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PHOTOCHEMICAL REACTIONS—XX*

SOLID STATE PHOTOCHEMISTRY OF 3-DEHYDRO-GIBBERELLIN A_3 METHYL ESTER; LIGHT-CATALYZED TOPODIMERIZATION AND SUBSEQUENT AROMATIZATION

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Abstract—UV-irradiation ($\lambda > 300$ nm) of 3-dehydro-gibberellin A_3 methyl ester **1** in the crystalline state leads *via* [2+2] cycloaddition to two cyclobutane-type photodimers **2** and **6**. Further irradiation of both compounds gives, with loss of carbon dioxide, the corresponding ring A aromatic dimers. Photolysis of **1** as a thin film causes intramolecular photodecarboxylation to give the monomeric phenolic ester **8**.

Several reports, especially the elegant investigations of Schmidt *et al*[1] have shown that cyclobutane-type dimerization in some cases proceeds efficiently in the crystalline state, and can be expected to arise by a lattice-controlled stereospecific process.[2] In this communication we report the crystal state photolysis of 3-dehydro-gibberellin A_3 methyl ester **1** representing a further example of topophotochemical dimerization which is in remarkable contrast to the solution photochemistry[3,4] as well as, to the crystal state photolysis, of the corresponding free enone acid of **1**.[5]

UV-irradiation of crystalline methyl ester **1** in the $n \rightarrow \pi^*$ absorption region of the enone chromophore ($\lambda > 300$ nm) yields a mixture of the four new photoproducts **2**, **4**, **6** and **7**, besides some unchanged **1** and untractable polymeric material. Upon silica gel chromatography the pure compounds have been obtained in 39, 12·5, 6 and 3·6% yield, respectively, based on starting material consumed. Slow formation of photoproduct **2** is also detectable upon exposure of crystalline **1** to diffuse daylight. Further irradiation of **2** and **6** in the crystalline state or as a thin film converts both these photodimers, with loss of carbon dioxide, to **4** and **7**, whereas prolonged irradiation causes transformation to polymers in all four cases.

The structure of the main photodimer **2** was assigned on the basis of the following evidence.[6] The mass spectra (positive and negative ionization) show a peak of highest mass number at *m/e* 672 (M-44), indicating the dimeric nature of **2**. On the other hand, elemental analysis give the composition of a normal dimerization product $C_{40}H_{44}O_{12}$ indicating that the above mentioned peak at *m/e* 672 cannot be the molecular ion peak but results from a dominating mass spectral fragmentation process involving elimination of carbon dioxide. Other prominent peaks in the cation mass spectrum appear at *m/e* 654 (M^+-CO_2-H_2O), 640 (M^+-CO_2-CH_3OH), 626 (M^+-CO_2-CO-H_2O), 612 (M^+-CO_2-CH_3COOH), 594 (M^+-CO_2-CH_3COOH-H_2O), 566 (M^+-CO_2-COOH-H_2O-CO) and 548 (M^+-CO_2-CH_3COOH-$2H_2O$-CO) following the typical fragmentation pattern of the corresponding gibberellin functional groups[7] remaining after photolysis. A further series of peaks with *m/e* 340, 330, 314, 299, 286, 272 and 254 corresponds to the mass spectrum of starting enone **1** showing that cleavage to the monomeric compound takes place, similar to the mass spectral behaviour of some other photodimers.[8] The IR spectrum (chloroform) of **2** exhibits absorption typical of terminal methylene (902, 1660 and 3080), α,β-unsaturated ketone (1610 and 1702), methyl ester (1175), carbonyl (1735) as well as strong γ-lactone (1785) and hydroxyl (3595 cm^{-1}). In comparison with the starting ketone **1** the UV spectrum of the photodimer **2**, besides remaining enone absorption at 227 and 325 (ϵ 6900 and 80, respectively) shows an additional maximum near 285 nm (ϵ 230)[9] attributed to the presence of a newly formed saturated carbonyl function.

Acylation of **2** under conditions for esterification of the tertiary 13-hydroxyl group (8 days at 20°)[12] yields the monoacetyl derivative **3**, whose cation and anion mass spectrum similar to **2** shows again not the molecular ion, but a peak at highest mass number at *m/e* 714 (758–44) in both cases resulting again from a preferred loss of carbon dioxide. In the IR, besides O-acetyl at 1263 cm^{-1}, a free hydroxyl group at 3598 cm^{-1} is indicated which must be

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present in a highly steric hindered environment. The 100 MHz NMR spectrum of **3** is characterized by signals at $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7·25 (d, 9·5 Hz, 1-H), 6·03 (d, 9·5 Hz, 2-H), 5·09 and 4·98 (17'-H_2), 3·76 and 3·71 (singlets of 7- and 7'-methyl ester-H_3), 2·01 (s, 13'-O-acetyl-H_3), 1·26 (s, 18-H_3) and 1·22 ppm (s, 18'-H_3).

