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THE STRUCTURE OF ALEURIAXANTHIN*

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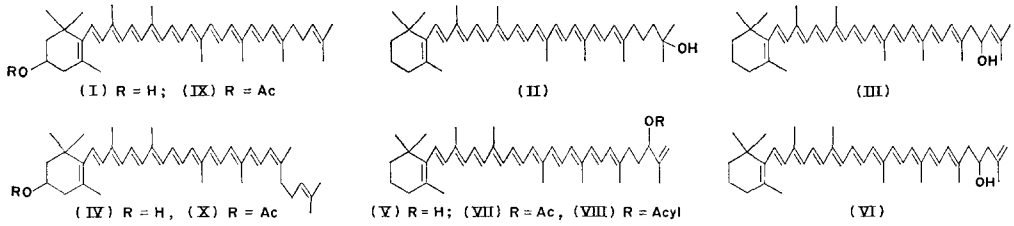
Key Word Index—*Aleuria aurantia*; fungus; carotenoid; aleuriaxanthin; chemical structure; NMR and IR spectra.

Abstract—The structure of aleuriaxanthin ex. *Aleuria aurantia* has been shown to be 1′,2′-dihydro-1′,16′-didehydro-β,ψ-caroten-2′-ol (V) by means of chemical and spectroscopic evidence.

THE CAROTENOIDS of *Aleuria aurantia* (Fr.) Fuckel (*Peziza aurantia*) have previously been investigated by Lederer,[1] Valadon,[2] and Liaaen-Jensen.[3] The major xanthophyll of *A. aurantia* with a β,ψ-carotene chromophore, previously identified as rubixanthin,[2] was shown to be a natural ester. The free alcohol was different from rubixanthin (I) and 1′,2′-dihydro-β,ψ-caroten-1′-ol (II).[3] This xanthophyll, named aleuriaxanthin,[3] did not appear to contain any hydroxy groups allylic to the polyene chain, since no products with elongated chromophores were formed on treatment with acidified chloroform or allylic oxidation with *p*-chloranil.[3] By exclusion the tentative constitution β,ψ-caroten-3′-ol (III) was considered for aleuriaxanthin. Without direct comparison a possible identity of aleuriaxanthin and gazaniaxanthin was not excluded.[3] Gazaniaxanthin has later been shown to be the 5′,6′-*cis* isomer (IV) of rubixanthin (I).[4,5]



(I) R = H; (IX) R = Ac (II) (III)

(IV) R = H, (X) R = Ac (V) R = H; (VII) R = Ac, (VIII) R = Acyl (VI)

Several attempts in this laboratory during the last decade to arrive at an unambiguous constitution for aleuriaxanthin, using diverse spectroscopic and chemical evidence, have failed, mainly due to the small amounts of sample available and the general instability of the

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[1] LEDERER, E. (1938) *Bull. Soc. Chim. Biol.* **20**, 611.
[2] VALADON, L. R. G. (1964) *Biochem. J.* **92**, 19 P.
[3] LIAAEN-JENSEN, S. (1965) *Phytochemistry* **4**, 925.
[4] BROWN, B. O. and WEEDON, B. C. L. (1968) *Chem. Commun.* 382.
[5] ARPIN, N. and LIAAEN-JENSEN, S. (1969) *Phytochemistry* **8**, 185.

compound. Based on earlier unreported studies the alternative structures 1′,2′-dihydro-1′,16′-didehydro-β,ψ-caroten-2′ or 3′-ol (V,VI) have been advanced.[6,7]

In a recent reinvestigation, aleuriaxanthin was obtained in sufficient quantity for full PMR characterization and unequivocal structural assignment. We now report the results of several isolations which have led to the constitution 1′,2′-dihydro-1′,16′-didehydro-β,ψ-caroten-2′-ol (V) for aleuriaxanthin with a novel end group among carotenoids.

A total synthesis of aleuriaxanthin acetate (VII) and aleuriaxanthin (V) itself has confirmed the present assignment.[8] The new nomenclature rules for carotenoids recommended by IUPAC[9] have been used.

RESULTS AND DISCUSSION

Aleuria aurantia contained *ca.* 0·13% total carotenoids, based on the dry acetone extracted residue. Aleuriaxanthin ester constituted *ca.* 20% of the total. The ester (VIII) was isolated in the usual manner and purified by column or TLC. The visible light absorption spectrum had spectral characteristics typical of a β,ψ-carotene chromophore.

