

# PHOTODIMERIZATION OF DIMETHYL 3-DEHYDROGIBBERELLENATE AND SUBSEQUENT PHOTOEPIMERIZATION AND CLEAVAGE REACTIONS

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 the GDR, 402 Halle (Saale), German Democratic Republic

(Received in UK 17 May 1980)

**Abstract**—Irradiation ( $\lambda > 300$  nm) of dimethyl 3-dehydrogibberellenate 1, as a heteroannular dienone, in *t*-BuOH ( $10^{-2}$  M) for 2 hr led to cyclobutane-type photodimer A in 85% yield. However, irradiation of 1 under the same conditions but for 3 hr gave not only photodimer A but also two other photodimers B and C which were found to be the products of photoepimerization reaction of A. The stereochemistry of A, B and C was fully elucidated on the basis of physico-chemical techniques. At lower concentration ( $10^{-4}$  M) of A in *t*-BuOH, irradiation with  $\lambda$  254 nm and  $\lambda$  313 nm resulted in  $\beta$ -cleavage to 1.

While photodimerization of  $\alpha,\beta$ -unsaturated ketones has been extensively investigated, little is known about photodimerization of  $\alpha,\beta,\gamma,\delta$ -unsaturated ketones which has been studied in steroidal systems only.<sup>1-3</sup> Rubin *et al.*<sup>2,3</sup> studied the photodimerization of a number of 4,6-diene-3-ketosteroids, and of 3,5-diene-7-ketosteroids respectively. For each system only one of the twenty possible dimers was observed. In the former the dimer was found to involve the addition of the  $\alpha,\beta$ -double bond of one monomer unit to the  $\gamma,\delta$ -double bond of a second, while in the latter it was found to involve the addition of the  $\alpha,\beta$ -double bond of the two molecular units of the dimer.

The present work is aimed at investigating further the photochemical behaviour of a heteroannular dienone as exemplified by dimethyl 3-dehydrogibberellenate 1 as well as elucidating possible photoreaction paths involving the dienone chromophore in an environment with (a) fused 5-membered ring which may possibly affect the mode of dimerization, and (b) an asymmetric centre in the molecule allowing for photoepimerization reaction of the expected photodimer.

## RESULTS AND DISCUSSION

A solution of 700 mg ( $2.7 \times 10^{-2}$  M) of dimethyl 3-dehydrogibberellenate 1 in 70 ml of *t*-butanol was irradiated at  $\lambda > 300$  nm. After 2 hr irradiation, the starting material had been consumed, and tlc indicated the formation of photoproduct A.

Photoproduct A, crystallized from acetone-hexane as prisms to give 595 mg (85% yield with respect to the starting material), m.p. 212°, and was identified as a photodimer on the basis of physical measurements. NMR spectrum showed the absence of the olefinic protons of ring A, IR spectrum showed the presence of unconjugated CO band at  $1715\text{ cm}^{-1}$ , instead of the original conjugated CO band at  $1680\text{ cm}^{-1}$ , and C=C stretching at  $1660\text{ cm}^{-1}$ , UV spectrum gave  $n \rightarrow \pi^*$  absorption of saturated cyclic ketones, and finally the mass spectrum gave a parent molecular ion peak at  $m/e$  744, which is twice the monomeric value, indicating the dimeric nature of A.

The NMR, IR and UV data excluded completely the possibility of dimerization through oxetane formation, or that involving the interaction of the olefinic group exocyclic to ring D of one molecule with  $\alpha,\beta$ - or  $\gamma,\delta$ -double bond of a second molecule.

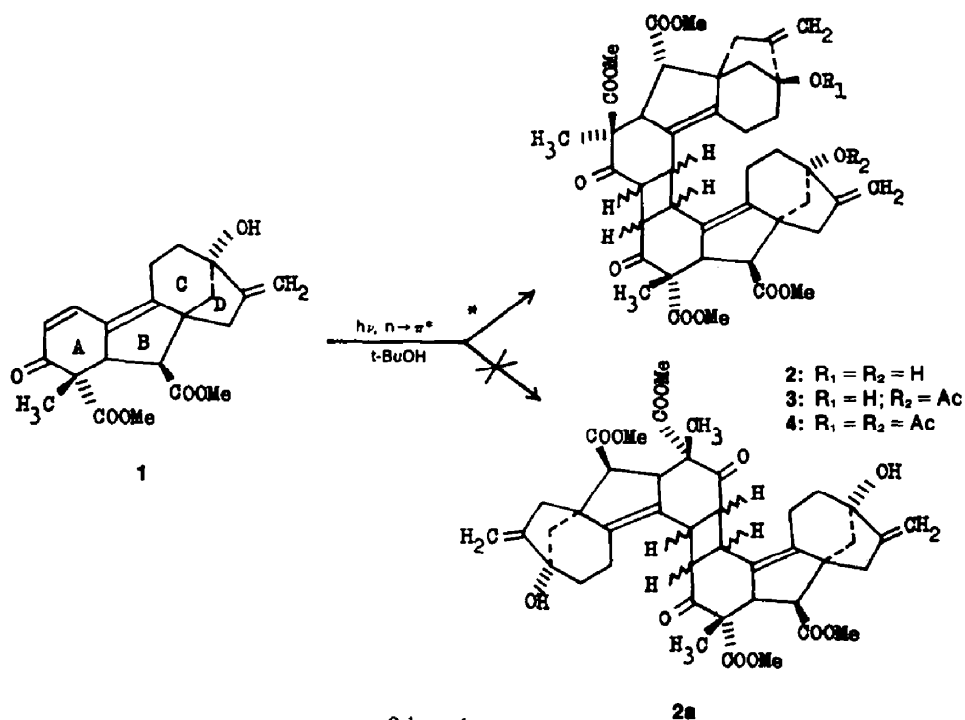
In view of these facts and the well known tendency of conjugated carbonyl compounds to undergo photodimerization giving cyclobutane derivatives,<sup>4</sup> it seemed likely that A was a dimer of the cyclobutane type formed by the reaction of  $\alpha,\beta$ -double bond of two molecules of the dienone, and could possibly be either 2 or 2a (Scheme 1).