These data, coupled with elemental analysis, lead to the conclusion that the main photodimer must have a cyclobutane type constitution as indicated in formulae **2** arising from a [2+2] photocycloaddition of the excited Δ^1-enone double bond to the terminal methylene group of a second enone molecule, spatially favoured in the crystal lattice.

Dimer **6**, m.p. above 298° (dec), and $[\alpha]_D^{20}+33{\cdot}7°$, displays in the mass spectrum the highest mass number at *m/e* 672 and nearly the same fragmentation pattern as that of **2**. Also in this case elemental analysis indicates $C_{40}H_{44}O_{12}$. The IR and UV data reveal the same functional groups as **2** (especially an enone function) as well as a newly created saturated carbonyl (IR: $\nu_{\max}^{\mathrm{CHCl_3}}$ 1610 and 1706 cm^{-1}; UV: $\lambda_{\max}$ at 228, 285 and 330 nm with ϵ 6000, 240 and 65, respectively). The NMR spectrum exhibits signals at $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 7·25 (d, 10 Hz, 1-H), 6·00 (d, 10 Hz, 2-H), 5·13 and 4·94 (17'-H_2), 3·72 and 3·68 (singlets of 7- and 7'-methyl-ester-H_3), 1·27 and 1·21 ppm (singlets of 18- and 18'-H_3). This shows that compound **6** belongs to the same cycloadduct type as **2** and differs only in the cyclobutane environment.

With regard to the more difficult problem of the structure and stereochemistry about the cyclobutane ring in the dimers **2** and **6**, stereochemical considerations together with ORD results are useful. Supposing a cis-annelation[13] of the cyclobutane ring, [2+2] photocycloaddition of the Δ^1 enone double bond to the terminal ethylenic linkage of a second molecule gives rise to four different structural types **a–d**, and for each of them again two stereoisomeric possibilities differing in the α- or β-cyclobutane fusion at ring A' are possible. From these eight cycloadducts five already could be eliminated because of drastic steric hindrance in such highly voluminous and rigid systems leading to unusual short atom distances. Applying the octant rule to the three remaining structural possibilities as shown in Fig 2 the cyclobutane structure and stereochemistry for **2** and **6** was assigned. The ORD curves of both cycloadducts should be the result of an additive overlapping of the corresponding enone Cotton effect, well known[14] for **1**, and the increment of the newly created saturated 3'-carbonyl group in the other half of the dimer. As indicated in Fig 1 the positive Cotton effect in the 280 nm carbonyl region of both photodimers is decreased in comparison to the ground curve of **1** (a = +41) which must be due to negative 3'-carbonyl Cotton effects for which the increments of the molecular amplitudes can be calculated with $a_2 - a_1 = 22 - 41 = -19$ for dimer **2** and $a_6 - a_1 = 6{\cdot}8 - 41 \approx -34$ for the minor cycloadduct **6**. Because the carbonyl Cotton effect of 3-keto-gibberellins with a cis 1,2-annelated cyclobutane ring shows, even in the case of an α-cyclobutane orientation, a positive value (a = +81)[15] both the observed negative 3'-carbonyl increments rule out the structural alternative **9** for which one must expect a strong positive Cotton effect from the octant rule. On the other hand, the octant projection of the remaining two structural possibilities **2** and **6** leads to the conclusion that the main photodimer with the larger positive amplitude a = +22 has structure **2** and the minor dimer showing a ~ +6·8 has structure **6**.

