Carotenoids and Related Polyenes. Part 2.[1] Photoisomerization of an Allenic Carotenoid, Peridinin, and Allenic Model Compounds

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Iodine-catalysed photoisomerization of peridinin **1a** gave the novel (6*S*)-allenic isomer **1b** whose structure was confirmed by chemical synthesis. In addition, the photochemical behaviour of several model compounds having a part structure of allenic carotenoids was investigated. From these results, photoisomerization of the allenic double bond in allenic carotenoids was discussed.

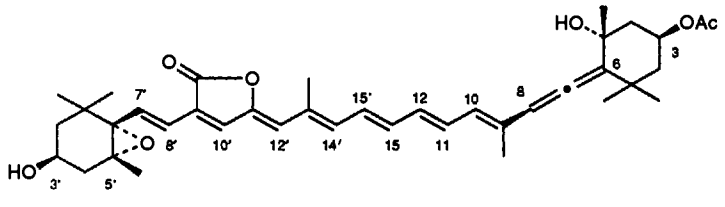
Of approximately 600 naturally occurring carotenoids of known structure,[2] about 13 allenic carotenoids having 6*R* and/or 6′*R* chirality are included. Peridinin **1a**[3] in dinoflagellates and fucoxanthin **2a**[4] in brown algae are representative allenic carotenoids. These are known as auxiliary light-harvesting pigments for photosynthesis[5] in the sea.

Isoe *et al.*[6] in 1971 suggested that allenic-bond formation in allenic carotenoids might be initiated by a similar mechanism to the photosensitized oxidation of 3-hydroxy-β-ionol, providing an allenic compound of established relative configuration. A subsequent *S*-to-*R* isomerization of the allenic bond would then be required in order to account for the chirality of natural allenic carotenoids. In 1974 the isolation of the minor, presumed (6′*S*)-allenic, isomer **2b** of fucoxanthin **2a** was claimed from iodine-catalysed stereomutation mixtures of fucoxanthin **2a** and from the brown alga *Fucus serratus*.[7] However, the identification of compound **2b** has since been disproved[8,9] following reinvestigation of the previously reported ^{1}H NMR data, including our synthetic allenic apocarotenals.[10] In consequence, it was suggested that a chemical-shift difference of allenic protons between 6′*R* and 6′*S* isomers is < 0.17 ppm ($CDCl_3$), and that 0.5 ppm downfield shifts for the allenic proton coincide with a 9′*Z* configuration. In a previous paper, we have reported[11] the first isolation of a novel (6*S*)-allenic isomer **1b** from the photoirradiation mixture of peridinin **1a**, and its structural determination by chemical methods. This was the first time that *R*-to-*S* isomerization of the allenic bond in conjugated polyene compounds has been achieved. In the present paper, we describe the experimental details and further studies on the photoisomerization of allenic model compounds, which support the proposed biosynthetic mechanism[6] for allenic carotenoids.

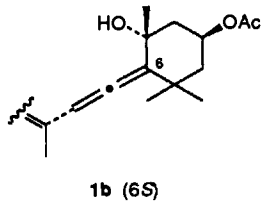
Results

Isolation and Characterization of a Novel Photoproduct of Peridinin, a (6S)-*Allenic Isomer* **1b**.—(a) *Photoisomerization of peridinin* **1a**. Photoisomerization of peridinin **1a** was carried out in benzene solution containing a catalytic amount of iodine by the light of a daylight fluorescent lamp (15 W) for 25 min. As was revealed by HPLC with a system designed for separation of synthetic peridinin and its isomers, several isomers were observed [Fig. 1(a)]. A photo-steady-state was achieved after 25 min when the time course of the photoisomerization was followed by HPLC (Fig. 2). The proportions of isomers [I : II (**1a**) : III : IV] were ~5 : 8 : 3 : 1. Photoisomerization of peridinin **1a** in benzene solution in the absence of iodine proceeded very slowly and only a small amount of the isomer I was detected after irradiation for 3 h [Fig. 1(b)]. Isomers isolated by preparative HPLC were identified respectively by visible, FT–IR and ^{1}H NMR spectroscopy (see Experimental section). Spectral properties of isomer IV were in good accord with those of (11′*E*)-peridinin recently synthesized.[1] Isomer III was regarded as the (9*Z*)-isomer from a strong downfield shift[8] (~0.5 ppm) of the allenic proton in the ^{1}H NMR data. The ^{1}H NMR spectrum of isomer I was similar to that of peridinin **1a** except for the allenic proton (0.1 ppm downfield shift).[8] It was therefore expected to be the new (6*S*)-allenic isomer **1b**.

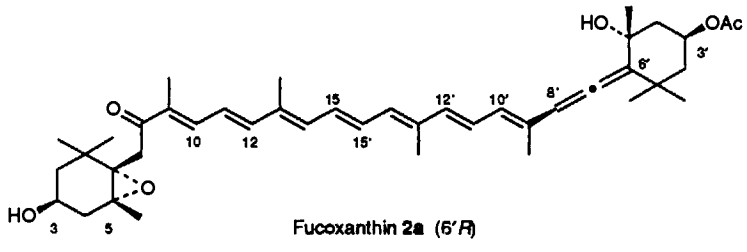
(b) *Characterization of the* (6S)-*isomer of peridinin by chemical synthesis.* In order to confirm the structure of the novel allenic isomer I (**1b**) of peridinin **1a**, synthesis of (6*S*)-peridinin was accomplished according to the same methodology as applied in the synthesis of (6*R*)-peridinin **1a**[1] [condensation between the aldehydo ester **5** and the (6*R*)-allenic sulfone **3b**] as follows (Scheme 1).



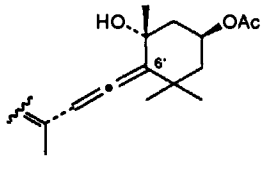
Peridinin **1a** (6*R*)



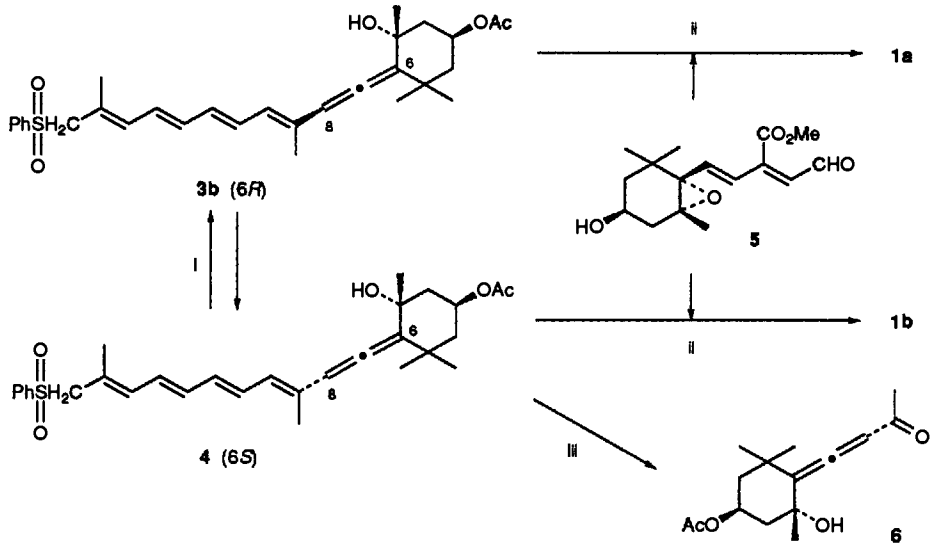
1b (6*S*)



Fucoxanthin **2a** (6′*R*)



2b (6′*S*)



Scheme 1 *Reagents and conditions:* i, *hv*, benzene; ii, LDA, THF–hexane (1:1), −78 °C; iii, O_3, MeOH, −78 °C

The (6*S*)-allenic sulfone **4**, the key intermediate for the synthesis of (6*S*)-peridinin **1b**, was obtained by direct irradiation of its (6*R*)-epimer **3b**, which was carried out in benzene solution in the presence of iodine catalyst and using the light of a daylight fluorescent lamp (15 W) for 2 h to give a photoequilibrium mixture (72%; **3b**:**4** ~1:1). In addition, direct irradiation of (6*R*)-allenic sulfone **3b** by use of a high-pressure mercury lamp (300 W; Pyrex filter) provided the same mixture quantitatively in a shorter time (8 min). Unlike peridinin **1a**, iodine-catalysed photoreaction of compound **3b** provided a complex mixture.

The ^{1}H NMR signal of the allenic proton of the newly isolated isomer **4** was further downfield (0.12 ppm) than that of the (6*R*)-form **3b**, suggesting that compound **4** was the (6*S*)-allenic isomer. The chirality of compound **4** was chemically confirmed by ozonolysis to give the allenic ketone **6**, whose spectral data, including chiroptical properties, were identical with those of an authentic specimen prepared according to the literature.[12]

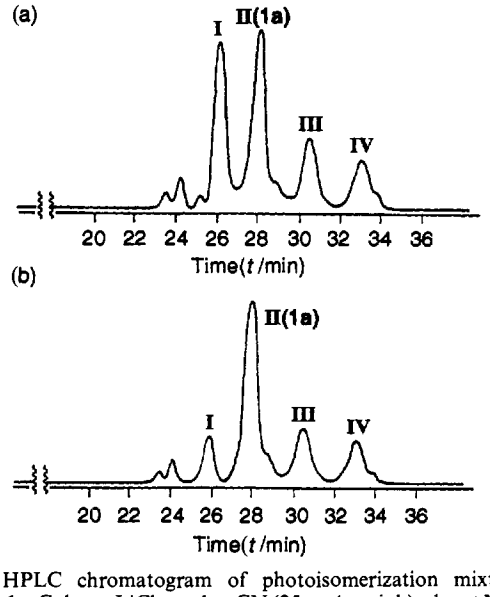


Fig. 1 HPLC chromatogram of photoisomerization mixture of peridinin **1a**. Column LiChrospher CN (25 × 4 cm i.d.); eluent MeOH–acetone–hexane (1:10:89); flow rate 1.5 cm^3 min^{-1}; detection λ 450 nm. (a) Irradiation of **1a** in the presence of iodine catalyst for 25 min; (b) Irradiation of **1a** in the absence of iodine catalyst for 3 h.

Based on the synthesis of peridinin **1a**, the (6*S*)-allenic sulfone **4** was condensed with the aldehydo ester **5** in the presence of lithium diisopropylamide (LDA) at −78 °C to provide condensation products, repeated purification of which by preparative HPLC in the dark led to (6*S*)-peridinin **1b** and its (11′*E*)-isomer in pure form. Spectral properties of synthetic **1b** were in good agreement with those of the isomer I isolated from the photoisomerization mixture of natural (6*R*)-peridinin **1a**. This is the first structural characterization of (6*S*)-peridinin **1b**.

