methyl-fucose, tentatively L-configurated. The differentiation of species in the genus *Oscillatoria*, causing natural blooms in eutrophic lakes, was supported by their carotenoid pattern when including the differences in sugar moiety of the carotenoid glycosides.

INTRODUCTION

Blue-green algae (Cyanobacteria) synthesize specific monocyclic and aliphatic carotenoid glycosides [1, 2]. The carotenoid aglycone is either myxol (**1**) [3] of established chirality [4] or oscillol (**2**) [3] of unestablished chirality [4, 5]. Biogenetically 2,2′-*S*-chirality for **2** is predicted [4].

Myxoxanthophyll, first isolated from *Oscillatoria rubescens* [6], was upon direct comparison considered identical with a sample from *Arthrospira* sp. [7]. In 1969 myxoxanthophyll *ex Arthrospira* sp. was assigned the L-rhamnoside constitution **3** [8]. The identification of the sugar moiety was based on mass spectrometry and ^{1}H NMR (100 MHz, no spin decoupling) of the tetraacetate **3a**. Furthermore rhamnose was identified as the major sugar by paper chromatography after glycoside hydrolysis. A minor sugar component was identified as glucose by paper chromatography, consistent with the mass spectrum of acetylated myxoxanthophyll (**3a** + **4a**), revealing the presence of a hexoside **4**.

Oscillaxanthin, first isolated from *O. rubescens* [9] was upon direct comparison considered identical with a sample from *Arthrospira* sp. [7], subsequently assigned the dirhamnoside constitution **5** [10]. ^{1}H NMR correlations with the methyl triacetyl-α- and β-L-rhamnosides were later attempted [11].

In *O. limosa* [3] and *O. bornetii* f. *tenuis* [12] myxol and oscillol are glycosidically bound to an *O*-methylmethylpentoside, **6** and **7** respectively, judged from the molecular ions, prominent oxonium ions at *m/z* 245 and fragment ions thereof in the mass spectra of the acetylated carotenoid glycosides **6a** and **7a**. The known distribution of carotenoid glycosides in blue-gree algae until 1980 has been summarized [1, 13].

Recently new glycosides were reported from *Spirulina* sp. with myxol and oscillol mainly linked to α-L-chinovose and partly to α-L-fucose according to a 400 MHz ^{1}H NMR study [14]. The carbohydrate moiety in these glycosides (**8**–**11**) was partly esterified with fatty acids.

RESULTS AND DISCUSSION

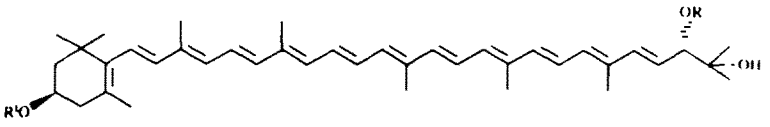
The sugar moieties bound to myxol and oscillol

The availability of 400 MHz ^{1}H NMR and the spin–spin decoupling technique has prompted a ^{1}H NMR study of the carbohydrate moieties in the available myxoxanthophyll-like glycoside from *O. agardhii* [15] and of the myxol *O*-methyl-methylpentoside from *O. bornetii* f. *tenuis*. ^{1}H NMR data for the tetraacetate **12a** (see Fig. 1) of myxoxanthophyll *ex O. agardhii* was consistent with the α-chinovoside structure **12**.

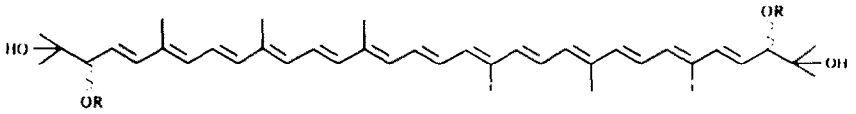
Thus the ^{1}H NMR signals for the myxol aglycone agreed with previous reports [3, 8]. The multiplicity and coupling constants, in addition to spin decoupling experiments for the metine and methyl protons of the carbohydrate moiety (Fig. 1), were consistent with the $^1C_4$ conformation (provided L-configuration) of a triacetyl 6-deoxy-α-glucoside (α-chinovoside, *A*). The identity of the carbohydrate moiety was confirmed by glycoside hydrolysis followed by acetylation of the reducing sugar and comparative GLC studies with D-chinovose tetraacetate, L-rhamnose tetraacetate and L-fucose tetraacetate. Attempts to separate enantiomeric acetylated carbohydrates on a chiral GLC column failed.