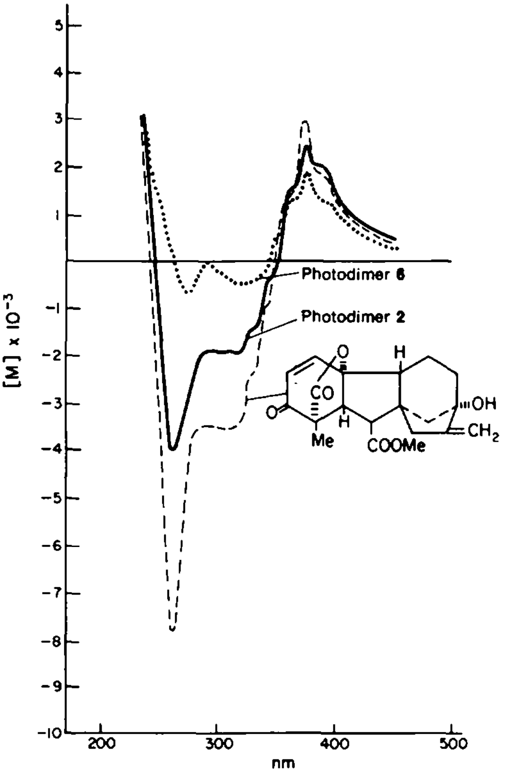
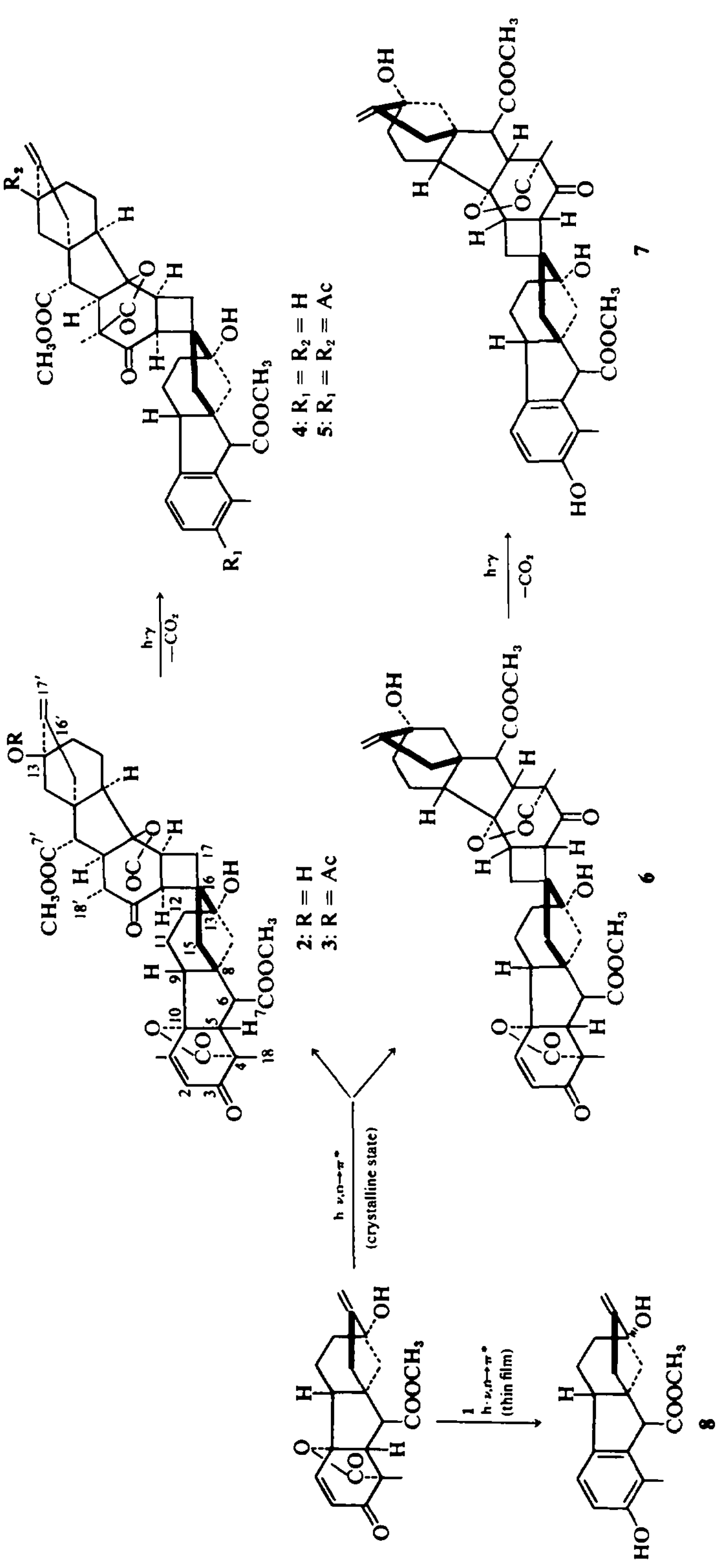


Fig 1. ORD curves of enone **1** and photodimers **2** and **6**.

