

Nuclear magnetic resonance and UV spectral probe of photochemical steady states of vitamin K₁

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Abstract

Steady state photochemistry of vitamin K₁ has been examined using a ¹H nuclear magnetic resonance probe on solutions in CDCl₃, acetone-*d*₆, benzene-*d*₆ and acetonitrile-*d*₃, and a UV probe on solutions in acetone, pentane and ethanol. A rationale for formation of the major photoproduct, *i.e.* chromenol (1), based on electron transfer from the side-chain olefinic bond to the naphthoquinone moiety in vitamin K₁, has been suggested. The new mechanistic scheme implicates, *inter alia*, quinone methide (6) as the precursor of 1. Attempted separation of photolysis mixture using flash chromatography has led to isolation of 9 and an oxygen adduct 10 of chromenol (1). The photoconversion of the vitamin is accelerated with catalytic amounts of triethylamine.

1. Introduction

Photochemical studies on vitamin K₁ have assumed importance on account of its unique biological characteristics [1-5] and the fact that the vitamin possesses a highly photolabile chromophore [6-8]. The literature records sporadic investigations of UV-light-induced transformations in vitamin K₁ and its analogues such as plastoquinone-1 and menaquinone-1. However, most of the reported information generally has come from application of lasers transient techniques [9-14]. Studies on steady state irradiation of vitamin K₁ have been beset with numerous difficulties and the nature of the primary photoproducts formed, particularly under anaerobic irradiation conditions, at best remains unsettled. Nevertheless, based on available reports, the choice of photolysis products is narrowed down to structures 1-6 (Fig. 1) [9, 11, 15]; for the *o*-quinone methides, proposed as important intermediates in vitamin K₁ photochemistry and, with reported half-lifetimes of up to 30 min [9, 11], three structures (4-6) have been suggested.

We describe, in this paper, the photochemical steady states of vitamin K₁ using nuclear magnetic resonance (NMR) and UV spectroscopy as probes. Also, incorporated herein are the results of attempted isolation of various products of anaerobic irradiation of vitamin K₁, and catalytic influence of triethylamine on its photoconversion.

2. Experimental procedure

Vitamin K₁ (50 mg; Sigma) was dissolved in dry CDCl₃, benzene-*d*₆, acetone-*d*₆ or CD₃CN (1.5 ml; Aldrich) in an NMR tube, the solution was protected from light and purged with dry oxygen-free N₂ for 3 min and then the tube was sealed. Its ¹H NMR spectrum was recorded (JEOL-JNM-FX-100 NMR spectrometer). It was then exposed to UV light by placing the sample tube at a distance of 10 cm from the source (125 W medium pressure Hg arc placed inside a water-cooled jacket of Pyrex glass) for 10 min and its ¹H NMR spectrum was recorded again. The above operations were repeated after intervals of 10 min and continued as long as the sample gave a clear NMR spectrum (total time of irradiation varied with different solvents). ¹³C NMR spectra were obtained after final irradiation in each solvent. UV spectral measurements were carried out, at 10 min intervals, on solutions (10⁻⁴-10⁻⁵ M) of vitamin K₁ in spectroscopic grade *n*-pentane, ethanol and ace-

