

COMPETITION BETWEEN SINGLET STATE PHOTOREDUCTION AND TRIPLET STATE PHOTODIMERIZATION OF DIMETHYL 3-DEHYDROGIBBERELLENATE

H. K. AL-EKABI and G. A. W. DERWISH*

Department of Chemistry, College of Science, University of Baghdad, Adamiya, Baghdad, Iraq

and

G. ADAM and K. SCHREIBER

Institute of Plant Biochemistry of the Academy of Sciences of GDR 402 Halle (Saale), German Democratic Republic

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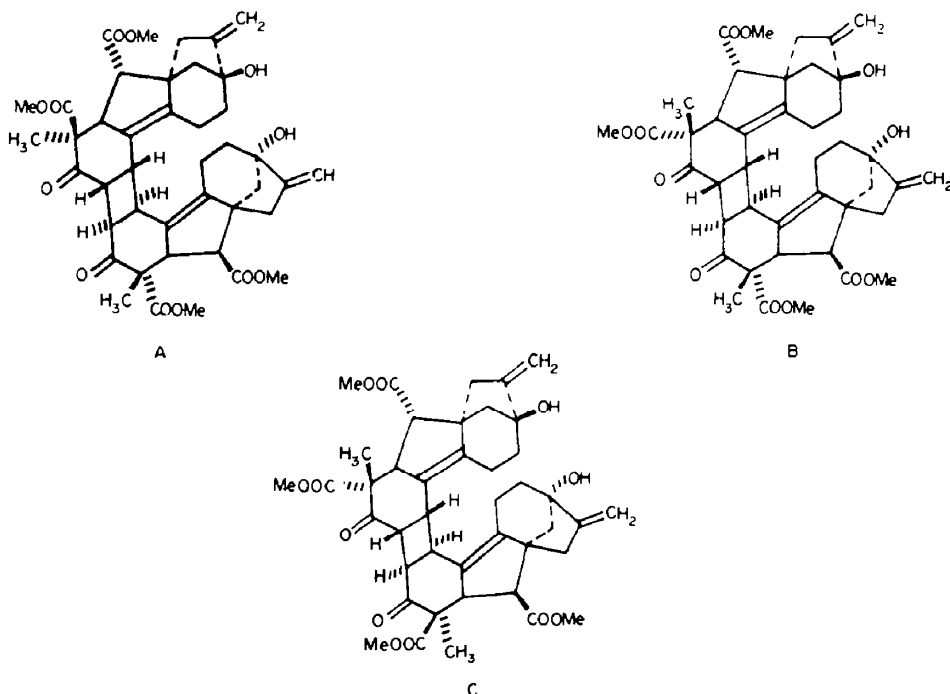
Abstract—Photolysis of dilute solutions (10^{-4} M) of dimethyl 3-dehydrogibberellenate **1**, in MeOH, EtOH, *i*-PrOH, *t*-BuOH and 2, 2, 2-trifluoroethanol, showed that while the last two solutions underwent photodimerization reactions only; the other solutions gave photoreduction products **2** and **3**, besides some photodimerization product. It is further shown that while photodimerization proceeded through triplet excited state, photo-reduction, surprisingly, proceeded only through singlet excited state.

It has been reported that the alkanone (n, π^*) singlet state (S_1) is at least two or three orders of magnitude less reactive than the (n, π^*) triplet state (T_1) toward intermolecular hydrogen abstraction.¹⁻³ A recent theoretical model of photochemical reactions, in fact, suggests that intermolecular hydrogen abstraction should be much less efficient from alkanone S_1 states than alkanone T_1 states.⁴ However, Turro *et al.* reported recently that alkanone S_1 and T_1 states have comparable reactivity (but not necessarily efficiency) toward intermolecular hydrogen abstraction.⁵ We would like to present evidence from stu-

dies of photolysis of dilute solutions of dimethyl 3-dehydrogibberellenate **1** in MeOH, EtOH, *i*-PrOH, *t*-BuOH and 2, 2, 2-trifluoroethanol that intermolecular photoreduction proceeded through singlet state only.

RESULT AND DISCUSSION

It was observed that photolysis of relatively concentrated solution (2.7×10^{-2} M) of dimethyl 3-dehydrogibberellenate **1** with $\lambda > 300$ nm for 3 hr in *t*-BuOH gave three photodimers designated as A, B and C (Scheme 1) in 65, 12 and 7% yields, respectively.⁶



Scheme 1. Photodimers A, B and C.