(c) *Reversible photoisomerization of* (6S)-*peridinin* **1b** *and the* (6S)-*allenic sulfone* **4**. (6*S*)-Peridinin **1b** was also isomerized in benzene solution by irradiation in the presence of iodine to give a similar quasi-equilibrium mixture as in the case of peridinin **1a**. In addition, *S*-to-*R* isomerization of the allenic bond in the (6*S*)-allenic sulfone **4** was observed under the same irradiation conditions as in the case of compound **3b**. Thus, the photochemical behaviour of compounds **1a**, **1b**, **3b** and **4** supports the proposed biosynthetic mechanism[6] for allenic carotenoids.

Synthesis and Photoisomerization of Allenic Model Compounds.—The photochemical behaviour of several allenic model compounds **3**, **8**, **11** and **14** (Scheme 2) possessing a part structure of allenic carotenoids was investigated. On the other end of an allenic group in model conjugated systems, a formyl group (**a**) (a carbonyl group is contained in compounds **1** and **2**), a sulfonylmethyl group (**b**) (remarkable photoisomerization

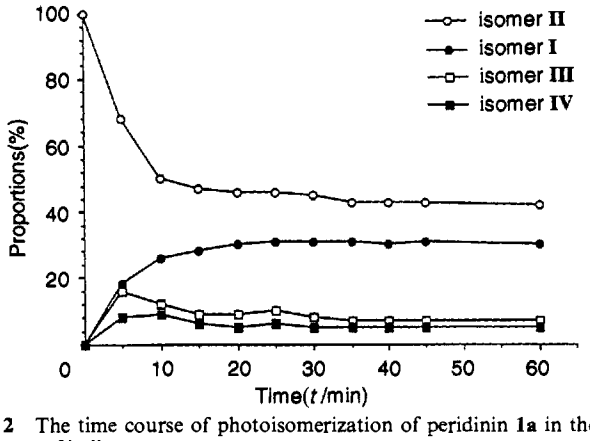
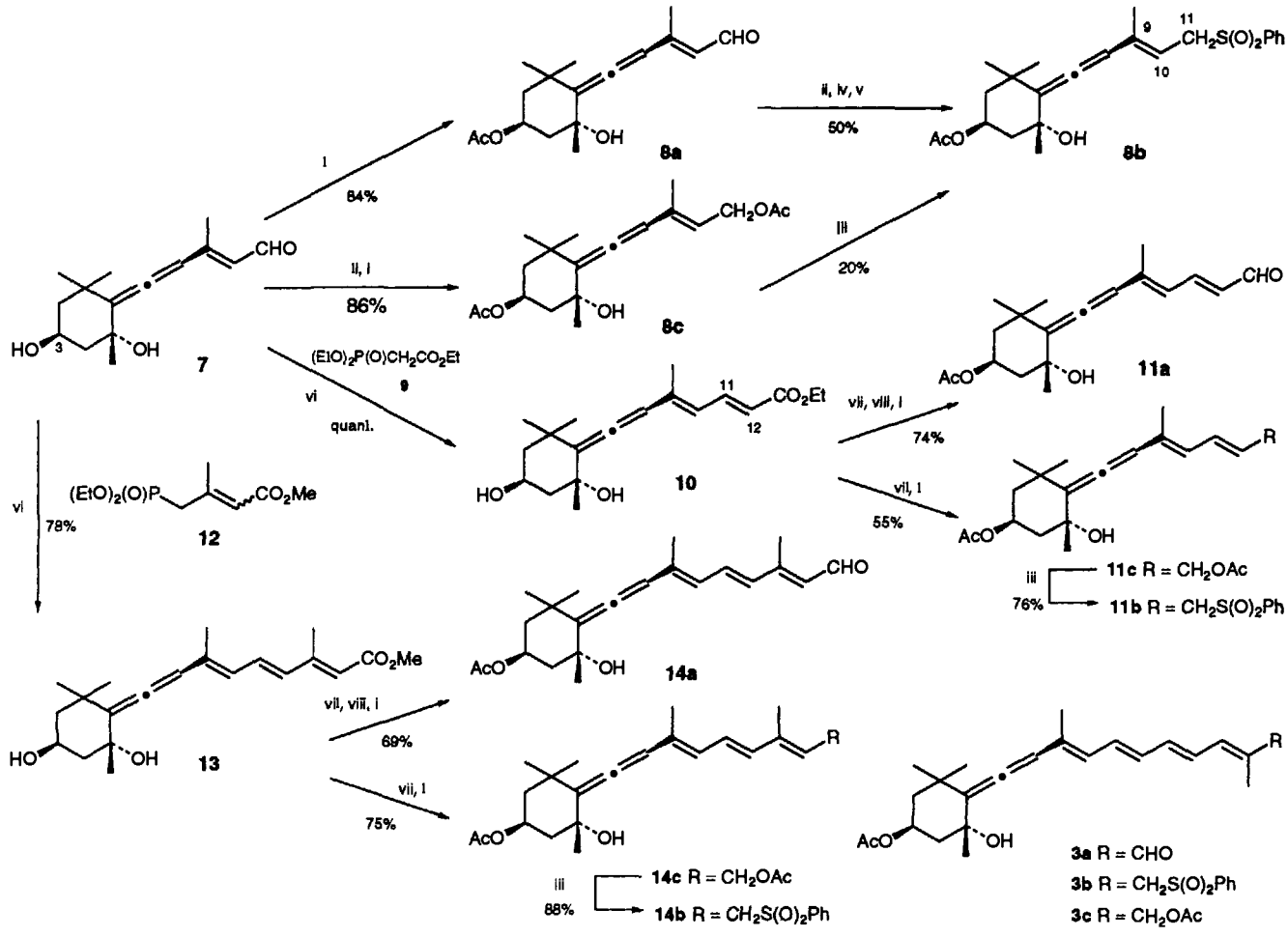


Fig. 2 The time course of photoisomerization of peridinin **1a** in the presence of iodine



Scheme 2 *Reagents and conditions:* i, Ac_2O, Py; ii, $NaBH_4$, MeOH; iii, $PhSO_2Na$, propan-2-ol–water, reflux; iv, MsCl, LiCl, γ-collidine, DMF; v, $PhSO_2Na$, DMF, room temp.; vi, BuLi, THF; vii, LAH, THF; viii, MnO_2, THF

was observed in the irradiation of compound **3b**) and an acetoxymethyl group (**c**) (acetoxy compounds were synthetic intermediates of sulfones) were selected respectively. These compounds were synthesized from the known C_{15}–allenic aldehyde **7**.[1]

(a) *Synthesis of allenic model compounds.* The 3-acetoxy allenic aldehyde **8a** was prepared from the corresponding 3-hydroxy compound **7** by acetylation (84%). Reduction of the formyl group in compound **7** with $NaBH_4$ followed by acetylation gave the diacetate **8c** (86%), which was converted in low yield into the sulfone **8b** containing its (9*Z*)-isomer using sodium benzenesulfinate in propan-2-ol–water under reflux for 48 h. Thus, compound **8a** was reduced with $NaBH_4$ to give the allenic alcohol, which was transformed into the desired sulfone **8b** (50% from **7**) *via* the corresponding allylic chloride as shown in Scheme 2. Stereochemistry of these isomers was confirmed by ^1H NMR spectroscopy including a 2D NOESY experiment: in the (9*E*)-sulfone **8b**, cross-peaks between 9-Me and 11-H_2 were observed. On the other hand, cross-peaks between 8-H and 11-H_2, 9-Me and 10-H were observed in the (9*Z*)-isomer of sulfone **8b**.

Dienyl allenic model compounds **11a–c** were synthesized from the dienyl ester **10**, which was prepared by an Emmons–Horner reaction of aldehyde **7** with the phosphonate **9** using butyllithium in a quantitative yield. An *E*-configuration was assigned to the newly formed 11,12-double bond of compound **10** from the coupling constants (15 Hz) between 11- and 12-H in the ^1H NMR spectrum. Reduction of the ester group in compound **10** with lithium aluminium hydride (LAH) followed by MnO_2 oxidation and subsequent acetylation of the 3-hydroxy group gave the 3-acetoxy allenic dienal **11a** (74%). The ester **10** was also reduced with LAH followed by acetylation to afford the diacetate **11c** (55%), which was refluxed with sodium benzenesulfinate in propan-2-ol–water to give the sulfone **11b** (76%).

Trienyl allenic model compounds **14a–c** were synthesized through the trienyl ester **13** in the same manner as in the case of the synthesis of **11a–c** as shown in Scheme 2.

Preparation of tetraenyl allenic model compounds **3a–c** was previously reported.[1]

(b) *Photoisomerization of allenic model compounds.* Photoisomerization of allenic model compounds **3**, **8**, **11** and **14** was carried out in benzene solution (3–4 mmol) by direct irradiation using a high-pressure mercury lamp (300 W; Pyrex filter). The irradiation was continued until the isomer ratio was unchanged (HPLC). Proportions and yields of isomers were calculated by HPLC analysis. Separation of the photoisomerization mixture by preparative HPLC provided each pure isomer, whose structures were confirmed on the basis of their spectral data (see Experimental section). Configuration of the allenic bond on each isomer was confirmed by ozonolysis to the (6*S*)-allenic ketone **6** or (6*R*)-one **15** prepared according to the literature.[12]

The results summarized in Table 1 show a distinct effect between functional end-groups and the number of conjugated double bonds on photoisomerization of the allenic bond. In aldehydes [Table 1(*a*)], selective photoisomerization of the allenic bond occurred as the length of the conjugated double-

Table 1 Photoisomerization of allenic model compounds

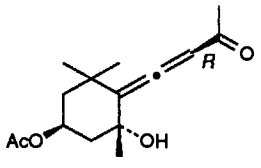
(*a*) In the case of aldehydes

Substrate	Degree of conjugation	Products	Proportions	Yield (%)	Irradiation time (*t*/min)
8a	1	(6*R*) + (6*S*)	1:1	63	8
11a	2	(6*R*) + (6*S*) + (9*Z*)	1:1:trace	quant.	15
14a	3	(6*R*) + many isomers			8
3a	4	(6*R*) + (6*R*, 13*Z*)	9:7	85	8

(*b*) In the case of sulfones and acetates

Substrate	Degree of conjugation	Products	Proportions	Yield (%)	Irradiation time (*t*/min)
8b	1	no isomerization			180
8c	1	(6*R*) + (6*R*, 9*Z*)	5:2	71	120
11b	2	(6*R*) + (6*R*,9*Z*) + (6*S*) + (6*S*, 9*Z*)	1:1:1:1	21	120
11c	2	(6*R*) + (6*R*, 9*Z*) + (6*S*) + (6*S*, 9*Z*)	1:1:1:1	68	90
14b	3	(6R) + (6*S*)	9:7	73	8
14c	3	(6*R*) + (6*S*)	9:7	quant.	15
3b[a]	4	(6*R*) + (6*S*)	1:1	quant.	8
3c	4	(6*R*) + (6*S*)	1:1	83	15

[a] The same result was obtained using a daylight fluorescent lamp (15 W) for 1 h.