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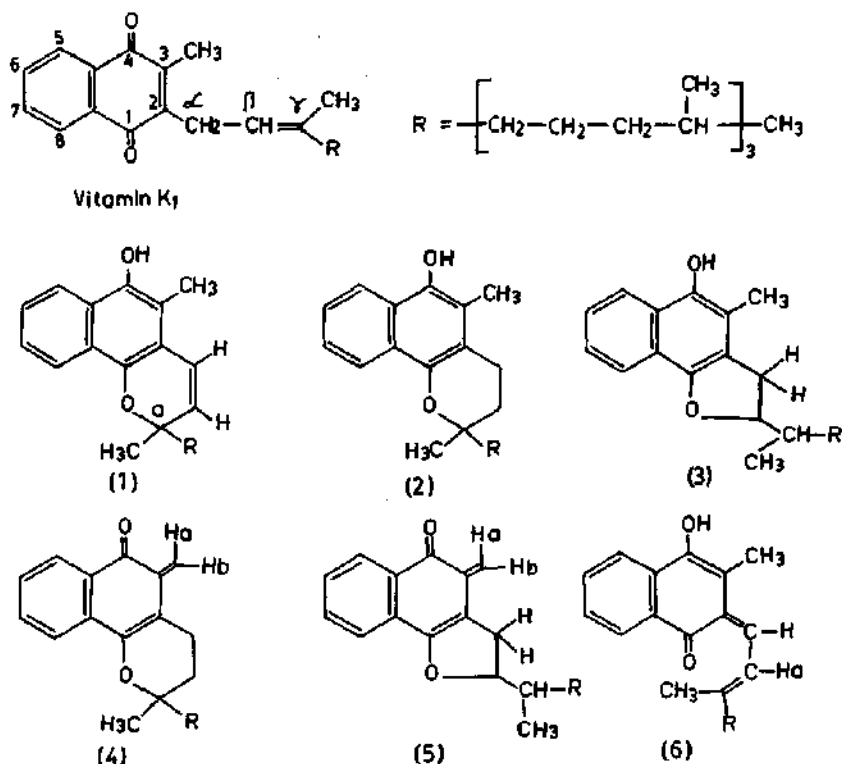


Fig. 1. Structures 1-6.

tone solvents which were irradiated under above conditions in a cell of 1 cm width of a CE-588 CECIL UV-visible spectrophotometer. For isolation of photoproducts, a solution of vitamin K₁ (500 mg) in *n*-pentane (350 ml) was irradiated (under N₂) for ½ h in a Pyrex reactor using a 125 W medium pressure Hg arc. The solvent was then removed under reduced pressure and the yellow oily residue was flash chromatographed (silica gel 60; E. Merck; 230-400 mesh; hexane). As the products were unstable, they were rechromatographed, with unavoidable exposure to air. Irradiations of the vitamin under catalytic influence of triethylamine were carried out as above in NMR tubes, using chloroform-*d* and acetone-*d*₆ solvents, for collateral studies with direct irradiations.

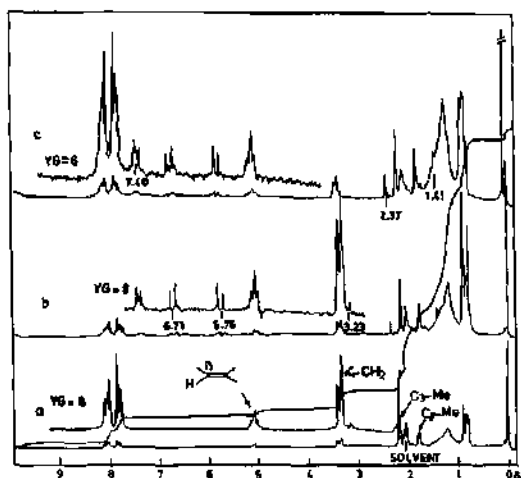
3. Results

3.1. NMR spectral studies

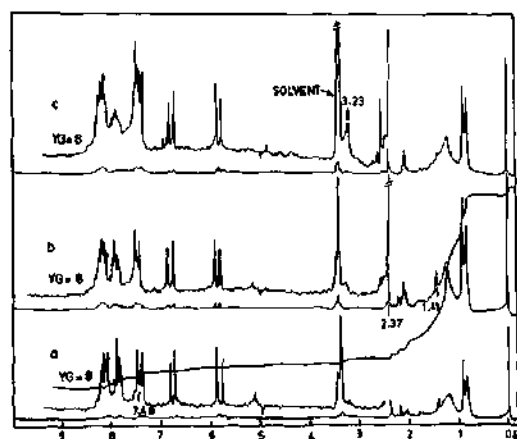
The ¹H NMR spectrum of a solution of vitamin K₁ in CDCl₃, taken after irradiation for 10 min, displays two doublets in the olefinic region, at δ=6.62 and 5.67 ppm (*J*=10.0 Hz), coupled to each other (decoupling experiments). The intensity

