(IIf) ~130°, (IIc) ~ 120°, (IIk) ~ 150°. As a result, mercaptoalkyl esters with a five-membered ring are more resistant to thermal decomposition than compounds with a six- or seven-membered ring. A small amount of one of the mercaptoalkyl esters (IIk) with a five-membered ring could be obtained by vacuum-distillation.

EXPERIMENTAL

O-2-Mercaptoalkyl Esters of Cyclic Phosphorus Thioacids (IIa-m). A mixture of the phosphorus thioacid and a double excess of the alkylene oxide in ether solution was refluxed for 20-30 min. The volatile substances were removed at first at 10 torr, and then at 0.2 torr and ~ 25°, and analyzed immediately. The constants of compounds (IIa-m) are given in Table 1.

CONCLUSIONS

The S-2-hydroxyalkyl esters of cyclic P(V) thioacids, which were obtained by reacting a cyclic phosphorus monothioacid with an alkylene oxide, are converted to the 2-mercaptoalkyl esters of cyclic phosphorus acids independent of the size of the ring.

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TRANSFORMATIONS OF GIBBERELLIN A_3 DERIVATIVES IN PRESENCE OF PALLADIUM COMPOUNDS

É. P. Serebryakov

UDC 542.97:547.9

It is known that CH_2N_2 in the presence of $Pd(OAc)_2$ easily reacts with styrene [1] and α,β-enones [2, 3] to give cyclopropane derivatives. In the present paper, in order to obtain analogs of gibberellin A_3 (I) with a cyclopropane ring instead of a double bond, we studied the reaction of the known [4] p-methoxyphenacyl ester of gibberellin A_3 (II) with excess CH_2N_2 in the presence of catalytic amounts of $Pd(OAc)_2$ in THF solution (18-20°C, 2 h). Here, instead of the desired product (III), was formed a mixture of five compounds (IV)-(VIII), which were separated by preparative TLC, but not one of them corresponded to the cyclopropanation product.

The main product (yield 55-60%) proved to be ester (IV), which in its R_f value and PMR spectrum coincided with one of the minor products of the O-methylation of ester (II) [4]. The reduction of (IV) with Zn in glacial AcOH gave 3-O-methylgibberellin A_3 (IX), which was synthesized previously [4] in six steps from (I). The reaction of (II) with CH_2N_2 and $Pd(OAc)_2$ permits obtaining (IX) from (I) in three steps in better yield.

The next three products, isolated in respective yields of 2, 25, and 13%, were identified as being the known [4] dimethyl ester (V) and p-methoxyphenacyl esters (VI) and (VII), which belong to the isogibberellin A_3 (X) series. The structure of (VI) and (VII) was proved via their spectra and conversion to the corresponding acids (XI) and (X) by treatment with Zn in glacial AcOH. The PMR spectra of compounds (VI), (VII), and (XI), like the spectrum of (X) [5], contain the characteristic signals of an olefinic proton at C^1 (δ ~5.7 ppm, m) and an allylic proton at C^2 (δ ~ 4.7 ppm, triplet from a doublet of doublets, $J_{observed}$ ~6 Hz). The fifth reaction product (VIII), isolated in 2% yield, based on the IR spectral data, lacks a lactone grouping, but retains an exocyclic double bond and tertiary OH group (ν 1110 and 905 cm^{-1}). Its PMR spectrum has signals (δ, ppm) at 3.56 s (3H, methyl ester), at ~ 5.2 m (1H), and at 3.31 d (1H, J = 4.5 Hz), which must be assigned to the proton of the MeOCHCH grouping in the cyclopropane ring. The signals at 4.90 and 5.04 ppm (2H) confirm the retention of the exocyclic double bond. The mass spectrum of (VIII) (M^+ 464) corresponds to the loss of CO_2 and insertion of CH_2 into the (II) molecule. The treatment of (VIII) with Zn in glacial AcOH gives the monobasic acid (XII), which was additionally characterized as the methyl ester (XIIa), from whose mass spectra (M^+ 316 and M^+ 330) it follows that changes in the gibberellin portion of the molecule fail to occur when