Direct comparison of the 400 MHz and 100 MHz ^{1}H NMR spectra of the tetraacetate **12a** of myxol-α-

*Part 11 in the series "Carotenoids of Blue-green Algae". For Part 10 see *Phytochemistry* (1981) **19**, 2167.



1 R = R' = H, MYXOL
3 R = L-rhamnosyl, R' = H
3a R = L-rhamnosyl (Ac)$_3$, R' = Ac
4a R = glucosyl (Ac)$_4$, R' = Ac
6 R = OMe-methylpentosyl, R' = H
6a R = OMe-methylpentosyl (Ac)$_2$, R' = Ac
8 R = α-L-chinovosyl (acyl), R' = H
9 R = α-L-fucosyl (acyl), R' = H
12 R = α-L-chinovosyl, R' = H
12a R = α-L-chinovosyl (Ac)$_3$, R' = Ac



2 R = H, OSCILLOL
5 R = L-rhamnosyl
5a R = L-rhamnosyl (Ac)$_3$
7 R = OMe-methylpentosyl
7a R = OMe-methylpentosyl (Ac)$_3$
10 R = α-L-chinovosyl (acyl)
11 R = α-L-fucosyl (acyl)
13 R = α-L-chinovosyl
13a R = α-L-chinovosyl (Ac)$_3$

chinovoside and of the previously recorded 100 MHz ^{1}H NMR spectrum of oscillaxanthin hexaacetate *ex Arthrospira* sp. [10] revealed the presence of the same carbohydrate moiety. Reassignment of the proton signals [11] in favour of the α-chinovoside structure **13a** for oscillaxanthin hexaacetate on the basis of the spin decoupling experiments may now be made, and requires a revision of the α-L-rhamnoside structure **5** to the α-chinovoside structure **13**. Chinovose and rhamnose are C-2 epimers.

It appears plausible that myxoxanthophyll *ex* the same *Arthrospira* sp. also is an α-chinovoside (**12**). Rhamnose and chinovose should then exhibit closely similar R_f-values [8].

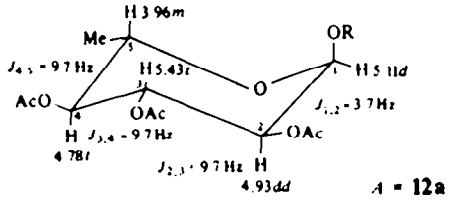
Turning now to the myxol *O*-methyl-methylpentoside (**6**) *ex O. bornetii* f. *tenuis* the ^{1}H NMR spectrum of the triacetate (**6a**) was compatible with a myxol-*O*-methyl-α-fucoside. The multiplicity and coupling constants, together with spin decoupling experiments for the methine and methyl protons of the carbohydrate moiety (Fig. 1), were consistent with the $^1C_4$ conformation (provided L-configuration) of a diacetyl 6-deoxy-α-galactoside (α-fucoside, *C*). The 4,5-coupling constant could not directly exclude the C-5 epimeric 6-deoxy-β-D-altroside in the $^1C_4$ conformation. However, this glycoside would prefer the thermodynamically more favoured $^4C_1$ conformation, which is ruled out by the ^{1}H NMR data. Allocation of the methoxyl group to C-3 of the carbohydrate moiety in the natural glycoside followed from ^{1}H NMR correlation with tetraacetyl α-L-fucose (*D*, Fig. 1), pentaacetyl α-D-glucose *F* and tetraacetyl 3-*O*-methyl-α-D-glucose (*E*).