of the doublets increases for a total irradiation time of up to 40 min, remains almost constant for the next 20 min and then decreases on further irradiation; the signals are lost in the noise after a total irradiation time of 100 min. The aromatic region reveals a new multiplet at δ=7.56-7.32 ppm with concomitant decrease in intensity of the original aromatic proton resonances (δ=7.72-7.60 ppm). The appearance of singlets at δ=2.45, 2.36 and 1.36 ppm (methyl groups in a changed environment) is accompanied by gradual disappearance of signals due to side-chain olefinic H (δ=5.03 ppm) and α-CH₂ group (δ=3.37 ppm). In the short-irradiation-time spectra, a weak doublet at δ=3.52 ppm, a multiplet at δ=4.75 ppm and weak signals in the olefinic region, which did not develop further with increase in irradiation time, are observed.

The ¹H NMR spectrum of an irradiated solution of the vitamin in acetone-*d*₆ (Fig. 2) shows two new doublets at δ=6.71 and 5.76 ppm (*J*=10.0 Hz), methyl singlets at δ=2.37 and 1.41 ppm, a multiplet (due to aromatic protons) at δ=7.40 ppm, and a weak multiplet in the olefinic region at δ=6.64 ppm, which is soon obliterated with further increase in irradiation time. Other im-



(a)



(b)

Fig. 2. (a) ^1H NMR spectra of vitamin K_1 in acetone- d_6 : curve a, before irradiation; curve b, after irradiation for 10 min; curve c, after irradiation for 30 min. (b) ^1H NMR spectra of vitamin K_1 in acetone- d_6 : curve a, after irradiation for 60 min; curve b, after irradiation for 80 min; curve c, after irradiation for 100 min.

portant changes include the appearance of a broad singlet around $\delta=3.23$ ppm and weak resonances at $\delta=6.6\text{--}6.8$ ppm. The overall reaction is much smoother in this solvent, and disappearance of signals due to side-chain olefinic H ($\delta=5.10$ ppm) and $\alpha\text{-CH}_2$ ($\delta=3.36$ ppm), C(3)-methyl ($\delta=2.17$ ppm), $\text{C}\gamma$ -methyl ($\delta=1.78$ ppm) and aromatic H atoms at $\delta=7.96\text{--}7.80$ ppm could be monitored. However, on irradiation, the aromatic proton multiplet at $\delta=8.29\text{--}8.00$ ppm (in the spectrum of the vitamin) did not show any variation in intensity, although the pattern became rather more complex.

In benzene- d_6 , the olefinic H doublets and the new multiplet (due to aromatic protons) appear

at $\delta=6.50$ and 5.50 ppm ($J=10.0$ Hz) and $\delta=7.40\text{--}7.00$ ppm respectively; the latter signal overlapped with the multiplet at $\delta=7.20\text{--}7.00$ ppm owing to C(6)-H and C(7)-H. Additional signals include a doublet at $\delta=4.50$ ppm ($J=8.0$ Hz), a multiplet at $\delta=6.08$ ppm, a doublet at $\delta=6.36$ ppm ($J=8.0$ Hz) and a singlet at $\delta=6.52$ ppm amidst the doublet at $\delta=6.50$ ppm. However, the spectrum (in C_6D_6) became complex after 60 min and could not be studied further after a total irradiation time of 90 min.

In CD_3CN , the reaction follows a less recognizable path. Initially, the ^1H NMR spectrum recorded the appearance of doublets, in the olefinic region, at $\delta=6.86$ and 5.71 ppm ($J=10.0$ Hz) and a new multiplet due to aromatic protons at $\delta=7.40\text{--}7.28$ ppm. However, after irradiation for 30 min, the above features are lost and new signals are observed (a multiplet around $\delta=3.65$ ppm and two triplets at $\delta=2.28$ and 2.45 ppm). Further irradiation of the sample results in a poorly resolved spectrum.