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bond chain decreased, whereas double bonds tended to isomerize predominantly in the case of the highly conjugated compound. In contrast, when the end-groups were alkyl groups [Table 1(*b*)], increasing the number of conjugated double bonds tended to raise the selectivity on stereomutation of the allenic bond and to decrease the photoequilibration time.

Discussion

The novel (6*S*)-allenic isomer **1b** was isolated from the iodine-catalysed photoisomerization mixture of peridinin **1a**. This was the first time that *R*-to-*S* isomerization of an allenic bond in conjugated polyene compounds had been found. However, by direct irradiation, neither peridinin **1a** [Fig. 1(b)] nor the highly conjugated allenic model compounds possessing a carbonyl group in the polyene chain [Table 1(*a*)] gave the (6*S*)-allenic isomers. These results were very similar to those for the photoisomerization of fucoxanthin **2a** recently reported by Haugan and Liaaen-Jensen.[13] As they mentioned, it has been demonstrated for fucoxanthin **2a**, as for peridinin **1a**, that *R*/*S* isomerization of the allenic double bond may be effected under appropriate light conditions in the presence of iodine, presumably *via* iodated radicals.

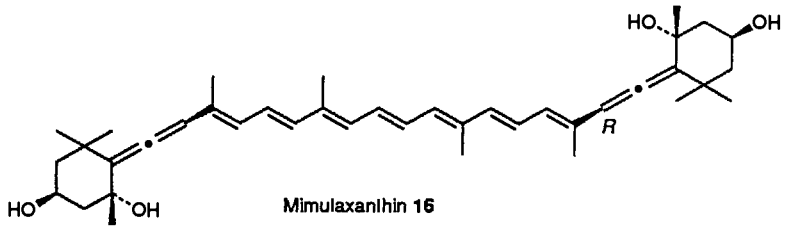
On the other hand, in direct photoirradiation of the highly conjugated allenic model compounds (**3b**, **c** and **14b**, **c**) which do not contain a carbonyl group in the polyene chain, selective isomerization of the allenic double bond occurred [Table 1(*b*)]. Especially in the case of compound **3b**, photoequilibration ($R \rightleftharpoons S$) was observed. This suggests that photoisomerization of the allenic double bond in allenic carotenoids (*i.e.*, mimulaxanthin **16**, neoxanthin **17**) might similarly proceed as in the proposed biosynthetic mechanism[6] for allenic carotenoids.

^{1}H *NMR Spectral Properties of Allenic Model Compounds.*—Configuration of the allenic bond in a number of allenic model compounds prepared in the present work was determined by ozonolysis to the known (6*S*)-allenic ketone **6**[12] or (6*R*)-one **15**.[12] Consequently, characteristic properties were found in the ^{1}H NMR chemical shifts of allenic protons (8-H) and 9-methyl protons in these compounds (Table 2). In (6*S*)-isomers, ^{1}H NMR signals of 8-H (~ 0.1 ppm) and 9-methyl protons (~ 0.05 ppm) were further downfield than those of (6*R*)-isomers. These results could be effectively applied to confirm the stereochemistry of the allenic bond in allenic compounds of this type.

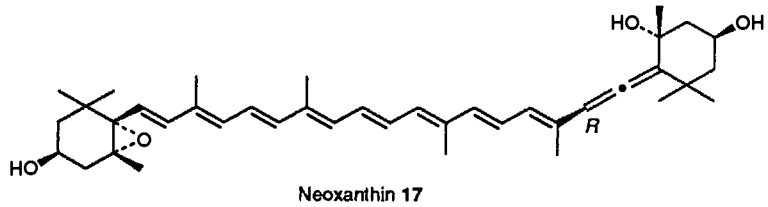
Experimental

UV–VIS spectra were recorded on a JASCO Ubest-55 instrument. IR spectra were measured on a Shimadzu IR-27G spectrometer for chloroform solutions, and FT–IR spectra on a Shimadzu FTIR-4200 by a diffuse reflectance method in KBr crystals. ^{1}H NMR spectra at 200, 400 or 500 MHz were taken on a Varian XL-200, a Varian Gemini-200, a JEOL GX-400 or a Varian VXR-500 superconducting FT-NMR spectrometer, respectively, for deuteriochloroform solutions unless otherwise stated (tetramethylsilane as internal reference). *J* Values are given in Hz. Mass spectra were recorded on a Hitachi M-80, a Hitachi M-4100 or a JEOL JMS-SX 102 spectrometer. Optical rotations were measured on a JASCO DIP-181 polarimeter ($[\alpha]_D$ values are in units of 10^{-1} deg cm^2 g^{-1}), and CD spectra on a JASCO J-500C. Short-column chromatography (SCC) was performed on silica gel (Merck Art. 7739) under reduced pressure. Preparative TLC (PTLC) was conducted on silica gel plates (Merck silica gel $60F_{254}$ precoated plates, 0.5 mm thickness). Analytical and preparative HPLC (PHPLC) was carried out on Shimadzu LC-3A, 6A and Waters Model 510 instruments with a UV–VIS detector. Photoirradiations were carried out with a daylight fluorescent lamp (15 W) or a high-pressure (300 W) mercury lamp through a Pyrex filter (PIH-300, Eikosha, Osaka, Japan).

Extracts from the reaction mixture were dried over anhydrous sodium sulfate and all operations were carried out under nitrogen or argon. Evaporation of the extract or the filtrate was carried out under reduced pressure. Ether refers to diethyl ether and hexane to *n*-hexane. NMR assignments are given using the carotenoid numbering system.



Mimulaxanthin **16**



Neoxanthin **17**

Table 2 Characteristic ^1H NMR spectral data of allenic compounds [in $CDCl_3$ except for **1a, b** (in C_6D_6)]

	8-H		9-Me	
	6*R*	6*S*	6*R*	6*S*
1a, b	6.00	6.10	1.73	1.78
6, 16	5.88	5.96	2.19	2.26
3b	6.03	6.14	1.77	1.82
3c	6.03	6.14	1.78	1.83
8a	6.09	6.19	2.16	2.21
11a	6.10	6.21	1.94	1.99
11b	5.96	6.07	1.65	1.69
(9*Z*)-**11b**	6.27	6.36	1.76	1.84
11c	5.99	6.10	1.76	1.81
(9*Z*)-**11c**	6.48	6.57	1.78	1.83
14b	6.04	6.14	1.77	1.81
14c	6.03	6.14	1.79	1.84
	Δ ~ 0.1 ppm		Δ ~ 0.05 ppm	

Photoisomerization of Peridinin **1a** *in the Presence of Iodine Catalyst.*—(a) *Isolation of photoisomerization products.* Peridinin **1a** (5 mg) was dissolved in benzene (260 cm^3) and then a solution of iodine in benzene (1%, w/v; 17 mm^3) was added. The solution was irradiated with a daylight fluorescent lamp (15 W) at a distance of 10 cm for 20 min at room temperature. Evaporation of the solvent and subsequent SCC [acetone–hexane (3:7)] gave a photoisomerized mixture (isomers I:II:III:IV ~5:8:3:1) in quantitative yield. The same procedure was repeated 3 times and the combined mixture was separated by PHPLC [LiChrosorb CN (7 μm) 1 × 25 cm; MeOH–acetone–hexane (1:10:89)] to afford each pure isomer. *Isomer* I [(6*S*)-peridinin **1b**]: λ_{max}(EtOH)/nm 475; λ_{max}(hexane)/nm 426sh, 452 and 480; ν_{max}(KBr)/cm^{-1} 3460 (OH), 1929 (C=C=C), 1744 (C=O) and 1524 (C=C); δ_H(400 MHz; C_6D_6; 5 °C) 1.09 (6 H, s), 1.10, 1.13, 1.18 and 1.49 (each 3 H, s) (1- and 1′-*gem*-Me, 5- and 5′-Me), 1.74 (3 H, s, OAc), 1.78 (3 H, s, 9-Me), 2.15 (3 H, s, 13′-Me), 3.78 (1 H, m, 3′-H), 5.21 (1 H, s, 12′-H), 5.70 (1 H, m, 3-H), 6.10 (1 H, s, 8-H), 6.12 (1 H, d, *J* 12, 10-H), 6.13 (1 H, s, 10′-H), 6.28 (1 H, dd, *J* 14 and 10, 12-H), 6.35 (1 H, d, *J* 10.5, 14′-H), 6.45 (1 H, dd, *J* 14 and 10, 15-H), 6.49 (1 H, dd, *J* 14 and 10.5, 15′-H), 6.59 (1 H, d, *J* 15.5, 8′-H), 6.65 (1 H, dd, *J* 14 and 12, 11-H) and 7.61 (1 H, d, *J* 15.5, 7′-H) (Found: M^+, 630.356. $C_{39}H_{50}O_7$ requires M, 630.355).

Isomer II (peridinin **1a**): δ_H(400 MHz; C_6D_6; 5 °C) 1.08, 1.10, 1.11, 1.14, 1.18 and 1.46 (each 3 H, s, 1- and 1′-*gem*-Me, 5- and 5′-Me), 1.73 (3 H, s, 9-Me), 1.75 (3 H, s, OAc), 2.16 (3 H, s, 13′-Me), 3.78 (1 H, m, 3′-H), 5.21 (1 H, s, 12′-H), 5.71 (1 H, m, 3-H), 6.00 (1 H, s, 8-H), 6.13 (1 H, s, 10′-H), 6.15 (1 H, d, *J* 12, 10-H), 6.31 (1 H, dd, *J* 14 and 10, 12-H), 6.36 (1 H, d, *J* 11, 14′-H), 6.44 (1 H, dd, *J* 14 and 10, 15-H), 6.50 (1 H, dd, *J* 14 and 11, 15′-H), 6.59 (1 H, d, *J* 15.5, 8′-H), 6.64 (1 H, dd, *J* 14 and 12, 11-H) and 7.61 (1 H, d, *J* 15.5, 7′-H).

Isomer III [(9*Z*)-isomer of **1a**]: λ_{max}(EtOH)/nm 467; λ_{max}(hexane)/nm 426sh, 452 and 480; ν_{max}(KBr)/cm^{-1} 3460 (OH), 1929 (C=C=C), 1746 (C=O) and 1524 (C=C); δ_H(400 MHz; C_6D_6; 5 °C) 1.16, 1.18, 1.19, 1.22, 1.24 and 1.48 (each 3 H, s, 1- and 1′-*gem*-Me, 5- and 5′-Me), 1.82 (3 H, s, OAc), 1.83 (3 H, s, 9-Me), 2.26 (3 H, s, 13′-Me), 3.78 (1 H, m, 3′-H), 5.21 (1 H, s, 12′-H), 5.70 (1 H, m, 3-H), 6.01 (1 H, d, *J* 12, 10-H), 6.12 (1 H, s, 10′-H), 6.25 (1 H, dd, *J* 14 and 10, 12-H), 6.30 (1 H, d, *J* 11, 14′-H), 6.49–6.53 (2 H, m, 15- + 15′-H), 6.48 (1 H, s, 8-H), 6.59 (1 H, d, *J* 15.5, 8′-H), 6.75 (1 H, dd, *J* 14 and 12, 11-H) and 7.61 (1 H, d, *J* 15.5, 7′-H) (Found: M^+, 630.356).

