Tetrahedron. Vol. 27, pp. 5901 to 5909. Pergamon Press 1971. Printed in Great Britain

PHOTOCHEMICAL TRANSFORMATIONS OF GIBBERELLIN A_3 DERIVATIVES

AROMATIZATION OF RING A

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(*Received in the UK* 2 *June* 1971; *Accepted for publication* 16 *July* 1971)

Abstract—The photolysis of the 3-keto derivative of gibberellin A_3 methyl ester (I) in t-BuOH or benzene gives rise to the tetracyclic phenol (III) while in benzyl alcohol I is transformed into the tricyclic phenol (X) and the reduced ketone (XI). The epoxy ketone (II) upon photolysis in dioxan affords the resorcinol (XII); at higher temperature the latter is accompanied by the hydroxy ketone (XIII). Some mechanistic aspects of the photoaromatization are discussed.

THE well-known hydrolytic aromatization of gibberellic acid[1,2] yields products with no OH group in the aromatized ring A. The introduction of this function requires several steps[3] and is hardly compatible with the retention of the original structure of rings C and D. The present report concerns the photo-induced aromatization of ring A in the 3-keto derivative of gibberellin A_3 methyl ester[4] (I) and in the corresponding epoxy ketone[5] (II) which affords phenolic products with rings C and D untouched.

Irradiation of I in t-butyl alcohol (in quartz at 28–30°, under argon) brings about noticeable evolution of carbon dioxide and gives a mixture of products from which a phenolic compound, $C_{19}H_{22}O_4$ (III), was isolated in 42% yield as a chromatographically pure amorphous solid. The mass spectrum of this compound displays an intense peak of molecular ion at 314 mu and the base peak with *m/e* 255 (M—$CH_3OCO\cdot$) but otherwise is relatively simple. The aromatic character of III is further confirmed by its UV and IR spectra (λ_{max} 229 and 291 nm, ν_{max} 1609 and 1503 cm^{-1}). A methyl ether (IIIa) and a monoacetate (IIIb) were obtained upon methylation or acetylation of III under standard conditions. The *ortho* position of two aromatic hydrogens and hence the *ortho* position of Me and OH groups in the ring A follows from the IR spectra of III and IIIa (ν_{max} 830 or 824 cm^{-1}, respectively) and from the NMR spectra of III and its monoacetate IIIb where the signals of two aromatic protons appear as an AB-system with $J_{AB} = 7$ or 9 c/s, respectively. Moreover, the passage from III to IIIb involves a diamagnetic shift of the signal belonging to the Me group in the benzene nucleus; such shifts are characteristic of *ortho*-cresols.[6] The remaining part of the molecule must be structurally the same as in the initial ketone I since the IR and NMR spectra of III, IIIa and IIIb show the presence of an exocyclic methylene together with an OH group. Accordingly, the compound $C_{19}H_{22}O_4$ was formulated as a tetracyclic phenol (III) the stereochemistry at C_6 and C_9 being deduced in the following manner.

Successive treatment of III with OsO_4 in pyridine-benzene and then with H_2S in ether afforded in low yield a phenolic triol (IV), characterized by its UV, IR and

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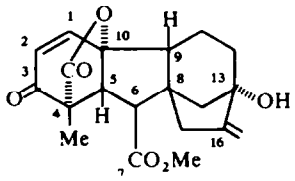
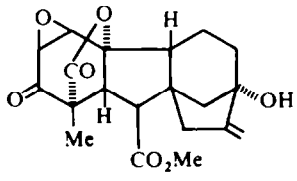
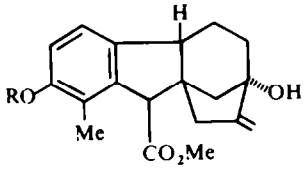