The absolute configuration of the α-chinovoside and 3-*O*-methyl-α-fucoside moieties were not determined, but L-configuration is common for 6-deoxy hexoses from prokaryotes [16]. Methyl pentoses reported from prokaryotes include L-rhamnose, L-fucose, 3-*O*-methyl-L-rhamnose and 2-*O*-methyl-L-fucose [16].

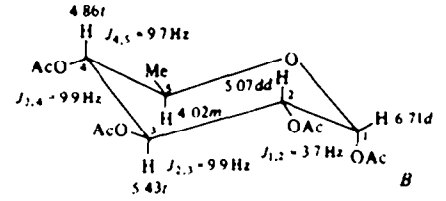
In conclusion it appears that myxol (**1**) in natural carotenoids is glycosidically bound to acylated α-L-chinovose (**8**) and acylated α-L-fucose (**9**) [14], to α-L-chinovose (**12**, major component in myxoxanthophyll), glucose (**4**, minor component in myxoxanthophyll) or to 3-*O*-methyl-α-L-fucose (**6**). Except for glucose, oscillol (**2**) occurs glycosidically bound to the same sugars (**10**, **11** and **13** = oscillaxanthin).

Taxonomic and phylogenetic applications

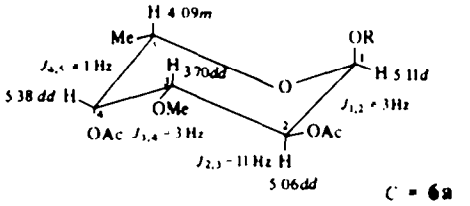
Planktic species of *Oscillatoria* are major contributors to the phytoplankton of Norwegian inland waters. More than fifteen species have been reported, and some develop algal blooms [17]. The limitations of morphological and cytological characteristics complicate the classification of *Oscillatoriaceae* [18–20], and chemosystematic approaches are obvious. Carotenoid distribution patterns may represent a useful tool [21, 22]. Previous microscopic examination of the strains, involving the trichome type, cell size and shape and cellular inclusions, had resulted in a division into the *O. agardhii/rubescens* group and *O. bornetii* group [23] (Table 1). In line with the morpholo-



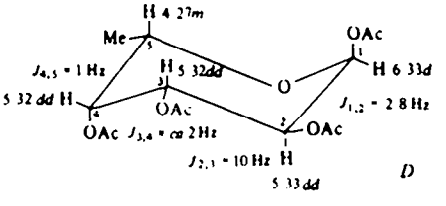
6 Deoxy-α-L-glucopyranoside (α-L-chinovoside) triacetate



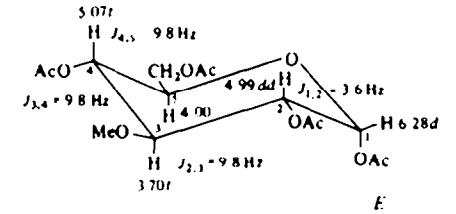
6 Deoxy-α-D-glucopyranose (α-D-chinovose) tetraacetate



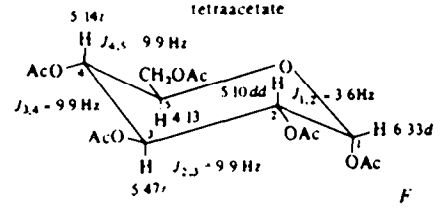
3-*O*-Methyl-6-deoxy-α-L-galactopyranoside (α-L-fucoside) diacetate



6-Deoxy-α-L-galactopyranose (α-L-fucose) tetraacetate



3-*O*-Methyl-α-D-glucopyranose tetraacetate



α-D-Glucopyranose pentaacetate

Fig. 1. ^{1}H NMR spectral data for the acetylated sugar moieties of carotenoid glycosides and relevant model compounds.

gical differences the members of the *O. agardhii/rubescens* group are all strictly planktic, whereas *O. limosa* [24, 25] and *O. bornetii* prefer a benthic mode of living, but may develop a planktic phase.