A good ^{13}C NMR spectrum was obtained only for solutions in acetone- d_6 . Important spectral features are as follows: signals in the regions $\delta=134\text{--}121$ (weak), $48\text{--}12$ and 108.25 ppm; no signals are observed in the region $\delta=108\text{--}50$ ppm.

3.2. UV absorption spectral investigations

Irradiation of vitamin K_1 in ethanol for 10 min leads to suppression of the original UV spectrum (Fig. 3) and the appearance of new bands at 230 and 259 nm and an inflection around 280 nm. Further irradiation for 10 min produces an overall decrease in band intensities, although the band at 280 nm decays rather rapidly. Continued irradiation leads to a steady state spectrum with bands at 230 and 280 nm, a shoulder at 290 nm and an inflection at 305 nm. Towards the long-wavelength side, the spectrum has a tail up to 330 nm.

A rather similar spectrum is obtained in n -pentane, although with slightly shifted band positions (Fig. 4). However, the photodecay of the substrates in n -pentane is relatively slow. In acetone, no new spectral features are observed (Fig. 5) except a band at 330 nm (after irradiation for 4 h) which may be the continuum of the 305–330 nm band observed in the ethanol and n -pentane solvents.

4. Discussion

In the ^1H NMR spectrum of the photolysate, the presence of two doublets at $\delta(\text{acetone-}d_6)=6.71$

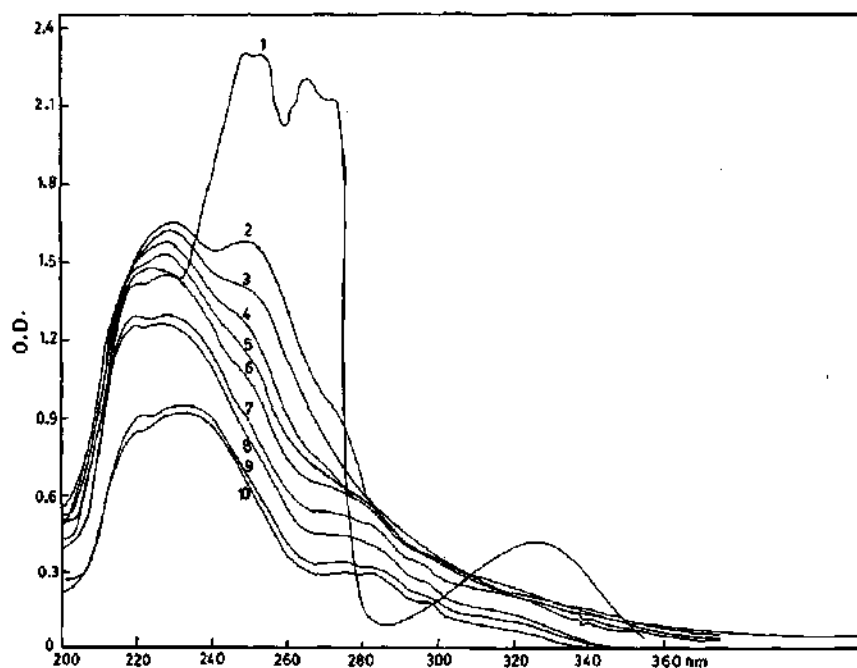


Fig. 3. UV spectra of vitamin K_1 in ethanol. (1) Original spectrum; (2)–(10) after the following irradiation times: (2) 10 min; (3) 20 min; (4) 30 min; (5) 40 min; (6) 50 min; (7) 60 min; (8) 90 min; (9) 120 min; (10) 150 min.