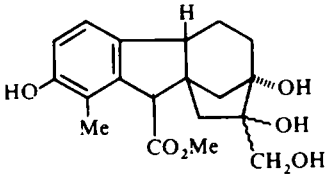
I



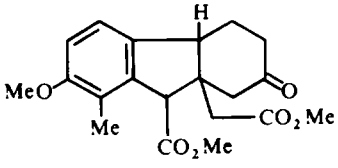
II



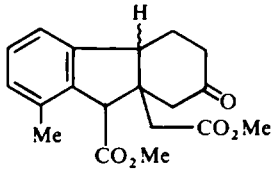
III: R = H
IIIa: R = Me; IIIb: R = Ac



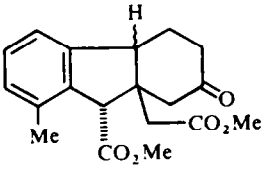
IV



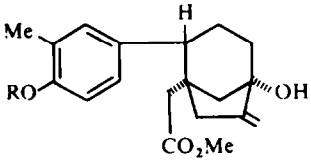
V



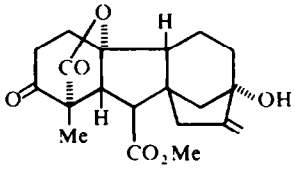
VI: 9α—H
VII: 9β—H



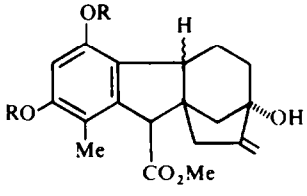
VIII: 9β—H
IX: 9α—H



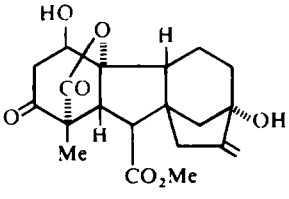
X: R = H
Xa: R = Me; Xb: R = Ac



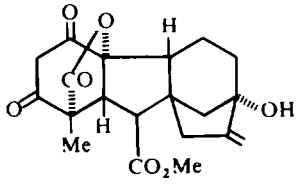
XI



XII: R = H
XIIa: R = Me



XIII



XIV

CHART 1

mass spectra. Oxidative scission of ring D in this triol with $NaBiO_3$ followed by methylation of the crude acidic product with diazomethane and plate chromatography gave an oily substance which was formulated as V on the basis of its UV, IR and mass spectra. A comparison of its ORD curve with that recorded earlier[7] for keto diesters (VI, VII, VIII and IX) derived from allogibberic and epiallogibberic acids (Fig 1) implies that in ketone V the carbomethoxy group in ring B must be β- rather than α-oriented, while the amplitude of the positive Cotton effect exhibited by V is more compatible with a 9β-H configuration (as in VII) than with a 9α-H configuration (as in VI). In accordance with this approach, the stereochemistry of III may be described as 6R, 9R. Further indirect evidence in the favour of 9β-H configuration may be seen in the failure of III to undergo photosensitized oxygenation at C_{15}. This

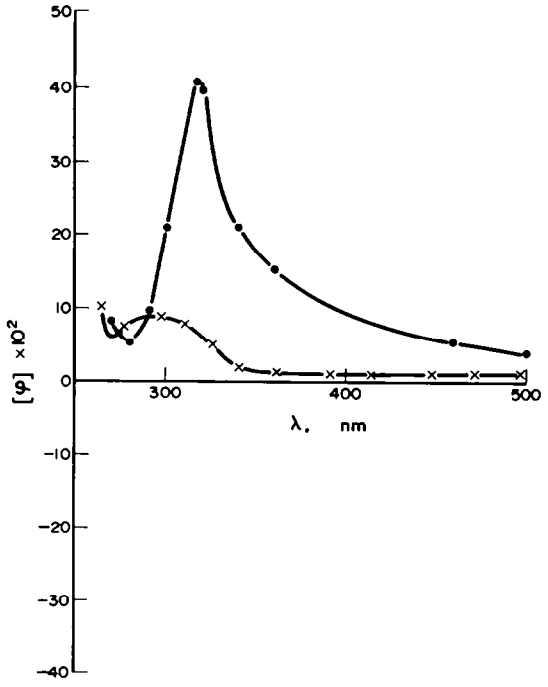


FIG 1a. ORD-curves (in φ) of the keto diester V (———) and the parent phenol III*a* (X—X—X)

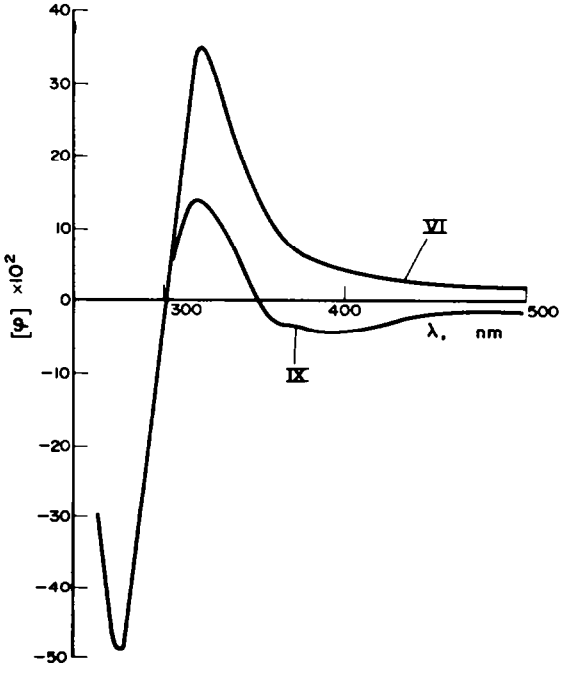


FIG 1b. ORD-curves for compounds VI and IX (9α-H)[7]

