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PHOTOCHEMISTRY OF BERTYADIONOL AND RELATED COMPOUNDS†

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Abstract—Irradiation of the macrocyclic diterpene bertyadionol resulted in a single photoisomer (2) the formation of which was rationalised in terms of a novel photorearrangement resulting in transannular bond formation. The structure of this photoproduct was elucidated by a combination of chemical and spectroscopic methods. Two related compounds, diterpene B and D, and their acetate derivatives when photolysed underwent E→Z isomerisation of the conjugated double bond and epimerization about one centre of the cyclopropyl moiety.

In previous publications[1-4] on the diterpenoid constituents of *Bertya cupressoidea* evidence was presented for the structure and absolute stereochemistry of three novel macrocyclic diterpenes, bertyadionol (1), diterpene B (14) and D (17). During the early part of this work we became aware of the presence of another compound which often accompanied bertyadional and appeared to arise by the action of light on 1. Photochemical studies have confirmed that this compound is in fact a photoproduct of bertyadionol. This report presents chemical and spectroscopic evidence for the structure of the bertyadionol photoproduct (2), which arises by a novel sequence involving interaction of the conjugated diene system with the cyclopropyl enone double bond. The photochemistry of the related diterpenes, epoxylathyrol (4) and its parent alcohol (5), which present only the cyclopropyl enone system as the major chromophore, has been studied by Balmain and Ourisson[5] who showed that two major products were formed. Both arise after E to Z isomerisation of the cyclopropyl enone double bond followed either by fission of the cyclopropane to give a carbene which inserts into the carbonyl group leading to the furan (6) or by epimerisation of the cyclopropyl group to give a photostable isomer (7). For comparison we have studied the photochemistry of diterpene B (14) and D (17) and their acetate derivatives which contain a chromophore analogous to that in 4 and 5.

Only one major product was formed from either 14 or 17. Spectroscopic evidence suggested that in both cases structures analogous to that of 7 were formed. These results are presented in this report. X-ray diffraction studies on the photoproduct of diterpene D acetate (19) have confirmed the stereochemistry of the double bond and identified the stereochemistry of the cyclopropyl group in 19. These are reported in the accompanying paper.

RESULTS AND DISCUSSION

Photolysis of bertyadionol (1) gave good yields of a single photoisomer (2), $C_{20}H_{26}O_3$, whose formation was found to be independent of the solvent and wavelength used for the irradiation. The NMR spectrum of the photoproduct (2) differed markedly from that of 1 showing the presence of only one vinyl Me group but no signals for vinylic protons. The spectrum included resonances for three tertiary and one secondary Me group and for a hydroxymethine proton. The IR spectrum of 2, apart from the absorption due to an OH group, showed significant absorption at 1700, 1620 and 1615 cm^{-1}. The first of these was assigned to a cyclopentenone moiety. The other two absorptions and the nature of the third oxygen in 2 could not, at this stage, be assigned although the UV spectrum of this compound suggested that the 1,4-enedione system was still present. Overall the UV spectrum of 2 [λ_{max} 218 nm (ϵ, 14600), 256 (9600), 263 (13800) 332 (4600)] qualitatively was not dissimilar to that of bertyadionol (1) [228 (14300), 263 (9100), 288 (4200), 338 (1800)]. The ^{13}C NMR spectrum of 2 clearly showed the presence of two CO carbons (δ 214.1, 194.6) and four olefinic carbons (δ 158.9, 153.4, 143.9 and 139.4).[6] This information allows the proposal that 2 consists of a tetracyclic structure containing a diene dione system. The presence of a 1,4-enedione system was confirmed by reduction of the photoproduct (2) with Zn/AcOH. The dihydro compound (8) obtained showed IR absorptions at 1735 cm^{-1}, characteristic of a cyclopentanone CO group, and at 1680 cm^{-1} assigned to a conjugated CO [UV: λ_{max} 261 nm (ϵ 6000)]. This CO presumably gave rise to the absorption at 1620 cm^{-1} (or 1615 cm^{-1}) in the IR spectrum of the photoproduct and this could best be rationalized by assuming it to be part of an $\alpha\beta$, $\alpha'\beta'$-unsaturated carbonyl system. The dihydroacetate (9) could be obtained by treatment of 2 under reductive acetylation conditions ($Zn/Ac_2O/NaOAc$) after chromatography on silicic acid. Attempts to purify 9 by chromatography with alumina led to a mixture of compounds whose spectral data was consistent with the suggestion that epimerisation of the secondary Me group had occurred. This indicated that this Me was α- to CO as in the parent compound. In fact, treatment of 2 with 2N NaOD/dioxan gave a product (10) which, from its MS, was shown to have incorporated only one D atom, and whose NMR spectrum showed that the signal for the secondary Me group had collapsed to a broad singlet. When the NMR spectrum of 10 was recorded using C_5H_5N or C_6H_6 as solvents a separation of the resonance of two of the tertiary Me groups was noted suggesting that the product contained a mixture of epimers. The relative heights indicated a 1:1 ratio of the two epimers. Similar mixtures were observed for the products arising after alumina chromatography of the dihydroacetate (9) or of the photoproduct (2).

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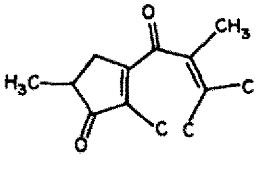
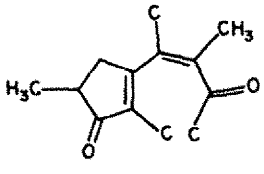
The part structure (A) which can be written for the photoproduct, on the basis of the results given above, maintains the cyclopentenone ring and the 1,4-enedione system present in bertyadionol. The vinylogous enedione system (B) could not be excluded at this stage.



A

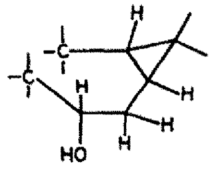


B

The nature of the third oxygen had already been established as an OH group from the NMR spectrum, and by formation of the acetate (3) of the photoproduct and the dihydroacetate (9). To obtain information regarding the environment of the OH group in 2 two derivatives were prepared. Treatment of the dihydroalcohol (8) with $POCl_3$/pyridine gave the dehydration product (11) whose NMR spectrum showed resonances for two newly introduced vinylic protons (δ 5.65 and 5.81) which were mutually coupled with J 10 Hz, appropriate for a double bond in a 6 or larger-membered ring. The lower field proton showed a second coupling (2 Hz) which was shown to originate from a proton assigned to one of the cyclopropane protons (9-H) resonating at δ 1.41 as a doublet of doublets ($J_{8,9}$ 2 and $J_{9,11}$ 8 Hz). The UV spectrum of 11 was similar to that of 8 indicating the new centre of unsaturation to be remote from the existing conjugated chromophore shown in part structure A.