In the present work six selected strains were cultivated under identical and controlled laboratory conditions. The carotenoid pattern was analyzed quantitatively with particular emphasis on the carbohydrates bound to myxol (**1**) and oscillol (**2**): methylpentose (chinovose) or *O*-methylmethylpentose (3-*O*-methylfucose) as determined by mass spectroscopy of the acetylated carotenoid glycosides (Table 1).

The results clearly support differences between the species of the two algal groups. Thus, the algae in the *O. bornetii* group all contained carotenoid glycosides based on the *O*-methyl-methylpentose identified as 3-*O*-methyl-α-L-fucose in *O. bornetii* f. *tenuis* from Lake Mjøsa. By contrast the *O. agardhii/rubescens* group all contained glycosides of methylpentoses considered as the common myxoxanthophyll (**12**) and oscillaxanthin (**13**).

EXPERIMENTAL

Biological materials. Algal samples were collected from selected localities of Norwegian inland waters. The dominant forms were isolated and cultured; NIVA strains: CYA 29, Lake Gjersjøen, 1968, isolated by R. Romstad; CYA 56/1, Lake Steinsfjorden 1978, isolated by T. Källqvist; CYA 65, Lake Vansjø 1979; CYA 60, Lake Mjøsa 1978; CYA 33/6, Lake Mjøsa 1976 and CYA 70, River Glåma 1980. The four latter strains were isolated by R. Skulberg. The cultures are deposited in the culture collection of algae at the Norwegian Institute for Water Research (NIVA) [26].

The cultures were grown at identical conditions in medium Z8 [26, 27] under 14–17 μE m^{-2} sec^{-1} fluorescent illumination with a 12/12 hr light/dark cycle at 15°. Cells were harvested by centrifugation and lyophilized or deep-frozen until pigment extraction.

Materials and methods. These were as commonly employed in the NTH Laboratory [28]. R_f values refer to TLC (silica gel), eluent Me_2CO in hexane (AH). If not otherwise specified VIS spectra are recorded in Et_2O. For the mass spectra only prominent and diagnostically useful ions are cited.

Individual carotenoids. These are treated in order of increasing adsorption upon TLC.

β,β-Carotene. R_f = 1.00 (30% AH), R_f = 0.81 (5% AH, special plates [29], inseparable from authentic β,β-carotene; VIS λ_{max} nm: (420), 448, 475; MS *m/z* (rel. int.): 536 [M]$^+$ (100), 444 [M − 92]$^+$ (10).

Echinenone (β,β-caroten-4-one). R_f = 0.83 (30% AH), inseparable from an authentic standard; VIS λ_{max} nm: 453, (474); MS *m/z* (rel. int.): 550 [M]$^+$ (100), 458 [M − 92]$^+$ (10).