The MS of several preparations of the natural ester exhibited molecular ions at *m/e* 932, 858, 840, 814 and 790. However, none of the preparations exhibited the same prominent molecular ions. After saponification or reduction with lithium aluminium hydride the molecular ion was observed at *m/e* 552, thus indicating that the esterifying fatty acids were C_{25}-saturated hydroxy, C_{21}-monounsaturated, C_{20}-triunsaturated, C_{18}-diunsaturated, and C_{16}-saturated fatty acids, respectively. These results may reflect chemical variation between fungi from different localities or seasonal variations. The PMR spectrum of the natural ester confirmed the presence of unsaturated esterifying acid(s).

Due to the general instability of free aleuriaxanthin the pigment was purified via the acetate, which after TLC and crystallization from acetone–methanol was obtained as purple prisms of m.p. 134·5–135·5°. The visible light absorption spectrum was identical with those of the natural ester and free aleuriaxanthin. The IR spectrum exhibited characteristic acetate absorption at 1740 cm^{-1} and a medium strength absorption at 900 cm^{-1} beside common carotenoid absorptions. The PMR data, including signal assignments are given in Table 1. Features of special interest are a 6 proton singlet at δ 1·02 which was ascribed to the *gem.*-dimethyl groups of an unsubstituted β-end group, a 1 proton multiplet at δ 5·15 which was ascribed to a methine proton of a secondary acetate, and a signal at δ 4·95 integrating for 2 protons. The molecular ion on electron impact was observed at *m/e* 594·4438 (Calc. for $C_{42}H_{58}O_2$: 594·4436) consistent with a monoacetate of a $C_{40}H_{56}O$ alcohol.

Saponification of aleuriaxanthin acetate (VII) or the natural ester (VIII) afforded free aleuriaxanthin (V), which after purification by TLC and crystallization from ether–light petrol. had m.p. 122–122·5°. The visible light absorption spectrum was typical of a β,ψ-carotene chromophore.[10] The IR spectrum exhibited characteristic absorptions at

[6] LIAAEN-JENSEN, S. (1971) in *Carotenoids* (ISLER, O., ed.), p. 61, Birkhäuser, Basel.
[7] LIAAEN-JENSEN, S (1973) Proc. 3rd. International Symposium on Carotenoids other than Vitamin A, Cluj, Romania, 1972, *Pure Appl Chem.* **35**, 81.
[8] KJØSEN, H. and LIAAEN-JENSEN, S (1973) *Acta Chem. Scand* in press.
[9] ANON (1971) IUPAC Commission on the Nomenclature of Organic Chemistry and IUPAC–IUB Commission on Biochemical Nomenclature: Tentative Rules for the Nomenclature of Carotenoids. *Biochemistry* **10**, 4827.
[10] VETTER, W., ENGLERT, G., RIGASSI, N. and SCHWIETER, U. (1971) in *Carotenoids* (ISLER, O., ed), p 189, Birkhauser, Basel.

3300 cm^{-1} (bonded OH) and 897 cm^{-1} apart from common carotenoid CH vibrations. The PMR data (Table 1) showed a 6 proton singlet at δ 1·02 ascribed to the *gem.*-dimethyl groups of a β-end group. The fact that this signal was not affected by acetylation demonstrated that the β-end group was unsubstituted (see Ref. 5). A 1 proton signal at δ 4·07 may be ascribed to the methine proton of a secondary alcohol. However, the coupling pattern could not initially be established due to the lack of material. Two broad signals at δ 4·97 and δ 4·88 integrating for one proton each were attributed to a terminal methylene group,[11] an assumption supported by the absorption at 897 cm^{-1} in the IR. Other tentative PMR assignments are given in Table 1. The MS of aleuriaxanthin showed the molecular ion at *m/e* 552·4334 (Calc. for $C_{40}H_{56}O$: 552·4331) in agreement with its formulation as a C_{40}-monool. Aleuriaxanthin is thus a structural isomer of rubixanthin (III) and gazaniaxanthin (IV).