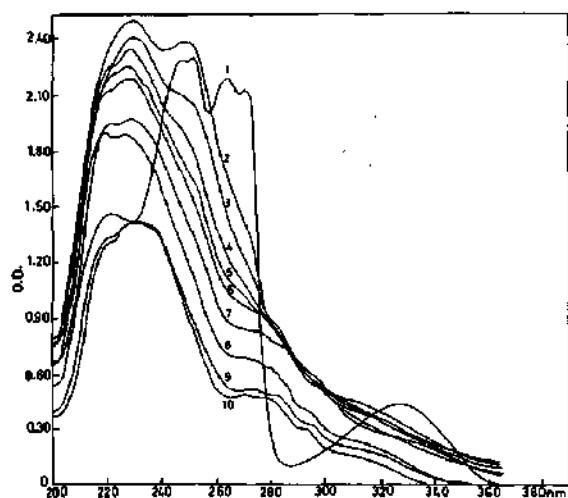


Fig. 4. UV spectra of vitamin K_1 in *n*-pentane. (1) Original spectrum; (2)–(10) after the following irradiation times: (2) 10 min; (3) 20 min; (4) 30 min; (5) 40 min; (6) 50 min; (7) 60 min; (8) 120 min; (9) 150 min; (10) 180 min.

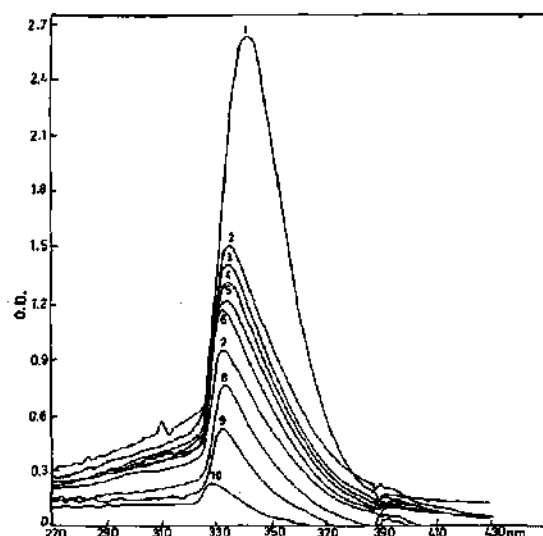
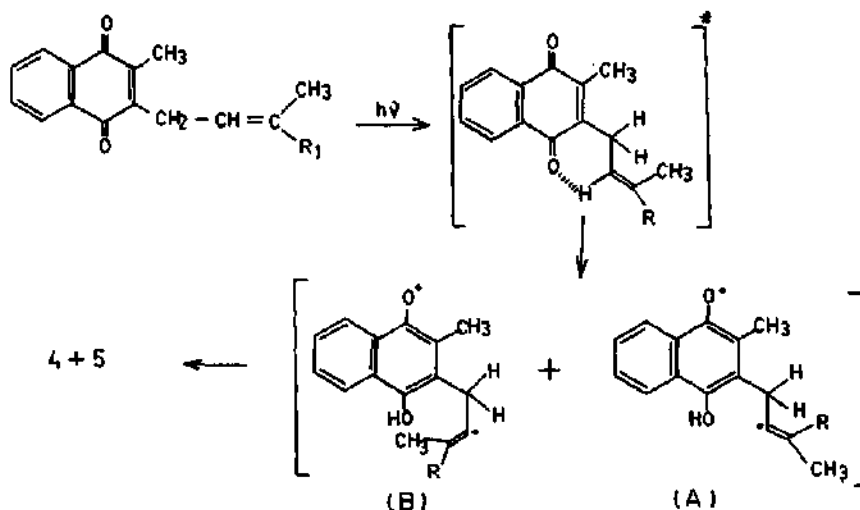


Fig. 5. UV spectra of vitamin K_1 in acetone. (1) Original spectrum; (2)–(10) after the following irradiation times: (2) 10 min; (3) 20 min; (4) 40 min; (5) 80 min; (6) 100 min; (7) 120 min; (8) 150 min; (9) 180 min; (10) 240 min.

and 5.76 ppm ($J=10.0$ Hz) alludes to olefinic moieties as in structures (1) (compare ref. 16) and (6) (Fig. 2). Although for the *o*-quinone methide structures 4 and 5 a chemical shift difference of around 1 ppm is anticipated for exomethylene protons H_a and H_b , the observed value of coupling

constant (10.0 Hz) is inconsistent with these structural formulations [17–19]. However, the structure 1 is supported by non-observance of any homoallylic couplings, as might be anticipated for H_a in struc-