Cryptoxanthin (β,β-caroten-3-ol). R_f = 0.69 (30% AH), in-

Table 1. Carotenoid distribution pattern in some species of *Oscillatoria*

Species	Carotenoid (% of total)													References	Taxonomic category
	β,β-Carotene	Cryptoxanthin (β,β-caroten-3-ol)	Zeaxanthin (β,β-carotene-3,3'-diol)	Echinenone (β,β-caroten-4-one)	3'-Hydroxy-β,β-caroten-4-one	Canthaxanthin (β,β-carotene-4,4'-dione)	Mutatochrome 5,8-Epoxy-5,8-dihydro-β,β-carotene)	Myxoxanthophyll	Oscillaxanthin	Myxol-2'-*O*-methyl-methyl-pentoside	Oscillol-2,2'-di(*O*-methyl)-methylpentoside	Unidentified			
O. rubescens (NIVA-CYA 1)	29	4	8	19	1	—	—	30	10	—	–		[7]		
O. rubescens var. (Lake Steinsfjorden)	37	—	9	19	1	—	—	20	14	—	—		[5]		
O. agardhii var. (Lake Kolbotnvatn)	26	-	12	18	1	—	—	22	23	—	–	-	[5]		*Oscillatoria agardhii/ rubescens* group
O. agardhii (Lake Arungen)	35	4	9	8	1	—	1	33	10	-	—	—	[15]		
O. agardhii (NIVA-CYA 29)	54	1	12	12	1	—	--	16	3			1	•		
O. agardhii var. isothrix (NIVA-CYA 65)	62	2	10	11	<1	—	-	12	2	-	—	<1	•		
O. agardhii var. isothrix (NIVA-CYA 56/1	52	2	17	12	<1	—	—	14	3	—	–	—	•		
O. bornetii f. *tenius* (NIVA-CYA 33/1)	39	2	12	15	—	1		—	—	25	3	2	[12]		
O. bornetii (NIVA-CYA 60)	60	<1	12	12	<1	—	—		1	12	2	—	•		*Oscillatoria bornetii* group
O. bornetti f. *tenuis* (NIVA-CYA 70)	75	1	4	9	<1	—	—	-	1	9	1	—	•		
O. bornetii f. *tenuis* (NIVA-CYA 33/6)	61	<1	10	9	1	-	-	—	2	14	2	—	•		
O. limosa (River Nidelva)	17	1	22	23		7	—	–	—	27	9	—	[3]		*Oscillatoria limosa*

*Present work

separable from an authentic standard; VIS λ_{max} nm: (420), 447, 473; MS *m/z* (rel. int.): 552 [M]$^+$ (20), 460 [M − 92] (5), 91 (100).

3'-Hydroxy-β,β-caroten-4-one. R_f = 0.64 (30% AH), inseparable from an authentic standard *ex Arthrospira* sp. [7, 30]; VIS λ_{max} nm: 452 (475); MS *m/z* (rel. int.): 566 [M]$^+$ (10), 95 (100).

Zeaxanthin (*β,β-carotene-3,3'-diol*). R_f = 0.50 (30% AH), inseparable from authentic zeaxanthin; VIS λ_{max} nm: (420) 448, 476; MS *m/z* (rel. int.): 568 [M]$^+$ (100), 476 [M − 92] (10), 462 [M − 106] (1).

Unidentified. R_f = 0.45 (60% AH); VIS λ_{max} nm: (446), 473, 503.

Myxol-2'-O-methyl methylpentoside (**6**). R_f = 0.32 (60% AH); VIS λ_{max}^{MeOH} nm: 445, 470, 501. The triacetate **6a** was prepared by standard acetylation [3], R_f = 0.82 (50% AH); VIS λ_{max} nm: 445, 471, 502; MS *m/z* (rel. int.): 870 [M]$^+$ (5), 812 [M − 58]$^+$ (2), 778 [M − 92]$^+$ (1), 764 [M − 106]$^+$ (3), 331 (100), 245 (50); ^{1}H NMR ($CDCl_3$, 400 MHz, sample *ex O. bornetii* f. *tenuis* NIVA-CYA 33/1): δ 1.02 (3H, *d*, *J* = 6.5 Hz, Me at C-6, carbohydrate moiety), 1.08 (3H, *s*, Me-16/17), 1.11 (3H, *s*, Me-16/17), 1.17 (3H, *s*, Me-16'/17'), 1.21 (3H, *s*, Me-16'/17'), 1.72 (3H, *s*, Me-18), 1.93 (3H, *s*, Me-18'), 1.98 (12H, Me-19, 20, 19', 20'), 2.06 (3H, *s*, OAc at C-3), 2.11 and 2.15 (3 + 3H, OAc at C-2 and C-4 in carbohydrate), 2.47 (1H, *dd*, J_1 = 5 Hz, J_2 = 13 Hz, H-4), 2.60 (1H, *br s*, OH at C-1'), 3.38 (3H, *s*, OMe in carbohydrate), 3.70 (1H, *dd*, J_1 = 3 Hz, J_2 = 11 Hz, H-3 in carbohydrate), 3.75 (1H, *d*, *J* = 9 Hz, H-2'), 4.09 (1H, *m*, H-5 in carbohydrate), *ca* 5.1 (1H, *m*, H-3), 5.06 (1H, *dd*, J_1 = 3 Hz, J_2 = 11 Hz, H-2 in carbohydrate), 5.11 (1H, *d*, *J* = 3 Hz, H-1 in carbohydrate), 5.38 (1H, *br d*, *J* = 3 Hz, H-4 in carbohydrate), 5.63 (1H, *dd*, J_1 = 9 Hz, J_2 = 15 Hz, H-3'), 6.1–6.7 (*ca* 16H, *m*, olefinic H). All proton proton spin couplings in the carbohydrate moiety was determined by spin decoupling experiments (see *C*, Fig. 1).