Oxidation of the photoproduct (2) with Jones' reagent gave the trione (12) in good yield. The IR spectrum of this compound, compared to that of 2, showed the presence of a new CO absorption at 1705 cm^{-1}, in agreement with the previous suggestion as to the size of the ring containing the original OH group. Base catalysed deuterium exchange of 12 resulted in the introduction of 3 D atoms, two of which must be located α- to the new CO function. INDOR analysis of the NMR spectrum of the trione (12) demonstrated the presence of three discrete methylene groups in the molecule which were identified by their characteristic geminal coupling constants of 18, 16.5 and 16.4 Hz. One of these (at δ 3.03 and 2.25) was assigned to C-1 because of its coupling to the C-2H which is also coupled to the secondary Me protons. Another with resonances centred at δ 2.88 and 2.51 was shown to be coupled to one of the cyclopropane protons (H-9). The third showed resonances at δ 2.85 and 2.44 (J geminal 16.4 Hz) with only small (<2 Hz) long range coupling. One proton (H-11), resonating at δ 1.61 was observed directly as a broadened doublet and a coupling constant (J 8 Hz) similar to one of those observed for H-9 in the dehydration product (11). These results are analogous to those obtained for bertyadionol and related compounds.[3]

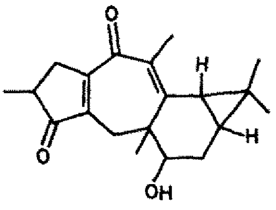
Thus the relationship between C-6, 7, 8, 9 and 11 appear to have been maintained in the photoproduct as shown in part structure C.



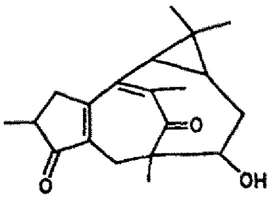
C

The third methylene group was assigned to the C-5 protons following examination of the NMR spectrum of the dihydroalcohol (13) formed as a single epimer by $NaBH_4$ reduction of 9. The absence of absorption for the cyclopentanone group in the IR spectrum of 13 indicated that this was the CO reduced by $NaBH_4$. INDOR analysis of the 3-hydroxymethine proton (δ 3.61; apparent triplet, J 5 Hz) allowed the C-4 and C-15 proton resonance signals to be differentiated. The former resonates as a multiplet centred at δ 2.68, spread over a range of 30 Hz, whereas the latter appears as a multiplet at δ 3.16 with a spread of 25 Hz. Even allowing for the magnitude of the coupling between the 3 and 4-H (5 Hz) the range (30 Hz) and complexity of the 4-H signal can only be interpreted by assuming coupling with methylene protons. The 15-H multiplet which is coupled to H-4 and the C-1 methylene protons shows signals spread over a similar range. Hence a methylene group can be placed adjacent to C-4 and this corresponds to that giving signals at δ 2.44 and 2.85 in the trione (11). At this point, consideration of the structure of the starting material (1), the multiplicity of the C-5 methylene protons in the trione (12) and of the C-7 proton in 2 and the dehydration product (11) indicates that one of the tertiary Me groups must be located between C-5 and C-7.

Two possible structures can now be considered for the photoproduct as shown in D and E.



D



E

A distinction between these two structures can be made by consideration of the UV spectra of the dihydro derivatives, 8, 9, 11 and 13, of the photoproduct (2). Comparison of the absorption maxima of these compounds (λ_{max} 260–263 nm) with those calculated (λ_{max} 249 nm) using Woodward's rules[7] indicates the contribution of a hyperconjugative influence of the cyclopropyl group on the conjugated ketone. The variation in the conjugative influence of a cyclopropyl group as part of a chromophore has been discussed by Pete,[8] and the magnitude of the contribution to the UV absorption maximum has been related to the angle that the cyclopropyl group subtends to the adjacent π system. For the dihydro derivatives of structure D molecular models show that for conformations in which steric interactions are minimized the angle between the cyclopropyl and double bond system is approximately 120°. Following the method used by Pete the calculated value of the position of the absorption maximum is 267 nm, in reasonable agreement with the observed value (λ_{max} 260–263 nm). On the other hand structure E, apart from being a highly strained and crowded system, has the C-14 carbonyl group almost orthogonal to the 13,14-double bond. A similar orientation is observed in the corresponding 4,15-dihydro derivatives. Since this would prevent any effective conjugation of these two functionalities this compound would not be expected to give rise to the observed UV.

The structure **D** which retains the cyclopropyl enone chromophore was assigned to the photoproduct. This has now been confirmed by X-ray diffraction studies which are reported in the accompanying paper.

One point that deserves comment is the unusual IR and UV spectra of the parent photoproduct **2**. The 1620 cm^{-1} absorption for a CO functionality is particularly low, and no precedent could be found. Furthermore, with respect to the UV, the origin of the 332 nm maximum is puzzling. Although this is in the region for a displaced $n \rightarrow \pi^*$ transition of the carbonyl group, the extinction co-efficient is too high and it can only be thought of as an electron transfer transition of an extensively conjugated ketone. In general, the prediction and rationale of absorption maxima are complicated on the introduction of cross conjugating units,[7] and no adequate model could be found for this system. However one possible explanation lies in the indication from models that a through space interaction of the C-4, 15 and C-12, 13 bonds may be possible and the shift may be analogous to that found in the case of norbornadiene.[9]

Photochemistry of diterpenes B and D and their acetate derivatives. Irradiation of a benzene solution of diterpene D monoacetate (**18**) gave, in good yield, a single crystalline photoisomer (**19**) the mass spectrum of which was identical to that of the starting material. The IR spectrum indicated no alteration in the assignment of the oxygen functionalities. The NMR spectrum contained the type resonances for the starting material with some differences in the chemical shifts (Table 1).

Of particular significance was the shift of the 12-H in **18** from δ 7.32 to δ 5.22 for the equivalent protons in **19**, consistent with the loss of the large deshielding of that proton by the 15-OH group. An examination of Dreiding models demonstrated that an $E \rightarrow Z$ isomerisation of the 12-ene readily rationalized the result since the proton in question was then remote from and would not be effected by the anisotropy of the OH group.

The UV maximum of **19** (Table 1) showed a 5 nm hypsochromic shift with respect to that for **18**. Although consistent with the situation generally observed between *cis* and *trans* isomers[7] it may also reflect a decrease in the hyperconjugative contribution of the cyclopropyl group.[8] In turn, the 80% decrease in the associated extinction co-efficient was consistent with the suggestion from models that a high degree of twist had been introduced between the CO and the vinyl π systems that would make the $\pi \rightarrow \pi^*$ electron transition less favoured.

Photolysis of diterpene B (**14**), its mono-(**15**) and diacetate (**16**), and diterpene D (**17**) gave the photoisomers **21**, **22**, **23** and **20** respectively. The spectral data (Table 1) indicated that an argument parallel to that for **19** applied in each case for an $E \rightarrow Z$ isomerisation of the 12-double bond.