The NMR spectrum of A showed that the photodimer molecule was quite symmetric since it gave a rather simple spectrum similar to that of the parent dienone, except for the absence of the olefinic protons in ring A due to the opening of  $\alpha,\beta$ -double bonds of the two dienone molecules in forming the cyclobutane ring of the dimer.

In order to check the symmetric nature of the photodimer, the monoacetyl and the diacetyl derivatives of A were prepared by acetylation with acetic anhydride-pyridine for 8 days at room temperature. The two possible products were separated by column chromatography and were characterized as 3 and 4. Examination of their NMR spectra showed clearly that the diacetate 4 exhibited again the simple spectrum encountered for the parent dimer, while the spectrum of the monoacetate 3 was less simple due to the asymmetric nature of the molecule, since in this case the spectrum showed four signals of the non-equivalent methyl esters.

Generally,  $\alpha,\beta$ -unsaturated ketones give upon photoirradiation "head-to-head" and/or "head-to-tail" dimers.<sup>5-7</sup> In the present case these descriptions are to be understood with respect to the dienone chromophore only, i.e. structures 2 and 2a, respectively. Both structures could have *cis*- or *trans*-fused cyclobutane rings. In addition, the relationship of the two dienone halves might be either *syn* or *anti* about the cyclobutane ring.

In order to check whether A was "head-to-head" or "head-to-tail" isomer, it was reduced to the corresponding 3,3-dihydroxy derivatives using  $\text{NaBH}_4$  in methanol



Scheme 1.

solution at room temperature for a short reaction time as checked by tlc. Three reduction products corresponding to the following possible stereochemical products:  $3\alpha,3'\alpha$ -;  $3\alpha,3'\beta$ -;  $3\beta,3'\alpha$ - and  $3\beta,3'\beta$ -dihydroxy derivatives were obtained (examination of the models showed the identity of  $3\alpha,3'\beta$ - and  $3\beta,3'\alpha$ -dihydroxy derivatives). The products were separated by column chromatography on silica gel and were identified on the basis of usual physical measurements (IR, UV, NMR and MS data).

It was expected for the  $3\alpha,3'\alpha$ - and  $3\beta,3'\beta$ -dihydroxy derivatives of the "head-to-head" dimer, that intramolecular H-bonding might be formed.<sup>8</sup> It was thought that examination of the IR spectrum of dilute solution of the  $3\alpha,3'\alpha$ - and  $3\beta,3'\beta$ -dihydroxy derivatives in  $\text{CCl}_4$  and  $\text{CHCl}_3$  would clarify this point. Unfortunately, due to the insolubility of these products in either  $\text{CCl}_4$  or  $\text{CHCl}_3$ , the IR spectrum could not be measured. For this reason, the diacetyl derivative of the photodimer was reduced to the corresponding  $3,3'$ -dihydroxy derivatives under similar conditions as for the photodimer. The IR spectrum of the isolated reaction product mixture was measured and showed that the products exhibited OH...OH bonding ( $3465\text{ cm}^{-1}$ ),<sup>9,9</sup> OH... $\pi$  bonding ( $3550\text{ cm}^{-1}$ )<sup>10</sup> and a free OH ( $3645\text{ cm}^{-1}$ ), thus proving that the reduction products of the diacetyl derivative of the photodimer was of the "head-to-head" type.

Examination of stereo-model showed that the formation of the *syn*-form seemed to be extremely unattainable because of the drastic steric hindrance due to the very short distances between groups of both halves of the molecule. It could therefore be, safely, concluded that photodimer A is a "head-to-head" dimer of the *anti*-form, *viz* structure 2.

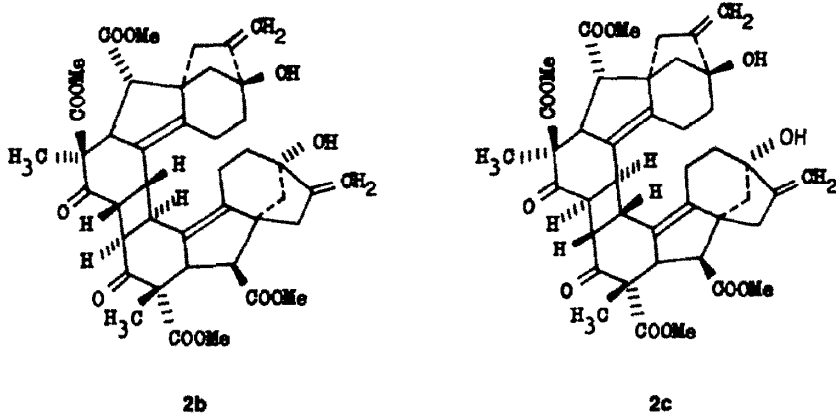
Treatment of fused cyclobutane ring with methanolic MeONa or alumina, distinguishes between the *trans*- and the *cis*-fused junctions. The former, because of ring strain, is highly unstable toward such treatment. When A

was treated with these reagents it showed remarkable stability, indicating that it has a *cis*-fused cyclobutane ring. Therefore, of the four possible structures, the two *syn*-forms have already been excluded on the basis of steric hindrance. The preference of one of the two remaining structural possibilities 2b and 2c (Scheme 2) have been judged by using ORD technique. Thus, applying the octant rule to the remaining two structural possibilities one could predict that while structure 2b would give positive Cotton effect, structure 2c would give negative Cotton effect. ORD measurement which gave positive Cotton effect was in good agreement with structure 2b which was therefore accepted as the structure for photodimer A.