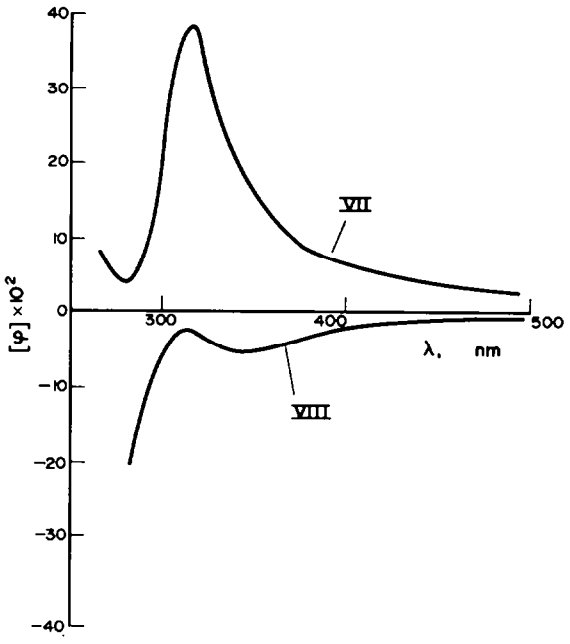


FIG 1c. ORD-curves for compounds VII and VIII (9β-H)[7]

reaction has been recommended as a sensitive probe for the stereochemistry at C_9 in ent-gibberell-16-enes.[8] 9α H-epimers being oxidized and 9β H-epimers remaining untouched. Therefore, phenol III may be regarded as methyl 3-hydroxy-epialogibberate.

The same tetracyclic phenol III was isolated in 21% yield upon photolysis of I in benzene. The formation of III both in t-BuOH and in benzene is accompanied by extensive dimerization and/or polymerization leading to lactone-containing amorphous products which were not studied in detail.† This process accounts for 40 to 60% of the starting material.

In benzyl alcohol, which is known as a hydrogen donating solvent,[9] the photolysis of I proceeds differently. Here a new phenolic substance, $C_{19}H_{24}O_4$(X), was isolated in 41% yield‡ together with a keto lactone (XI) obtained in 14% yield. The latter product was identical with the previously described[10] 3-keto-derivative of gibberellin A_1 methyl ester on the basis of TLC analysis and a comparison of IR and mass spectra. In addition, traces of the tetracyclic phenol III were detected by combined gas chromatography–mass spectrometry. The dimerization of I was also observed in this solvent to the extent of 40%.

The structure of phenol X is based on the following evidence. In the mass spectrum of X the peak of molecular ion appears at 316 mu. The phenolic nature of this substance is revealed by its UV and IR spectra (λ_{max}227 akd 282 nm, ν_{max}1610, 1515 and

† In one case very small amounts of a crystalline dimer with m.p. 248–251° was obtained upon photolysis of I in t-BuOH.

‡ 60% yield was erroneously stated in our preliminary note.[11]

830 cm^{-1}). By analogy with III. phenol X was transformed into a methyl ether (Xa) and a monoacetate (Xb). The NMR spectra of X and Xb show the presence of three benzene protons in a 1,2,4-position (J_{ortho} = 8–9 cs and $J'_{meta} \approx 0{\cdot}6$ cs), the most shielded one (δ 6·7 ppm) being ortho-coupled. The signal of the Me group at C_4 is shifted by 0·07 ppm upfields on passage from X to Xb. The data imply that compound X is a 4-substituted *o*-cresol. The IR and NMR spectra of X, Xa and Xb indicate that ring D remains undisturbed in the course of photolysis; on the other hand, the cleavage of ring B is supported by NMR spectra of X and Xb (2-proton broad singlets with δ 2·60–2·61 ppm. most probably —$C\underline{H}_2COOMe$) and by the mass spectra of X. Xa and Xb where noticeable peaks M-73 seem to correspond to the ejection of $\cdot CH_2COOMe$. Since in the NMR spectra of X and Xb the signal of the benzylic proton (formerly at C_9) appears as a distinct part of an ABC-system with ($J_{AC} + J_{BC}$) = 6·5 c/s, this proton must nearly bisect the angle between the protons of the neighbouring CH_2 group. Two conformations with an axial aryl group agree with the observed splitting, the one corresponding to the retention of original configuration at C_9 (Fig. 2a) and the other arising from its inversion (Fig. 2b). Examination of respective Dreiding models shows that the former conformation should be more stable than its equatorial boat-form counterpart, while in the second pair the axial conformer is particularly hindered. It is likely, therefore, that the benzylic proton in X is β-oriented.