Isomer IV [(11′*E*)-isomer of **1a**]: Spectral properties of this isomer IV were in good accord with those of synthetic (11′*E*)-peridinin;[1] λ_{max}(EtOH)/nm 475; λ_{max}(hexane)/nm 428sh, 455 and 484; ν_{max}(KBr)/cm^{-1} 3460 (OH), 1929 (C=C=C), 1750 (C=O) and 1524 (C=C); δ_H(400 MHz; C_6D_6; 5 °C) 1.08, 1.10, 1.11, 1.14, 1.15 and 1.45 (each 3 H, s, 1- and 1′-*gem*-Me, 5- and 5′-Me), 1.58 (3 H, s, 13′-Me), 1.73 (3 H, s, 9-Me), 1.75 (3 H, s, OAc), 3.78 (1 H, m, 3′-H), 5.70 (1 H, m, 3-H), 6.00 (1 H, s, 8-H), 6.10 (1 H, d, *J* 11, 14′-H), 6.15 (1 H, d, *J* 12, 10-H), 6.25 (1 H, s, 12′-H), 6.31–6.40 (2 H, m, 12- + 15-H), 6.45 (1 H, t-like, *J* 12, 15′-H), 6.58 (1 H, d, *J* 15.5, 8′-H), 6.64 (1 H, t-like, *J* 12, 11-H), 6.71 (1 H, s, 10′-H) and 7.71 (1 H, d, *J* 15.5, 7′-H) (Found: M^+, 630.356).

(b) *The time course of photoisomerization* (*Fig.* 2). A solution of peridinin **1a** (1 mg) in benzene (50 cm^3) containing iodine catalyst (1%, w/v in benzene; 2.3 mm^3) was exposed according to the photoisomerization procedure described above. The isomerization was followed by analytical HPLC at 5 min intervals. A chromatogram of the photoisomerized mixture of compound **1a** after 25 min is shown in Fig. 1(a).

Photoisomerization of Peridinin **1a** *in the Absence of Iodine Catalyst.*—A solution of peridinin **1a** (1 mg) in benzene (50 cm^3) was irradiated with a daylight fluorescent lamp (15 W) for 3 h at room temperature. The isomerization was monitored by analytical HPLC. The chromatogram is shown in Fig. 1(b).

Photoisomerization of (6R)-*Allenic Sulfone* **3b**.—A solution of allenic sulfone **3b**[1] (455 mg) in benzene (900 cm^3) was irradiated with a daylight fluorescent lamp (15 W) at room

temperature. The isomerization was monitored by analytical HPLC. After irradiation for 2 h, the solvent was evaporated off to give a residue, which was purified by SCC [acetone–hexane (3:7)] to afford an isomeric mixture (**3b**:**4** ~ 1:1). PHPLC separation [LiChrosorb Si 60 (7 μm) 2.5 × 25 cm; tetrahydrofuran (THF)–hexane (1:3)] of the mixture provided the (6*S*)-allenic sulfone **4** (177 mg, 39%) and recovered starting material **3b** (148 mg, 33%) as pale yellow solids. *Compound* **4**: $[\alpha]_D^{19}$ −18.3 (*c* 0.33, MeOH); λ_{max}(EtOH)/nm 320sh, 337, 353 and 373; λ_{max}(hexane)/nm 320sh, 335, 352 and 372; ν_{max}/cm^{-1} 3600–3200 (OH), 1930 (C=C=C), 1725 (OAc), 1305 and 1145 (SO_2); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.34 (3 H, s, 5-Me), 1.38 (1 H, t, *J* 12, 2-H^{ax}), 1.41 (3 H, s, 1-Me^{ax}), 1.48 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.82 (3 H, d, *J* 1, 9-Me), 1.89 (3 H, d, *J* 0.5, 15′-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.24 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 3.81 (2 H, s, 14′-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.71 (1 H, br d, *J* 11, 15-H), 6.07 (1 H, dd-like, *J* 11.5 and 1, 10-H), 6.14 (1 H, s, 8-H), 6.16 (1 H, dd, *J* 14.5 and 11, 13-H), 6.26 (1 H, dd, *J* 14.5 and 11, 12-H), 6.32 (1 H, dd, *J* 14.5 and 11, 14-H), 6.52 (1 H, dd, *J* 14.5 and 11.5, 11-H), 7.54 (2 H, t, *J* 8, ArH), 7.64 (1 H, tt, *J* 8 and 1.5, ArH) and 7.85 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M$^+$, 510.244. $C_{30}H_{38}O_5S$ requires M, 510.244).

Ozonolysis of (6S)-*Allenic Sulfone* **4**.—Ozone gas was introduced into a stirred solution of sulfone **4** (73 mg) in MeOH at −78 °C until the spot for compound **4** disappeared on TLC. Nitrogen gas was bubbled into the reaction solution for 10 min, and dimethyl sulfide (50 mm^3) was added to it at −78 °C. After the mixture had been stirred for 40 min at 0 °C, the solvent was evaporated off. The residue was purified by PTLC [ether–hexane (1:1)] to give (6*S*)-allenic ketone **6** (9.3 mg, 24%) as a solid. Spectral data including chiroptical properties were identical with those of an authentic specimen prepared according to the literature.[12] CD (*c* 6.8 × 10^{-5}, 1,4-dioxane) Δε nm +7.3 (228), 0 (241), −3.7 (254) and 0 (280) [lit.,[12] CD; (1,4-dioxane) Δε nm +7.1 (227) and −4.1 (253)].

Preparation of (6S)-*Peridinin* **1b**.—A solution of BuLi (1.60 mol dm^{-3} in hexane; 0.438 cm^3, 0.70 mmol) was added to a stirred solution of diisopropylamine (0.097 cm^3, 0.69 mmol) in dry THF (3 cm^3)–hexane (3 cm^3) at −78 °C, and the mixture was stirred for a further 20 min. To this LDA solution was added a solution of the (6*S*)-allenic sulfone **4** (168 mg, 0.33 mmol) in dry THF (5 cm^3)–hexane (5 cm^3). After being stirred for 10 min at −78 °C, the mixture was treated with a solution of the aldehydo ester **5**[1] (65 mg, 0.22 mmol) in dry THF (5 cm^3)–hexane (5 cm^3) at the same temperature. The reaction mixture was stirred at −78 °C for 15 min before being allowed to warm to room temperature over a period of *ca.* 10 min. After being quenched with saturated aq. NH_4Cl, the mixture was extracted with ether. The extracts were washed with brine, dried, and evaporated to give a residue, which was purified by PTLC [acetone–hexane (35:65)] to afford an isomeric mixture [**1b**: its (11′*E*)-isomer ~ 1:1] (20 mg, 15% from **5**). PHPLC separation [LiChrosorb CN (7 μm) 1 × 25 cm; MeOH–acetone–hexane (1:10:89)] of the mixture provided **1b** and its (11′*E*)-isomer, each as a red glass. Spectral properties of **1b** were identical with those of (6*S*)-peridinin isolated from the photoisomerization mixture of peridinin **1a**. (11′*E*)-*Isomer* of **1b**: λ_{max}(EtOH)/nm 477; λ_{max}(hexane)/nm 430sh, 456 and 485; ν_{max}(KBr)/cm^{-1} 3460 (OH), 1929 (C=C=C), 1742 (C=O) and 1522 (C=C); δ_H(500 MHz; C_6D_6; 5 °C) 1.08, 1.10, 1.11, 1.13, 1.17 and 1.49 (each 3 H, s, 1- and 1′-*gem*-Me, 5- and 5′-Me), 1.56 (3 H, s, 13′-Me), 1.73 (3 H, s, OAc), 1.79 (3 H, s, 9-Me), 3.77 (1 H, m, 3′-H), 5.71 (1 H, m, 3-H), 6.09 (1 H, s, 8-H), 6.10 (1 H, d, *J* 11.5, 14′-H), 6.13 (1 H, d, *J* 9, 10-H), 6.25 (1 H, s, 12′-H), 6.30–6.37 (2 H, m, 12- + 15-H), 6.46 (1 H, t-like, *J* 12, 15′-H), 6.58 (1 H, d, *J* 15.5, 8′-H), 6.67 (1 H, t-like, *J* 12, 11-H), 6.69 (1 H, s, 10′-H) and 7.71 (1 H, d, *J* 15.5, 7′-H) (Found: M$^+$, 630.357. $C_{39}H_{50}O_7$ requires M, 630.355).

Photoisomerization of (6S)-*Peridinin* **1b** *in the Presence of Iodine Catalyst*.—In the same manner as described for the photoisomerization of peridinin **1a**, a solution of (6*S*)-peridinin **1b** (1 mg) in benzene (50 cm^3) containing iodine catalyst (1% w/v in benzene; 2.3 mm^3) was irradiated. The HPLC chromatogram of the photoisomerization mixture after 30 min was similar to that of peridinin **1a** as shown in Fig. 1(a).

(E)-5-[(1R,2R,4S)-4-*Acetoxy*-2-*hydroxy*-2,6,6-*trimethylcyclohexylidene*]-3-*methylpenta*-2,4-*dienal* **8a**.—Acetic anhydride (3 cm^3) was added to a stirred solution of the allenic aldehyde **7**[1] (50 mg, 0.20 mmol) in pyridine (Py) (5 cm^3) at 0 °C. The mixture was stirred at room temperature for 3 h, poured into ice–water, and extracted with ether. The extracts were washed successively with aq. 3% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by SCC [acetone–hexane (1:3)] to afford the *acetate* **8a** (49 mg, 84%) as a pale yellow solid, λ_{max}(EtOH)/nm 287; λ_{max}(hexane)/nm 275; ν_{max}/cm^{-1} 3600 and 3440 (OH), 1932 (C=C=C), 1725 (OAc), 1658 (conj. CHO) and 1605 (C=C); δ_H(500 MHz) 1.10 (3 H, s, 1-Me^{eq}), 1.38 (3 H, s, 5-Me), 1.41 (3 H, s, 1-Me^{ax}), 1.42 (1 H, t, *J* 12, 2-H^{ax}), 1.52 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 2.02 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.05 (3 H, s, OAc), 2.16 (3 H, d, *J* 0.5, 9-Me), 2.32 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 5.95 (1 H, br d, *J* 8, 10-H), 6.09 (1 H, s, 8-H) and 10.03 (1 H, d, *J* 8, CHO) (Found: M$^+$, 292.168. $C_{17}H_{24}O_4$ requires M, 292.167).