TABLE 1. PMR DATA ($CDCl_3$) FOR ALEURIAXANTHIN (V) AND ALEURIAXANTHIN ACETATE (VII) WITH PRELIMINARY ASSIGNMENTS

Signal (δ-value)		
Aleuriaxanthin (V)	Aleuriaxanthin acetate (VII)	Proton assignments
7·0–5·8 (15 H)	7·0–5·8 (15 H)	Conj. olefinic
~5·0, ~4·9 (2 H)	~4·95 (2 H)	Non-conj. olefinic
	~5·2 *m* (1 H)	Methine *sec.* acetate
~4·1 *m* (1 H)		Methine *sec.* alcohol
	2·02 *s* (3 H)	Acetate Me
1·97 *s* (12 H)	1·97 *s* (12 H)	In-chain Me
1·82 *s* (3 H)	1·72 *s* (3 H)	End-of-chain Me
1·72 *s* (6 H)	1·82 *s* (6 H)	Me at C-5 of β-ring and Me at isolated double bond
~1·55 *m*	~1·55 *m*	Non-allylic CH_2
1·02 *s* (6 H)	1·02 *s* (6 H)	*gem*-Me at unsubst. β-ring

Considering the methyl signals of the PMR spectrum (Table 1) and the β,ψ-carotene chromophore of aleuriaxanthin the terminal methylene group was restricted to the 16′- or 17′-positions. The position of the hydroxy group, however, was not directly evident from the spectroscopic data available. From the PMR evidence the hydroxy group was secondary and not located in the β-end of the molecule. No signal associated with the methylene protons of a primary alcohol or methyl groups adjacent to tertiary hydroxy groups, but a methine proton of a secondary alcohol, with the expected down-field shift on acetylation (Table 1) was observed.

The secondary character of the hydroxy group was confirmed by acetylation and silylation data. Additional chemical reactions were utilized in attempts to establish the exact position of the hydroxy function in the aliphatic terminus. As previously observed[3] attempted oxidation with *p*-chloranil[12] and treatment with acidified chloroform[13] did not give products with elongated chromophores, indicating that the hydroxy function was not allylic to the

[11] ARPIN, N., FIASSON, J.-L., BOUCHEZ-DANGYE-CAYE, M. P., FRANCIS, G. W. and LIAAEN-JENSEN, S. (1971) *Phytochemistry* **10**, 1595.
[12] WARREN, C. K. and WEEDON, B. C. L. (1958) *J. Chem. Soc.* 3972.
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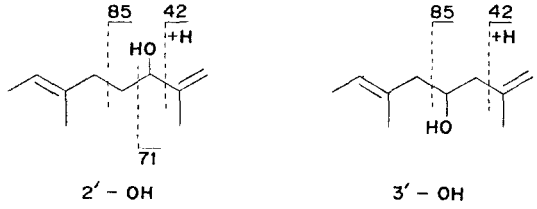
main chromophore, i.e. not at C-4', leaving C-2' or C-3' as likely possibilities. The reactions with other reagents capable of allylic oxidation to isolated double bonds were studied. Oxidation with nickel peroxide[14] resulted in a product with virtually the same chromophore as the starting compound and a MW of 550 as judged from the MS. This product could, however, not be converted back to aleuriaxanthin upon reduction with lithium aluminium hydride.

Attempted allylic oxidation with silver carbonate,[15] manganese dioxide,[16] or dicyanodichlorobenzoquinone (DDQ)[17] only led to severe decomposition of the pigment and no identifiable products were obtained. Attempted dehydration of aleuriaxanthin with phosphorous oxychloride[18] or β-elimination[19] by tosylation and alkali treatment resulted in decomposition of the pigment, as did attempted allylic rearrangement under acidic conditions.

Comparative hydrolysis of aleuriaxanthin acetate (VII) and rubixanthin acetate (IX) showed that the latter compound was hydrolysed twice as fast as (VII) indicating that the hydroxy function of aleuriaxanthin (V) was in a more hindered position than that of rubixanthin (III). However, the chemical behaviour of aleuriaxanthin did not allow a distinction between 2'- or 3'-hydroxy substitution to be made.

Careful examination of the mass spectrometric fragmentation pattern[20] seemed to give a slight precedence for 2'-hydroxy rather than 3'-hydroxy substitution due to the losses of 42, 71 and 85 m.u. from the molecular ion (Scheme 1).



SCHEME 1.