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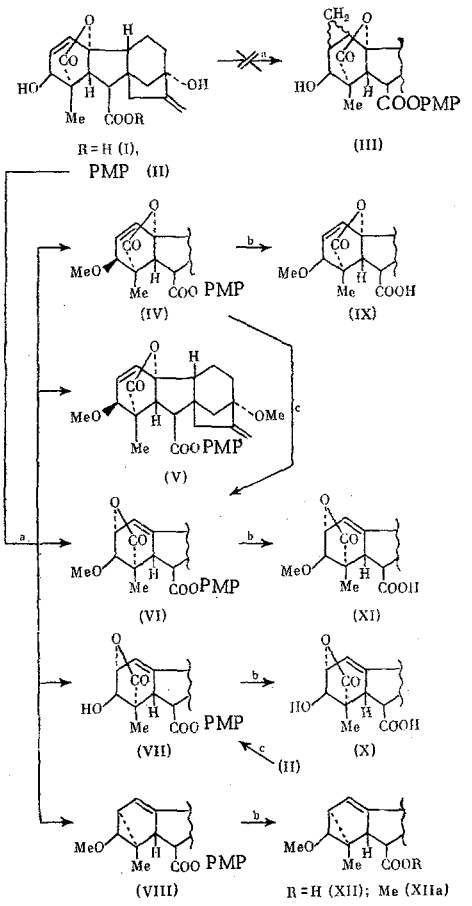
removing the p-methoxyphenacyl protection. Finally, the PMR spectra of (VIII) and its derivatives, (XII) and (XIIa), have, together with the signal of an olefinic proton at ~ 5.2 ppm, a signal at ~ 0.6 ppm m (1H). The presented data are in agreement with structure (VIII) (Scheme 1).

Scheme 1



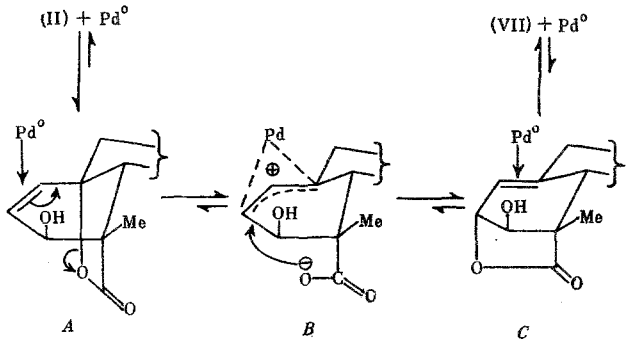
a) $CH_2N_2/Pd(OAc)_2$, b) Zn/AcOH, c) $Pd(PPh_3)_4$, PMP = p-$MeOC_6H_4COCH_2$.

When (VII) is treated with excess CH_2N_2 in the presence of $Pd(OAc)_2$, the hydroxyl at C^3 is not methylated even after long exposure. Evidently, only the allylic hydroxyl in the (II) molecule is methylated under these conditions. There is noticeable competition between this reaction and the isomerization of the double bond [(II) → (VII) and (IV) → (VI)], which is analogous to the known isomerization of (I) to (X) in weakly basic medium [6].

In the absence of CH_2N_2 the $Pd(OAc)_2$ does not cause the isomerization (II) → (VII) or (IV) → (VI) even after long exposure. Apparently, the isomerization catalyst here are traces of colloidal Pd, which is formed by the reduction of $Pd(OAc)_2$ with diazomethane. To verify this possibility we studied the effect of the complex $Pd(PPh_3)_4$ [7] on esters (II) and (IV) (18-20°, 15 min). It is proved that they are rapidly isomerized respectively to (VII) and (VI). This isomerization can be explained by a two-step mechanism, according to which the lactone fragment first plays the role of the leaving group (A → B), and then it again cyclizes at C^2 (B → C). A similar mechanism was proposed for the alkylation of allylic acetates by soft nucleophiles in the presence of Pd [8].