Scheme 1.

ture 6. Other features of the ^1H NMR spectrum which support structure 1 are (a) the observance of a new aromatic proton multiplet at $\delta(\text{acetone-}d_6) = 7.40$ ppm (C(6)-H, C(7)-H) with concomitant disappearance of the original aromatic proton multiplet ($\delta(\text{acetone-}d_6) = 7.95\text{--}7.76$ ppm), signifying complete destruction of the naphthoquinone system in the above phototransformation [17, 20], and (b) the observed shift changes for methyl resonances; a change from the naphthoquinone system to chromenol (1) is anticipated to bring about a downfield shift of C(3)-methyl resonance and upfield shift of C γ -methyl resonance, since the latter methyl group is no longer attached to an sp^2 carbon in chromenol (1). The non-observance of a ^{13}C NMR signal in the region $\delta = 200\text{--}50$ ppm (anticipated region for C_α in 1), is not considered to be a pointer against formulation 1¹, since even for methine carbon atoms observed in the aromatic-olefinic region the intensity was low. As such, the quaternary carbon (C_α in 1) may have remained indistinguishable from the spectral noise.

The chromenol structure 1 is corroborated by the UV spectrum which showed characteristic bands at 230 nm and in the region 280–330 nm [22–25].

No definite spectral conclusions regarding the minor reaction products formed by irradiation of vitamin K_1 in CDCl_3 and acetone- d_6 solvents can

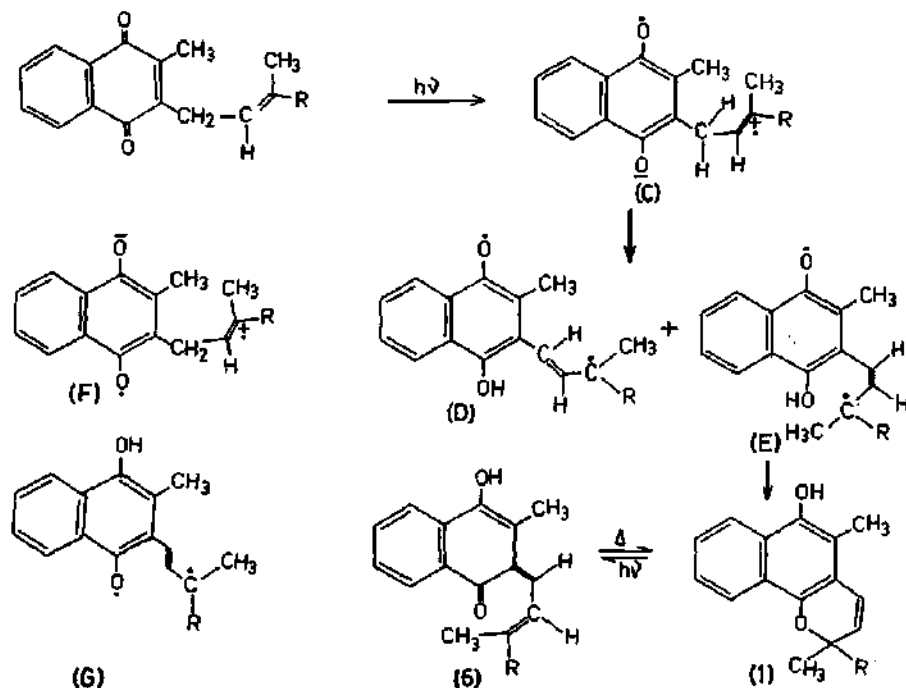
yet be made. However, in the low irradiation time ^1H NMR spectrum in benzene- d_6 , the presence of two additional doublets at $\delta = 4.50$ and 6.36 ppm ($J = 8.0$ Hz) may be attributed to chance observance of quinone methide (6). Again, in the ^1H NMR spectrum in CD_3CN , the presence of triplets at $\delta = 2.28$ and 2.45 ppm are in consonance with a structure such as 2.

