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TOPOPHOTODIMERIZATION OF A GIBBERELLIN DERIVATIVE (1)

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Recently, the n → π* photochemistry of the α,ß-unsaturated gibberellin ketone I in solution has been studied in which photoaddition of solvent molecules e.g. alcohol (2) and dioxane (3) to the activated Δ^1-double bond (4) or intramolecular cycloaddition in this position (3) play an important role. We wish to report that the enone I is photoreactive also in solid state yielding a cyclobutane photodimer as a main product, for which structure II is proposed.

Thus, crystalline I (70 mg) was irradiated through pyrex under rotation and vacuum at 25-35° C for 36 hrs. using a 500 Watt high pressure mercury lamp. After silicagel chromatography by elution with methylene chloride and increasing amounts of ethyl acetate a new compound with m.p. (corr.) 251-253° (dec.) and $[\alpha]_D^{18}$ +52.8° (c = 0.510, chloroform) has been isolated in 32 % yield. While elemental analysis corresponds with the composition of a normal dimerization product $C_{40}H_{44}O_{12}$ mass spectra (positive and negative ionization) show peaks of highest mass number at m/e 672 (M-44) probably due to a thermal loss of carbon dioxide. Other prominent peaks in the cation mass spectrum appear at m/e 654 (M^+-CO_2-H_2O),

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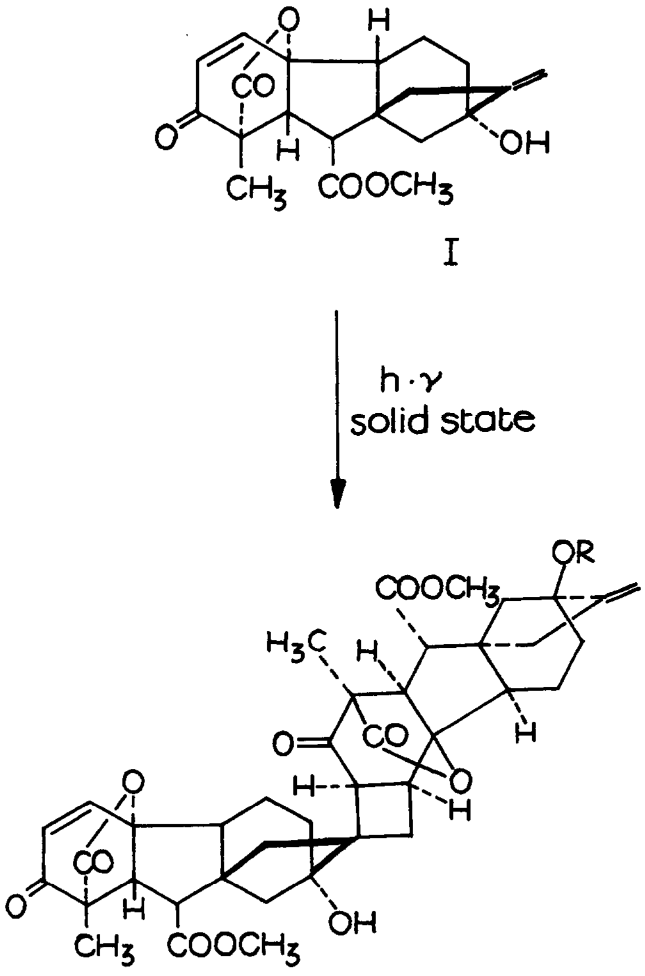
[+] Dedicated to Professor Dr. Dr.h.c. K. Mothes on the occasion of his 70th birthday.

640 (M^+-CO_2-CH_3OH), 626 (M^+-CO_2-H_2O-CO), 612 (M^+-CO_2-CH_3COOH), 594 (M^+-CO_2-CH_3COOH-H_2O), 566 (M^+-CO_2-CH_3COOH-H_2O-CO), 548 (M^+-CO_2-CH_3COOH-$2H_2O$-CO) typical of the corresponding gibberellin functions (5) which remained untouched during photolysis. These groups are also established by IR-bands (chloroform) near 902 (>C=CH_2), 1175 ($COOCH_3$), 1610 (conj. C=C), 1660 (C=C), 1702 (conj. C=O), 1735 (C=O), 1785 (γ-lactone C=O), 3080 (>C=CH_2) and 3595 cm^{-1} (OH). Different from the starting ketone I the UV spectrum (methanol) of the photodimer II, besides enone absorption at 227 and 325 nm (ε 6900 and 80, respectively) shows a further maximum near 285 nm (ε 230) attributed to the presence of a saturated carbonyl function. The increased ε value results from a homoconjugation effect with the γ-lactone carbonyl found by us also in other gibberellin 3-ketones (3). The rotatory dispersion curve (methanol) with extrema of $[M]_{390}$ +2050°, $[M]_{373}$ +2530°, $[M]_{358}$ +1450°, $[M]_{343}$ -300°, $[M]_{328}$ -1600°, $[M]_{296}$ -1950°, $[M]_{264}$ -4200°, $[M]_{237}$ +20 700° and $[M]_{225}$ +9750° is quite similar to I but superimposed by an additional Cotton effect in the saturated carbonyl region (275 nm, a ~ -19). Acetylation of II with acetic anhydride/pyridine for 8 days at room temperature and silicagel chromatography yield a monoacetyl derivative III with m.p. 240-243° (dec.) and $[\alpha]_D^{18}$ +30.9° (c = 0.547) which exhibits IR maxima at 901 (>C=CH_2), 1180 ($COOCH_3$), 1263 ($OCOCH_3$), 1618 (conj. C=C), 1678 (C=C), 1705 (shoulder, conj. C=O), 1740 (C=O), 1790 (γ-lactone C=O) and 3598 cm^{-1} (OH). The cation mass spectrum again shows no molecular ion peak but prominent fragments at m/e 655 (M^+-CO_2-CH_3COO), 637 (M^+-CO_2-CH_3COO-H_2O), 623 (M^+-CO_2-CH_3COO-CH_3OH), 609 (M^+-CO_2-CH_3COO-H_2O-CO) and 549 (M^+-CO_2-CH_3COO-CH_3COOH-CO). The 100 MHz NMR spectrum is characterized by signals at $\delta^{CDCl_3}_{TMS}$ 7.25 (d, 9.5 Hz, 1-H), 6.03 (d, 9.5 Hz, 2-H), 4.98 and 5.09 (17'-H_2), 3.76 and 3.71 (two singlets of 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).


O
H
CO
O
H
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CH3
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COOCH3
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OH
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II: R = H
III: R = Ac

The above physical data of the photodimer and its acetyl derivative lead to the conclusion that during irradiation of I photocycloaddition of the excited enone to the terminal olefin part of a second molecule must have taken place. From the eight structural and spatial possibilities of such a cycloadduct six already could be excluded by considerations on Dreiding models because of steric hindrance in these highly voluminous systems. Applying the octant rule to the remaining two isomers the observed negative carbonyl Cotton effect ($a \sim -19$) is in agreement with structure II, which on that account is assumed for the photoproduct and its acetyl derivative III, respectively. An independent confirmation of this structure by X-ray analysis is in progress.

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