This communication deals with the photolysis of dilute solutions (10^{-4} M) of 1 in MeOH, EtOH, *i*-PrOH, *t*-BuOH and 2, 2, 2-trifluoroethanol, as solvents, at 313 nm in 10 nm quartz cell. The reactions were followed by UV and tlc techniques. Tlc data and UV measurements showed that while *t*-BuOH and 2, 2, 2-trifluoroethanol gave the previously reported photodimer A together with trace amounts of photodimers B and C; solutions in MeOH, EtOH and *i*-PrOH gave, besides the photodimer A, a new photoproduct F.

The reaction in MeOH, EtOH and *i*-PrOH were followed, as mentioned above, by the change in their UV spectra. Thus, during the course of photolysis, the initial absorption max at 312 nm disappeared and a new max at 254 nm appeared with the concomitant appearance of two isosbestic points at 242 and 269 nm in case of MeOH solution; at 238 and 271 nm in case of EtOH solution and at 238 and 272 nm in case of *i*-PrOH solution (Fig. 1).

The disappearance of the initial absorption max at 312 nm in *t*-BuOH and at 317 nm in 2, 2, 2-trifluoroethanol solutions were not accompanied with the appearance of new band at 254 nm or any other region within the range covered in this work.

The new photoproduct F was identified on the basis of comparison of its UV spectrum with that of NaBH_4 -reduction products of 1 in MeOH† and with the known UV spectrum of dimethyl gibberellenate,⁷ and found to be a photoreduction product obtained from intermolecular photoreduction of the carbonyl group of 1. The UV spectra of the three samples indicated the presence of highly intense band centred at 254 nm (Fig. 2). However, while for the known dimethyl gib-

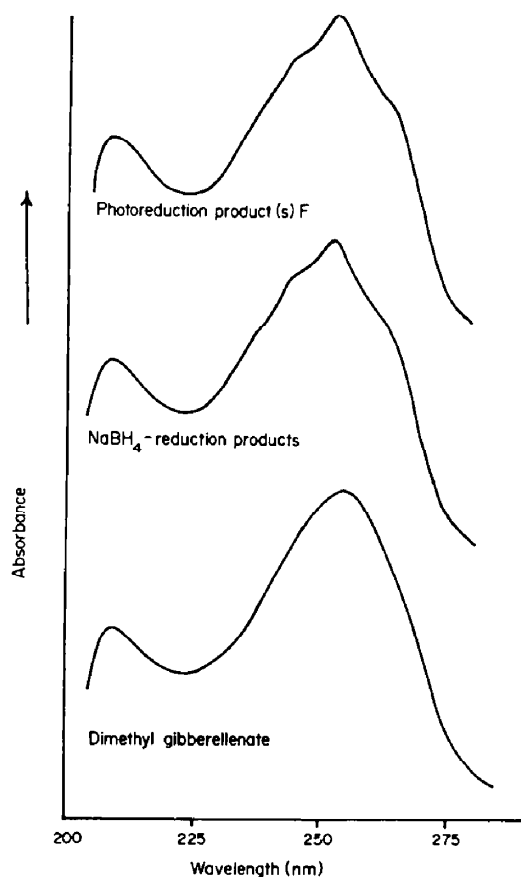


Fig. 2. UV-spectra of dimethyl gibberellenate, NaBH_4 -reduction products and photoreduction product(s).

†The starting material was reduced to the corresponding 3-hydroxy derivatives using NaBH_4 in methanol solution at room temperature for short reaction time as checked by tlc.