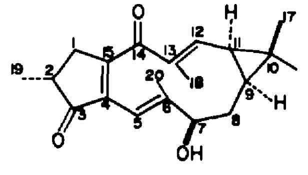
The outstanding stereochemical question pertaining to these photoproducts was the chirality of the C-9 and C-11 centres and no clear solution was possible from the available data on the compounds. While NOE studies were possible, models indicated that although different conformations of the macrocyclic ring could be differentiated, different configurations about the cyclopropyl ring fusion could not. In light of the photostability of these compounds and the comparable situation reported for epoxylathyrol (**4**),[5] it was tempting to postulate a similar isomerisation/epimerisation process, but the only definitive solution to this structural problem lay in an X-ray analysis. Accordingly, crystals of diterpene D monoacetate photoproduct (**19**) were subjected to an X-ray analysis. The results are reported in the accompanying paper and indicate that the structure and stereochemistry of this compound is as shown in **19**.

Mechanism. The isomerisations observed for **14** and **15** are examples of well documented photochemical processes and parallel the formation of the analogous Z isomer from irradiation of epoxylathyrol.[5] In that case, the initial isomerisation of the conjugated double bond, which occurred via a $\pi \rightarrow \pi^*$ triplet diradical was followed by epimerisation of the cyclopropyl group (stereochemistry undefined) which occurred via an $n \rightarrow \pi^*$ triplet diradical. With respect to this process, it is interesting to note that if a similar mechanism occurs for the *Bertya* diterpenoids, since breakage of the C-10,11 bond would give rise to the more stable radical pair, the directing factor to the observed cleavage must be the

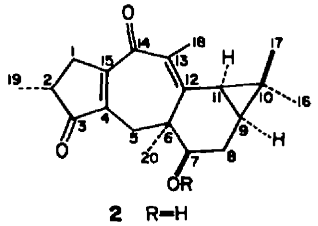
Table 1. NMR data for diterpene B, D, their derivatives and photoproducts

	Chemical shifts (δ) with couplings (Hz) in parenthesis				U.V. data
	12-H	5-H	18-CH_3	20-CH_3	λ_{max} nm(ϵ)
Diterpene B (**14**)	7.31	5.82	1.83	1.60	284 (15,000)
	(11.0, 1.2)	(10.6, 1.2)	(1.2)	(1.2)	
photoproduct (**21**)	5.06	5.70	1.98	1.57	275 (5,820)
	(10, 1.5)	(9.5, < 1)	(1.5)	(< 1)	
Diterpene B monoacetate (**15**)	7.35	5.74	1.83	1.63	282 (10,000)
	(11.4, 1.2)	(10.6, 1.2)	(1.2)	(1.2)	
photoproduct (**22**)	5.16	5.66	2.02	1.58	278 (2,310)
	(10.0, 1.5)	(9, < 1)	(1.5)	(< 1)	
Diterpene B diacetate (**16**)	6.73	5.77	1.85	1.60	
	(11.2, 1.2)	(10.6, 1.2)	(1.2)	(1.2)	
photoproduct (**23**)	5.03	5.63	1.90	1.61	
	(11, 1.5)	(8, 1.2)	(1.5)	(1.5)	
Diterpene D (**17**)	7.31	5.72	1.79	1.49	280 (5,170)
	(11.6, 1.2)	(10.0, 1.2)	(1.2)	(1.2)	
photoproduct (**20**)	5.12	5.53	1.97	1.53	
	(~9, 1.5)	(~ 10, 1.2)	(1.5)	(1.2)	
Diterpene D monoacetate (**18**)	7.32	5.64	1.81	1.52	278 (10,400)
	(11.8, 1.2)	(10, 1.2)	(1.2)	(1.2)	
photoproduct(**19**)	5.22	5.40	2.00	1.60	274 (1,930)
	(9.3, 1.5)	(10.0, 0.8)	(1.5)	(0.8)	

principle of maximum orbital overlap of the cyclopropyl-π systems as determined by geometric constraints. However, in the absence of sensitiser/quenching studies on these systems, the possibility of carbene formation cannot be discounted, since it could also give rise to the observed product. No direct precedence could be found in the literature for the phototransformation observed for bertyadionol. However in terms of known processes the pathways shown in Scheme 1 can be considered. The formation of the cyclobutyl intermediate (path a Scheme 1) is an example of the well-documented[2+2] cycloaddition reaction.[10] On the basis of orbital symmetry correlations and considered as a concerted excited state process this may occur in either a $[{}_{\pi}2_{s}+{}_{\pi}2_{s}]$ or a $[{}_{\pi}2_{a}+{}_{\pi}2_{a}]$ sense.[11] For bertyadionol, where the orientation of the C-5 and C-12 double bonds relative to each other approaches the orthogonality requirement for the addition, the former process seems most likely since the