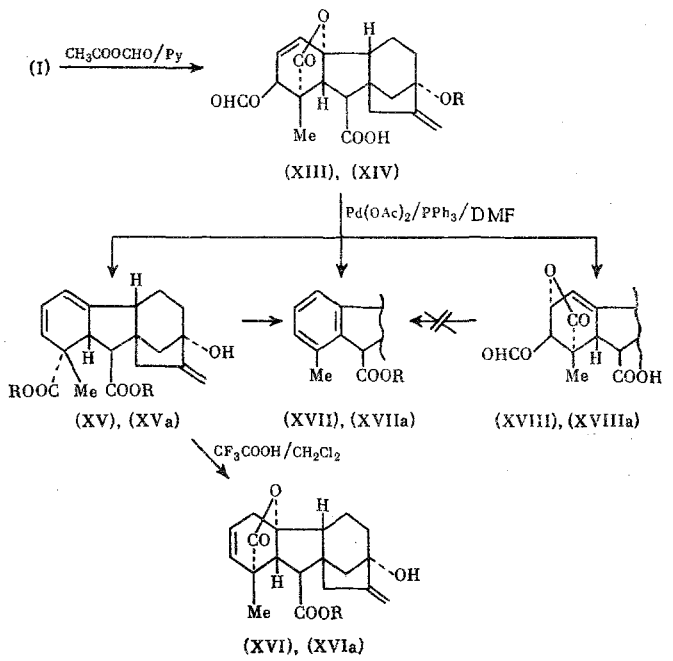
The formation of (VIII) can be explained as being another way of stabilizing the B system, which is related to the elimination of CO_2 and the formation of a bond between C^4 and C^2.

The selective methylation of the hydroxyl at C^3 and the isomerization of the double bond in ring A revealed that the Pd is coordinated preferentially at the Δ^1 bond. We decided to use this selectivity to remove the hydroxyl function at C^3 using Pd catalysis. It is known [9, 10] that aliphatic allyl formates when heated with $Pd(OAc)_2$ lose CO_2 and are converted to olefinic hydrocarbons; here the probability of allylic migration of the double bond depends on the structure of the starting allylic alcohol.



The 3-monoformate of gibberellin A_3 (XIII) was obtained by reacting (I) with acetic formic anhydride (85% yield); diformate (XIV) is formed as a by-product. CO_2 was evolved and three products were formed when (XIII) was heated with catalytic amounts of $Pd(OAc)_2$ and $P(C_6H_5)_3$ in DMF (reactant ratio = 20:1:15, 85-115°, 5 h, Ar). The main reaction product (46% yield) proved to be the previously unknown* (–) gibberella-1(10),2,16-trien-13α-ol-7,19-dioic acid (XV); the homoangular arrangement of the diene system in (XV) followed from the PMR spectrum of its dimethyl ester (XVa) and their UV spectra (λ_{max} 275.5 nm, ε 4000). In the PMR spectrum of diester (XVa) the protons at C^1 and C^2 have $J_{vic} \simeq 5.3$ Hz, the protons at C^2 and C^3 have $J_{cis} = 9.5$ Hz, and the protons at C^1 and C^3 have the long-range SSC constant $J_{1,5} = 2.0$ Hz. Chemical proof for the structure of (XV) was its conversion to gibberellin A_5 (XVI) in 46% yield by treatment with CF_3COOH in abs. CH_2Cl_2 (5:95 by volume, 0-5°, 72 h). The by-products of the reaction of (XIII) with $Pd(OAc)_2$ proved to be the known [12] epiallogibberoic acid (XVII) and the 3-monoformate of isogibberellin A_3 (XVIII), which were additionally characterized as the methyl esters (XVIIa) and (XVIIIa). The yield of (XVII) is nearly quantitative when diene (XV) is heated with $Pd(OAc)_2$ and $P(C_6H_5)_3$ in DMF under the above indicated conditions. The homoallylic formate (XVIII) remains unchanged under the same conditions. Apparently, only the allylic formates are capable of decarboxylation when treated with $Pd(OAc)_2$ (Scheme 2).