In another set of experiments where irradiation of 1 was carried out under the same conditions as before but for 3 hr, the results gave, as indicated by tlc, beside the photoproduct A, a rather substantial amount of a second photoproduct B and lesser amount of a third photoproduct C. The three photoproducts were clearly separated by column chromatography.

Photoproduct A was eluted 65% yield (with respect to the starting material), m.p.  $212^\circ$ . Photoproduct B was eluted in 12% yield, m.p.  $220$ – $222^\circ$ , and photoproduct C was eluted in 7% yield, m.p.  $228$ – $230^\circ$ . The last two photoproducts were identified by the same spectroscopic methods, and were found to be quite similar to photodimer A with the exception of minor differences in their NMR spectra.

It is evident, from the above results that photodimer A was formed as the primary photoproduct (stereospecific) with the other two photodimers (*viz* B and C) as a secondary and tertiary photoproducts, respectively. To verify this conclusion, independent experiments on the photolysis of photodimers A, B and C as bichromophoric systems were carried out in *t*-butanol. Thus, irradiation of 250 mg of photodimer A for 8 hr, under the same conditions as indicated for the parent compound, gave

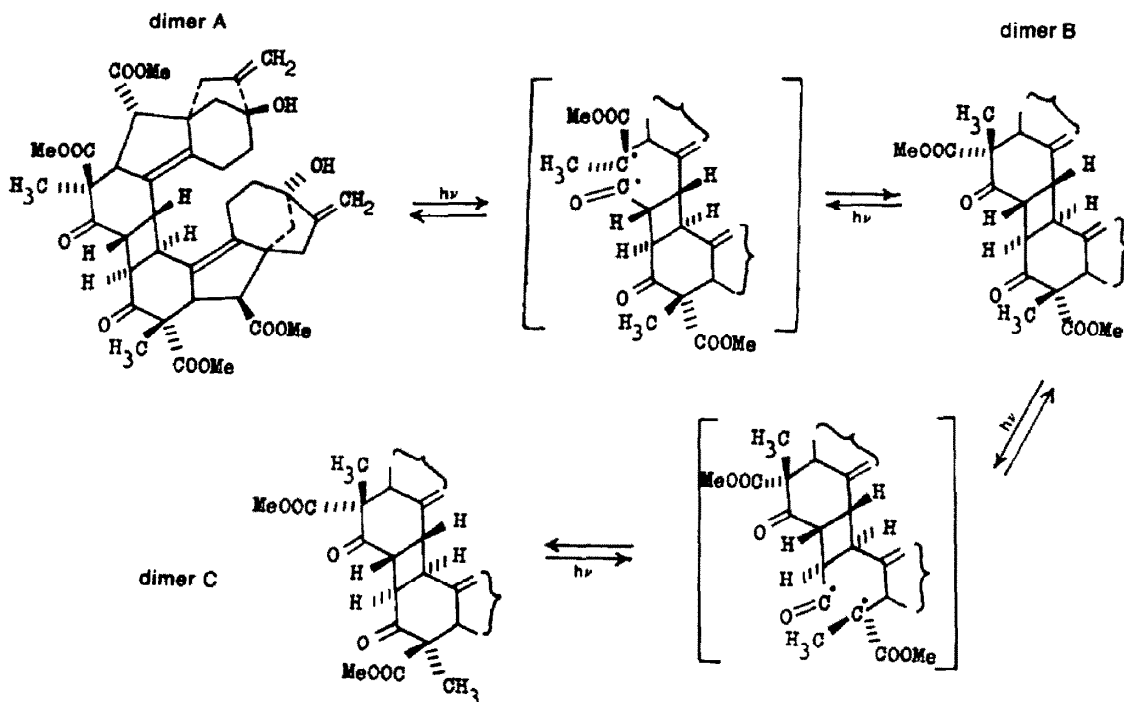


Scheme 2.

besides 85 mg (34%) of the starting material, 25 mg (10% yield) of photodimer B, and 20 mg (8% yield) of photodimer C. Irradiation for 5 hr of 50 mg of photodimer B, under the same conditions of irradiation as for the parent compound, gave 13 mg (26% yield) of photodimer A, 12 mg (24%) of the starting material (i.e. photodimer B) and 5 mg (10% yield) of photodimer C. Also, irradiation of photodimer C (2 mg/2 ml), under similar conditions of irradiation, gave photodimers A and B (in this case the reaction was followed by tlc only). Such behaviour suggests the possibility that the three photodimers might be of similar structures and were in a state of photochemical equilibrium.