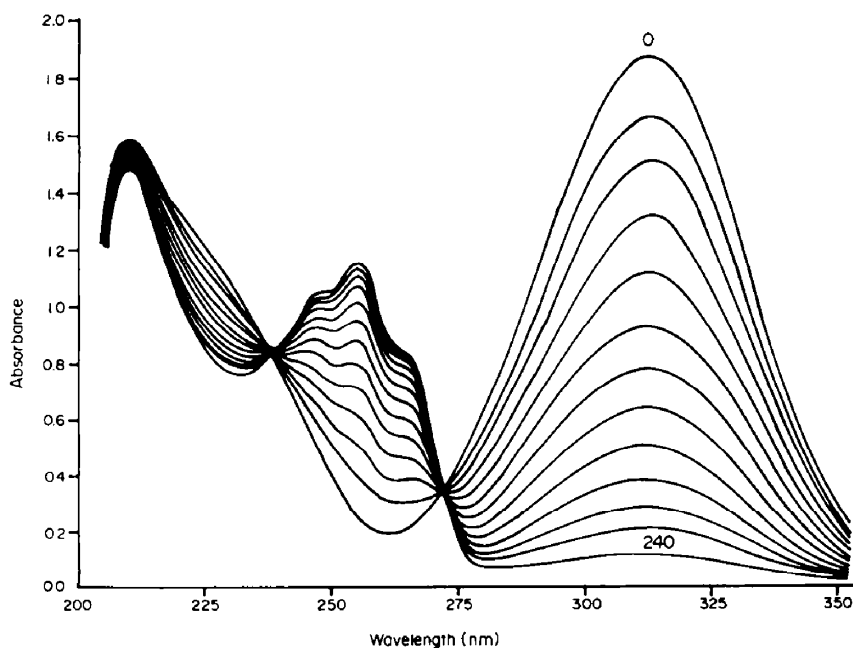


Fig. 1. UV-spectra of irradiated dienone (10^{-4} M solution in isopropanol freshly prepared, 313 nm, exposure times 0, 20, 40, ... min.).

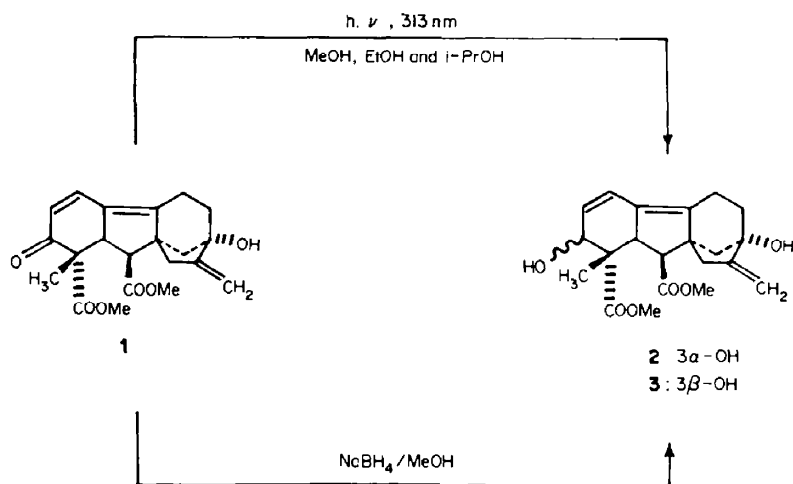
berellenate, the band centred at 254 nm was quite smooth, the photoreduction product **F** and NaBH_4 -reduction products showed the presence of two side shoulder at 246 and 264 nm, characteristic of many heteroannular dienes.⁶ Therefore, it is reasonable to conclude that the compounds in the three cases have the same structure but different configurations of the 3-OH group resulting in the presence or absence of the two side shoulders.

Although, the comparison of the NMR spectrum of NaBH_4 -reduction products mixture with that of the known dimethyl gibberellenate (3β -OH) as a reference, showed the presence of the expected two epimers (i.e. 3α -OH and 3β -OH) with 3:2 ratio, respectively, however, checking by tlc in different solvents mixtures (7:3 benzene-AcOH or 5:4:1 CHCl_3 , EtOAc-AcOH) showed that dimethyl gibberellenate (3β -OH), the photoreduction

product(s) and the NaBH_4 -reduction products have the same position on tlc plate in both solvent mixtures.

Since the UV spectrum of the known dimethyl gibberellenate (3β -OH) has quite smooth band centred at 254 nm and that of NaBH_4 -reduction products and the photoreduction product(s) have, in addition to this principal band, an extra two side shoulders, therefore, it seemed likely that the photoreduction product was the 3α -epimer of dimethyl gibberellenate or at least a mixture of 3α - and 3β -OH dimethyl gibberellenate (i.e. **2** and **3**; Scheme 2), in which the 3α -OH epimer was the predominant form.

Because, in dilute solutions the photoreactions were followed by UV measurements, the choice of suitable quencher was limited to oxygen, which has no absorption in the absorption regions of the initial and final species. Also, butadiene as quencher was excluded, because the



Scheme 2. Photoreduction and NaBH_4 -reduction of dimethyl 3-dehydro-gibberellenate 1.