The structures of both secondary photoproducts **4** and **7**, obtained on further irradiation of **2** and **6**, respectively, with UV > 300 nm in the crystalline state or as a thin film, were deduced from spectral data. From IR and UV, it follows that an enone chromophore is no longer present. Instead a newly formed aromatic system with two o-hydrogens is indicated in both cases (IR: $\nu_{\max}$ near 830, 1500 and 1615 cm^{-1}; UV: $\lambda_{\max}$ 286 with ϵ 1500 and 1800, respectively) which must result from a decarboxylation involving the lactone bridge in ring A. This loss of carbon dioxide is also confirmed by the mass spectral behaviour of **4** and **7** with the peak at


h ν,n→π* (crystalline state)
1 h·ν,n→π* (thin film)
hγ −CO₂
hγ −CO₂
2: R = H
3: R = Ac
4: R₁ = R₂ = H
5: R₁ = R₂ = Ac
6
7
8

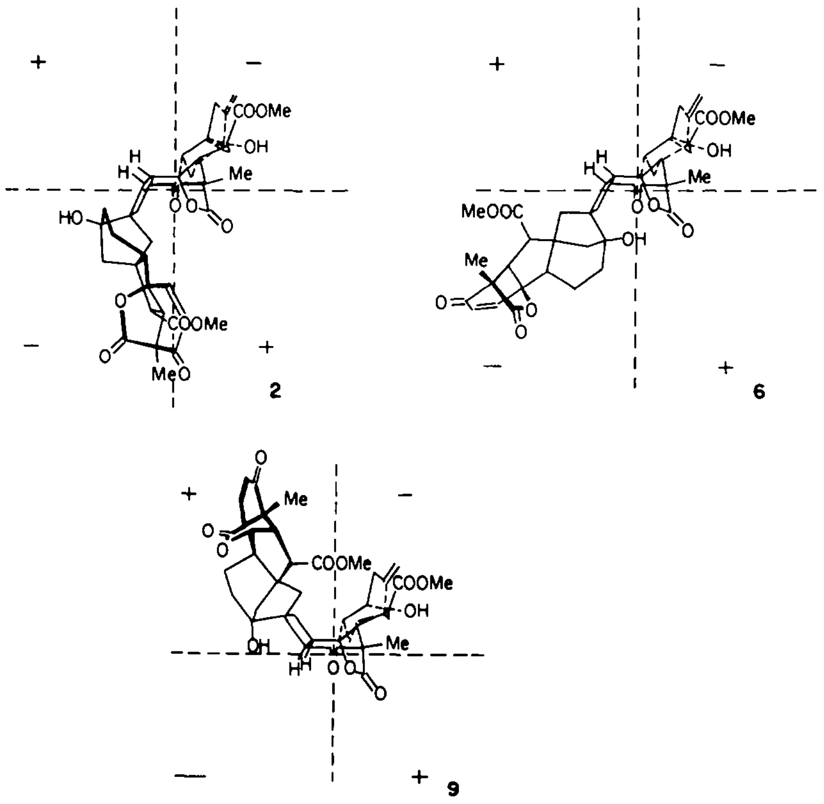
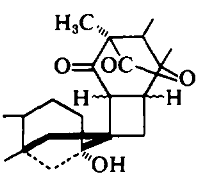
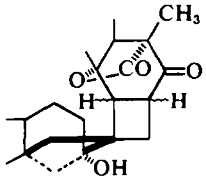


Fig 2. Octant projections of the three possible cycloadducts from 1.


a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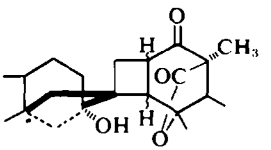
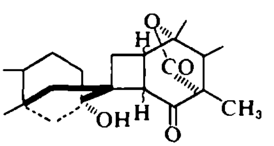

c


d

highest mass number at *m/e* 672 representing, in contrast to 2 and 6, the molecular ion.

The results demonstrate that further excitation of the remaining enone chromophore results in photoaromatization of ring A, and confirm structures 4 and 7. The process is analogous to the smooth mass spectral decarboxylation of 2 and 6 causing absence of the corresponding molecular ion peaks, and indicates another parallelism between photochemical and mass spectral fragmentation behaviour.[16]

In contrast to the crystal state photodimerization, upon photolysis ($\lambda > 300$ nm) of the enone ester 1 as a thin film intramolecular photodecarboxylation leading to the well known[3,5] monomeric phenolic ester 8 (isolated in 28% yield based on recovered starting material) becomes the preferred reaction, whereas the cycloaddition products **2** and **6** could be detected only in minor amounts (3 and 1·4% yield, respectively, besides polymeric material). Such photoaromatization has been observed by us as the main reaction in the crystal state photolysis of the free 3-dehydro gibberellic acid,[5] which differs remarkably from the dimerization tendency of its methyl ester**1**. Decarboxylation in ring A has also been found to be one of the solvent photolysis processes of **1**[3,4] and shown to proceed in these cases via the lowest excited singlet state.[4]