Since photodimers B and C were very stable towards methanolic MeONa or alumina, therefore they must have similar *cis*-fused cyclobutane ring as for photodimer A, and the only point where they could differ in their stereochemistries was at the asymmetric centers C<sub>4</sub> and

C<sub>1</sub>. This point could be demonstrated by consideration of Norrish process I type photochemical reaction. The  $n \rightarrow \pi^*$  photochemistry of photodimer A could lead through Norrish process I-cleavage (i.e.  $\alpha$ -cleavage) and subsequent internal rotation followed by recombination to give photodimer B. However, dimer C could not be formed directly from dimer A by a similar sequence of steps. But, dimer B could undergo Norrish process I at the two equivalent positions of the two identical halves of the dimer. For one of the positions, it would lead back to dimer A, and for the other position on the other half of the dimer molecule, it could lead to the formation of dimer C (Scheme 3). There are two known experimental facts that clearly showed the reversibility of the fission step and then support our conclusion. First, the quantum yield was small, indicating that energy was lost in a repetition of the first step.<sup>11</sup> More important, however, was the observed photochemical epimerization in com-



Scheme 3. Photoepimerization of photodimers A, B and C.

pounds that bear centres of asymmetry adjacent to the CO function.<sup>12</sup>

It was expected on steric grounds, by close examination of stereo-models of dimers A, B and C, that dimer A was the least strained while dimer C was the most strained, because of the proximity of the bulky methyl esters groups on positions 4 and 7 and 4' and 7'. Dimer B might take up an intermediate position in this respect. This behaviour could explain the relative yields of these isomers.

It was expected, from applying the octant rule technique to photodimers A, B and C, that all the three dimers must give positive Cotton effects with molecular amplitudes increasing in the order  $A < B < C$ . ORD measurements showed that all the photodimers gave such positive Cotton effects together with the expected trend of the molecular amplitudes, *viz* photodimer A ( $a = 65$ ) < Photodimer B ( $a = 74$ ) < Photodimer C ( $a = 78$ ) (Fig. 1).

In more dilute solutions ( $10^{-4}$  M) photodimer A on irradiation with  $\lambda_{254}$  or  $\lambda_{313}$  nm underwent photochemical cleavage ( $\beta$ -cleavage) to the corresponding dienone as checked by UV and tlc techniques.

Thus, when  $10^{-4}$  M solution of photodimer A was irradiated at 254 nm, a photostationary state was reached within 10 min between the photodimer and the dienone; analysis by UV spectral measurements indicated the presence of 39% dimer A and 61% dienone. However when  $10^{-4}$  M solution of photodimer A was irradiated at 313 nm again a photostationary state was reached, but within 105 min between the photodimer and the dienone; and analysis by UV spectral measurements indicated the formation of 41% dienone and the presence of 59% dimer A.

Since at 254 nm the extinction coefficient for dimer A is more than that of the dienone ( $\epsilon_{\text{dimer A}}^{254}$  2250;  $\epsilon_{\text{dienone}}^{254}$  1835), the quantum yield for the cleavage of dimer A would be expected to be more than that for the photodimerization of the dienone. At 313 nm the ratio of

extinction coefficients drops to about 0.005 ( $\epsilon_{\text{dimer A}}^{313}$  99;  $\epsilon_{\text{dienone}}^{313}$  18695), so the stationary state is displaced in favour of photodimerization. Therefore, it seemed reasonable to conclude that the energy of excitation as well as the extinction coefficients of reactant and product could be considered as important factors in the dienone-photodimer photochemical dichotomy.<sup>13</sup> Thus, the considerable change in ratio's of the extinction coefficients of the monomer to the dimer (at 254 nm the ratio 1:1.25 while at 313 nm the ratio 200:1) was reflected by the time needed to reach equilibrium, as well as, by the relative concentration of the two species at equilibrium at the respective wavelength. Also, the recombination of the dienone monomers to reform the dimer is governed by the requirement that the produced two monomer halves must remain within the reaction sphere of one another.

The contrast in the behaviour of photodimer A upon irradiation at  $\lambda > 300$  or 313 nm at high ( $> 10^{-2}$  M) and low ( $10^{-4}$  M) concentrations could be explained on the following basis: at high concentration the excited dimer may undergo two possible processes: (a)  $\beta$ -cleavage of the  $C_2-C_2'$  bond of the dimer giving the original dienone and (b)  $\alpha$ -cleavage of the  $C_3-C_4$  or  $C_3'-C_4'$  bond of the dimer giving photodimer B. However, because of the high reactivity of the dienone at high concentration towards photodimerization reaction, especially when the produced two dienone monomers remain within the reaction sphere of one another, therefore, the produced dienone monomers will tend to dimerize much faster than they can diffuse away from one another.

The present work provides further insight on the mode of dimerization, and its stereospecificity, in that due to the rather sterically hindered position of the 5-membered ring, dimerization through  $\alpha,\beta$ -double bond of the two dienone molecules was the preferred mode.

#### EXPERIMENTAL

M.p.s were corrected. UV spectra were run in MeOH and IR spectra were taken in nujol. A Varian Associate A-60 was used to record NMR spectra. All spectra were run in  $CD_3COCD_3$  soln, HMDS as an internal standard. Electron-attachment mass spectragraph of the Research Institute Manfred Von Ardenne, Dresden was used to record MS spectra. ORD curves were run in MeOH on a JASCO ORD/UV-5 spectrometer. Tlc: Silica gel G (Merck) developed with benzene-AcOH 70:30; detection with 85%  $H_2SO_4$ , heating for 15 min at 120°. Column chromatography: silica gel Woelm for partition chromatography.