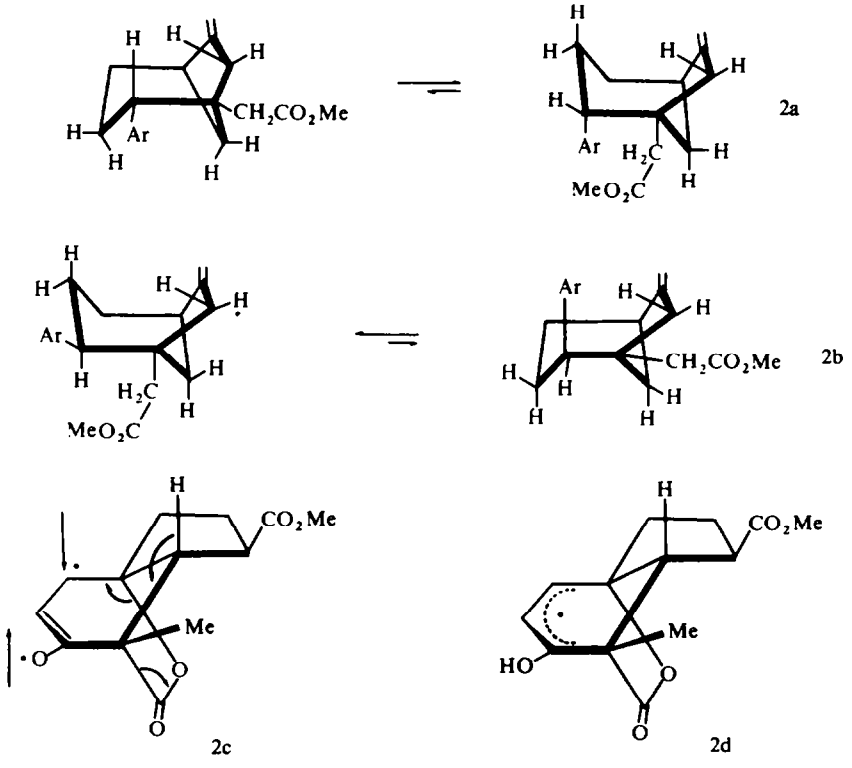


FIG 2.

In order to exclude the possibility (however small) that X is formed by direct hydrogenolysis of the C_5—C_6 bond in III. the latter was photolysed in benzyl alcohol under the same conditions as I. No change occurred, the purity of the recovered III being controlled by IR. NMR and mass spectra. Therefore, the formation of X proceeds without intermediacy of the tetracyclic phenol III.

The formation of III from I in t-BuOH or in benzene is not inhibitited by oxygen and hence may be supposed to take place via the singlet rather than triplet state. Since III possesses the same configuration at C_6 and C_9 as the starting ketone I the elimination of the lactone bridge may be conceived as a concerted process facilitated by the *trans*-diaxial arrangement of 5 β-H and the eliminated group (Fig 2c). Surprisingly, this mechanism does not take place when I is photolysed in benzyl alcohol. Here the primary reactive species must be a resonance-stabilized ketyl radical (Fig 2d), but the reason for the preferential cleavage of the C_5—C_6 bond is not understood.

The easy loss of the lactone bridge upon UV excitation of I must be due to the strong overlap between the σ-orbital of the C_{10}—O bond and the π-orbitals of the enone system. In the UV spectrum of I (in EtOH) this interaction is reflected by the position of the $n \rightarrow \pi^*$ band which displays a partly resolved vibrational structure with λ_{max}338 (ε 56), 354 (ε 54) and 370 (ε 36) nm. As noted.[12] the orthogonality of the lactone bridge with the plane of the C=C—C=O system greatly facilitates the elimination of the lactone group.