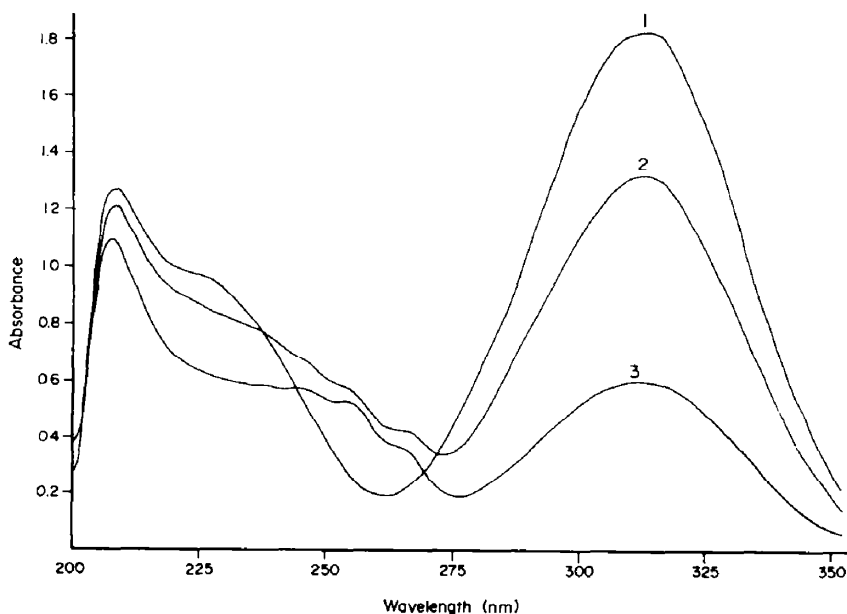


Fig. 3. UV-spectra of: 1. Freshly prepared dienone in isopropanol. 2. As in 1 but after 1 hour irradiation at 313 nm. 3. Deaerated solution irradiated for 1 hour at 313 nm.

excited dienone was found to add easily to it upon irradiation.†

Solution of **1** in *i*-PrOH (10^{-4} M) was treated for 30 min with nitrogen while another was used as a freshly prepared solution. The two samples were irradiated simultaneously for 1 hr at 313 nm. The results showed that the rate of disappearance of dienone in partially deoxygenated solution was faster than that of freshly prepared solution (Fig. 3). Similar results were also obtained in case of MeOH and EtOH. In addition, informative results were obtained from irradiation of **1** in MeOH, EtOH and *i*-PrOH under different conditions as presented in the Table.

Photoreduction yields were calculated on the assumption that the known dimethyl gibberellenate (3β -OH) and its 3α -OH epimer have the same extinction coefficient at 254 nm ($\epsilon = 22500$). Corrections for the relatively weak absorption at 254 nm of the dienone ($\epsilon = 1865$) and its dimer A ($\epsilon = 2250$) were neglected because of their opposing effects on the calculation.

The data presented in Table 1 (where yields are taken as an indication of the rates of the reactions) showed clearly that the yields of the photoreduction product obtained in case of irradiation in the presence of oxygen were about twice the yields obtained in case of irradiation in the absence of oxygen. However, the amounts of the reacted dienone reduced to less than half of that in the absence of oxygen. On the other hand, while the reacted dienone in partially deoxygenated solutions was much more than that in non-deoxygenated solution, the

photoreduction product behaved differently. Such behaviour indicated the competition between photodimerization and photoreduction reactions resulting from different excited states. The results showed that while photoreduction proceeded through singlet excited state, photodimerization proceeded through triplet excited state. That photoreduction proceeded through the singlet excited state is a very rare case since the singlet excited state is too short-lived to undergo efficiently intermolecular reaction and thus photoreduction usually proceeds through the triplet excited state.⁹

Hydrogen photoabstraction reactions are generally of two types, i.e. charge-transfer and radical-like abstraction.¹⁰ In the first type the rates are strongly dependent on the ionization energy of the substrate, whereas in the second type the rates are a function of the strength of the weakest C-H bond of the substrate.¹¹ Thus, the order of reactivity for charge-transfer can be predicted from the ionization potential of the alcohol, i.e. *t*-BuOH > *i*-PrOH > EtOH > MeOH, whereas the order of reactivity for radical-like abstraction can be predicted from the strength of the weakest C-H bond of the alcohols, i.e., *i*-PrOH > EtOH > MeOH > *t*-BuOH.^{11,12} In the case when a mixed mechanism is thought to be operative¹³, the usual sequence was found to be *i*-PrOH > EtOH > *t*-BuOH > MeOH.⁵

The results obtained in this work showed clearly that yields of photoreduction product(s) increased as the strength of the weakest C-H bond in alcohol decreased. Thus, the reactivity increased in going from MeOH (primary α -C-H) to EtOH (secondary α -C-H) to *i*-PrOH (tertiary α -C-H) and no photoreduction product was observed in *t*-BuOH. Therefore, these results indicate that the reaction is of the radical-like abstraction type, otherwise photoreduction product might be obtained in *t*-BuOH solvent.