The results represent a striking difference between the crystal state, thin film and solution[3,4] photochemistry of an α,β-unsaturated ketone. The observed topophotodimerization leading to **2** and **6** appears to be a lattice geometry-controlled process preceded by π complex formation[17] between the Δ^1 enone double bond and the terminal olefinic group of a suitably placed second molecule. Direct excitation of such a complex could explain intermolecular photocycloaddition in preference to the "normal" photoaromatization which can follow only as a slower secondary photoprocess leading to the ring A phenolic dimers **4** and **7**. The effects of crystal structure on the photochemistry of such 3-dehydro gibberellic acid derivatives are being investigated by X-ray analysis.

EXPERIMENTAL

M.ps are corrected. Specific rotations in chloroform. IR: UR 10 spectrophotometer (Zeiss Jena); UV: Ultrascan (Hilger & Watts) in methanol; NMR: Varian HA 100 in $CDCl_3$ with TMS as internal standard; MS: Electron attachment mass spectrograph of the Research Institute Manfred von Ardenne, Dresden. ORD: JASCO ORD/UV 5 instrument in methanol. TLC: Silicagel G (Merck) developed with chloroform-methanol 95:5 v/v; detection with 85% sulphuric acid, heating for 2 hr at 120°. Column chromatography: Silicagel Woelm for partition chromatography.

Photolysis of crystalline 3-*dehydro gibberellin* A_3 *methylester* **1**

Crystalline enone ester **1**[18] (85 mg) was irradiated in a rotating 100 ml pyrex flask under argon at 25–30° for 36 hr using an external 500 W high-pressure mercury arc lamp Th U 500 (distance 6 cm). After this time the TLC showed, besides some starting **1** (R_F 0·57) four new spots with R_F 0·51 and 0·40 (both greenish-yellow) as well as 0·35 and 0·33 (brownish). The collected photoproducts of four such runs were adsorbed on celite (700 mg) with methylene chloride and chromatographed on 32 g of silica gel (10 ml fractions). Elution with methylene chloride–ethyl acetate 85:15 afforded 62 mg starting enone ester **1** (R_F 0·57). Elution with methylene chloride–ethyl acetate 7:3 gave 109 mg (39% yield based on recovered starting material) main photodimer **2** (R_F 0·51) as plates (from acetone–hexane) m.p. 251–253° (dec), $[\alpha]_D^{18}+52{\cdot}8°$ ($c = 0{\cdot}510$). (Calc for $C_{40}H_{44}O_{12}$ C, 67·03; H, 6·19. Found: C, 67·38; H, 5·99). IR (chloroform): ν_{max} 902 (>C=CH$_2$), 1175 (COOCH$_3$), 1610 (conj. C=C), 1660 (C=C), 1702 (conj. C=C), 1735 (C=O), 1785 (γ-lactone), 3080 (>C=CH$_2$) and 3595 cm^{-1} (OH). UV: λ_{max} 227, 285, 325 nm (ϵ 6900, 230, 80). MS (positive ionization, T_v 100°): *m/e* 672 (M^+-44), 654, 640, 626, 612, 594, 566, 548, 355, 340, 341, 332, 330, 323, 314, 299, 286, 272, 259, 254. MS (negative ionization, T_v 90°); *m/e* 672 (M^--CO_2), 656, 644, 628, 614, 538, 360, 340, 330, 314, 299, 282, 272. ORD ($c = 0{\cdot}191$): $[M]_{390}+2050°$, $[M]_{373}+2530°$, $[M]_{358}+1480°$, $[M]_{343}-300°$; $[M]_{328}-1600$, $[M]_{296}-2000°$; $[M]_{264}-4200°$ ($a = +22$); $[M]_{237}+20700°$; $[M]_{225}+9750°$. NMR: δ 7·25 (d, 10 Hz, 1-H), 6·05 (d, 10 Hz, 2-H), 5·12 and 4·98 (17′-H$_2$), 3·73 and 3·71 (s, 7- and 7′-methyl ester-H$_3$), 1·28 (s, 18-H$_3$) and 1·22 ppm (s, 18′-H$_3$).