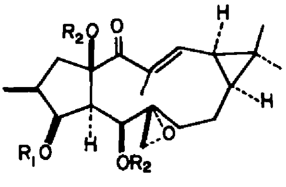


1



2 R=H

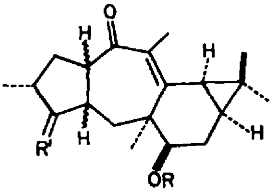
3 R=Ac



4 R_1=PhCH$_2$CO

R_2=Ac

5 R_1,R_2=H

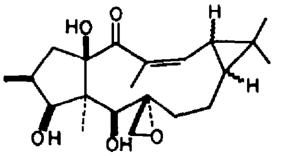


8 R=H,R'=O

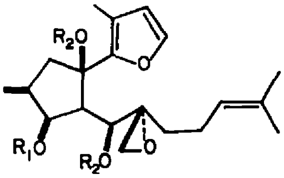
9 R=Ac,R'=O

11 7-ene,R'=O

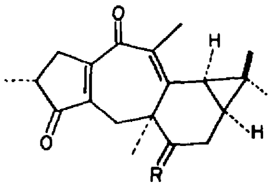
13 R=Ac,R'=$<^{OH}_{H}$



7

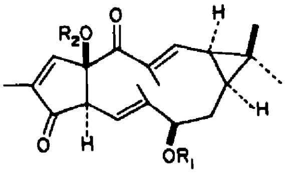


6



10 R=$<^{OH}_{H}$2-D

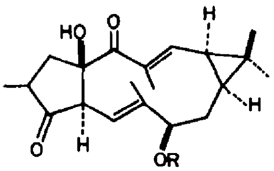
12 R=O



14 R_1,R_2=H

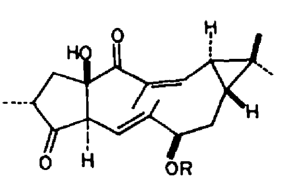
15 R_1=Ac,R_2=H

16 R_1,R_2=Ac



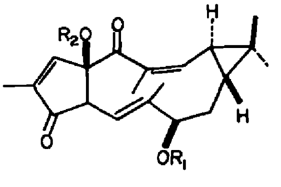
17 R=H

18 R=Ac .



19 R=Ac

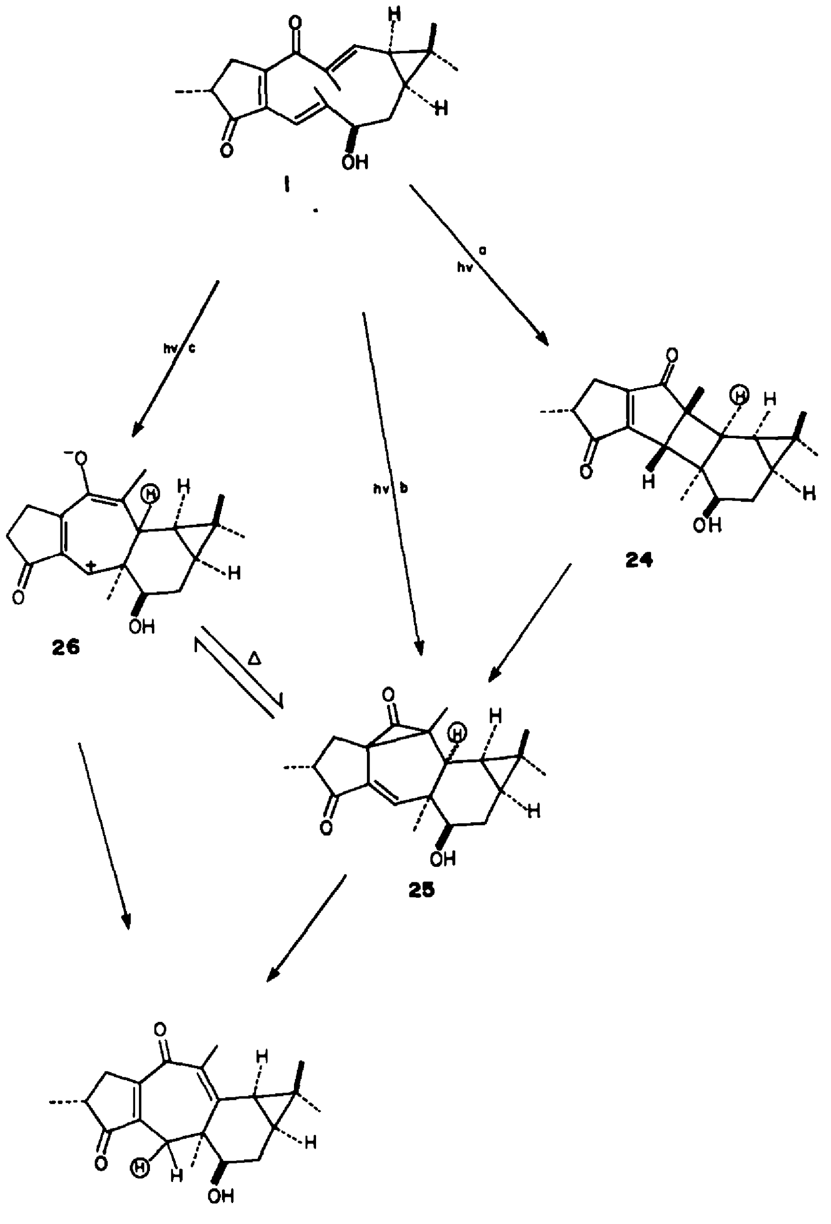
20 R=H



21 R_1,R_2=H

22 R_1=Ac,R_2=H

23 R_1,R_2=Ac



Scheme 1

orientation of the 2-Me group relative to the plane of the macrocyclic ring does not change. Formation of the cyclopropanone (25) from the cyclobutyl intermediate (24) has a precedent in the work of Cargill *et al.*[12] on the photochemistry of bicylo[3.2.0]hept-2-en-2-ones. They observed a set of products derived from a cyclopropanone intermediate whose formation was shown to occur by a concerted $[_\sigma 2 + _\pi 2]$ cycloaddition.

Alternatively the cyclopropane intermediate (25) could result from a photochemical Diels–Alder reaction (path b), which, if concerted, may occur through either the symmetry allowed $[_\pi 2_s + _\pi 4_s]$ or $[_\pi 2_a + _\pi 4_a]$ processes.

The two sequences would lead to two structures which differ in the relative orientation of the C-12H and the C-6 Me group. It is possible that either reaction type A or B could be preceeded by E→Z isomerisation. If the cyclopropanone is in fact the immediate precursor to the photoproduct an unlikely antarafacial homo [1,5] sigmatropic shift would have to be assumed. Given the thermal instability of cyclopropanones[13,14] it would seem more reasonable to assume *thermal* ring opening of the cyclopropanone[14] to generate the zwitterion (26) which then undergoes a [1,6] suprafacial sigmatropic shift of the 12-H to C-5. This step is clearly intramolecular since no deuterium incorporation was observed from photolysis of 1 in EtOD. The zwitterion may also arise from an electrocyclic reaction to 1 (path c). With respect to the overall pathway two points deserve further comments. The postulated involvement of the cyclopropanone intermediate (or the tautomeric zwitterion) assumes that the subsequent sigmatropic shift occurs faster than diffusion control since no products arising from nucleophilic attack were observed when the photolysis was carried out in a polar solvent. (e.g. EtOH). Secondly, photolysis of 1 in the presence of naphthalene as a triplet quencher or acetone or benzophenone as triplet sensitisers had no observable effect on the course of the reaction. It is therefore difficult to speculate whether a singlet or an unquenchable triplet state or a combination of both is involved in the transformation.

EXPERIMENTAL

General experimental details are as quoted in a previous publication.[2] For the photochemical experiments an Oliphant Photochemical Reactor was used. Solns were deoxygenated by purging with N_2. The temp. inside the reactor rose to approximately 34°. Photolyses were monitored by NMR and/or TLC and in no case was any evidence found to suggest the formation of any intermediate products. In all cases periods of extended irradiation resulted in gradual degradation of the product(s). The UV spectra recorded in this paper were run on a Varian Techtron 635 UV-Visible Spectrophotometer. Chemical Shifts marked with an asterisk indicate that the resonance position and multiplicity were determined by double resonance methods.