(1R,3S,6R)-6-[(E)-5-*Acetoxy*-3-*methylpenta*-1,3-*dienylidene*]-1,5,5-*trimethylcyclohexane*-1,3-*diol* 3-*Acetate* **8c**.—$NaBH_4$ (24 mg, 0.63 mmol) was added to an ice-cooled solution of aldehyde **7** (52 mg, 0.21 mmol) in MeOH (5 cm^3). The mixture was stirred at 0 °C for 1 h, then was poured into ice–water and extracted with ether. The extracts were washed with brine and dried. Evaporation of the solvent gave the triol, which without purification was dissolved in pyridine (5 cm^3)–acetic anhydride (3 cm^3). The mixture was stirred at room temperature for 16 h, poured into ice–water, and extracted with ether. The extracts were washed successively with aq. 3% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts provided the *diacetate* **8c** (60 mg, 86%) as a solid, λ_{max}(EtOH)/nm 227 and 240sh; λ_{max}(hexane)/nm 226 and 240sh; ν_{max}/cm^{-1} 3600 and 3450 (OH), 1940 (C=C=C), 1740sh and 1725 (OAc); δ_H(200 MHz) 1.07 (3 H, s, 1-Me), 1.35 and 1.38 (each 3 H, s, 1- and 5-Me), 1.71 (3 H, s, 9-Me), 2.04 and 2.07 (each 3 H, s, OAc × 2), 2.29 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 4.68 (2 H, d, *J* 7, 11-H_2), 5.37 (1 H, tt, *J* 11 and 4, 3-H), 5.54 (1 H, br t, *J* 7, 10-H) and 5.98 (1 H, s, 8-H) (Found: M$^+$, 336.191. $C_{19}H_{28}O_5$ requires M, 336.193).

(1R,3S,6R)-6-[(E)-5-*Benzenesulfonyl*-3-*methylpenta*-1,3-*dienylidene*]-1,5,5-*trimethylcyclohexane*-1,3-*diol* 3-*Acetate* **8b**.—(a) *From the diacetate* **8c**. To a solution of the diacetate **8c** (39 mg, 0.12 mmol) in propan-2-ol (4 cm^3) were added water (1 cm^3) and $PhSO_2Na{\cdot}2H_2O$ (35 mg, 0.18 mmol), and the mixture was refluxed for 48 h. After cooling, the reaction mixture was diluted with ether, washed with brine, dried and evaporated. The residue was purified by SCC [acetone–hexane (3:10)] to give an isomeric mixture of the sulfones. PHPLC separation [LiChrosorb CN (7 μm) 1 × 25 cm; MeOH–ether–hexane (1:40:59)] of the mixture provided the (9*E*)-sulfone **8b** (8.5 mg, 17%) and its (9*Z*)-isomer (1.4 mg, 3%) as solids.

(b) *From the enal* **8a**. $NaBH_4$ (30 mg, 0.79 mmol) was added to an ice-cooled solution of aldehyde **8a** (132 mg, 0.45 mmol) in MeOH (5 cm^3). The mixture was stirred at 0 °C for 30 min, then

poured into ice–water and extracted with ether. The extracts were washed with brine and dried. Evaporation of the solvent gave a residue, which was purified by SCC [acetone–hexane (2:5)] to afford the allenic alcohol (85 mg).

A solution of lithium chloride (13.5 mg, 0.32 mmol) in dry dimethylformamide (DMF) (0.1 cm^3) was added to a stirred solution of the allenic alcohol (85 mg) in 2,4,6-trimethylpyridine (γ-collidine) (0.047 cm^3) at 0 °C and the mixture was stirred at 0 °C for 15 min. To this reaction mixture was added methanesulfonyl chloride (MsCl) (0.025 cm^3, 0.35 mmol) and the mixture was stirred at 0 °C for a further 1.5 h before being poured into ice–water and extracted with ether. The organic layer was washed successively with aq. 3% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extract provided a residue, which was purified by SCC [ether–hexane (2:1)] to afford the corresponding chloride (91 mg) as an oil; ν_{max}/cm^{-1} 3600 and 3450 (OH), 1938 (C=C=C) and 1726 (OAc); δ_H(200 MHz) 1.07, 1.35 and 1.38 (each 3 H, s, *gem*-Me and 5-Me), 1.49 (1 H, dd, *J* 13 and 11.5, 4-H^{ax}), 1.74 (3 H, d, *J* 1, 9-Me), 2.00 (1 H, ddd, *J* 12.5, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.30 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 4.20 (2 H, d, *J* 8, 11-H_2), 5.37 (1 H, tt, *J* 11.5 and 4, 3-H), 5.62 (1 H, br t, *J* 8, 10-H) and 5.98 (1 H, s, 8-H).

$PhSO_2Na{\cdot}2H_2O$ (87 mg, 0.42 mmol) was added to a solution of this chloride (91 mg, 0.28 mmol) in DMF (5 cm^3) and the mixture was stirred at room temperature for 1 h before being diluted with ether and washed with brine. Evaporation of the dried solution gave a residue, which was purified by SCC [ether–hexane (3:7)] to afford the *sulfone* **8b** (95 mg, 50% from **8a**), λ_{max}(EtOH)/nm 217 and 246; λ_{max}(hexane)/nm 216, 231 and 242; ν_{max}/cm^{-1} 3570 and 3450 (OH), 1935 (C=C=C), 1725 (OAc), 1300 and 1145 (SO_2); δ_H(500 MHz) 0.99 (3 H, s, 1-Me^{eq}), 1.23 (3 H, d, *J* 1, 9-Me), 1.28 (3 H, s, 1-Me^{ax}), 1.31 (1 H, t, *J* 12, 2-H^{ax}), 1.36 (3 H, s, 5-Me), 1.41 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.02 (3 H, s, OAc), 2.24 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 3.91 (2 H, d, *J* 8, 11-H_2), 5.34 (1 H, tt, *J* 12 and 4, 3-H), 5.40 (1 H, br t, *J* 8, 10-H), 5.95 (1 H, s, 8-H), 7.51 (2 H, t, *J* 8.5, ArH), 7.63 (1 H, tt, *J* 8.5 and 1.5, ArH) and 7.87 (2 H, dd, *J* 8.5 and 1.5, ArH) (Found: M^+, 418.182. $C_{23}H_{30}O_5S$ requires M, 418.181).

(9Z)-*Isomer* of **8b**: λ_{max}(EtOH)/nm 218 and 244; λ_{max}(hexane)/nm 217 and 245; ν_{max}/cm^{-1} 3550 and 3400 (OH), 1935 (C=C=C), 1725 (OAc), 1300 and 1145 (SO_2); δ_H(500 MHz) 0.93 (3 H, s, 1-Me^{eq}), 1.21 (3 H, s, 1-Me^{ax}), 1.31 (3 H, s, 5-Me), 1.32 (1 H, t, *J* 12, 2-H^{ax}), 1.42 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.71 (3 H, d, *J* 1, 9-Me), 1.95 (1 H, ddd, *J* 12, 4.5 and 2.5, 2-H^{eq}), 2.02 (3 H, s, OAc), 2.24 (1 H, ddd, *J* 13, 4.5 and 2.5, 4-H^{eq}), 3.94 (2 H, d, *J* 8, 11-H_2), 5.28 (1 H, br t, *J* 8, 10-H), 5.32 (1 H, tt, *J* 12 and 4.5, 3-H), 5.81 (1 H, s, 8-H), 7.53 (2 H, t, *J* 8, ArH), 7.62 (1 H, tt, *J* 8 and 1.5, ArH) and 7.88 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M^+, 418.182).

Ethyl (2E,4E)-7-[(1R,2R,4S)-2,4-*Dihydroxy*-2,6,6-*trimethylcyclohexylidene*]-5-*methylhepta*-2,4,6-*trienoate* **10**.—BuLi (1.60 mol dm^{-3} in hexane; 2.38 cm^3, 3.8 mmol) was added to a stirred solution of ethyl (diethoxyphosphoryl)acetate **9** (896 mg, 4.0 mmol) in dry THF (10 cm^3) at 0 °C and the mixture was stirred at 0 °C for 30 min. To this mixture was added dropwise a solution of the aldehyde **7**[1] (501 mg, 2.0 mmol) in dry THF (10 cm^3) at 0 °C and the mixture was stirred at room temperature for 2.5 h. The reaction was quenched with saturated aq. NH_4Cl. After evaporation off of THF, the residue was extracted with ether. The extracts were washed with brine, dried and evaporated. The residue was purified by SCC [acetone–hexane (1:3)] to afford the *dienyl ester* **10** (640 mg, quant.) as a pale yellow solid, λ_{max}(EtOH)/nm 316; ν_{max}/cm^{-1} 3605 and 3450 (OH), 1930 (C=C=C), 1695 (conj. CO_2Et) and 1615 (C=C); δ_H(200 MHz) 1.07 (3 H, s, 1-Me), 1.31 (3 H, t, *J* 7, OCH_2Me), 1.34 (6 H, s, 1- + 5-Me), 1.88 (3 H, s, 9-Me), 1.96 (1 H, br d, *J* 12, 2-H^{eq}), 2.28 (1 H, br d, *J* 12, 4-H^{eq}), 4.22 (2 H, q, *J* 7, OCH_2Me), 4.32 (1 H, m, 3-H), 5.85 (1 H, d, *J* 15, 12-H), 6.04 (1 H, s, 8-H), 6.12 (1 H, br d, *J* 12, 10-H) and 7.61 (1 H, dd, *J* 15 and 12, 11-H) (Found: M^+, 320.199. $C_{19}H_{28}O_4$ requires M, 320.199).

(2E,4E)-7-[(1R,2R,4S)-4-*Acetoxy*-2-*hydroxy*-2,6,6-*trimethylcyclohexylidene*]-5-*methylhepta*-2,4,6-*trienal* **11a**.—A solution of ester **10** (96 mg, 0.30 mmol) in dry THF (10 cm^3) was added dropwise to a stirred suspension of LAH (34 mg, 0.89 mmol) in dry THF (12 cm^3) at 0 °C and the mixture was stirred at 0 °C for 30 min. The excess of LAH was decomposed by dropwise addition of water. The mixture was extracted with ethyl acetate and the extracts were washed with brine and dried. Evaporation off of the solvent gave the hydroxy compound, which without purification was dissolved in THF and shaken with active MnO_2 (2 g) at room temperature for 1 h. The mixture was filtered through Celite. Evaporation of the filtrate gave the aldehyde, which without purification was dissolved with pyridine (7 cm^3)–acetic anhydride (5 cm^3). The mixture was stirred at room temperature for 12 h, poured into ice–water and extracted with ether. The extracts were washed successively with aq. 3% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts provided a residue, which was purified by SCC [acetone–hexane (1:3)] to afford the 3-*acetoxy allenic aldehyde* **11a** (71 mg, 74%) as a pale yellow solid, λ_{max}(EtOH)/nm 330; λ_{max}(hexane)/nm 321; ν_{max}/cm^{-1} 3600 and 3420 (OH), 1930 (C=C=C), 1725 (OAc), 1665 (conj. CHO) and 1605 (C=C); δ_H(500 MHz) 1.09 (3 H, s, 1-Me^{eq}), 1.37 (3 H, s, 5-Me), 1.40 (3 H, s, 1-Me^{ax}), 1.42 (1 H, t, *J* 12, 2-H^{ax}), 1.51 (1 H, dd-like, *J* 12.5 and 12, 4-H^{ax}), 1.94 (3 H, d, *J* 1, 9-Me), 2.02 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.31 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 6.10 (1 H, s, 8-H), 6.16 (1 H, dd, *J* 15 and 8, 12-H), 6.28 (1 H, br d, *J* 12, 10-H), 7.43 (1 H, dd, *J* 15 and 12, 11-H) and 9.61 (1 H, d, *J* 8, CHO) (Found: M^+, 318.184. $C_{19}H_{26}O_4$ requires M, 318.183).