Other losses of 29 and 57 as well as the commonly observed losses of 79, 92 (toluene), 106 (xylene), and 158 (dimethylcyclodecapentaene) m.u.[21] were also observed. The mass spectrum of the acetate did not give any information as regards the position of the acetoxy function. Losses of 42 (ketene), 43 (acetyl) and 60 (acetic acid) m.u. from the molecular ion were observed in addition to the typical carotenoid losses. Direct comparison of the MS of rubixanthin (I) and gazaniaxanthin (IV) and their acetates (IX and X) showed that they differed considerably from those of aleuriaxanthin (V) and its acetate (VII).[20]

In order to obtain additional mass spectrometric information the preparation of aleuriaxanthin methyl ether was attempted using methyl iodide and silver oxide in dimethylformamide.[22] Besides unreacted aleuriaxanthin, a product which had unchanged spectral

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[15] FETIZON, M. and GOLFIER, M (1968) *Compt. Rend.* **267***c*, 900.
[16] ATTENBURROW, J , CAMERON, A. F B., CHAPMAN, J. H., EVANS, R. H , HEMS, B. A., JANSEN, A B A. and WALKER, T. (1952) *J. Chem. Soc.* 1094.
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[19] KUHN, R. and WINTERSTEIN, A (1934) *Ber.* **67**, 344.
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[21] ENZELL, C. R., FRANCIS, G. W. and LIAAEN-JENSEN, S. (1969) *Acta Chem. Scand.* **23**, 727.
[22] KUHN, R., TRISCHMANN, H and LOW, I. (1955) *Angew. Chem* **67**, 32.

characteristics in visible light was obtained in small quantity. However, the molecular ion of this product occurred at *m/e* 610 (expected M = 566 for the methyl ether).

A final reisolation of aleuriaxanthin from *A. aurantia* provided sufficient material of a purity which allowed detailed PMR spectra of both the free alcohol and the acetate to be obtained (Fig. 1). The methine protons are seen to resonate as sharp triplets (J 6 Hz) at δ 4·07 and δ 5·14, respectively, a coupling pattern which can only be accommodated with the hydroxy and acetoxy functions at C-2′. We therefore conclude that aleuriaxanthin is 1′,2′-dihydro-1′,16′-didehydro-β,ψ-caroten-2′-ol (V).

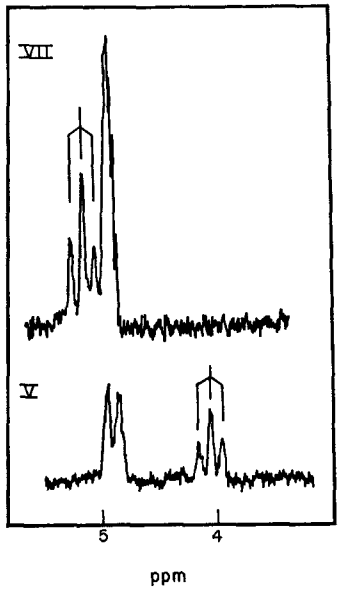


FIG. 1. PMR SIGNALS OF THE METHINE AND TERMINAL METHYLENE PROTONS OF ALEURIAXANTHIN AND ALEURIAXANTHIN ACETATE IN $CDCl_3$ SOLUTION.