Finally, similar aromatization of ring A takes place upon photolysis of the epoxy ketone (II). When irradiated at 28–30° in dioxan, it gives a new phenolic substance, $C_{19}H_{22}O_5$ (XII). in 23% yield. In addition, about 35% of unreacted II can be recovered together with more polar products of higher molecular weight (~40%). One of these products was tentatively identified as a 1:1 adduct of II with dioxan by combined gas chromatography–mass spectrometry (M^+ 446).

The phenolic nature of XII is revealed by its UV and IR spectra (λ_{max} 290 nm. bathochromic shift in 0·1N NaOH; ν_{max} 1615 and 1520 cm^{-1}). The mass spectrum of XII is relatively simple and displays an abundant molecular peak at 330 mu. On treatment with diazomethane XII gives a dimethyl ether (XIIa), characterized by its UV. NMR and mass spectra. The NMR spectra of XII and XIIa show only one strongly shielded aromatic proton (δ = 6·33 or 6·24 ppm, respectively); in the case of XII the latter is quickly exchanged on standing with MeOD. The peak M—H_2O in the mass spectrum of XII is negligible while it is known to be abundant in the case of pyrocathechol type phenols.[13] Accordingly, compound XII is formulated as the tetracyclic resorcinol.

The photolysis of II in boiling dioxan affords resorcinol XII in nearly the same yield (26%) but in addition it gives in 18% yield a hydroxy ketone (XIII) which was found to be identical with the previously described[5] sample by its m.p., R_f, $[\alpha]_D$, IR and mass spectra. The axial orientation of the OH group at C_1 was confirmed by the NMR spectra of XIII at 60 and 100 MHz, where protons at C_1 and C_2 form an ABX-system with $(J_{AX} + J_{BX})$ = 7c/s (at both frequencies); the found splittings J_{AX} = 5c/s and J_{BX} = 2 cs exclude the axial position of the proton at C_1.

It appears that the photo-excited epoxy ketone (II) undergoes two mechanistically different transformations: (i) elimination of carbon dioxide and aromatization and (ii) abstraction of hydrogen from the solvent. Only the latter of these is temperature-dependent. Since many α, β-epoxy ketones are known to give β-dicarbonyl compounds

(with or without sceletal rearrangement) upon UV irradiation[14] the formation of resorcinol XII may proceed via the enolizable β-diketone (XIV) which rapidly delactonizes in a manner analogous to the formation of III from I.

When phenolic compounds III and XII were bioassayed on dwarf pea and lettuce seeds they showed no gibberellin-like or antigibberellinic activity.

EXPERIMENTAL

Unsaturated ketone I used in this work had m.p. 182–184° and $[\alpha]_D$ +46°. The corresponding epoxy ketone II had m.p. 182–185° and $[\alpha]_D$ +16°. It was free from the admixture of II (UV and mass spectra). Two high-pressure mercury lamps PRK-4 (220 watt each) placed horizontally at the bottom of the cylindrical reflector were used as the light source. Irradiations were carried out in flat-bottomed quartz vessels under dry argon, the temp of solns being kept at 28–30° by fan cooling. IR spectra: UR-10 instrument (Zeiss, Jena), in KBr pellets. UV spectra: Unicam SP 700 instrument, in EtOH. NMR spectra; Varian DA-60 or JEOL-100, in $CDCl_3$ if not stated otherwise. Mass spectra: MX-1303 instrument with all-glass inlet system (160–230°, 70 eV). Specific rotations: Hilger polarimeter, in acetone. ORD curves: Cary-60 instrument, in EtOH (*c*. 0·25). Silica gel KSK and neutral alumina (grade III/IV) were used as adsorbents.

Photolysis of enone I *in t-butanol*

Ketone I (500 mg) in abs t-BuOH (150 ml) was irradiated for 8 hr. The combined residue from two such operations (1·0 g, after vacuum evaporation at 45°) was chromatographed on silica gel (50 g). Elution with benzene–chloroform (3:7 and 2:8) gave III (370 mg) as a white solid foam, m.p. 105–115°. $[\alpha]_D^{19}$ +34°. IR spectrum: 3450, 1725, 1662, 1609, 1503, 830 cm^{-1}; UV spectrum: 229 (ε 5·890) and 291 (ε 2·070) nm; Mass spectrum: M^+ 314, *m/e* 255 (base peak), 240, 239, 226, 225, 211, 197, 185, 171 mu; NMR spectrum: δ 2·08 (3H, s); 3·63 (3H, s); 4·98 and 5·12 (2H, broad singlets); 6·59 and 6·74 (2H, AB-system, J_{AB} = 7c/s) ppm. (Found: C, 72·31; H, 7·21. $C_{19}H_{22}O_4$ requires: C, 72·59; H, 7·05%). More polar eluents afforded 450 mg of amorphous solid with strong lactonic IR absorption. Fractions eluted with chloroform–ethyl acetate (8:2) partly crystallized on standing and after washing with cold EtOAc gave needles (0·5 mg), m.p. 248–251°; Mass spectrum: *m/e* 686, 672 (M–CO_2, base peak) 654, 640, 626, 614, 613, 612, 594, 566, 539, 355, 341 and 332 mu.