(1R,3S,6R)-6-[(3E,5E)-7-*Acetoxy*-3-*methylhepta*-1,3,5-*trienylidene*]-1,5,5-*trimethylcyclohexane*-1,3-*diol* 3-*Acetate* **11c**.—A solution of the dienyl ester **10** (82 mg, 0.26 mmol) in dry THF (10 cm^3) was added dropwise to a stirred suspension of LAH (29 mg, 0.76 mmol) in dry THF (10 cm^3) at 0 °C and the mixture was stirred at 0 °C for 30 min. The excess of LAH was decomposed by dropwise addition of water. The mixture was extracted with ethyl acetate and the extracts were washed with brine and dried. Evaporation of the solvent gave the hydroxy compound, which without purification was dissolved in pyridine (3 cm^3)–acetic anhydride (2 cm^3) and the mixture was stirred at room temperature for 16 h, poured into ice–water and extracted with ether. The extracts were washed successively with aq. 3% HCl, saturated aq. $NaHCO_3$ and brine. Evaporation of the dried extracts gave a residue, which was purified by SCC [ether–hexane (2:3)] to afford the *diacetate* **11c** (52 mg, 55%) as an oil, λ_{max}(EtOH)/nm 277; λ_{max}(hexane)/nm 277 and 290sh; ν_{max}/cm^{-1} 3610 and 3470 (OH), 1935 (C=C=C) and 1730 (OAc); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.34 (3 H, s, 5-Me), 1.38 (3 H, s, 1-Me^{ax}), 1.40 (1 H, t, *J* 12, 2-H^{ax}), 1.50 (1 H, t, *J* 12, 4-H^{ax}), 1.76 (3 H, s, 9-Me), 1.99 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 and 2.07 (each 3 H, s, OAc × 2), 2.28 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 4.63 (2 H, br d, *J* 7, 13-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.76 (1 H, dt, *J* 15 and 7, 12-H), 5.99 (1 H, s, 8-H), 6.01 (1 H, br d, *J* 11.5, 10-H) and 6.58 (1 H, ddt, *J* 15, 11.5 and 0.5, 11-H) (Found: M^+, 362.211. $C_{21}H_{30}O_5$ requires M, 362.209).

(1R,3S,6R)-6-[(3E,5E)-7-*Benzenesulfonyl*-3-*methylhepta*-1,3,5-*trienylidene*)-1,5,5-*trimethylcyclohexane*-1,3-*diol* 3-*Acetate* **11b**.—To a solution of the diacetate **11c** (47 mg, 0.13 mmol) in propan-2-ol (5 cm^3) were added water (2 cm^3) and $PhSO_2Na{\cdot}2H_2O$ (39 mg, 0.20 mmol), and the mixture was

refluxed for 24 h. After cooling, the reaction mixture was diluted with ether, washed with brine and evaporated. The residue was purified by SCC [acetone–hexane (2:3)] to afford the *sulfone* **11b** (44 mg, 76%) as an oil, λ_{max}(EtOH)/nm 287; λ_{max}(hexane)/nm 286; ν_{max}/cm^{-1} 3600 and 3450 (OH), 1935 (C=C=C), 1725 (OAc), 1310sh, 1300 and 1140 (SO_2); δ_H(500 MHz) 1.05 (3 H, s, 1-Me^{eq}), 1.33 (3 H, s, 5-Me), 1.38 (3 H, s, 1-Me^{ax}), 1.39 (1 H, t, *J* 11.5, 2-H^{ax}), 1.48 (1 H, dd-like, *J* 12 and 11.5, 4-H^{ax}), 1.65 (3 H, d, *J* 0.5, 9-Me), 1.98 (1 H, ddd, *J* 11.5, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.28 (1 H, ddd, *J* 11.5, 4 and 2, 4-H^{eq}), 3.88 (2 H, br d, *J* 7.5, 13-H_2), 5.37 (1 H, tt, *J* 11.5 and 4, 3-H), 5.53 (1 H, dt, *J* 15.5 and 7.5, 12-H), 5.96 (1 H, s, 8-H), 5.96 (1 H, br d, *J* 11.5, 10-H), 6.35 (1 H, ddt, *J* 15.5, 11.5 and 0.5, 11-H), 7.56 (2 H, t, *J* 8, ArH), 7.66 (1 H, tt, *J* 8 and 1.5, ArH) and 7.88 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M$^+$, 444.197. $C_{25}H_{32}O_5S$ requires M, 444.197).

Methyl (2E,4E,6E)-9-[(1R,2R,4S)-2,4-*Dihydroxy*-2,6,6-*trimethylcyclohexylidene*]-3,7-*dimethylnona*-2,4,6,8-*tetraenoate* **13**.—BuLi (1.60 mol dm^{-3} in hexane; 1.25 cm^3, 2.0 mmol) was added to a stirred solution of methyl 4-(diethoxyphosphoryl)-3-methylbut-2-enoate **12**[14] (*E*:*Z* 5:1) (500 mg, 2.0 mmol) in dry THF (5 cm^3) at −78 °C. After this mixture had been stirred for 15 min at −78 °C, a solution of the allenic aldehyde **7** (250 mg, 1.0 mmol) in dry THF (5 cm^3) was added dropwise at −78 °C and the mixture was stirred for a further 1 h before being poured into saturated aq. NH_4Cl and extracted with ether. The extracts were washed with brine, dried and evaporated. The residue was purified by SCC [ethyl acetate–hexane (1:1)] to afford the *trienyl ester* **13** (270 mg, 78%) as a pale yellow solid, λ_{max}(EtOH)/nm 345; ν_{max}/cm^{-1} 3600 and 3400 (OH), 1930 (C=C=C), 1710 (conj. CO_2Me), 1650 and 1590 (C=C); δ_H(200 MHz) 1.07 (3 H, s, 1-Me), 1.34 and 1.35 (each 3 H, s, 1- and 5-Me), 1.83 (3 H, s, 9-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.27 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 2.34 (3 H, d, *J* 1, 13-Me), 3.72 (3 H, s, OMe), 4.32 (1 H, tt, *J* 12 and 4, 3-H), 5.78 (1 H, br s, 14-H), 6.04 (1 H, s, 8-H), 6.12 (1 H, br d, *J* 11, 10-H), 6.27 (1 H, d, *J* 15, 12-H) and 6.90 (1 H, dd, *J* 15 and 11, 11-H) (Found: M$^+$, 346.213. $C_{21}H_{30}O_4$ requires M, 346.214).

(2E,4E,6E)-9-[(1R,2R,4S)-4-*Acetoxy*-2-*hydroxy*-2,6,6-*trimethylcyclohexylidene*]-3,7-*dimethylnona*-2,4,6,8-*tetraenal* **14a**.—In the same manner as described for the preparation of aldehyde **11a** from ester **10**, reduction of the trienyl ester **13** (86 mg) with LAH and successive oxidation with MnO_2 followed by acetylation produced a crude product, which was purified by SCC [acetone–hexane (1:3)] and then PHPLC [LiChrosorb CN (7 μm) 1 × 25 cm; MeOH–ether–hexane (0.5:35:64.5)] to afford the *allenic trienal* **14a** (62 mg, 69%) as a yellow solid, λ_{max}(EtOH)/nm 371; λ_{max}(hexane)/nm 327sh, 350 and 367; ν_{max}/cm^{-1} 3600 and 3450 (OH), 1930 (C=C=C), 1725 (OAc), 1650 (conj. CHO) and 1585 (C=C); δ_H(200 MHz) 1.08 (3 H, s, 1-Me), 1.36 and 1.40 (each 3 H, s, 1- and 5-Me), 1.87 (3 H, s, 9-Me), 2.05 (3 H, s, OAc), 2.32 (3 H, s, 13-Me), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 5.98 (1 H, br d, *J* 8, 14-H), 6.07 (1 H, s, 8-H), 6.17 (1 H, br d, *J* 11, 10-H), 6.36 (1 H, d, *J* 16, 12-H), 7.04 (1 H, dd, *J* 16 and 11, 11-H) and 10.12 (1 H, d, *J* 8, CHO) (Found: M$^+$, 358.216. $C_{22}H_{30}O_4$ requires M, 358.214).

(1R,3S,6R)-6-[(3E,5E,7E)-9-*Acetoxy*-3,7-*dimethylnona*-1,3,5,7-*tetraenylidene*]-1,5,5-*trimethylcyclohexane*-1,3-*diol* 3-*Acetate* **14c**.—Following the procedure as described for the preparation of diacetate **11c** from ester **10**, reduction of the trienyl ester **13** (120 mg) with LAH and subsequent acetylation produced a crude product, which was purified by SCC [acetone–hexane (1:3)] and then PHPLC [LiChrosorb CN (7 μm) 1 × 25 cm; MeOH–ether–hexane (0.5:40:59.5)] to afford the *diacetate* **14c** (106 mg, 75%) as a yellow solid, λ_{max}(EtOH)/nm 295sh, 311 and 325; λ_{max}(hexane)/nm 295sh, 311 and 325; ν_{max}/cm^{-1} 3590 and 3420 (OH), 1932 (C=C=C) and 1725 (OAc); δ_H(500 MHz) 1.07 (3 H, s, 1-Me^{eq}), 1.35 (3 H, s, 5-Me), 1.38 (3 H, s, 1-Me^{ax}), 1.41 (1 H, t, *J* 12, 2-H^{ax}), 1.51 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.79 (3 H, d, *J* 0.5, 9-Me), 1.88 (3 H, d, *J* 0.5, 13-Me), 1.99 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 and 2.07 (each 3 H, s, OAc × 2), 2.28 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 4.73 (2 H, d, *J* 7, 15-H_2), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 5.62 (1 H, br t, *J* 7, 14-H), 6.03 (1 H, s, 8-H), 6.07 (1 H, br d, *J* 11, 10-H), 6.27 (1 H, d, *J* 15, 12-H) and 6.54 (1 H, dd, *J* 15 and 11, 11-H) (Found: M$^+$, 402.241. $C_{24}H_{34}O_5$ requires M, 402.241).