#### Photolysis of dimethyl 3-dehydrogibberellenate (1) for 2 hours

A soln of 700 mg of 1<sup>4</sup> in 70 ml t-BuOH was irradiated in pyrex flask ( $\lambda > 300$  nm), under argon at 25–30° using an external (500 W) high-pressure mercury arc lamp THU 500 (distance 6 cm). After 2 hr, 1 had been consumed, and tlc showed the formation of one yellow-brownish spot. After evaporation of t-BuOH under reduced pressure, the residue was crystallized from acetone-hexane in prisms to give 595 mg (85% yield based on recovered starting material) of the photodimer A, m.p. 212°. UV:  $\lambda_{\text{max}}(\epsilon)$  208 (20521), 245 (3410) and 305 nm (74). IR:  $\nu_{\text{max}}$  895 ( $\text{C}=\text{CH}_2$ ), 1175 ( $\text{COOCH}_3$ ), 1665 (C=C), 1715 (unconj. C=O),

1735 ( $\text{COOCH}_3$ ), 3075 ( $\text{C}=\text{CH}_2$ ) and  $3500\text{cm}^{-1}$  (OH). 100-MHz. NMR:  $\delta_{\text{HMDS}}^{\text{acetone-d}_6}$  1.16 (s, 18- and 18'- $\text{CH}_3$ ), 3.62 and 3.66 (s, 7-, 7'-, 19- and 19'-methylsters- $\text{H}_3$ ) and 4.78 and 5.04 ppm (17- and 17'- $\text{H}_2$ ). MS (positive ionization,  $T_v = 145^\circ\text{C}$ ):  $m/e$  744 ( $\text{M}^+$ ), 713 ( $\text{M}^+-\text{OCH}_3$ ), 684 ( $\text{M}^+-\text{CH}_3\text{COOH}$ ), 625 ( $\text{M}^+-\text{CH}_3\text{COOH}-\text{COOCH}_3$ ), and 565 ( $\text{M}^+-2\text{CH}_3\text{COOH}-\text{COOCH}_3$ ). ORD (C=O 0.8523):

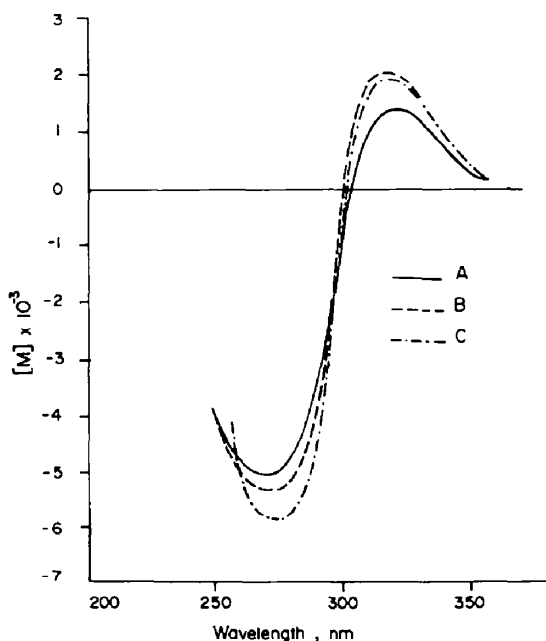


Fig. 1. ORD spectra of photodimers A, B and C.

$$[M]_{319} = +1395, [M]_{302} = 0 \text{ and } [M]_{270} = -5073.$$

**Acetylation of photodimer A**

A soln of 150 mg of A was dissolved in 1.5 ml abs pyridine. Ac<sub>2</sub>O (1.5 ml) was added to the soln. The mixture was left at room temp for 8 days. It showed the complete disappearance of A and formation of two new spots. The products, after evaporation of the solvent, adsorbed on celite (300 mg) with acetone and chromatographed on 7.5 gm of silica gel. Elution (5 ml fractions) with benzene-ether 8:2 gave 100 mg (66% yield) diacetyl of A as crystals (from acetone-hexane), m.p. 130–132° UV:  $\lambda_{\max}(\epsilon)$  212 (9556), 248 (3801) and 305 nm (109). IR:  $\nu_{\max}$  906 ( $\text{>C=CH}_2$ ), 1168 (COOCH<sub>3</sub>), 1268 (O-acetyl), 1660 (C=C), 1715 (unconj. C=O), 1740 (COOCH<sub>3</sub>) and 3090 cm<sup>-1</sup> ( $\text{>C=CH}_2$ ). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.16 (s, 18- and 18'-CH<sub>3</sub>), 1.95 (s, 13- and 13'-O-acetyl-H<sub>3</sub>), 3.62 and 3.66 (s, 7-, 7'-, 19- and 19'-methylesters-H<sub>3</sub>) and 4.88 and 4.96 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 115°): m/e 828 (M<sup>+</sup>), 797 (M<sup>+</sup>-OCH<sub>3</sub>), 769 (M<sup>+</sup>-OCH<sub>3</sub>-CO) and 737 (M<sup>+</sup>-OCH<sub>3</sub>-CH<sub>3</sub>OH). MS (negative ionization, T<sub>v</sub> = 110°): m/e 842 (M<sup>-</sup>+O<sub>2</sub>), 828 (M<sup>-</sup>), 810 (M<sup>-</sup>-H<sub>2</sub>O), 796 (M<sup>-</sup>-CH<sub>3</sub>OH), 768 (M<sup>-</sup>-CH<sub>3</sub>COOH) and 737 (M<sup>-</sup>-CH<sub>3</sub>COOH-OCH<sub>3</sub>).