The data presented in the table are perhaps best dis-

†The addition of **1** to dienes will be detailed in a forthcoming communication.

Table 1. Solvent dependence of photoreduction product yields in photolysis of dimethyl 3-dehydrogibberellenate^(a)

Solvent	Photoreduction yield ^(b) , %	Percent of reacted dienone ^(c) , %
Methanol ^(d)	16	36
Methanol ^(e)	30	21
Ethanol ^(d)	17	67
Ethanol ^(e)	45	29
Ethanol ^(f)	48	26
<i>i</i> -Propanol ^(d)	20	67
<i>i</i> -Propanol ^(e)	50	28

(a) 0.0001 M, 313 light.

(b) Relative to amount of dienone reacted as determined by UV for one hour irradiation.

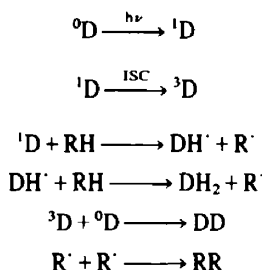
(c) Relative to amount of dienone used initially.

(d) Partially deoxygenated solution by bubbling of N_2 for one hour before irradiation.

(e) Freshly prepared (not treated with nitrogen).

(f) Saturated solution with O_2 by bubbling of O_2 for one hour before irradiation.

cussed in terms of the processes shown below



The initially generated dienone excited singlet (${}^1\text{D}$) undergoes an intersystem crossing (ISC) to the excited triplet (${}^3\text{D}$) or in the presence of reactive solvent (hydrogen donating solvent, RH), undergoes an intermolecular reaction given the photoreduction product (DH_2). The excited triplet (${}^3\text{D}$) may interact with ground state dienone (${}^0\text{D}$) to form the photodimer (DD). Recombination of the radicals (R^\cdot) gives (RR).

It was expected that since *t*-BuOH has no α -H atom, and because of the difficulties of the hydrogen abstraction from the much stronger OH bond¹⁰, therefore photodimerization rather than photoreduction would be the preferred mode in this solvent.

Although, 2, 2, 2-trifluoroethanol has two α -H atoms, however, they are made unavailable for photoreduction due to their possible strong involvement in intermolecular and intramolecular H-bonding with the F atoms of the alcohol. This explain why photoreduction product was not observed and only photodimerization product was obtained in this solvent.

EXPERIMENTAL

Quantum yield photoreactor 2001 (Applied Photophysics Ltd.) was used. It was supplied with high pressure mercury lamp (250 W), quartz lens, quartz soln-filter cell and quartz cuvette.

For irradiation at 313 nm, aqueous soln of potassium chromate was used as filter.¹⁴ The soln is known to have a good transmission max at 313 nm¹⁴ where a group of strong mercury lines are located. The filter was prepared from potassium chromate (0.20 g) dissolved in one liter soln of 0.05 N NaOH in order to prevent the formation of dichromate which is known to have different adsorption spectrum. The UV spectrum of the chromate soln was measured in 10 mm quartz cell and found to give a

transmission max at 313 nm of about 60%. The temp. at the cuvette holder was found to remain in the range 25–30°.

UV Spectra were measured in 10 mm rectangular quartz cells using Unicam SP-800 (Pye Unicam) spectrophotometer.

A Varian Associates A-60 was used to record NMR spectra. The spectra were run in CD_2COCD_2 soln, HMDS as an internal standard.

MeOH, EtOH, *i*-PrOH and 2, 2, 2-trifluoroethanol solvents used for photolysis were of highest purity (Merck's, special for spectroscopy). They were used without further treatment. *t*-BuOH was also of high purity (Fluka's puriss) and was used without further treatment.

The reactions in all solvents were followed by UV and tlc technique. Thus, the disappearance of 1^{15} was followed by UV measurements and when the dienone was completely consumed, the soln of five identically irradiated samples were collected and concentrated by evaporating of solvent under reduced pressure and was checked by tlc.

Tlc silica gel G(Merck) were developed, unless otherwise stated, with benzene-AcOH 70:30 v/v. Detection was made under UV light, after the developed plate was sprayed with 85% H_2SO_4 and heated for 15 mins at 120°.

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