(1R,3S,6R)-6-[(3E,5E,7E)-9-*Benzenesulfonyl*-3,7-*dimethylnona*-1,3,5,7-*tetraenylidene*]-1,5,5-*trimethylcyclohexane*-1,3-*diol* 3-*Acetate* **14b**.—According to the procedure given for sulfone **11b**, treatment of the diacetate **14c** (65 mg) with $PhSO_2Na$ followed by purification by SCC [ethyl acetate–hexane (2:5)] and then by PHPLC [LiChrosorb CN (7 μm) 1 × 25 cm; MeOH–EtOAc–hexane (0.5:15:84.5)] provided the *sulfone* **14b** (68 mg, 88%) as a pale yellow solid, λ_{max}(EtOH)/nm 305sh, 318 and 330sh; λ_{max}(hexane)/nm 305sh, 318 and 333; ν_{max}/cm^{-1} 3570 and 3425 (OH), 1928 (C=C=C), 1725 (OAc), 1300 and 1145 (SO_2); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.35 (3 H, s, 5-Me), 1.38 (3 H, s, 1-Me^{ax}), 1.40 (1 H, t, *J* 12, 2-H^{ax}), 1.48 (3 H, s, 13-Me), 1.50 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.77 (3 H, d, *J* 0.5, 9-Me), 1.99 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.28 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 3.96 (2 H, d, *J* 8.5, 15-H_2), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 5.44 (1 H, br t, *J* 8.5, 14-H), 6.03 (1 H, s, 8-H), 6.05 (1 H, br d, *J* 11, 10-H), 6.23 (1 H, d, *J* 15, 12-H), 6.46 (1 H, dd, *J* 15 and 11, 11-H), 7.54 (2 H, t, *J* 8, ArH), 7.64 (1 H, tt, *J* 8 and 1, ArH) and 7.85 (2 H, dd, *J* 8 and 1, ArH) (Found: M$^+$, 484.228. $C_{28}H_{36}O_5S$ requires M, 484.228).

Photoisomerization of Allenic Model Compounds **3a–c**, **8a–c**, **11a–c** *and* **14a–c**.—*General procedure.* An ice-cooled solution (3–4 mmol dm^{-3}) of each allenic compound in benzene was irradiated using a high-pressure (300 W) mercury lamp (Pyrex filter), with nitrogen bubbling. The isomerization was monitored by analytical HPLC (Table 3) under the indicated conditions. The irradiation was continued until a change in the isomer ratio was not observed on HPLC. Proportions of the isomers and yields were calculated by peak areas.

Isolation of photoproducts. Evaporation of the above reaction mixture provided a mixture of photoproducts, which was separated by PHPLC [column: **3b**: LiChrosorb CN (7 μm) 1 × 25 cm, other compounds: LiChrosorb Si 60 (7 μm) 1 × 25 cm; eluent: the same eluent as described for analytical HPLC (Table 3)] to give each pure isomer.

(13Z)-*Isomer* of **3a**: λ_{max}(EtOH)/nm 271 and 396; λ_{max}(hexane)/nm 267, 340sh, 359, 377 and 399; ν_{max}/cm^{-1} 3600–3200 (OH), 1925 (C=C=C), 1720 (OAc), 1660 (conj. CHO), 1610 and 1570 (C=C); δ_H(500 MHz) 1.08 (3 H, s, 1-Me^{eq}), 1.36 (3 H, s, 5-Me), 1.39 (3 H, s, 1-Me^{ax}), 1.41 (1 H, t, *J* 12, 2-H^{ax}), 1.51 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.84 (3 H, s, 9-Me), 1.88 (3 H, s, 15′-Me), 2.00 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.29 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 6.07 (1 H, s, 8-H), 6.19 (1 H, br d, *J* 11.5, 10-H), 6.41 (1 H, t, *J* 11.5, 14-H), 6.53 (1 H, t, *J* 11.5, 13-H), 6.74 (1 H, dd, *J* 14.5 and 11.5, 11-H), 6.83 (1 H, dd, *J* 14.5 and 11.5, 12-H), 7.35 (1 H, br d, *J* 11.5, 15-H) and 9.52 (1 H, s, CHO) (Found: M$^+$, 384.228. $C_{24}H_{32}O_4$ requires M, 384.230).

(6S)-*Isomer* of **3c**: λ_{max}(EtOH)/nm 312sh, 329, 345 and 364; λ_{max}(hexane)/nm 312sh, 328, 344 and 363; ν_{max}/cm^{-1} 3575 and 3425 (OH), 1925 (C=C=C) and 1725 (OAc); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.34 (3 H, s, 5-Me), 1.38 (1 H, t, *J* 12, 2-H^{ax}), 1.41 (3 H, s, 1-Me^{ax}), 1.48 (1 H, t, *J* 12, 4-H^{ax}), 1.82 (3 H, d, *J* 1, 15′-Me), 1.83 (3 H, d, *J* 1, 9-Me), 1.96 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 and 2.09 (each 3 H, s, OAc × 2), 2.24 (1 H, ddd, *J* 12, 4 and 2, 4-

Table 3 Analytical HPLC conditions in the general procedure for photoisomerization

Compound	Column[a]	Eluent[b] (proportions)		Flow rate (cm^3 min^{-1})	Detection (λ/nm)
3a	I	A	(1:25:74)	1.5	360
3b	II	B	(25:75)	1.2	360
3c	I	A	(0.5:20:79.5)	1.5	320
8a	I	A	(0.5:35:64.5)	1.5	280
8b	I	A	(1:35:64)	1.0	220
8c	I	A	(1:40:59)	1.5	230
11a	I	A	(0.5:30:69.5)	1.5	310
11b	I	A	(1:35:64)	1.8	280
11c	I	A	(0.5:15:84.5)	1.5	290
14a	I	A	(0.5:35:64.5)	1.5	360
14b	I	A	(0.5:20:79.5)	1.5	310
14c	I	A	(0.5:40:59.5)	1.5	300

[a] I = LiChrosorb CN (5 μm) 0.4 × 25 cm; II = LiChrosorb Si 60 (5 μm) 0.4 × 30 cm. [b] A = MeOH–ether–hexane; B = THF–hexane.

H^{eq}), 4.55 (2 H, s, 14'-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 6.08 (1 H, dd-like, *J* 11.5 and 1, 10-H), 6.13 (1 H, dd-like, *J* 11 and 1, 15-H), 6.14 (1 H, s, 8-H), 6.28–6.38 (2 H, m, 12- + 13-H), 6.44 (1 H, dd, *J* 14 and 11, 14-H) and 6.54 (1 H, dd, *J* 14 and 11.5, 11-H) (Found: M^+, 428.255. $C_{26}H_{36}O_5$ requires M, 428.256).

(6S)-*Isomer* of **8a**: λ_{max}(EtOH)/nm 287; λ_{max}(hexane)/nm 277; ν_{max}/cm^{-1} 3610 and 3460 (OH), 1935 (C=C=C), 1725 (OAc), 1660 (conj. CHO) and 1605 (C=C); δ_H(500 MHz) 1.10 (3 H, s, 1-Me^{eq}), 1.38 (3 H, s, 5-Me), 1.40 (1 H, t, *J* 12, 2-H^{ax}), 1.45 (3 H, s, 1-Me^{ax}), 1.51 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.97 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.21 (3 H, d, *J* 1, 9-Me), 2.26 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.97 (1 H, br d, *J* 8, 10-H), 6.19 (1 H, s, 8-H) and 10.05 (1 H, d, *J* 8, CHO) (Found: M^+, 292.167. $C_{17}H_{24}O_4$ requires M, 292.167).

(9Z)-*Isomer* of **8c**: λ_{max}(EtOH)/nm 224sh and 237; λ_{max}(hexane)/nm 225 and 236; ν_{max}/cm^{-1} 3600 and 3425 (OH), 1935 (C=C=C) and 1730 (OAc); δ_H(200 MHz) 1.08 (3 H, s, 1-Me), 1.36 and 1.38 (each 3 H, s, 1- and 5-Me), 1.77 (3 H, s, 9-Me), 1.99 (1 H, ddd, *J* 12, 4.5 and 2, 2-H^{eq}), 2.04 and 2.07 (each 3 H, s, OAc × 2), 2.28 (1 H, ddd, *J* 12, 4.5 and 2, 4-H^{eq}), 4.70 (2 H, d, *J* 7, 11-H_2), 5.37 (1 H, m, 3-H), 5.41 (1 H, br t, *J* 7, 10-H) and 6.31 (1 H, s, 8-H) (Found: M^+, 336.196. $C_{19}H_{28}O_5$ requires M, 336.194).

(6S)-*Isomer* of **11a**: λ_{max}(EtOH)/nm 330; λ_{max}(hexane)/nm 319; ν_{max}/cm^{-1} 3580 and 3450 (OH), 1930 (C=C=C), 1725 (OAc), 1665 (conj. CHO) and 1605 (C=C); δ_H(500 MHz) 1.08 (3 H, s, 1-Me^{eq}), 1.36 (3 H, s, 5-Me), 1.40 (1 H, t, *J* 11.5, 2-H^{ax}), 1.44 (3 H, s, 1-Me^{ax}), 1.50 (1 H, t, *J* 11.5, 4-H^{ax}), 1.97 (1 H, ddd, *J* 11.5, 4 and 2, 2-H^{eq}), 1.99 (3 H, d, *J* 1, 9-Me), 2.04 (3 H, s, OAc), 2.26 (1 H, ddd, *J* 11.5, 4 and 2, 4-H^{eq}), 5.37 (1 H, tt, *J* 11.5 and 4, 3-H), 6.15 (1 H, dd, *J* 15 and 8, 12-H), 6.21 (1 H, s, 8-H), 6.29 (1 H, dd-like, *J* 11.5 and 1, 10-H), 7.46 (1 H, dd, *J* 15 and 11.5, 11-H) and 9.61 (1 H, d, *J* 8, CHO) (Found: M^+, 318.184. $C_{19}H_{26}O_4$ requires M, 318.183).

(9Z)-*Isomer* of **11a**: λ_{max}(EtOH)/nm 223 and 324; λ_{max}(hexane)/nm 219, 311 and 319sh; ν_{max}/cm^{-1} 3580 and 3400 (OH), 1928 (C=C=C), 1725 (OAc), 1658 and 1652 (split) (conj. CHO) and 1590 (C=C); δ_H(500 MHz) 1.10 (3 H, s, 1-Me^{eq}), 1.38 (3 H, s, 5-Me), 1.40 (1 H, t, *J* 12, 2-H^{ax}), 1.43 (3 H, s, 1-Me^{ax}), 1.50 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.97 (3 H, s, 9-Me), 1.98 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.26 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 6.12 (1 H, dd, *J* 15 and 8, 12-H), 6.21 (1 H, br d, *J* 12, 10-H), 6.70 (1 H, s, 8-H), 7.54 (1 H, dd, *J* 15 and 12, 11-H) and 9.60 (1 H, d, *J* 8, CHO) (Found: $M^{\bullet}$, 318.183).