Further elution with benzene-ether 8:1 gave 50 mg (33% yield) monoacetyl of A as amorphous substance. UV:  $\lambda_{\max}(\epsilon)$  213 (10884), 248 (4066) and 305 (370). IR:  $\nu_{\max}$  910 ( $\text{>C=CH}_2$ ), 1178 (COOCH<sub>3</sub>), 1254 (O-acetyl), 1668 (C=C), 1715 (shoulder, C=O, 6-membered ring), 3075 ( $\text{>C=CH}_2$ ) and 3600 cm<sup>-1</sup> (OH). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.16 (s, 18- and 18'-CH<sub>3</sub>), 1.9 (s, 13- or 13'-O-acetyl-H<sub>3</sub>), 3.62, 3.64 and 3.66 (7-, 7'-, 19- and 19'-methylesters-H<sub>3</sub>) and 4.78, 4.87, 4.97 and 5.03 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 120°): m/e 786 (M<sup>+</sup>), 755 (M<sup>+</sup>-OCH<sub>3</sub>) and 727 (M<sup>+</sup>-COOCH<sub>3</sub>). MS (negative ionization, T<sub>v</sub> = 120°): m/e 786 (M<sup>-</sup>), 754 (M<sup>-</sup>-CH<sub>3</sub>OH) and 726 (M<sup>-</sup>-CH<sub>3</sub>COOH).

**Reduction of photodimer A**

Photodimer A (250 mg) was dissolved in 35 ml MeOH. An excess of NaBH<sub>4</sub> (250 mg) was added to the soln. The reaction, as indicated by tlc, was very fast. After 2 min, the starting material had been consumed, and tlc showed the formation of three new blue spots. The soln was evaporated to half, acidified with 35 ml (1:5) AcOH and extracted by EtOAc. The residue, after evaporation of the solvent, was adsorbed on celite (500 mg) with acetone and chromatographed on 12.5 gm silica gel. Elution (5 ml fractions) with CHCl<sub>3</sub>-EtOAc 6:4 gave 56 mg (22% yield) of the first reduction product (i.e. the higher spot on tlc plate developed with CHCl<sub>3</sub>-CH<sub>3</sub>OH 90:10 v/v). IR:  $\nu_{\max}$  884 ( $\text{>C=CH}_2$ ), 1165 (COOCH<sub>3</sub>), 1660 (C=C), 1735 (COOCH<sub>3</sub>) and 3455 cm<sup>-1</sup> (OH). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.12 (s, 18- and 18'-CH<sub>3</sub>), 3.50 and 3.60 (s, 7-, 7'-, 19- and 19'-methylesters-H<sub>3</sub>) and 4.76 and 5.00 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 140°): m/e 730 (M<sup>+</sup>-H<sub>2</sub>O), 712 (M<sup>+</sup>-2H<sub>2</sub>O), 699 (M<sup>+</sup>-H<sub>2</sub>O-OCH<sub>3</sub>), 671 (M<sup>+</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>), 653 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O), 611 (M<sup>+</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>-CH<sub>3</sub>COOH), 593 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O-CH<sub>3</sub>COOH) and 533 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O-2CH<sub>3</sub>COOH). MS (negative ionization, T<sub>v</sub> = 130°): m/e 748 (M<sup>-</sup>), 730 (M<sup>-</sup>-H<sub>2</sub>O), 716 (M<sup>-</sup>-CH<sub>3</sub>OH), 688 (M<sup>-</sup>-CH<sub>3</sub>COOH) or (M<sup>-</sup>-CH<sub>3</sub>OH-CO) and 671 (M<sup>-</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>).

Further elution with CHCl<sub>3</sub>-EtOAc 6:4 gave 87 mg (35% yield) of the second reduction product (i.e. the middle spot on tlc plate developed by CHCl<sub>3</sub>-MeOH 90:10 v/v). IR:  $\nu_{\max}$  884 ( $\text{>C=CH}_2$ ), 1180 (COOCH<sub>3</sub>), 1660 (C=C), 1728 (COOCH<sub>3</sub>), 3085 ( $\text{>C=CH}_2$ ) and 3400 cm<sup>-1</sup> (OH). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.16 (s, 18- and 18'-CH<sub>3</sub>), 3.53 and 3.64 (s, 7-, 7'-, 19- and 19'-methylesters-H<sub>3</sub>) and 4.76 and 5.00 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 145°): m/e 730 (M<sup>+</sup>-H<sub>2</sub>O), 712 (M<sup>+</sup>-2H<sub>2</sub>O), 699 (M<sup>+</sup>-H<sub>2</sub>O-OCH<sub>3</sub>), 689 (M<sup>+</sup>-COOCH<sub>3</sub>), 671 (M<sup>+</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>), 653 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O), 611 (M<sup>+</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>-CH<sub>3</sub>COOH), 593 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O-CH<sub>3</sub>COOH) and 533 (M<sup>+</sup>-COOCH<sub>3</sub>-

2H<sub>2</sub>O-2CH<sub>3</sub>COOH). MS (negative ionization, T<sub>v</sub> = 130°): m/e 748 (M<sup>-</sup>), 730 (M<sup>-</sup>-H<sub>2</sub>O), 716 (M<sup>-</sup>-CH<sub>3</sub>OH), 688 (M<sup>-</sup>-CH<sub>3</sub>COOH) and 671 (M<sup>-</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>).