For ^{1}H NMR comparison the tetraacetate of α-L-fucose (*D*, Fig. 1), 3-*O*-methyl α-D-glucopyranose tetraacetate (*E*) and the pentaacetate of α-D-glucopyranose (*F*) were prepared. All spin-spin couplings were determined by double irradiation, δ($CDCl_3$, 400 MHz) and *J*, see Fig. 1.

3-*O*-methyl-α,β-D-glucopyranose (**16**) was prepared via 1.2:5.6 di-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (**15**) from 1.2:5.6-di-*O*-isopropylidene-α-D-glucofuranose (**14**, Fluka). Compound **14** (100 g), methylated with dimethylsulphate–NaOH provided **15** as a yellow syrup in 95% yield; ^{1}H NMR ($CDCl_3$ 400 MHz): δ 5.87 (1H-1, *d*, $J_{1,2}$ = 3.74 Hz), 4.57 (1H-2, *d*, $J_{2,3}$ = 0), 3.78 (1H-3, *d*, $J_{3,4}$ = 3.03 Hz), 4.12 (1H-4, *dd*, $J_{4,5}$ = 6.93 Hz), 4.30 (1H-5, *m*, $J_{5,6a}$ = 6.16 Hz, $J_{5,6b}$ = 5.37 Hz), 4.09 (1H-6a, *dd*, J_{gem} = 8.60 Hz), 4.01 (1H-6b, *dd*), 3.46 (3H-OMe, *s*), 1.50 and 1.32 [3H-2 × Me (1,2-isoprop.)], 1.36 and 1.44 [3H-2 × Me (5,6-isopr.)] Compound **15** (3.0 g), hydrolysed with 0.8% H_2SO_4 at 80° for 13 hr, provided **16** as a colourless syrup in 85% yield. Compound **16** upon acetylation provided the tetraacetate (α + β); ^{1}H NMR data for the α-anomer see *E*, Fig. 1.