5. Mechanistic considerations

An earlier mechanistic rationale for phototransformation of vitamin K_1 was postulated by Serdobov [11] and is based on transient techniques involving electron spin resonance (ESR) studies. This implicates a diradical pair (Scheme 1, A and B) deemed to be formed through side-chain olefinic H abstraction by the quinone moiety. The above rationale led to products formulated as 4 and 5 for which, however, no conclusive proof was adduced.

However, we take into account the fact that photochemically excited quinones are strong oxidizing agents [26, 27] and recent understanding of the photochemical electron transfer processes [28–33] and, in particular, studies involving covalently linked quinones and porphyrins, especially naphthoquinones [33–39], and the first step in the above phototransformation is now suggested to be an electron transfer process. This will also explain the overwhelmingly important role of the side-chain double bond in this phototransformation; the double bond may in fact be implicated in the

¹The reported highly reactive nature of *o*-quinone methides [21] further led to elimination of structure 6. However, 1 and 6 are interconvertible under the present conditions (*vide infra*).



Scheme 2.

hopping of electrons [40] in electron transport processes involving vitamin K_1 [2, 5, 6, 41]. This view is in agreement with the observation of the formation (with a low yield) of chromenol-type products in CD_3CN solvent. This is attributed to the well-known tendency of acetonitrile to solvate the radical ions, thereby increasing their lifetime, and leading eventually to dissociative chemistry of radical ions [28–30, 34–36, 42]. Again, strong contact ion pairing, which should occur in acetone [34–36] explains the excessive formation of **1** in this solvent. In the projected Scheme 2, the radical ion C appears to be short lived and this step is followed by hydrogen abstraction from the α - CH_2 group to yield *cis* biradicals D and *trans* biradicals E. The intervention of radical ions of type F and biradical species of type G are precluded by the observed distance of 5.2 Å between odd electrons, based on the ESR studies reported by Lazarev *et al.* [10].

Again, the involvement of the biradicals D and E explains the formation of vitamin K_1 hydroxides and hydroperoxides under aerobic photolytic conditions [15, 43, 44]. These biradicals can collapse to *o*-quinone methide of type 6 with the same or different geometric arrangement around the side-chain double bond. The biradical E, as envisaged



Scheme 3.

in the projected Scheme 2, should directly lead to chromenol (1). Alternatively, **1** arises through cyclization under irradiation conditions. The literature records a few examples of facile thermal cyclization of structures of type 6 to (2H)-pyrans resembling chromenol (1) (see 7→8, Scheme 3) [45].

The projected route to chromenol (1) finds support in the present observation of high stability of **1** in acetone- d_6 ; acetone with its UV cut-off point at 330 nm should prevent the conversion of chromenol (1) back into 6.

It may be mentioned here that a comparison of results of irradiation experiments (carried out under identical conditions) on vitamin K_1 in NMR tubes in $CDCl_3$ and acetone- d_6 solvents, with and without the presence of a catalytic amount of triethylamine, revealed a faster photoconversion

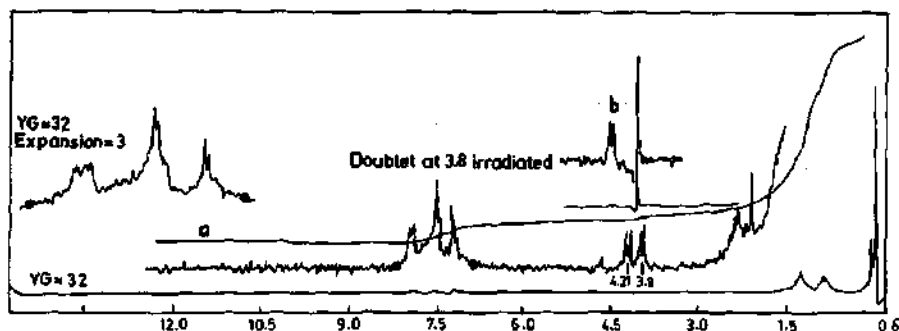
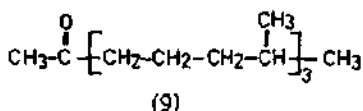


Fig. 6. ^1H NMR spectra of **10** in CDCl_3 : curve a, normal spectrum; curve b, homodecoupled spectrum.