Phenol III (80 mg) was treated with AcO–pyridine (20°, 25 hr). The volatile products were vacuum-evaporated, the residue dissolved in EtOAc and washed with dil HCl and water. Chromatography on silica gel (4 g) afforded IIIb (52 mg) as a chromatographically pure oil. $[\alpha]_D^{19}$ +45·4°; IR spectrum: 3460, 1760, 1731, 1662, 1220, 1197 cm^{-1}; UV spectrum: 270 (ε 616) and 278 (ε 610) nm; Mass spectrum: M^+ 356, *m/e* 314, 296 (base peak), 255, 254, 239, 211, 197, 185, 171 mu; NMR spectrum: δ 2·02 (3H, s); 2·25 (3H, s); 3·61 (3H, s); 4·98 and 5·06 (2H, broad singlets); 6·85 and 6·92 (AB-system, J_{AB} = 9 cs) ppm.

The treatment of III with diazomethane in ether (manyfold excess, 14 hr) followed by chromatography on silica gel gave IIIa in 50% yield as an oil. IR spectrum: 3440, 1732, 1662, 1615, 1488, 824 cm^{-1}; UV spectrum: 233 (ε 5·010) and 286 (ε 1·644) nm; Mass spectrum: M^+ 328, *m/e* 313, 299, 268 (base peak), 253, 251, 239, 225, 211, 199, 185 and 173 mu.

Photolysis of enone I *in benzene*

Ketone I (500 mg) in dry benzene (150 ml) was irradiated for 8 hr and the products were chromatographed on silica gel (25 g). Elution with benzene-chloroform 4:6 and 3:7) gave III (100 mg). This sample was identical in all respects (R_f, $[\alpha]_D$, IR, UV, NMR and mass spectra) with the previous specimen and gave the same acetate IIIb on acetylation. Less polar eluents (benzene–chloroform, 6:4) recovered 60 mg of the starting ketone I while chloroform-EtOAc mixtures afforded amorphous lactone-containing dimerization products (~600 mg).

Photolysis of I *in the presence of oxygen*

Soln of I (134 mg) in pure t-BuOH (40 ml) was saturated with O_2 and then photolysed for 8 hr in the slow stream of O_2-argon (1:39 v/v). Preparative plate chromatography on alumina (benzene–MeOH 9:1) afforded starting material (40 mg) and phenol III (46 mg) identified by their IR, UV and mass spectra. Two additional zones of unidentified products were also observed while the yield of "dimers" was somewhat lower (35 mg). Analogous result was obtained upon photolysis of I in oxygenized benzene.

Oxidative degradation of phenol III

Phenol III (182 mg) was dissolved in a mixture of pyridine (5 ml) and benzene (60 ml) and treated with OsO_4 (135 mg). After prolonged stirring (20–23°, 14 days) the dark soln was diluted with ether (140 ml) and saturated with H_2S, then filtered and evaporated to dryness. The residue (82 mg) upon plate chromatography on alumina (chloroform–MeOH 4:1, elution of the zone with R_f 0·35–0·50) afforded IV (16 mg), m.p. 195–202° (dec); IR spectrum: 3430–3220 (broad), 1722, 1610, 1500, 1170, 1100 cm^{-1}; UV spectrum: 289 nm (ε 1·710); Mass spectrum: M^+ 348, *m/e* 330, 312, 289, 273, 272 (base peak, presumably M-ring D-2H), 244, 228, 213, 185, 171 mu. Without further purification this triol (14 mg) was stirred with sodium bismuthate (20 mg) in AcOH (5 ml). Three more 20 mg portions of $NaBiO_3$ were added every 10 hr. After 40 hr at 20–23° the solvent was evaporated in vacuum and the residue suspended in 30 ml EtOAc. The filtered organic soln was shaken with Na_2CO_3 aq (4 × 5 ml), the carbonate layer was acidified to pH2 and re-extracted with EtOAc (4 × 15 ml). The acidic gum (8 mg) obtained after washing with water, drying and evaporation, was repeatedly treated with diazomethane in ether (20°, 15 hr). Plate chromatography on alumina (benzene–acetone 9:1, elution of the upper zone) afforded the desired V (5·1 mg) as a chromatographically pure oil; IR spectrum: 1730, 1705 (sh), 1610, 1495, 835 cm^{-1}; UV spectrum: 284 nm (ε 1·570); Mass spectrum: M^+ 360, *m/e* 318, 301, 300, 287, 286 (base peak, presumably McLaferty ion M-CH_3COOCH_3), 243, 185, 171 mu ORD: $[\alpha]_{460}$ +165°; $[\alpha]_{350}$ +430°; $[\alpha]_{340}$ +580°; $[\alpha]_{320}$ +1100°; $[\alpha]_{317}$ +1125°; $[\alpha]_{300}$ +575°; $[\alpha]_{290}$ +278°; $[\alpha]_{280}$ +165°; $[\alpha]_{270}$ +245°. Amplitude = +34·55°.