Photolysis of bertyadionol (1)

(a) *Direct irradiation.* Bertyadionol (1, 1 g) was dissolved in $CHCl_3$ (100 ml) and irradiated with light of narrow bandwidth centred at 350 nm (10 hr). The solvent was evaporated and the residue crystallised from $CHCl_3$ as yellow needles of the *photoisomer* (2, 930 mg) m.p. 213–214°, $[\alpha]_D + 307°$ (*c*, 11.0). Further quantities of the photoproduct (40 mg) were obtained by concentration and crystallisation of the mother liquors. (Found: C, 76.5, H, 8.3. $C_{20}H_{26}O_3$ requires: C, 76.4, H, 8.3%). IR ($\nu_{max}^{CHCl_3}$ cm^{-1}): 1700 (s, CO); 1620 (m) and 1615 (m, double bonds, CO). UV: (λ_{max} nm) 218 (ϵ, 14560), 256 (9630), 263 (13840), 332 (4570). MS (80°, 70 eV): *m/e* (%), 314 (M^+, 95), 296 (80), 286 (75), 281 (50), 271 (80), 268 (80), 254 (base peak). NMR ($CDCl_3$, 90 MHz): δ 3.68 (7-$\underline{H}$, br.d of d, H_{7-8a} = 12.0 Hz, J_{7-8b} = 4.0 Hz); 1.89 (18-$C\underline{H}_3$, s); 1.22 (19-$C\underline{H}_3$, d, J_{19-2} = 7.1 Hz); 1.23, 1.21 and 0.90 (16, 17 and 20-$C\underline{H}_3$, s). (C_6H_6, 60 MHz) δ 3.41 (7-$\underline{H}$, br.d of d, J_{7-8a} = 12.1 Hz, J_{7-8b} = 4.0 Hz); 1.95 (18-H_3, s); 0.99 (19-H_3, d, J_{19-2} = 7.0 Hz); 1.16, 0.98 and 0.75 (16, 17 and 20-$C\underline{H}_3$, s). ^{13}C NMR: ($CDCl_3$, 22.63 MHz) δ 214.1 (3-$\underline{C}$); 194.6 (14-$\underline{C}$); 158.9, 153.4, 143.9 and 139.4 (vinyl carbons); 76.9 (7-$\underline{C}$); 41.2, 39.8, 34.7, 27.9, 26.8, 26.4, 25.1, 24.8, 21.2, 18.0, 17.6, 16.7 and 14.4 (remaining carbons).

The photolysis was repeated using ethanol, and then benzene as solvent. In both cases a single photoisomer, identical to that described above was obtained. The same result was obtained using a Hanovia medium mercury lamp, with or without a pyrex filter.

(b) *With acetone or benzophenone as sensitisers.* A 1% acetone soln of bertyadionol was irradiated as described above (350 nm) and the same single photoproducts was obtained. Similarly, a 1% benzene solution of 1 (0.23 mmol) containing benzophenone was irradiated. The solvent was removed and the benzophenone separated by silicic acid (20 g, 80–100 mesh) chromatography to yield the single photoisomer (2) described above.

(c) *With naphthalene as triplet quencher.* A 1% benzene soln of 1 (0.48 mmol) and naphthalene (14 mmol) was irradiated (350 nm) for 5.5 hr. The solvent was evaporated and the naphthalene separated by chromatographing the residue on silicic acid. The NMR spectrum of the products showed it to be a mixture of starting material and photoproduct, judged to be present in the ratio of 15:85 respectively.

Acetylation of the photoproduct

The photoproduct (2, 100 mg) was dissolved in pyridine and Ac_2O and left for 12 hr at room temp. Recovery of the product gave the *acetate* (3, 96 mg) as an oil which crystallised from n-pentane/ether as needles, m.p. 131–132° $[\alpha]_D + 288°$ (*c*, 2.96). (Found: C, 74.1, H, 7.8; $C_{22}H_{28}O_4$ requires: C, 74.1, H, 7.9%). IR ($\nu_{max}^{CS_2}$ cm^{-1}): 1750 (s, acetate); 1710 (s, CO). UV (λ_{max} nm): 217 (ϵ 1400), 263 (14620), 330 (5790). NMR ($CDCl_3$, 60 MHz): δ 4.80 (7-$\underline{H}$, br.d of d, J_{7-8a} = 11.5 Hz, J_{7-8b} = 3.5 Hz); 2.08 (acetate); 1.89 (18-$C\underline{H}_3$, s); 1.23 (19-$C\underline{H}_3$, d, J_{19-2} = 7.5 Hz); 1.23, 1.11 and 0.91 (16, 17 and 20-$C\underline{H}_3$, s).

Photolysis of bertyadionol acetate in deuterated ethanol

Bertyadionol acetate (100 mg) was photolysed as described above, but using EtOD as solvent (10 ml). All initial transfer operations were carried out in a dry N_2 atmosphere. The crystalline photoproduct acetate (3, 75 mg) was isolated and shown to be identical in all respects to the acetate derivative of the bertyadionol photoproduct. The mass spectrum of this product demonstrated that no deuterium had been incorporated during the phototransformation.

Zinc-acetic acid reduction of the photoproduct (2)

Zn dust was added to a glacial AcOH (20 ml) soln of the photoproduct (2, 405 mg) and the mixture stirred at room temp. for 2 hr. The excess Zn dust was filtered off, and the product recovered with ether. After washing exhaustively with $NaHCO_3$ the ether was dried and evaporated and the resulting oil chromatographed on alumina (activity II) to give the *dihydroalcohol* (8, 264 mg) which crystallised from n-pentane ether as needles, m.p. 142–143°, $[\alpha]_D$ -14° (*c*, 2.48). (Found: C, 75.7, H, 8.8. $C_{20}H_{28}O_3$ requires: C, 75.9, H, 8.9%). IR ($\nu_{max}^{CHCl_3}$ cm^{-1}): 3610 (br, m, OH); 1735 (s) and 1680 (s, CO). UV (λ_{max} nm) 203 (ϵ, 2600), 261 (600). NMR ($CDCl_3$, 60 MHz): δ 3.83 (7-$\underline{H}$, d of d, J_{7-8a} = 7 Hz, J_{7-8b} = 2 Hz); 3.48 (4 or 15-$\underline{H}$, br.d of d, J = 11 and 7 Hz); 1.88 (18-$C\underline{H}_3$, d, J = 1.1 Hz); 1.11 (19-$C\underline{H}_3$, d, J_{19-2} = 6 Hz); 1.19, 1.12 and 1.03 (16, 17 and 20-$C\underline{H}_3$, s).

Reductive acetylation of the photoproduct (2)

Zn dust (500 mg) was added to a soln of the bertyadionol photoproduct (2, 550 mg) and NaOAc (600 mg) in Ac_2O (20 ml) and the mixture warmed on a steam bath for 30 min. The mixture was filtered and the filtrate poured into ice water and vigorously stirred for 2 hr before extracting with ether. The product was recovered in the normal manner as an oil, which after silicic acid chromatography crystallised from ether/n-pentane as needles of the *dihydroacetate* (9, 290 mg), m.p. 151–152°, $[\alpha]_D$ = +67° (*c*, 2.36). (Found: C, 73.9, H, 8.5. $C_{22}H_{30}O_4$ requires: C, 73.7, H, 8.4%). IR ($\nu_{max}^{CCl_4}$ cm^{-1}): 1740 (s) and 1735 (s, acetate and CO); 1680 (m, CO). UV (λ_{max} nm): 203 (ϵ, 3030), 260 (5530). MS (60°, 70 eV); *m/e* (%), 358 (M^+, 2), 298 (base peak), 283 (20), 265 (18), 256 (30), 255 (30), 227 (60). NMR ($CDCl_3$, 60 MHz): δ 4.82 (7-$\underline{H}$, d of d, J_{7-8a} = 7 Hz, J_{7-8b} = 2.8 Hz); 2.02 (acetate); 1.90 (18-$C\underline{H}_3$, d, = 1 Hz); 1.10 (19-$C\underline{H}_3$, d, J_{19-2} = 6.5 Hz); 1.18, 1.18, 1.10 and 1.02 (16, 17 and 20-$C\underline{H}_3$, s).