Further elution with EtOAc gave 93 mg (37% yield) of a third reduction product (i.e. the lowest spot on tlc plate developed by CHCl<sub>3</sub>-MeOH 90:10 v/v). IR:  $\nu_{\max}$  892 ( $\text{>C=CH}_2$ ), 1170 (COOCH<sub>3</sub>), 1660 (C=C), 1728 (COOCH<sub>3</sub>), 3085 ( $\text{>C=CH}_2$ ) and 3400 cm<sup>-1</sup> (OH). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.12 and 1.14 (s, 18- and 18'-CH<sub>3</sub>), 3.51, 3.61 and 3.63 (s, 7-, 7'-, 19- and 19'-methylesters-H<sub>3</sub>) and 4.75 and 5.00 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 135°): m/e 730 (M<sup>+</sup>-H<sub>2</sub>O), 712 (M<sup>+</sup>-2H<sub>2</sub>O), 699 (M<sup>+</sup>-H<sub>2</sub>O-OCH<sub>3</sub>), 689 (M<sup>+</sup>-COOCH<sub>3</sub>), 671 (M<sup>+</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>), 653 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O), 611 (M<sup>+</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>-CH<sub>3</sub>COOH) and 593 (M<sup>+</sup>-COOCH<sub>3</sub>-2H<sub>2</sub>O-CH<sub>3</sub>COOH). MS (negative ionization, T<sub>v</sub> = 135°): m/e 748 (M<sup>-</sup>), 730 (M<sup>-</sup>-H<sub>2</sub>O), 716 (M<sup>-</sup>-CH<sub>3</sub>OH), 688 (M<sup>-</sup>-CH<sub>3</sub>OH-CO) and 671 (M<sup>-</sup>-H<sub>2</sub>O-COOCH<sub>3</sub>).

**Identification of intramolecular hydrogen bonding in the products of diacetyl derivative of photodimer A**

Diacetyl derivative of A (20 mg) was dissolved in 1 ml MeOH. An excess of NaBH<sub>4</sub> (20 mg) were added to the soln. After 2 min. tlc showed that the diacetyl derivative of A was completely converted to three possible reduction products which may correspond to 3 $\alpha$ , 3' $\alpha$ -; 3 $\beta$ , 3' $\beta$ -; 3 $\alpha$ , 3' $\beta$ - or 3 $\beta$ , 3' $\alpha$ -dihydroxy derivatives. The soln was evaporated to half, acidified with 3 ml (1:5) AcOH and then extracted by EtOAc. The residue, after evaporation of the solvent under reduced pressure, was dissolved in CHCl<sub>3</sub> to examine the IR spectrum for the presence of intramolecular H-bonding which was to be expected to be formed in case of 3 $\alpha$ , 3' $\alpha$ - and 3 $\beta$ , 3' $\beta$ -dihydroxy derivatives of diacetyl of A. The reduction products exhibited OH...OH bonding (3465 cm<sup>-1</sup>), OH... $\pi$  bonding (3550 cm<sup>-1</sup>) and free OH (3645 cm<sup>-1</sup>).

**Photolysis of dimethyl 3-dehydrogibberellenate (1) for 3 hours**

A soln of 700 mg of 1 in 70 ml t-BuOH was irradiated for 3 hr. After this time the starting material had been consumed, and tlc showed the formation of three new yellow-brownish spots. After evaporation of t-BuOH under reduced pressure, the photo-products were adsorbed on celite (1.5 gm) with acetone and chromatographed on 35 gm of silica gel. Elution (20 ml fractions) with benzene-ether 6:4 gave 455 mg (65% yield) with respect to the starting material of photoproduct had the same physical properties (m.p., UV, IR, NMR and MS data) of the previously reported A.

Further elution with benzene-ether 4:6 gave 84 mg (12% yield) B as crystals (from acetone-hexane) m.p. 220–222°. UV:  $\lambda_{\max}(\epsilon)$  213 (10566), 247 (4758) and 315 nm (326). IR:  $\nu_{\max}$  890 ( $\text{>C=CH}_2$ ), 1170 (COOCH<sub>3</sub>), 1660 (C=C), 1714 (unconj. C=O), 1730 (COOCH<sub>3</sub>), 3080 ( $\text{>C=CH}_2$ ) and 3500 cm<sup>-1</sup> (OH). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.14 (s, 18- and 18'-CH<sub>3</sub>) and 4.86 and 5.11 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 125°): m/e 744 (M<sup>+</sup>), 726 (M<sup>+</sup>-H<sub>2</sub>O), 713 (M<sup>+</sup>-OCH<sub>3</sub>), 695 (M<sup>+</sup>-H<sub>2</sub>O-OCH<sub>3</sub>), 685 (M<sup>+</sup>-COOCH<sub>3</sub>) and 667 (M<sup>+</sup>-COOCH<sub>3</sub>-H<sub>2</sub>O). MS (negative ionization, T<sub>v</sub> = 110°): m/e 744 (M<sup>-</sup>), ORD (C = 1.0233):

$$[M]_{315} = +2036, [M]_{300} = 0 \text{ and } [M]_{275} = -5320.$$

Further elution with ether-MeOH 98:2 gave 49 mg (7% yield) C as crystal (from acetone-hexane) m.p. 228–230°. UV:  $\nu_{\max}(\epsilon)$  213 (10875), 249 (4503) and 325 nm (675). IR:  $\nu_{\max}$  890 ( $\text{>C=CH}_2$ ), 1170 (COOCH<sub>3</sub>), 1662 (C=C), 1710 (unconj. C=O), 1730 (COOCH<sub>3</sub>) and 3500 cm<sup>-1</sup> (OH). 100-MHz-NMR:  $\delta_{\text{HMS}}^{\text{Acetone-D}_6}$  1.15 (s, 18- and 18'-CH<sub>3</sub>) and 4.85 and 5.10 ppm (17- and 17'-H<sub>2</sub>). MS (positive ionization, T<sub>v</sub> = 120°): m/e 744 (M<sup>+</sup>), 726 (M<sup>+</sup>-H<sub>2</sub>O), 713 (M<sup>+</sup>-OCH<sub>3</sub>), 694 (M<sup>+</sup>-H<sub>2</sub>O-CH<sub>3</sub>OH), 685 (M<sup>+</sup>-COOCH<sub>3</sub>) and 667 (M<sup>+</sup>-COOCH<sub>3</sub>-H<sub>2</sub>O). ORD (C = 1.7100): [M]<sub>314</sub> = +1909, [M]<sub>301</sub> = 0 and [M]<sub>273</sub> = -5900.