(6S)-*Isomer* of **11b**: λ_{max}(EtOH)/nm 286; λ_{max}(hexane)/nm 285; ν_{max}/cm^{-1} 3600–3200 (OH), 1930 (C=C=C), 1720 (OAc), 1300 and 1140 (SO_2); δ_H(500 MHz) 1.05 (3 H, s, 1-Me^{eq}), 1.33 (3 H, s, 5-Me), 1.37 (1 H, t, *J* 12, 2-H^{ax}), 1.40 (3 H, s, 1-Me^{ax}), 1.48 (1 H, t, *J* 12, 4-H^{ax}), 1.69 (3 H, d, *J* 1, 9-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.24 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 3.88 (2 H, br d, *J* 7.5, 13-H_2), 5.36 (1 H, tt, *J* 12 and 4, 3-H), 5.55 (1 H, dt, *J* 15 and 7.5, 12-H), 5.97 (1 H, dd-like, *J* 11.5 and 1, 10-H), 6.07 (1 H, s, 8-H), 6.35 (1 H, br dd, *J* 15 and 11.5, 11-H), 7.56 (2 H, t, *J* 8, ArH), 7.66 (1 H, tt, *J* 8 and 1.5, ArH) and 7.88 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M^+, 444.199. $C_{25}H_{32}O_5S$ requires M, 444.197).

(9Z)-*Isomer* of **11b**: λ_{max}(EtOH)/nm 283; λ_{max}(hexane)/nm 283; ν_{max}/cm^{-1} 3600 and 3475 (OH), 1930 (C=C=C), 1725 (OAc), 1300 and 1140 (SO_2); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.34 (3 H, s, 5-Me), 1.38 (3 H, s, 1-Me^{ax}), 1.38 (1 H, t, *J* 12, 2-H^{ax}), 1.48 (1 H, t, *J* 12, 4-H^{ax}), 1.76 (3 H, s, 9-Me), 1.98 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.27 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 3.86 (2 H, d, *J* 7.5, 13-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.50 (1 H, dt, *J* 15 and 7.5, 12-H), 5.85 (1 H, dd-like, *J* 11 and 1, 10-H), 6.27 (1 H, d-like, *J* 0.5, 8-H), 6.43 (1 H, dd, *J* 15 and 11, 11-H), 7.56 (2 H, t, *J* 8, ArH), 7.65 (1 H, tt, *J* 8 and 1.5, ArH) and 7.88 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M^+, 444.196).

(6S,9Z)-*Isomer* of **11b**: λ_{max}(EtOH)/nm 283; λ_{max}(hexane)/nm 283; ν_{max}/cm^{-1} 3500 (OH), 1938 (C=C=C), 1728 (OAc), 1308 and 1150 (SO_2); δ_H(500 MHz) 1.05 (3 H, s, 1-Me^{eq}), 1.33 (3 H, s, 5-Me), 1.36 (1 H, t, *J* 12, 2-H^{ax}), 1.39 (3 H, s, 1-Me^{ax}), 1.47 (1 H, t, *J* 12, 4-H^{ax}), 1.84 (3 H, s, 9-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.24 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 3.86 (2 H, d, *J* 7.5, 13-H_2), 5.36 (1 H, tt, *J* 12 and 4, 3-H), 5.48 (1 H, dt, *J* 15 and 7.5, 12-H), 5.89 (1 H, br d, *J* 11, 10-H), 6.36 (1 H, s, 8-H), 6.45 (1 H, dd, *J* 15 and 11, 11-H), 7.56 (2 H, t, *J* 8, ArH), 7.64 (1 H, tt, *J* 8 and 1.5, ArH) and 7.88 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M^+, 444.196).

(6S)-*Isomer* of **11c**: λ_{max}(EtOH)/nm 278 and 289sh; λ_{max}(hexane)/nm 278 and 287sh; ν_{max}/cm^{-1} 3600–3300 (OH), 1925 (C=C=C) and 1725 (OAc); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.34 (3 H, s, 5-Me), 1.37 (1 H, t, *J* 12, 2-H^{ax}), 1.41 (3 H, s, 1-Me^{ax}), 1.48 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.81 (3 H, d, *J* 1, 9-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.03 and 2.07 (each 3 H, s, OAc × 2), 2.24 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 4.64 (2 H, dd, *J* 6.5 and 1, 13-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.76 (1 H, dt, *J* 15 and 6.5, 12-H), 6.02 (1 H, dd-like, *J* 11 and 1, 10-H), 6.10 (1 H, s, 8-H) and 6.60 (1 H, ddt, *J* 15, 11 and 1, 11-H) (Found: M^+, 362.210. $C_{21}H_{30}O_5$ requires M, 362.209).

(9Z)-*Isomer* of **11c**: λ_{max}(EtOH)/nm 274; λ_{max}(hexane)/nm 265sh and 274; ν_{max}/cm^{-1} 3580 and 3420 (OH), 1930 (C=C=C) and 1730 (OAc); δ_H(500 MHz) 1.08 (3 H, s, 1-Me^{eq}), 1.36 (3 H, s, 5-Me), 1.39 (3 H, s, 1-Me^{ax}), 1.39 (1 H, t, *J* 12, 2-H^{ax}), 1.48 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.78 (3 H, s, 9-Me), 1.98 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.03 and 2.08 (each 3 H, s, OAc × 2), 2.28 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 4.63 (2 H, d, *J* 7, 13-H_2), 5.37 (1 H, tt,

J 12 and 4, 3-H), 5.72 (1 H, dt, *J* 15 and 7, 12-H), 5.90 (1 H, dd-like, *J* 11 and 1, 10-H), 6.48 (1 H, d-like, *J* 1, 8-H) and 6.68 (1 H, br dd, *J* 15 and 11, 11-H) (Found: M^+, 362.211).

(6S,9Z)-*Isomer* of **11c**: λ_{max}(EtOH)/nm 275; λ_{max}(hexane)/nm 265sh and 274; ν_{max}/cm^{-1} 3550 and 3400 (OH), 1925 (C=C=C) and 1725 (OAc); δ_H(500 MHz) 1.07 (3 H, s, 1-Me^{eq}), 1.35 (3 H, s, 5-Me), 1.37 (1 H, t, *J* 12, 2-H^{ax}), 1.40 (3 H, s, 1-Me^{ax}), 1.48 (1 H, t, *J* 12, 4-H^{ax}), 1.83 (3 H, s, 9-Me), 1.96 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 and 2.08 (each 3 H, s, OAc × 2), 2.24 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 4.63 (2 H, d, *J* 6.5, 13-H_2), 5.38 (1 H, tt, *J* 12 and 4, 3-H), 5.72 (1 H, dt, *J* 15 and 6.5, 12-H), 5.93 (1 H, dd-like, *J* 11 and 1, 10-H), 6.57 (1 H, d-like, *J* 1, 8-H) and 6.68 (1 H, br dd, *J* 15 and 11, 11-H) (Found: M^+, 362.207).

(6S)-*Isomer* of **14b**: λ_{max}(EtOH)/nm 305sh, 320 and 335sh; λ_{max}(hexane)/nm 305sh, 319 and 337; ν_{max}/cm^{-1} 3600–3200 (OH), 1930 (C=C=C), 1725 (OAc), 1300 and 1145 (SO_2); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.34 (3 H, s, 5-Me), 1.38 (1 H, t, *J* 12, 2-H^{ax}), 1.40 (3 H, s, 1-Me^{ax}), 1.47 (3 H, d, *J* 1, 13-Me), 1.49 (1 H, dd, *J* 13 and 12, 4-H^{ax}), 1.81 (3 H, d, *J* 1, 9-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 (3 H, s, OAc), 2.24 (1 H, ddd, *J* 13, 4 and 2, 4-H^{eq}), 3.96 (2 H, d, *J* 8, 15-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.45 (1 H, br t, *J* 8, 14-H), 6.06 (1 H, dd-like, *J* 11 and 1, 10-H), 6.14 (1 H, s, 8-H), 6.23 (1 H, d, *J* 15, 12-H), 6.48 (1 H, dd, *J* 15 and 11, 11-H), 7.54 (2 H, t, *J* 8, ArH), 7.65 (1 H, tt, *J* 8 and 1.5, ArH) and 7.85 (2 H, dd, *J* 8 and 1.5, ArH) (Found: M^+, 484.227. $C_{28}H_{36}O_5S$ requires M, 484.228).

(6S)-*Isomer* of **14c**: λ_{max}(EtOH)/nm 295sh, 312 and 325; λ_{max}(hexane)/nm 295sh, 311 and 325; ν_{max}/cm^{-1} 3590 and 3440 (OH), 1930 (C=C=C) and 1725 (OAc); δ_H(500 MHz) 1.06 (3 H, s, 1-Me^{eq}), 1.35 (3 H, s, 5-Me), 1.38 (1 H, t, *J* 12, 2-H^{ax}), 1.41 (3 H, s, 1-Me^{ax}), 1.49 (1 H, t, *J* 12, 4-H^{ax}), 1.84 (3 H, d, *J* 0.5, 9-Me), 1.89 (3 H, d, *J* 0.5, 13-Me), 1.95 (1 H, ddd, *J* 12, 4 and 2, 2-H^{eq}), 2.04 and 2.07 (each 3 H, s, OAc × 2), 2.24 (1 H, ddd, *J* 12, 4 and 2, 4-H^{eq}), 4.73 (2 H, d, *J* 7, 15-H_2), 5.37 (1 H, tt, *J* 12 and 4, 3-H), 5.62 (1 H, br t, *J* 7, 14-H), 6.08 (1 H, dd-like, *J* 11 and 0.5, 10-H), 6.14 (1 H, s, 8-H), 6.27 (1 H, d, *J* 15, 12-H) and 6.56 (1 H, dd, *J* 15 and 11, 11-H) (Found: M^+, 402.241. $C_{24}H_{34}O_5$ requires M, 402.241).

Ozonolysis of Photoproducts of **3c**, **8c**, **11c**, **14b** *and* **14c**.—In the same manner as described for ozonolysis of sulfone **4**, each compound was oxidized with ozone gas. After removal of the solvent, the reaction products were analysed on HPLC [LiChrosorb CN (5 μm) 0.4 × 25 cm; MeOH–ether–hexane (0.5:35:64.5)]. Ozonolysis products of the (9*Z*)-isomers of compounds **8c**, **11b** and **11c** were identical with (6*R*)-allenic ketone **15**;[12] those of the (6*S*)-isomers of compounds **3c**, **11b**, **11c**, **14b** and **14c**, and those of the (6*S*,9*Z*)-isomers of compounds **11b** and **11c** were identical with (6*S*)-allenic ketone **6**[12] on HPLC.

Reduction and Subsequent Ozonolysis of Photoproducts of Compounds **3a**, **8a** *and* **11a**.—A solution of each compound in MeOH was treated with excess of $NaBH_4$ at 0 °C and the mixture was stirred for a further 30 min. The reaction mixture was diluted with ether and washed with brine. Evaporation of the dried solution gave hydroxy compounds, which without purification were oxidized with ozone gas in the same manner as described for ozonolysis of compound **4**. After removal of the solvent, the reaction products were analysed on HPLC [LiChrosorb CN (5 μm) 0.4 × 25 cm; MeOH–ether–hexane (0.5:35:64.5)]. The reaction product of the (13*Z*)-isomer of compound **3a** was identical with (6*R*)-allenic ketone **15**;[12] those of the (6*S*)-isomers of compounds **8a** and **11a** were identical with (6*S*)-allenic ketone **6**[12] on HPLC.

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