Isolation of the product by alumina chromatography (activity I) yielded an isomeric dihydroacetate, m.p. 187–188° (n-pentane/ether), $[\alpha]_D$ = +158° (*c*, 2.72). (Found: C, 73.7, H, 8.4. $C_{22}H_{30}O_4$ requires: C, 73.7, H, 8.4%. IR ($\nu_{max}^{CCl_4}$ cm^{-1}): as quoted above. UV (λ_{max} nm): 201 (ϵ, 3250), 261 (6450). MS: as quoted above. NMR ($CDCl_3$, 90 MHz): δ 4.59 (7-$\underline{H}$, br.d, J_{7-8a} = 7 Hz, J_{7-8b} < 2 Hz); 3.48 (4 or 15-$\underline{H}$, br.d of d, J = 7 and 11 Hz); 1.89 (18-CH_3 and acetate, s); 1.12 (19-$C\underline{H}_3$, d, J_{19-2} = 6.9 Hz); 1.27, 1.17 and 0.96 (16, 17 and 20-$C\underline{H}_3$, s).

Acetylation of the zinc-acetic acid reduction product (8)

The dihydroalcohol (8, 20 mg) was acetylated in the normal manner using Ac_2O in pyridine to give 9, (21 mg) identical in all respects to that epimer obtained by alumina chromatography following the reductive acetylation of the bertyadionol photoproduct.

C-2 *Epimerization of the bertyadionol photoproduct* (2)

Chromatography of the bertyadionol photoproduct on alumina or treatment with 2M NaOH in 50% dioxan under a N_2 atmosphere for 1 hr at room temp. resulted in a 50:50 mixture, as judged by NMR, of the C-2 eqimers of the photoproduct. The epimers co-crystallised from chloroform as yellow needles m.p. 212–215°, $[\alpha]_D$ = +331°, (*c*, 11.8). IR, UV, and MS: as quoted for 2. NMR ($CDCl_3$, 60 MHz): as quoted for 2. (C_6H_6, 60 MHz); as quoted for 2 but with a doubling of the signals attributable to the methyl groups δ 0.99 and 0.96 (19-$C\underline{H}_3$'s J_{19-2} = 7.0 Hz in each case); 1.20 (s); 1.16 (s); 0.95 (br.s); 0.75 (s); 0.71 (s, 16, 17 and 20 Me resonances).

Deuterium exchange on the bertyadionol photoproduct (2)

The photoproduct (2, 50 mg) was dissolved in dioxan (0.75 ml) and added to an approximately 2M NaOD soln (0.75 ml) and stirred under N_2 for 1 hr at room temp. The soln was poured into water and extracted with ether, which on evaporation gave the 2-d_1-photoproduct epimers (30 mg) which were purified by preparative TLC. MS (45°, 65 eV): *m/e* (%), 315 (60,d_1), 314 (25 d_0). NMR ($CDCl_3$, 60 MHz): The spectrum was analogous to that quoted for 2 except the secondary methyls doublet resonances had collapsed to a broad singlet at δ 1.22.

Dehydration of the dihydroalcohol (**8**)

The dihydroalcohol (**8**, 70 mg) was dissolved in pyridine (2 ml) and cooled in an ice bath prior to the addition of $POCl_3$ (0.2 ml). The mixture was allowed to stand for 5 hr (ice bath) then poured into ice water and extracted with ether. Workup in the normal manner gave an oil from which the *dehydro compound* (11, 50 mg) was isolated by preparative TLC. Crystallisation from n-pentane/ether gave the product as plates m.p. 185–186°. (Found: C, 80.3, H. 8.6. $C_{20}H_{26}O_2$ requires: C, 80.5, H, 8.8%). IR ($\nu_{max}^{CHCl_3}$ cm^{-1}): 1735 (s), 1675 (m) and 1670 (m, CO and double bonds). UV (λ_{max} nm): 200 (ϵ, 4270), 260 (5110). MS (25°, 70 eV): *m/e* (%), 298 (M^+, 60), 283 (30), 270 (30), 256 (40), 255 (40), 227 (50), 159 (base peak). NMR ($CDCl_3$, 90 MHz): δ 5.81 and 5.65 (7-$\underline{H}$ and 8-$\underline{H}$, ABX pattern, $J_{7-8} = 10$ Hz, further coupling to the lower field proton of 2 Hz from 9-H); 1.83 (18-$C\underline{H}_3$, d, $J = 1.1$ Hz); 1.41* (9-$\underline{H}$, d of d, J_{9-8} or $7 = 2$ Hz, $J_{9-11} = 8$ Hz); 1.09 (19-$C\underline{H}_3$, d, $J_{19-2} = 6.5$ Hz); 1.24, 1.16 and 0.84 (16, 17 and 20-$C\underline{H}_3$, s).

Jones' oxidation of the bertyadionol photoproduct (2)

The photoproduct (2, 90 mg) was dissolved in acetone (5 ml) and treated with Jones' reagent (0.5 ml) for 5 min at room temp. The excess reagent was destroyed by the addition of MeOH (1 ml) then the mixture diluted with H_2O and the organic product recovered with ether. Evaporation of the ether gave the *trione* (12, 75 mg) which crystallised from n-pentane/ether as plates m.p. 165–166°, $[\alpha]_D = +378°$ (*c*, 3.00). (Found: C, 76.7, H, 7.7. $C_{20}H_{24}O_3$ requires: C, 76.9, H, 7.7%). IR ($\nu_{max}^{CHCl_3}$ cm^{-1}): 1715 (s) and 1705 (s, CO); 1620 (m) and 1610 (m, CO, double bond). UV (λ_{max} nm): 223 (ϵ, 9440), 272 (7480), 318 (6560). MS (50°, 70 eV): *m/e* (%), 312 (M^+, base peak), 297 (30), 284 (30), 269 (98), 255 (20), 241 (80). NMR ($CDCl_3$, 90 MHz): δ 3.03 and 2.25* (-$C\underline{H}_2$, $J_{1Ha-Hb} = 18$ Hz, other couplings $J_{1Ha-2} = 3.1$ Hz, $J_{1Hb-2} = 2.1$ Hz); 2.88* and 2.51* (8-$C\underline{H}_2$, $J_{8Ha-Hb} = 16.5$ Hz, other couplings $J_{8Ha-9} = 6.0$ Hz, $J_{8Hb-9} = 2.5$ Hz); 2.85* and 2.44* (5-$C\underline{H}_2$, $J_{5Ha-Hb} = 16.4$ Hz); 2.00 (18-$C\underline{H}_3$, s); 1.61 (11-$\underline{H}$, br.d, $J_{11-9} = 8$ Hz); 1.52* (9-H, m); 1.22 (19-$C\underline{H}_3$, d, $J_{19-2} = 7.0$ Hz); 1.28, 1.24 and 0.86 (16, 17 and 20-$C\underline{H}_3$, s). (C_6H_6, 90 MHz): δ 3.07 and 2.45* (5-$C\underline{H}_2$, $J_{5Ha-Hb} = 16.2$ Hz); 2.96* and 1.93* (1-$C\underline{H}_2$, $J_{1Ha-Hb} = 18.0$ Hz, other couplings, $J_{1Ha-2} = 3.0$ Hz, $J_{1Hb-2} = 2.1$ Hz); 2.38* and 2.16* (8-$C\underline{H}_2$, $J_{8Ha-Hb} = 16.5$ Hz, other couplings $J_{8Ha-9} = 8.7$ Hz, $J_{8Jb-9} = 3.0$ Hz); 1.98 (18-$C\underline{H}_3$, s); 1.00 (19-$C\underline{H}_3$, d, $J_{19-2} = 7.0$ Hz); 1.01, 0.88 and 0.60 (16, 17 and 20-$C\underline{H}_3$, s), 0.81* (9-$\underline{H}$, M).