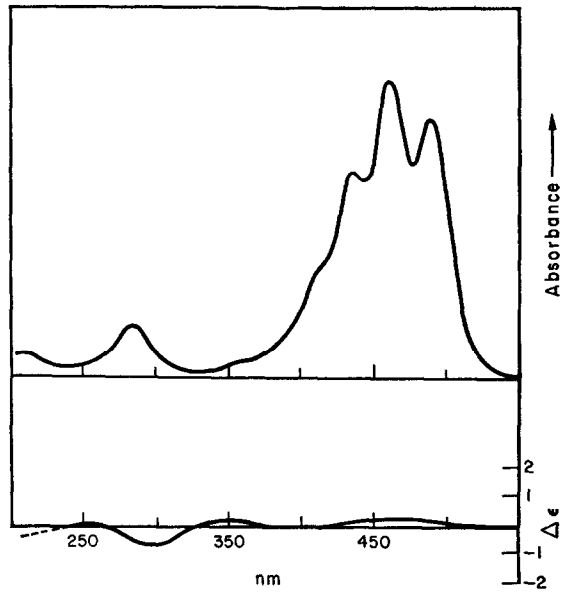


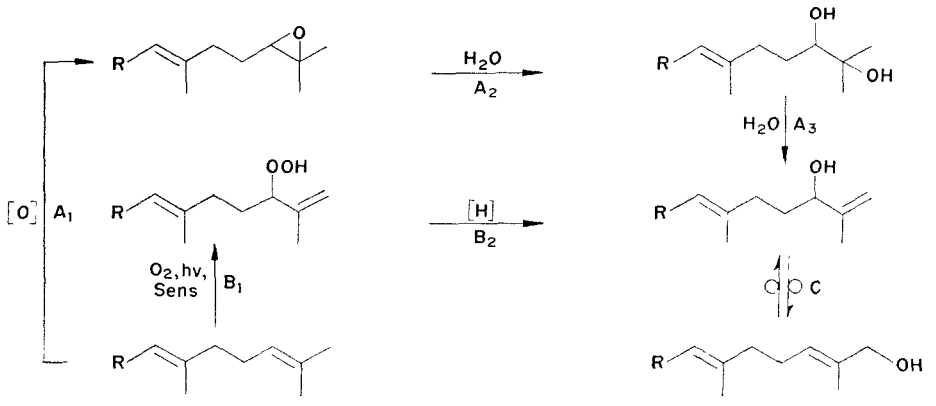
FIG. 2. VISIBLE LIGHT AND CD SPECTRA OF ALEURIAXANTHIN ACETATE (VII) IN EPA SOLUTION.

It was observed that the terminal methylene protons of aleuriaxanthin gave rise to two distinct signals at δ 4·97 and δ 4·88 whereas for the acetate only one signal at τ 5·04 was observed, obviously reflecting the anisotropic effect of the acetoxy function.

The present structural assignment for aleuriaxanthin has been confirmed by total synthesis.[8]

The CD spectrum of aleuriaxanthin has been recorded. However, no circular dichroism was observed within the range of the instrument. An optical rotation of +0·001–0·002° at 365 nm was within the limits of error of the polarimeter, but suggested a specific rotation of $[\alpha]_{365}^{RT}$ = *ca.* +100° as would be expected for this type of compound. The CD spectrum of aleuriaxanthin acetate (VII) is given in Fig. 2. These data may enable a future stereochemical correlation. At present the absolute configuration at C-2′ of aleuriaxanthin (V) is not settled.

The biosynthetic formation of the hydroxylated end group of aleuriaxanthin may be considered analogous to the formation of the same structural element in other classes of



SCHEME 2.

compounds.[23,24] For substituted coumarins a possible formation via an epoxide and a glycol has been proposed,[23] as adopted in A_{1-3} (Scheme 2). An alternative formation by photosensitized autoxidation has been considered for triterpenes,[24] adopted in B_{1-2} (Scheme 2). Among the carotenoids the close relationship between the aleuriaxanthin type end group and an end group of the lycoxanthin (ψ,ψ-caroten-16-ol) type is pointed out. These may be interconverted by simple allylic rearrangements (C, Scheme 2).

TABLE 2. R_fS ON CIRCULAR PAPER OF ALEURIAXANTHIN AND DERIVATIVES

Carotenoid	Schleicher & Schull No. 287				Schleicher & Schüll No. 288			
	0%*	1%	2%	5%	1%	2%	5%	10%
Aleuriaxanthin TMS ether			0 90	0·98		0·85		
Aleuriaxanthin natural ester	0 44	0·50	0·75		0·36	0·52		
Aleuriaxanthin acetate (VII)		0·55	0 73			0·56	0 81	0·94
Aleuriaxanthin (V)		0 24	0·33	0·56		0·10	0·30	0 62
Oxidation product A				>0·67				
Reduced product A				0 67				
Methylation product			0·70	0 83				

* Acetone in light petrol.

EXPERIMENTAL

Materials and methods were as usually employed in this laboratory and are summarized elsewhere.[25,26] Adsorptive properties of the compounds studied are compiled in Table 2.

Isolation Only details of the final isolation are given. *Aleuria aurantia* (*ca.* 4 kg wet wt) was collected near Grenoble, France, in September 1972 and extracted exhaustively with acetone at room temp., leaving 320 g dry extracted residue. The extracted pigments (427 mg) were transferred into light petrol. with aq. NaCl and

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[24] FOURREY, J. L., RONDEST, J. R. and POLONSKY, J (1970) *Tetrahedron* **26**, 3839.
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[26] LIAAEN-JENSEN, S. and JENSEN, A. (1971) *Methods Enzymol.* **23**, 586.

the extract washed, dried and the solvent evaporated. Some sterols were removed by precipitation with acetone. The carotenoids were chromatographed on alumina (Spence type H, activity grade 2[27]).