Acetylation of **2** with acetic anhydride-pyridine for 8 days at room temp followed by column chromatography on silica gel afforded monoacetate **3** with m.p. 240–243° (dec) from acetone-hexane, $[\alpha]_D^{18}+30{\cdot}9°$ ($c = 0{\cdot}547$). IR (chloroform): ν_{max} 901 (>C=CH$_2$), 1180 (COOCH$_3$), 1263 (O-acetyl), 1618 (conj. C=C), 1678 (C=C), 1705 (shoulder, conj. C=O), 1740 (C=O), 1790 (γ-lactone) and 3598 cm^{-1} (OH). MS (positive ionization, T_v 125°): *m/e* 714 (M^+-44), 686, 672, 655, 654, 636, 623, 622, 612, 609, 594, 566, 549, 400, 383, 374, 355, 341, 332, 314, 300, 282, 272, 254. MS (negative ionization, T_v 110°): *m/e* 714 (M^--44), 672, 340, 314, 296. NMR: δ 7·25 (d, 9·5 Hz, 1-H), 6·03 (d, 9·5 Hz, 2-H), 5·09 and 4·98 (17′-H$_2$), 3·76 and 3·71 (s, 7- and 7′-methylester-H$_3$), 2·01 (s, 13′-O-acetyl-H$_3$), 1·26 (s, 18-H$_3$) and 1·22 ppm (s, 18′-H$_3$).

Further elution with methylene chloride–ethyl acetate (65:35) gave 15 mg (6%) pure **4** (R_F 0·35) which crystallized from methylene chloride–hexane, m.p. 250–253° (dec), $[\alpha]_D^{18}+36{\cdot}2°$ ($c = 0{\cdot}354$). IR (nujol): ν_{max} 830 (aromatic with two ortho-H), 896 (>C=CH$_2$), 1170 (COOCH$_3$), 1503 and 1615 (aromatic), 1670 (C=C), 1736 (C=C), 1778 (γ-lactone) and 3350 cm^{-1} (broad, OH). UV: λ_{max} 213, 231, 286 nm (ϵ 6250, 4200 sh, 1500). MS (positive ionization, T_v 115°): *m/e* 672 (M^+), 611, 553, 355, 341, 332, 314, 297, 283, 272, 254. MS (negative ionization, T_v 100°): *m/e* 686 (M^-+14)[19], 672 (M^-), 656, 642, 626, 612, 372, 339, 330, 314, 298, 280, 271.

Acetylation of **4** with acetic anhydride–pyridine for 8 days at room temp followed by silica gel chromatography afforded diacetate **5** which crystallized from acetone–ether–hexane, m.p. 204–207° (dec), $[\alpha]_D^{18}+61{\cdot}3°$ ($c = 0{\cdot}293$) (Calc for $C_{43}H_{48}O_{12}$: C, 68·24; H, 6·39; Found C, 68·02; H, 6·11). IR (nujol): ν_{max} 908 (>C=CH$_2$), 1175 (COOCH$_3$), 1220 (phenolic acetate), 1250 (O-acetyl), 1670 (C=C), 1745 (C=O), 1792 (γ-lactone) and 3580 cm^{-1} (broad, OH). UV: λ_{max} 215, 270 (ϵ 12000, 2200).

Further elution with methylene chloride–ethyl acetate (6:4) yielded 34·7 mg (12·5%) photodimer **6** (R_F 0·40) which crystallized from methylene chloride–hexane, m.p., dec above 298°, $[\alpha]_D^{20}+33{\cdot}7°$ ($c = 0{\cdot}593$). (Calc. for $C_{40}H_{44}O_{12}$: C, 67·03; H, 6·19. Found: C, 67·37; H, 6·46). IR (chloroform): ν_{max} 903 (>C=CH$_2$, 1176 (COOCH$_3$), 1610 (conj. C=C), 1665 (C=C), 1700 (conj. C=O), 1708 (6-membered ring C=O), 1738 (C=O), 1786 (γ-lactone), 3085 (>C=CH$_2$) and 3600 cm^{-1} (OH). UV: λ_{max} 227, 281, 326 (ϵ 6000, 240, 65). MS (positive ionization, T_v 95°): *m/e* 672 (M^+-44), 640, 626, 610, 592, 430, 359, 341, 332, 323, 314, 300, 272, 254. NMR: δ 7·25 (d, 10 Hz, 1-H), 6·01 (d, 10 Hz, 2-H), 5·15 and 4·94 (17′-H$_2$), 3·72 and 3·68 (s, 7- and 7′-methyl ester-H$_3$), 1·27 and 1·21 ppm (s, 18- and 18′-H$_3$). ORD ($c = 0{\cdot}190$): $[M]_{389}+1330°$, $[M]_{370}+1530°$, $[M]_{360}+1370°$, $[M]_{343}+760°$, $[M]_{305}-500°$, $[M]_{283}-70°$, $[M]_{263}-750°$ ($a = +6{\cdot}8$), $[M]_{234}+1300°$, $[M]_{225}+10100°$.