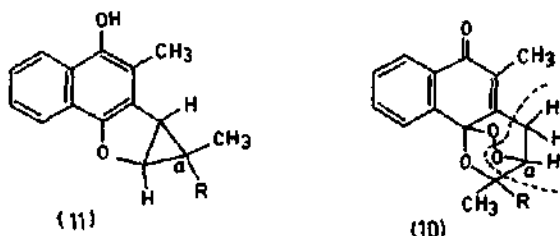
of the vitamin in the former case¹. For the formation of a charge transfer complex between triethylamine (TEA) and a triplet ketone, see ref. 46.

6. Attempted isolation of products

Flash chromatography of the photolysate led to isolation of three main products. The first major component (a thick oil), $\nu_{\text{max}}(\text{C}=\text{O}) = 1730 \text{ cm}^{-1}$, displayed in its ^1H NMR spectrum a triplet at $\delta = 2.42 \text{ ppm}$ (2H), a singlet at $\delta = 2.14 \text{ ppm}$ (3H), a broad multiplet at $\delta = 1.4 \text{ ppm}$ overlapping with another broad multiplet centred at $\delta = 1.21 \text{ ppm}$ and a broad doublet at $\delta = 0.85 \text{ ppm}$ (no signals were located in the lower field region of the spectrum). Considering its origin and the above spectral data, structure **9** (Scheme 4) is suggested for this compound.



Scheme 4.



Scheme 5.

¹In the present work, a similar acceleration of photoconversion of menaquinone-1 leading to the major compound **1** ($\text{R} = \text{CH}_3$), in CDCl_3 and acetone- d_6 solvents in NMR tubes using a catalytic amount of triethylamine (TEA), was observed.

The ^1H NMR spectrum of the second component (a thick yellow oil) displayed the following features: a double doublet at $\delta = 8.00\text{--}7.85 \text{ ppm}$ (1H, $J = 2.2$ and 8.0 Hz), a double doublet at $\delta = 7.61\text{--}7.14 \text{ ppm}$ (2H), a multiplet at $\delta = 7.32\text{--}7.15 \text{ ppm}$ (1H), doublets at $\delta = 4.21$ and 3.98 ppm ($J = 5.62$ and 5.47 Hz respectively; these were found, by double resonance experiments, to be not coupled to each other), and $\delta = 2.50\text{--}0.60 \text{ ppm}$ (a multiplet with a singlet at $\delta = 2.15 \text{ ppm}$ and a broad doublet at $\delta = 0.85 \text{ ppm}$) (Fig. 6). In its ^{13}C NMR spectrum, this showed multiple signals at $\delta = 133.0\text{--}125.2 \text{ ppm}$, two signals in the C-O region at $\delta = 68.2$ and 66.3 ppm , and other signals in the region $\delta = 47.4\text{--}11.0 \text{ ppm}$. Its IR spectrum displayed a broad band at 3400 cm^{-1} (O-H) and intense bands at 1680 and 1640 cm^{-1} . The above spectral data allude to **10** and **11** with two isomeric arrangements at C₄ atoms (Scheme 5). However, its mass spectrum showed the highest peak at $m/z = 439$ (corresponding to loss of 43 mass units from **10** as indicated, leading to formulation of **10** as an oxygen adduct of chromenol (**1**)).

The third (minor) component showed, in its ^1H NMR spectrum, multiplets at $\delta = 7.44\text{--}7.20$ and $2.70\text{--}0.8 \text{ ppm}$. The nature of the multiplets in the aromatic region pointed towards a naphthoquinonoid structure. However, its fuller structural details could not be examined.

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