Aleuriaxanthin ester was eluted with 20–30% C_6H_6 in light petrol. and was further purified by chromatography on silica plates developed with 2% acetone in light petrol. The zones were scraped out and the pigments desorbed with Et_2O. The homogeneous ester (71 mg) had λ_{max} (acetone) (440), 462 and 492 nm; % III/II[28] = 34; ν_{max} (liq) 3100–2800 (CH), 1735 (C=O), 1650, 1630, 1560 (C=C), 1450 (CH_2,Me) 1395, 1375, 1360 (Me), 1245, 1170 (C–O–) 1030, 1010, 965 and 955 (*trans* –CH=CH–), 910 (=CH_2), 828 (> C=CH–), and 735 (CH_2) cm^{-1}; δ ($CDCl_3$) 7·0–5·80 (15 H, olefinic, carotenoid) 3·5–3·2 (6 H, olefinic, acyl), 5·55 (1 H, methine H), 4·94 (2 H, =CH_2), 2·78 *m* (2 H, α-CH_2, acyl), 1·97 *s* (4 × 3 H, in-chain Me), 1·82 *s* (3 H, Me at C-5′), 1·72 *s* (2 × 3 H, Me at C-5 and C-1′) 1·52 *m* (non-allylic CH_2), 1·32 and 1·27 (*ca.* 18H, CH_2 of fatty acid residue), 1·03 *s* (2 × 3 H, *gem*-Me at C-1) and 0·88 *t* (3 H, *J* 7 Hz, terminal Me of acyl); *m/e* 840 (M), 748 (M-92), 734 (M-106), 552, 551, 550, 536. Other isolates gave the following values for the molecular ion: lot 2; *m/e* 814 (M_1), 790 (M_2) and lot 3; *m/e* 932 (M_3), 858 (M_4) and 814 (M_1). The ester was saponified with 5% KOH in Et_2O–MeOH (1:1, 100 ml) for 1 hr, and the reaction mixture worked up in the usual manner. The pigments were purified on silica plates using C_6H_6 as developer and then immediately acetylated with Ac_2O (1 ml) in dry pyridine (10 ml) for 24 hr in the usual manner.

Aleuriaxanthin acetate (VII, 52 mg) was purified by chromatography on silica plates developed with C_6H_6. Crystallization and recrystallization from acetone–MeOH gave the acetate as purple prisms of m.p. 134·5–135·5°; λ_{max} (acetone) (440), 462·5 ($E^{1\%}_{1cm}$ = 2500), and 493 nm; % III/II[28] = 56; ν_{max} (KBr) 3040–2800 (CH), 1740 (C=O), 1440 (CH_2, Me), 1370 (Me), 1230 (C–O–), 1020, 963 and 953 (*trans* –CH=CH–), 900 (=CH_2), and 825 (> C=CH–) cm^{-1}; δ ($CDCl_3$) 7·0–5·8 (15 H, olefinic), 5·14 *t* (1 H, *J* 6 Hz, H-2′), 4·96 *m* (2 H, W_H 6 Hz, H-16′), 2·05 *s* (3 H, Me, acetate), 1·97 *s* (4 × 3 H, in-chain Me), 1·85 *s* (3 H, Me at C-5′), 1·74 *s* (2 × 3 H, Me at C-5 and C-1′), 1·53 (2 × 2 H, non-allylic CH_2), 1·27 imp., and 1·02 *s* (2 × 3 H, *gem*-Me at C-1); *m/e* 594·4438 (M, Calc. for $C_{42}H_{58}O_2$: 594·4436), 552 (M-42), 551 (M-43), 550 (M-44), 534 (M-60), 502 (M-92), 488 (M-106) and 436 (M-158).