Further elution with methylene chloride–ethylacetate (50:50 and 45:55) gave after crystallization from methylene chloride–hexane 9·5 mg (3·6%) **7** (R_F 0·33), m.p., dec above 300°. $[\alpha]_D^{19}+47{\cdot}8°$ ($c = 0{\cdot}318$). IR (nujol):

ν_{max} 830 (aromatic with two ortho-H), 905 (>C═CH$_2$), 1175 (COOCH$_3$), 1500 and 1615 (aromatic), 1765 (C═C), 1730 (C═O), 1780 (γ-lactone) and 3440 cm^{-1} (broad, OH). UV: λ_{max} 218·5, 234, 286 nm (ϵ 5000, 3900, 1800). MS (negative ionization, T_e 150°): m/e 672 (M$^-$) 658, 630, 354, 340, 314, 300, 282, 272, 254.*

Subsequent elution of the column with methylene chloride–ethyl acetate (3:7, 2:8, 1:9) and pure ethyl acetate yielded 63 mg amorphous intractable polymeric material.

Solid state photolysis of dimer **2**

Crystalline photodimer **2** (50 mg) was irradiated through pyrex for 12 hr in a slow argon stream as described before. Evolution of carbon dioxide was observed by trapping with Ba(OH)$_2$. TLC indicated complete disappearance of **2** (R_F 0·51) and formation of compound **4** (R_F 0·35). Upon chromatography of the photolysis product on silica gel (15 g) and elution with methylene chloride–ethyl acetate (6:4) 19 mg (40%) **4** of m.p. 250–253° (dec) and $[\alpha]_D^{19}+35{\cdot}9°$ ($c=0{\cdot}481$) was obtained and shown to be identical in every respect with **4** produced upon direct photolysis of **1** as described. Further elution with increasing amounts of ethyl acetate yielded 23·6 mg polymeric material. A similar result was obtained upon photolysis of **2** as a thin film. Prolonged irradiation resulted in the disappearance also of **4** under formation of undefined polymeric material.

Solid state photolysis of dimer **6**

Photodimer **6** (2 mg) was irradiated in the crystalline state or as a thin film through pyrex as described above and the photoreaction controlled by TLC. After 1 hr starting **6** (R_F 0·40) was no longer present and a new spot of **7** (R_F 0·33) appeared. Prolonged irradiation resulted in the formation of undefined polymers.

Thin film photolysis of 3*-dehydrogibberellin* A$_3$ *methylester* **1**

Enone ester **1** (85 mg) was irradiated as a thin film in a 100 ml pyrex flask under rotation and argon for 36 hr as described in the crystalline state experiment. Evolving carbon dioxide was trapped by Ba(OH)$_2$. After this time TLC indicated, besides considerable amounts of **1**, the phenol **8** (R_F 0·45, brownish) as main product and only traces of the photodimers **2** (R_F 0·51, greenish-yellow) and **4** (0·35, brownish) could be detected. The collected photolysate of three such runs was chromatographed on 12 g silica gel. Elution with pure methylene chloride gave first 45 mg starting enone **1** (R_F 0·57). Further elution with methylene chloride yielded 49·5 mg (28%) monomeric phenol **8** (R_F 0·45) as chromatographically pure amorphous solid, $[\alpha]_D^{20}+32{\cdot}8°$ ($c=0{\cdot}435$), m/e 314 (M$^+$), which was shown to be identical in every aspect with an authentic specimen of **8**. Further elution with methylene chloride–ethyl acetate (9:1) afforded 6 mg (3%) dimer **2** (R_F 0·51), m.p. 250° (mixed m.p. and IR). Further elution with methylene chloride–ethyl acetate (8:2) afforded 2·5 mg (1·4%) phenolic dimer **4** (R_F 0·35), m.p. 249–252° (mixed m.p. and IR). Elution with more polar solvents gave 112 mg intractable polymeric solid.