**Photoepimerization of photodimer A**

A soln of 250 mg of A in 25 ml t-BuOH was irradiated for 8 hr. After this time, tlc showed besides the starting material (A) B and C were formed. The solvent was evaporated under reduced pressure and the residue was adsorbed on celite (500 mg) with acetone and chromatographed on 10 mg of silica gel. Elution (10 ml fractions) with benzene-ether 6:4 gave 85 mg starting material (A) which crystallized from acetone-hexane in prisms m.p. 212°.

Further elution with benzene-ether 4:6 gave 25 mg (10% yield) B which crystallized from acetone-hexane in prisms m.p. 220-222°.

Further elution with ether-MeOH 98:2 gave 20 mg (8% yield) C which crystallized from acetone-hexane, m.p. 228-230°.

**Photoepimerization of photodimer B**

A soln of 50 mg of B in 5 ml t-BuOH was irradiated for 5 hr. After this time, tlc showed besides the starting material (B), A and C were formed. The residue after evaporation of the solvent under reduced pressure was adsorbed on celite (100 mg) with acetone and chromatographed on 2 gm of silica gel. Elution (3 ml fractions) with benzene-ether 6:4 gave 18 mg (36% yield) A.

Further elution with benzene-ether 4:6 gave 12 mg starting B. Further elution with ether-MeOH 98:2 gave 7 mg (14% yield) C.

**Photoepimerization of photodimer C:**

A soln of 2 mg of C in 2 ml t-BuOH was irradiated for 4 hr. The reaction was followed by tlc only. After this time, tlc showed the formation of A and B besides the starting C.

**Photocleavage of photodimer A at 254 nm**

Photoreactor Reading Type 31 was used for irradiation of a soln of A ( $10^{-4}$  M) in t-BuOH at 254 nm. The irradiation was performed in a 5 mm rectangular quartz cell fitted with teflon stopper and placed at a fixed position, which was vacated by the removal of one of the two M-shaped lamps, and in the radiation field of the second lamp. The irradiation was continued until UV spectra of the soln showed no change with irradiation. An irradiation period of 10 min was required to attain equilibrium. In order to check the tlc of the reactoin, five identically irradiated solutions were collected and then concentrated by evaporating under reduced pressure. Tlc then showed that the reaction was very clean since only two spots, corresponding to the dimer A

and its monomer (dimethyl 3-dehydrogibberellenate), appeared on tlc plate. The composition was calculated from the extinction coefficient of the monomer at 312 (18700); and the product of irradiation of photodimer A was found to contain 39% of photodimer A and 61% of its monomer.

**Photocleavage of photodimer A at 313 nm**

A soln of A ( $10^{-4}$  M) in t-BuOH was irradiated in 5 mm quartz cell using Quantum Yield Photoreactor Model 2001 (Applied Photophysics Ltd) and potassium chromate filter<sup>15</sup> thus allowing irradiation at 313 nm. The irradiation was continued until UV spectra showed no change with further irradiation, and equilibrium was found to be attained after 105 min, tlc of the product showed again that the reaction was very clean. Composition was calculated from the extinction coefficient of the monomer at 312 nm, and the irradiation product was found to contain 59% of A and 41% of its monomer.

**REFERENCES**

- <sup>1</sup>H. P. Thronsdon, G. Cainelli, D. Arigoni and O. Jeger, *Helv. Chim. Acta* **45**, 2342 (1962).
- <sup>2</sup>M. B. Rubin, G. E. Hipps and D. Glover, *J. Org. Chem.* **29**, 68 (1964).
- <sup>3</sup>M. B. Rubin, D. Glover and R. G. Parker, *Tetrahedron Letters* 1075 (1964).
- <sup>4</sup>A. Mustafa, *Chem. Rev.* **51**, 1 (1952).
- <sup>5</sup>P. E. Eaton, *J. Am. Chem. Soc.* **84**, 2344 (1962).
- <sup>6</sup>G. Buchi and D. Knusten, Private communication noted in P. Yates and M. J. Jorgenson, *Ibid.* **85**, 2956 (1963).
- <sup>7</sup>B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner and O. Jeger, *Helv. Chim. Acta* **46**, 2473 (1963).
- <sup>8</sup>G. E. Lange and E. Neidert, *Tetrahedron Letters* 4215 (1971).
- <sup>9</sup>L. P. Kuhn, P. Von R. Schleyer, W. F. Baitinger and L. Ebersson, *J. Am. Chem. Soc.* **86**, 650 (1964).
- <sup>10</sup>M. Oki, H. Iwamura, T. Onoda and M. Iwamura, *Tetrahedron* **24**, 1905 (1968).
- <sup>11</sup>N. C. Yang and R. H. K. Chen, *J. Am. Chem. Soc.* **93**, 530 (1971).
- <sup>12</sup>H. Wehrli and K. Schaffner, *Helv. Chim. Acta* **45**, 385 (1962).
- <sup>13</sup>W. G. Dauben and M. S. Kellogg, *J. Am. Chem. Soc.* **93**, 3805 (1971).
- <sup>14</sup>J. S. Moffat, *J. Chem. Soc.* 3045 (1960).
- <sup>15</sup>M. Kasha, *J. Opt. Soc. Am.* **38**, 929 (1948).