Aleuriaxanthin (V). Aleuriaxanthin acetate (33 mg) was saponified with 5% KOH in Et_2O–MeOH (1:1 200 ml) for 3·5 hr. The products were worked up as usual and the pigments purified by chromatography on silica plates using C_6H_6 as developer; yield 28 mg (85%). Crystallization and recrystallization from Et_2O–light petrol. gave aleuriaxanthin of m.p. 122–122·5°; λ_{max} (acetone) (440), 462·5 ($E^{1\%}_{1cm}$ = 2440), and 493 nm, % III/II[28] = 53; ν_{max} (KBr) 3300 (bonded OH), 3030–2800 (CH), 1650, 1630, 1550 (C=C), 1440 (CH_2,Me), 1395, 1360 (Me), 1055–995 (OH), 960 (*trans* –CH=CH–), 897 (=CH_2) and 825 (> C=CH–) cm^{-1}; δ ($CDCl_3$) 7·0–5·8 (15 H, olefinic), 4·97 and 4·88 (1 + 1 H, W_H 4 Hz, H-16′), 4·07 *t* (1 H, *J* 6 Hz, H-2′), 1·97 *s* (4 × 3 H, in-chain Me), 1·85 *s* (3 H, Me at C-5′), 1·74 *s* (2 × 3 H, Me at C-5 and C-1′), 1·55 (2 × 2 H, non-allylic CH_2), 1·27 imp., and 1·02 *s* (2 × 3 H, *gem.* Me at C-1); *m/e* 552·4334 (M, Calc. for $C_{40}H_{56}O$: 552·4331), 537 (M-15), 534 (M-18), 523 (M-29), 510 (M-42), 509 (M-43), 495 (M-57), 481 (M-71), 467 (M-85), 460 (M-92), 446 (M-106) and 394 (M-158).

Aleuriaxanthin trimethylsilyl ether. Aleuriaxanthin (0·1 mg), was silylated at room temp. in the usual manner.[26] The TMS ether had the same spectral characteristics in visible light (acetone solution) as V; *m/e* 624 (M).

Oxidation with nickel peroxide.[14] Aleuriaxanthin (3·3 mg) and NiO_2 (27 mg, 4·3 × 10^{-5} g atom O) in dry Et_2O were stirred at room temp. for 75 min and the solution filtered; pigment recovery 23%. The products were separated on silica plates (10% Et_2O in light petroleum). One new product A had λ_{max} (acetone) (435), 454, 481 nm; % III/II = 9·5; *m/e* 550 (M). This product was reduced with excess $LiAlH_4$ in dry Et_2O. A product more polar than the starting product but less polar than aleuriaxanthin (Table 2) was obtained.

Oxidation with Ag_2CO_3–celite.[15] Aleuriaxanthin (1·4 mg) and Ag_2CO_3–celite (70 mg) in dry C_6H_6 (3 ml) were kept at 80° for 1 hr. The solution was filtered; pigment recovery 28%. Only unreacted aleuriaxanthin was recovered.

Oxidation with manganese dioxide.[16] Aleuriaxanthin (0·15 mg) and MnO_2 (7 mg) in light petrol. (2 ml) were stirred under N_2 at room temp. for 1·5 min at which time the sol. had turned completely colourless.

Oxidation with DDQ.[17] Aleuriaxanthin (0·1 mg) and DDQ (0·2 mg) in C_6H_6 (2 ml) were reacted at room temp. for 30 min and the reaction mixture chromatographed on a silica plate. Only decomposed pigments were obtained.

Attempted dehydration with $POCl_3$. Aleuriaxanthin (1·08 mg) and $POCl_3$ (0 05 ml) in dry pyridine (5 ml) were kept at room temp. for 20 min and the products extracted into light petrol. after addition of H_2O. Only products which did not migrate on kieselguhr paper or silica plates were obtained.

Attempted dehydration by tosylation followed by elimination. Aleuriaxanthin (0·15 mg) was treated with *p*-toluenesulfonyl chloride (0·4 mg) in dry pyridine at room temp. for 16 hr. The reaction mixture was worked up directly with excess 10% KOH in MeOH. The products had no carotenoid absorption in visible light.

Methylation of aleuriaxanthin.[22] Aleuriaxanthin (0·7 mg), Ag_2O (84 mg) and MeI (0·28 ml) in *N,N*-dimethylformamide (0·4 ml) were stirred at room temp. for 45 min and the products worked up as usual.

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Unreacted aleuriaxanthin (0·2 mg) was recovered. A product (0·2 mg) had R_f = 0 70 (Table 2); λ_{max} (acetone) (350), (435), 460 and 489 nm; % III/II = 24; *m/e* 610 (M, expected for the methyl ether M = 566).

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