Myxoxanthophyll (**12**). R_f = 0.24 (60% AH), inseparable from myxoxanthophyll *ex O. agardhii* Gom. var. Kolbotnvatn [5]; VIS λ_{max}^{MeOH} nm: (445), 471, 502. Myxoxanthophyll tetraacetate (**12a**) was prepared by acetylation of myxoxanthophyll (**12**). The tetraacetate had R_f = 0.70 (50% AH), inseparable from an authentic standard; VIS λ_{max} nm: (445), 471, 502; MS *m/z* (rel. int.): 898 [M]$^+$ (20), 856 [M − 42] (2), 840 [M − 58]$^+$ (3), 838 [M − 60] (2), 806 [M − 92] (3), 792 [M − 106] (10), 331 (100), 273 (60), ^{1}H NMR ($CDCl_3$, 400 MHz, sample *ex O. agardhii* var. Kolbotnvatn): δ 1.04 (3H, *d*, *J* = 6.2 Hz, Me at C-6, carbohydrate moiety), 1.08 (3H, *s*, Me-16/17), 1.11 (3H, *s*, Me-16/17), 1.16 (3H, *s*, Me-16'/17'), 1.21 (3H, *s*, Me-16'/17'), 1.72 (3H, *s*, Me-18), 1.92 (3H, *s*, Me-18'), 1.98 (12H, *br s*, Me-19, 20, 19', 20'), 2.01 *s*, 2.04 *s* and 2.05 *s* (3 + 3 + 3H, OAc at C-2, C-3 and C-4 in carbohydrate), 2.07 (3H, *s*, OAc at C-3), 2.48 (1H, *dd*, J_1 = 5 Hz, J_2 = 12 Hz, H-4), 2.50 (1H, *br s*, OH at C-1'), 3.75 (1H, *d*, *J* = 9 Hz, H-2'), 3.96 (1H, *m*, H-5 in carbohydrate), 4.78 (1H, *t*, J_1 = J_2 = 9.7 Hz, H-4 in carbohydrate), 4.93 (1H, *dd*, J_1 = 3.7 Hz, J_2 = 9.7 Hz, H-2 in carbohydrate), 5.08 (1H, *m*, H-3), 5.11 (1H, *d*, *J* = 3.7 Hz, H-1 in carbohydrate), 5.43 (1H, *t*, J_1 = J_2 = 9.7 Hz, H-3 in carbohydrate), 5.67 (1H, *dd*, J_1 = 9 Hz, J_2 = 15 Hz, H-3'), 6.1–6.7 (*ca* 16H, *m*, olefinic H). Addition of D_2O resulted in exchange of the δ2.5 proton. All proton-proton spin couplings in the carbohydrate moiety was determined by spin decoupling experiments (see *A*, Fig. 1).

For comparison the tetraacetate of α-D-chinovose was prepared; ^{1}H NMR ($CDCl_3$, 400 MHz) δ and *J* (determined by spin decoupling) (see *B*, Fig. 1).

Glycoside hydrolysis of myxoxanthophyll tetraacetate (1.0 mg *ex O. agardhii* var Kolbotnvatn) was carried out as previously described [15]. The resulting reducing carbohydrate was acetylated and submitted to comparative GLC (Varian 3300, BP-5 column, carrier gas H_2, flow 5 psi) R_t: authentic D-chinovose tetraacetate 7.35 min, acetylated hydrolysate 7.35 min (no separation upon co-chromatography with authentic D-chinovose tetraacetate), L-rhamnose tetraacetate 7.44 min, L-fucose tetraacetate 7.52 min.

Attempts to separate authentic D-chinovose tetraacetate and the acetylated hydrolysate on a chiral GLC column (Chirazil-Val., Pierce, H_2 carrier gas, 5 psi) failed (R_t 6.92 min). However, also D- and L-arabinose tetraacetate could not be separated in the same system.

Oscillol-2,2'-di-(O-methyl)-methylpentoside. R_f 0.05 (60% AH); VIS λ_{max}^{MeOH} nm: 460, 490, 525. The tetraacetate was prepared as previously described [3], R_f = 0.55 (50% AH); VIS λ_{max} nm: 462, 492, 526; MS *m/z* (rel. int.): 331 (80), 273 (80), 245 (80), 169 (100).

Oscillaxanthin. R_f 0.02 (60% AH); VIS λ_{max}^{MeOH} nm: 465, 492, 527. The hexaacetate was prepared by standard acetylation [7], R_f 0.50 (50% AH); VIS λ_{max} nm: 465, 492, 527; MS *m/z* (rel. int.): 331 (100), 273 (100), 169 (100).