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REFERENCES

[1] M. Lahar and G. M. J. Schmidt, *J. Chem. Soc.* (*B*) 239 (1967), and preceding papers in this series

[2] See, D. C. Neckers, *Mechanistic Organic Photochemistry*, p. 107. Reinhold, New York, (1967)

[3] I. A. Gurvich, N. S. Kobrina, E. P. Serebryakov and V. F. Kutcherov, *Tetrahedron* **27**, 5901 (1971)

[4] E. P. Serebryakov, N. S. Kobrina, V. F. Kutcherov, G. Adam and K. Schreiber, *Tetrahedron* **28**, 3819 (1972) and references cited therein

[5] G. Adam and B. Voigt, *Tetrahedron Letters* 4601 (1971)

[6] For a preliminary communication of this part, see G. Adam, *Tetrahedron Letters* 1357 (1971)

[7] For the mass spectroscopic behaviour of monomeric gibberellins see, N. S. Wulfson, V. I. Zaretskii, I. B. Papernaja, E. P. Serebryakov and V. F. Kutcherov, *Tetrahedron Letters* 4209 (1965); N. Takahashi, M. Murofushi, S. T. Tamura, N. Wasada, H. Hoshino, T. Tsuchiya, T. Aoyama and H. Moritz, *Tetrahedron Letters* 895 (1967); R. Binks, J. MacMillan and R. J. Price, *Phytochem.* **8**, 271 (1969); N. Takahashi, N. Murofushi, S. Tamura, N. Wasada, H. Hoshino, T. Tsuchiya, S.-I. Sasaki, T. Aoyama and E. Watanabe, *J. Org. Mass Spectrom.* **2**, 711 (1969)

[8] For the mass spectroscopic cleavage of other photodimers to the corresponding monomers, see H. Ziffer, H. M. Fales, W. A. Milne and F. H. Field, *J. Am. Chem. Soc.* **92**, 1597 (1970); C. Fenselau, S. Y. Wang and P. Brown, *Tetrahedron* **26**, 5923 (1970); R. D. Ricke and R. A. Copenhafer, *Tetrahedron Letters* 879 (1971); K. K. Ogilvie and J. W. Berestiansky, *Ibid.* 4667 (1972)

[9] The increased ϵ value is probably due to a homoconjugation effect between the 3- and γ-lactone carbonyl function, found by us also in some other gibberellin-3-ketones[4,10]

[10] G. Adam, *Z. Chem.* **10**, 140 (1970)

[11] For the numbering of the basic gibberellane ring system, see I. W. Rowe, *The Common and Systematic Nomenclature of Cyclic Diterpenes*, 3rd revision, Forest Product Laboratory, US Department of Agriculture, Madison, Wisconsin 1968.

[12] Under these acetylation conditions in monomeric gibberellins the tertiary hydroxyl in position 13 is also acetylated, see J. S. Moffat and M. Radley, *J. Sci. Food Agric.* **11**, 386 (1960) and lit.[16]

[13] Trans-fusion seems improbable in such a lattice controlled cycloaddition process and is excluded because no isomerization of **2** and **6** takes place with neutral alumina. For trans-fused adducts of cyclic hexenones and olefins in solution, see P. Boyle, I. A. Edwards and I. H. Fried, *J. Org. Chem.* **35**, 2560 (1970); G. R. Lenz, *Tetrahedron* **28**, 2195 (1972) and further references cited therein.

[14] I. A. Gurvič, S. S. Jufit, I. M. Milstejn and V. F. Kutcherov, *Izvest. Nauk USSR* (*Ser. Chim.*) 2233 (1966)

[15] G. Adam and B. Voigt, to be published

[16] For other analogies see, G. Adam, *Z. Chem.* **8**, 441 (1968) and references cited therein; R. C. Dougherty, *J. Am. Chem. Soc.* **90**, 5780 (1968); W. Benz and H. Dürr, *Tetrahedron* **24**, 6503 (1968); C. Fenselau, J. L. Young, S. Meyerson, W. R. Landis, E. Selke and L. C. Leitoh, *J. Am. Chem. Soc.* **91**, 6847 (1969)

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*A satisfactory cation mass spectrum could not be obtained from this compound.

[17] See, E. J. Corey, J. D. Bass, LeMahieu and R. B. Mitra, *J. Am. Chem. Soc.* **86**, 5570 (1964)

[18] B. E. Cross, *J. Chem. Soc.* 3022 (1960)

[19] This M + 14 peak may be due to an ion-molecule reaction with oxygen, see M. von Ardenne, K. Steinfelder and R. Tümmler, *Electronenanlagerungs-Massenspektrographie organischer Substanzen*, Springer Verlag, Berlin-Heidelberg-New York 1971, p. 124; G. Adam, K. Schreiber, R. Tümmler and K. Steinfelder, *J. prakt. Chem.* **313**, 1051 (1971)