Deuterium exchange on the Jones' oxidation product (12)

The trione (12, 10 mg) was dissolved in dioxan (0.5 ml) and an approximately 2M NaOD soln (0.5 ml) added. The mixture was stirred under N_2 for 20 min at room temp. before working up in the usual manner. The 3-d_1, 8-d_2-triones were isolated by preparative TLC. MS (35°, 70 eV): 315 (100, d_3), 314 (55, d_2), 313 (22, d_1), 312 (8, d_0).

Sodium borohydride reduction of the dihydroacetate (**9**)

The dihydroacetate (9, 100 mg) was dissolved in MeOH and the soln cooled (acetone/dry ice). Sodium borohydride (70 mg) was added and the solution stirred for 3 hr before pouring into water and isolating the products with ether in the normal manner. TLC and NMR indicated the formation of a single product which was purified by preparative TLC as a foam (13, 75 mg). IR ($\nu_{max}^{CCl_4}$ cm^{-1}): 3620 (w) and 3500 (br, w, OH); 1735 (s) and 1680 (m, CO). UV (λ_{max} nm): 263 (ϵ, 4820). MS: Calc. for $C_{22}H_{32}O_4$: 360.230. Found: 360.228. NMR ($CDCl_3$, 90 MHz): δ 4.58 (7-$\underline{H}$, br.d, $J_{7-8a} = 7.5$ Hz); 3.61 (3-$\underline{H}$, d of d, $J_{3-2} = 5$ Hz, $J_{3-4} = 5$ Hz); 3.16* (15-$\underline{H}$, m); 2.68* (4-$\underline{H}$, m); 2.41* and 1.67* (8-$C\underline{H}_2$, $J_{8Ha-Hb} = 17$ Hz, other couplings $J_{8Ha-7} = 7.5$ Hz, $J_{8Hb-9} = 8.5$ Hz); 2.03 (2-$\underline{H}$, m); 1.91 (acetate); 1.84 (18-$C\underline{H}_3$, d, $J_{18-15} = 1.1$ Hz); 0.97 (19-$C\underline{H}_3$, d, $J_{19-2} = 7.2$ Hz); 1.26, 1.16 and 0.96 (16, 17 and 20-$C\underline{H}_3$, s).

Photolysis of diterpene D monoacetate (**18**)

Diterpene D monoacetate (**18**, 420 mg) was dissolved in benzene (50 ml) and irradiated at 300 nm until no further conversion of the remaining trace quantities of starting material was observed (TLC, 3.75 hr). The solvent was evaporated and the residue recrystallised from n-pentane/ether to give the *photoisomer* (**19**) as needles (310 mg), m.p. 178-179°, $[\alpha]_D = -106°$ (*c*, 2.75). Found: C, 70.3, H, 7.8. $C_{22}H_{30}O_5$ requires: C, 70.6, H, 8.1%. IR ($\nu_{max}^{CCl_4}$ cm^{-1}): 3575 (m) and 3400 (br, OH); 1750 (br, s, acetate and carbonyl); 1700 (s, CO). UV (λ_{max} nm): 274 (ϵ, 1930). MS: The fragmentation pattern observed was identical to that quoted for diterpene D monoacetate (**18**).[3] NMR: ($CDCl_3$, 90 MHz): 5.40 δ* (5-$\underline{H}$, br.d, $J_{5-4} = 10$ Hz, $J_{5-20} = 0.8$ Hz); 5.30 (7-$\underline{H}$, br.d, $J_{7-8a} = 4$ Hz); 5.22 (12-$\underline{H}$, d of q, $J_{12-11} = 9.3$ Hz, $J_{12-18} = 1.5$ Hz); 3.77 (4-$\underline{H}$, d, $J_{4-5} = 10$ Hz); 2.11 (acetate); 2.00 (18-$C\underline{H}_3$, d, $J_{18-12} = 1.5$ Hz); 1.60 (20-$C\underline{H}_3$, d, $J_{20-5} \simeq 0.8$ Hz); 1.23 (19-$C\underline{H}_3$, d, $J_{19-2} = 6.8$ Hz); 1.12 and 1.01 (16 and 17-$C\underline{H}_3$, s); 0.97* and 0.49 (11 and 9-$\underline{H}$ respectively, $J_{9-11} \simeq 6.0$ Hz, other couplings $J_{11-12} = 9.3$ Hz, $J_{9-8a,8b} = 12$ and 4 Hz). (C_5D_5N, 90 MHZ): δ 6.15 (5-$\underline{H}$, br.d, $J_{5-4} = 9.5$ Hz); 5.44 (7-$\underline{H}$, br.d, $J_{7-8a,8b} = 4$ Hz and < 1 Hz); 5.24 (12-$\underline{H}$, d of q, $J_{12-11} = 10$ Hz, $J_{12-18} = 1.5$ Hz); 4.08 (4-$\underline{H}$, d, $J_{4-5} = 9.5$ Hz); 2.12 (18-$C\underline{H}_3$, d, $J_{18-12} = 1.5$ Hz); 1.70 (acetate): 1.62 (20-$C\underline{H}_3$, s); 1.30* and 0.77* (11 and 9-$\underline{H}$ respectively, $J_{9-11} \simeq 6$ Hz, other couplings $J_{11-12} = 10$ Hz, $J_{9-8a,8b} \simeq 9$ and 3 Hz); 1.07 and 0.93 (16 and 17-$C\underline{H}_3$, s).