REFERENCES

1. Goodwin, T. W. (1980) *The Biochemistry of the Carotenoids. Vol. I. Plants*, p. 232. Chapman & Hall, London.
2. Liaaen-Jensen, S. (1978) in *Marine Natural Products. Chemical and Biological Perspectives* (Scheuer, P., ed.) Vol. 2, p. 16. Academic Press, New York.
3. Francis, G. W., Hertzberg, S., Andersen, K. and Liaaen-Jensen, S. (1970) *Phytochemistry* **9**, 629.
4. Rønneberg, H., Andrewes, A. G., Borch, G., Berger, R. and Liaaen-Jensen, S. (1985) *Phytochemistry* **24**, 309.
5. Rønneberg, H., Foss, P., Ramdahl, T., Borch, G., Skulberg, O. and Liaaen-Jensen, S. (1980) *Phytochemsitry* **19**, 2167.
6. Heilbron, I. M. and Lythgoe, B. (1936) *J. Chem. Soc.* 1376.
7. Hertzberg, S. and Liaaen-Jensen, S. (1966) *Phytochemistry* **5**, 557.
8. Hertzberg, S. and Liaaen-Jensen, S. (1969) *Phytochemistry* **8**, 1259.
9. Karrer, P. and Rutschmann, J. (1944) *Helv. Chim. Acta* **27**, 1691.
10. Hertzberg, S. and Liaaen-Jensen, S. (1969) *Phytochemistry* **8**, 1281.
11. Hemmer, E. and Liaaen-Jensen, S. (1970) *Acta Chem. Scand.* 3019.
12. Hallenstvet, M., Liaaen-Jensen, S. and Skulberg, O. (1979) *Biochem. Syst. Ecol.* **7**, 1.
13. Hertzberg, S., Liaaen-Jensen, S. and Siegelman, H. W. (1971) *Phytochemistry* **10**, 3121.

14. Riesen, R. Pfander, H. and Schiedt, R. (1984) *Abstr. 7th Int. IUPAC Carotenoid Symposium*, München, P40.
15. Hertzberg, S. and Liaaen-Jensen, S. (1967) *Phytochemistry* **6**, 1119.
16. Wilkinson, S. G. (1977) in *Surface Carbohydrates of the Prokaryotic Cell* (Sutherland, I., ed.). Academic Press, London.
17. Skulberg, O. M. (1980) *Prog. Water Technol.* **12**, 121.
18. Baker, A. F. and Bold, H. C. (1970) *Taxonomic Studies in the Oscillatoriaceae. Phycological studies*, X, p. 1. Univ. Texas Publ., Austin, TX.
19. Rippka, R., Deruelles, J., Waterbury, J. B., Herdman, M. and Stanier, R. Y. (1979) *J. Gen. Microbiol.* **111**, 1.
20. Humm, H. J. and Wicks, S. R. (1980) *Introduction and Guide to the Marine Blue-green Algae*. Wiley, New York.
21. Liaaen-Jensen, S. (1977) in *Marine Natural Products Chemistry* (Faulkner, D. J. & Fenical, W. H., eds) p. 239. Plenum Press, New York.
22. Goodwin, T. W. (1980) *The Biochemistry of the Carotenoids. Vol. I. Plants*. Chapman & Hall, London.
23. Skulberg, O. M. and Skulberg, R. (1985) *Arch. Hydrobiol. Algol. Stud.* **38/39**, 157.
24. Geitler, L. (1932) in *Kryptogamenflora* Rabenhorst, L., ed.). XIV, Leipzig.
25. Rott, E. (1976) *Ber. Nat. Med. Ver. Innsbruck* **63**, 57.
26. Skulberg, O. M. (1983) *Culture Collection of Algae at Norwegian Institute for Water Research*. NIVA Publication, Oslo.
27. Hughes, E. O., Gorham, P. R. and Zehnder, A. (1958) *Can J. Microbiol.* **4**, 225.
28. Foss, P., Guillard, R. R. L. and Liaaen-Jensen, S. (1984) *Phytochemistry* **23**, 1629.
29. Skjetne, T., Bjørnland, T. and Liaaen-Jensen, S. (1984) *Abstr. 7th Int. IUPAC Carotenoid Symposium*, München p. 36.
30. Foss, P., Partali, V., Olsen, Y., Borch, G. and Liaaen-Jensen, S., *Acta Chem. Scand.* (in press).