Photolysis of enone I *in benzyl alcohol*

A soln of I (500 mg) in freshly distilled benzyl alcohol (50 ml) was irradiated for 8 hr. The solvent was distilled in vacuum and the residue chromatographed on 25 g of silica gel. Elution with benzene–chloroform (2:8) afforded X (180 mg) as a chromatographically pure oil; IR spectrum: 3425, 1725, 1665, 1610, 1515, 830 cm^{-1}; UV spectrum: 227 (ε 5·950) and 282 (ε 1·720) nm; bathochromic shift to 300 nm (ε 2·200) in 0·1N NaOH; Mass spectrum: M^+ 316, *m/e* 298, 285, 254 (base peak) 243, 165, 164, 149, 148, 147, 141, 134, 121 mu. NMR spectrum: δ 2·20 (3H, s); 2·61 (2H, broad singlet); 2·94 (1H); 3·63 (3H, s); 4·90 and 5·04 (2H, broad singlets), 6·63; 6·90 and 6·94 (3H; AB-system with J_{AB} = 9 c/s, overlapping in the downfield half with the third signal) ppm. (Found: C, 72·43; H, 7·59. $C_{19}H_{24}O_4$ requires: C, 72·12; H, 7·65%). From earlier fractions (elution with benzene–chloroform 4:6 and 3:7) the previously described[10] XI (70 mg) was obtained as white solid foam; IR spectrum: 3460, 1778, 1720, 1662, 905 cm^{-1}; Mass spectrum: M^+ 360, *m/e* 342, 328 (base peak), 316, 304, 301, 284, 258, 214, 135 mu. The elution of the column with chloroform–EtOAc afforded only the lactone-containing dimers (or polymers) of I.

Phenol X (71 mg) was treated with Ac_2O and pyridine (20°, 24 hr) and the acetylation product after usual working up was chromatographed on 4 g of silica gel to give Xb (57 mg) as a chromatographically pure oil. $[\alpha]_D^{19}$ −34·7°; IR spectrum: 3460, 1760, 1735, 1662, 1510, 1225 cm^{-1}; UV spectrum: 259 (ε 515), 266 (ε 596) and 274 (ε 505) nm; Mass spectrum: M^+ 358, *m/e* 340, 326, 316, 298 (base peak), 285, 284, 254 225, 224, 267, 148 mu; NMR spectrum: δ 2·13 (3H, s); 2·32 (3H, s); 2·60 (2H, broad singlet); 2·93 (1H, diffuse quartet shown to be the downfield part of an ABC-system by INDOR-resonance; $J_{AC} + J_{BC}$ = 6·5 c/s), 3·66 (3H, c); 4·88 and 5·04 (2H, unresolved triplets with $J \approx 1·5$ cs); 6·72, 7·09 and 7·07 (3H, an AB-system with J_{AB} = 9 c/s overlapping with the third signal); somewhat better resolution of three last signals was obtained in hexafluorobenzene (δ 6·73; 7·05 and 7·09 ppm. J_{ortho} = 9 c/s $J_{meta} = J'_{meta} \approx 0·6$ c/s).