Photolysis of diterpene D (**17**)

Diterpene D (**17**, 50 mg, homogeneous by NMR and TLC) was dissolved in benzene (10 ml) and irradiated at 300 nm. The photolysis was arrested at approximately 70% conversion of the starting material (TLC, NMR) since prolonged periods resulted in marked degradation of the mixture. Attempts to isolate the photoisomer (**20**) by chromatographic methods failed. The mixture was treated with acetic anhydride in pyridine in an attempt to isolate the compounds through their acetates, but resulted in an intractable mixture (TLC). The structure of the *photoisomer* (**20**) was assigned on the basis of the appearance in the NMR spectrum of the following signals: ($CDCl_3$, 60 MHz) δ 5.53 (br.d, $J = 10$ Hz); 5.12 (br.d, $J = 9$ Hz); 4.30 (br.s, $w/2 = 8$ Hz); 3.80 (d, $J = 10$ Hz); 1.97 and 1.53 (s). These were attributed to the C-5, 12, 7, 4, 18 and 20 protons respectively by analogy with the photomonoacetate (**18**).

Photolysis of diterpene B (14)

Diterpene B (14, 100 mg) in THF (10 ml) was irradiated at 300 nm. The progress of the reaction was followed by TLC and the irradiation terminated after approximately 30% conversion (2.5 hr) of the starting material. The solvent was evaporated and the product separated from the starting material by multiple preparative TLC. The identity of the latter compound was confirmed by NMR and TLC comparisons with an authentic sample. The *photoisomerised product* (21) was obtained as a foam (30 mg), $[\alpha]_D = +356°$ (*c*, 0.85, EtOH). IR ($\nu_{max}^{CHCl_3}$ cm^{-1}): 3600 (m) and 3400 (br, hydroxyl); 1720 (s) and 1700 (s, carbonyl). UV (λ_{max} nm): 275 (ϵ, 5820). MS: Calc. for $C_{20}H_{26}O_4$: 330.183. Found: 330.183. The fragmentation pattern was identical to that quoted for diterpene B (14).[3] NMR ($CDCl_3$, 90 MHz): δ 7.32 (1-$\underline{H}$, q, $J_{1-19} = 1.5$ Hz); 5.70 (5-$\underline{H}$, br.d, $J_{5-4} = 9.5$ Hz, $J_{5-20} < 1$ Hz); 5.06 (12-$\underline{H}$, d of q, $J_{12-11} = 10$ Hz, $J_{12-18} = 1.5$ Hz); 4.32 (7-$\underline{H}$, br.s, $w/2 = 9$ Hz); 3.69 (4-$\underline{H}$, d, $J_{4-5} = 9.5$ Hz); 1.98 (18-$C\underline{H}_3$, d, $J_{18-12} = 1.5$ Hz); 1.86 (19-CH_3, d, $J_{19-1} = 1.5$ Hz); 1.57 20-$C\underline{H}_3$, br.s, $J_{20-5} < 1$ Hz); 1.12 and 1.00 (16 and 17-$C\underline{H}_3$, s); 0.99* (11-$\underline{H}$, m); 0.61* (9-$\underline{H}$, m). The photolysis was repeated using 50% MeOH in benzene as solvent, and a Philips HPK 125 high pressure mercury lamp as the radiation source.[5] The reaction conditions resulted in a mixture of starting material and the photoisomerised product (21) shown by NMR and TLC comparisons to be analogous to that described above. Prolonged periods of irradiation under either set of reaction conditions resulted in severe degradation of the mixture (TLC, NMR).

Photolysis of diterpene B monoacetate (**15**)

Diterpene B monoacetate (**15**, 85 mg) was dissolved in benzene (10 ml) and irradiated at 300 nm for 5.5 hr. The solvent was evaporated and the *photoisomer* (**22**) separated from the starting material by preparative TLC as an oil (25 mg) which crystallised from n-pentane/ether as needles, m.p. 189–190°, $[\alpha]_D = +114°$ (*c*, 0.55, EtOH). (Found: C, 71.1, H, 7.7. $C_{22}H_{28}O_5$ requires: C, 70.9, H, 7.6%). IR ($\nu_{max}^{CS_2}$ cm^{-1}): 3380 (br, hydroxyl); 1740 (s, acetate), 1730 (s) and 1700 (s, CO). UV (λ_{max} nm): 278 (ϵ, 2310). MS: As quoted for diterpene B monoacetate (**15**).[3] NMR ($CDCl_3$, 90 MHz): δ 7.21 (1-$\underline{H}$, br.s, $w/2 \simeq 4$ Hz); 5.66 (5-$\underline{H}$, br.d, $J_{5\text{-}4} = 9$ Hz, $J_{5\text{-}20} < 1$ Hz); 5.36 (7-$\underline{H}$, m, $w/2 = 10$ Hz); 5.16 (12-$\underline{H}$, d of q, $J_{12\text{-}11} = 10$ Hz, $J_{12\text{-}18} = 1.5$ Hz); 3.70 (4-$\underline{H}$, d, $J_{4\text{-}5} = 9$ Hz); 2.13 (acetate); 2.02 (18-C$\underline{H}_3$, d, $J_{18\text{-}12} = 1.5$ Hz); 1.86 (19-C$\underline{H}_3$, d, $J_{19\text{-}1} = 1.5$ Hz); 1.58 (20-C$\underline{H}_3$, br.s, $J_{20\text{-}5} < 1$ Hz); 1.13 and 1.01 (16 and 17-C$\underline{H}_3$, s).

Acetylation of photoditerpene B (**21**)

Acetylation of photoditerpene B (**21**, 15 mg) in the normal manner using Ac_2O and pyridine resulted in an oil from which the monoacetate (10 mg) was isolated by preparative TLC. Comparison with an authentic sample of **22** by TLC, NMR, IR and MS showed the two to be identical.

Photolysis of diterpene B diacetate (**16**)

Diterpene B diacetate (**16**, 50 mg) was dissolved in $CHCl_3$ (5 ml) and irradiated at 300 nm for 3 hr. The *photoproduct* (**23**) was isolated by preparative TLC as an oil (8 mg) MS: Calc. for $C_{24}H_{30}O_6$: 414.204. Found: 414.200. Fragmentation pattern: as quoted for **16**.[3] NMR: ($CDCl_3$, 60 MHz) δ 7.53 (1-$\underline{H}$, br.s, $w/2 = 5$ Hz); 5.63 (5-$\underline{H}$, br.d, $J_{5\text{-}4} = 8$ Hz); 5.37 (7-$\underline{H}$, br.s, $w/2 = 8$ Hz); 5.03 (12-$\underline{H}$, br.d, $J_{12\text{-}11} = 11$ Hz); 3.41 (4-$\underline{H}$, d, $J_{4\text{-}5} = 8$ Hz); 2.11 (acetates); 1.90 (18 and 19-C$\underline{H}_3$, br.s); 1.61 (20-C$\underline{H}_3$, br.s); 1.12 and 0.97 (16 and 17-C$\underline{H}_3$).

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