On treatment with excess of diazomethane followed by chromatography on silica gel, X afforded as an oil Xa in ~50% yield; IR spectrum: 3440, 1732, 1662, 1615, 1510, 825 cm^{-1}; UV spectrum: 228 (ε 7·700) and 278 (ε 1·540) nm; Mass spectrum: M^+ 330, *m/e* 299, 268 (base peak), 257, 239, 167, 162, 148, 135, 133 mu.

The photolysis of phenol III *in benzyl alcohol*

Phenol III (100 mg) was dissolved in the freshly distilled benzyl alcohol (30 ml) and irradiated for 8 hr. The photolysate was chromatographed on silica gel (5 g) to give 69 mg of starting material and 27 mg of unidentified more polar products. The purity of the recovered III from the admixture of tricyclic phenol X was proved by its IR and NMR spectra and by combined gas chromatography–mass spectrometry (LKB instrument; no peaks corresponding to the fragmentation of X).

The photolysis of epoxy ketone II *in dioxan*

(i) A soln of II (350 mg) in abs dioxan (105 ml) was irradiated for 8 hr and the products of photolysis were chromatographed on silica gel (15 g). Elution with chloroform afforded 124 mg (35%) of starting material with m.p. 179–184°. Elution with chloroform–EtOAc (8:2) gave XII (72 mg) as amorphous white solid, m.p.

105–110°; IR spectrum: 3420. 1730. 1665. 1615. 1520 and 900 cm^{-1}; UV spectrum: 290 nm (ε 2·580); batochromic shift to 305 nm in 0·1 N NaOH; Mass spectrum: M^+ 330. *m/e* 270 (base peak). 242. 214. 135 mu; NMR spectrum (in d_6-acetone): δ 1·96 (3H. s). 3·61 (3H. s). 4·92 and 5·15 (2H. broad singlets) and 6·33 (1H. s. disappears on equilibrium in MeOD) ppm. Elution with more polar mixtures gave the chromatographically unseparable lactone-containing products of high molecular weight.

On standing with etheral diazomethane (~10 fold excess) for 6 days at +10° resorcinol XII (50 mg) gave a mixture of methylation products. Chromatography on alumina afforded XIIa (32 mg) as a white solid foam; UV spectrum: 285 nm (ε 2·860); Mass spectrum: M^+ 358. *m/e* 340. 327. 298 (base peak). 270 and 135 mu; NMR spectrum: δ 1·92 (3H. s); 3·55 (3H. s); 3.68 (3H. s); 3·71 (3H. s); 4·85 and 5·06 (2H. broad singlets). and 6·26 (1H. s).

(ii) Epoxy ketone II (500 mg) in boiling abs dioxan (140 ml) was irradiated for 8 hr and the photolysate was chromatographed on 25 g silica gel. Elution with chloroform gave XIII (92 mg). m.p. 240–242°. identified with the previously described sample by its IR and mass spectra; NMR spectrum (in d_6-acetone. 100 MHz): δ 1·00 (3H. s); 2·50 (1H. B-part of the ABX-system. J_{AB} = 17. J_{BX} = 2 c/s); 2·88 (1H. A-part of the ABX-system. J_{AB} = 17. J_{AX} = 5 c/s); 2·77 and 3·41 (2H. AB-system. J_{AB} = 10 c/s); 3·62 (3H. s); 4.35 (1H. X-part of the ABX-system. J_{AX} = 5 c/s. J_{BX} = 2 c/s); 4·80 and 5·10 (2H. diffuse triplets. J = ? 5 c/s)ppm. Elution with chloroform–EtOAc (9:1) afforded XIII (144 mg) identical with the previous sample in all respects. More polar eluents gave only lactone-containing products of high molecular weight.

Addendum. For brevity reason the nomenclature names of compounds used or obtained in this work were omitted throughout the text. In agreement with a recent suggestion,[8] we propose the names 20-nor-10α. 13α-dihydroxy-1β.2β-epoxy-3-oxo-ent-gibberell-16-ene-7.19-dioic acid 19 → 10 lactone. methyl ester (II); 19.20-dinor-3. 13α-dihydroxy-ent-gibberell-1.3.5(10). 16-tetraen-7-oic acid. methyl ester (III) and 19.20-dinor-5.6-seco-3.13α-dihydroxy-ent-gibberell-1.3.5(10). 16-tetraen-7-oic acid. methyl ester (X) for the representatives of each structural type.

Acknowledgement—We are very grateful to Dr. V. Pavlov for ORD-measurements. to Dr. B. Rosynov for mass spectroscopic determinations and to Mr. E. Prokofiev and Mr. V. Korenevsky for the recording of NMR-spectra.

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