Scheme 2



R=H (XIII), (XV), (XVI), (XVII), (XVIII), Me (XVa), (XVIa), (XVIIa), (XVIIIa), CHO (XIV).

From the obtained data it can be seen that the transformations of gibberellin A_3 under the influence of Pd compounds proceed exclusively at ring A, which can be used for the regiospecific synthesis of modified

* Acid (XV) was recently detected by the GLC–MS method as being one of the catabolism products of the gibberellins in pea seeds [11].

gibberellins. The preparation of (XVI) from (XV) formally represents the final step of the three-step synthesis of gibberellin A_5 from gibberellin A_3(I) → (XIII) → (XV) → (XVI) in an overall yield of 18% (cf. [13, 14]).

EXPERIMENTAL

All of the melting points are corrected. Chemapol L silica gel (40-100 μ) was used for the chromatography. The preparative TLC was run on plates with a layer size of 28 × 20 × 0.15 cm (loose). The IR spectra were taken on a UR-10 instrument. The PMR spectra were taken on a Varian HA-100 instrument. The mass spectra were taken on a Varian MAT-CH-6 instrument, equipped with a one-piece glass admittance system, at 170-210°C. The UV spectra were taken on a Specord UV-VIS instrument. The spectral data for the obtained products are given in Tables 1 and 2.

Reaction of (II) with CH_2N_2 and $Pd(OAc)_2$. A solution of 1.976 g (4 mmoles) of (II) in 30 ml of abs. THF was added to 60 ml of distilled CH_2N_2 solution in abs. ether (~20 mmoles of CH_2N_2), cooled to 0-2°. Then a saturated solution of 45 mg of $Pd(OAc)_2$ in abs. ether was added to the mixture, allowed to warm up to ~ 20° (2 h), the excess CH_2N_2 was distilled off, the obtained precipitate (15 mg) was filtered, and the filtrate was evaporated to dryness. The residue (2.226 g) was dissolved in 36 ml of acetone and aliquot portions of the solution were chromatographed on 12 preparative plates in the system: 4:2:1 benzene–ether–MeCN. From the zones with R_f 0.68 we isolated 41 mg (2%) of dimethyl ester (V) with mp 155-157°, which was identified via the R_f and the IR, PMR, and mass spectral data by comparing with the known specimen [4]. From the zones with R_f 0.59 we isolated (VIII) as an amorphous powder with mp 125-134°. Yield 38 mg (2%) (reprecipitated from CH_2Cl_2 solution with hexane). From the zones with R_f 0.45 we isolated monomethyl ester (IV) as an amorphous powder with mp 95-103°. Yield 1.21 g (59.5%) (reprecipritated from ethyl acetate (EA) solution with hexane). From the zones with R_f 0.32 we isolated 506 mg (25%) of glassy ester (VI) with mp 98-105°. From the zones with R_f 0.17 we isolated 238 mg (12%) of the p-methoxyphenacyl ester of isogibberellin A_3 (VII) as an amorphous powder with mp 132-134°.

Removal of p-Methoxyphenacyl Protection (General Method). With vigorous stirring, to a solution of 0.1-0.5 mmole of the p-methoxyphenacyl ester in 10-25 ml of glacial AcOH was added 0.5 g of Zn dust, the mixture was stirred for 4 h at 18-22°, filtered, the precipitate was washed with EA, and the solution was combined with the filtrate and evaporated in vacuo (5 mm) at 40-45°. The residue was dissolved in EA, the solution was extracted with 5% Na_2CO_3 solution, and the soda extract was acidified to pH 3.0 and extracted with EA. After washing with water, drying over Na_2SO_4, and evaporation of the extract in vacuo, the obtained acid was purified either by recrystallization or by reprecipitation.

From (IV) we obtained (IX) in 70% yield, mp 227-229° (crystals from EA–hexane) (cf. [4]).

From (VI) we obtained (XI) in 70% yield, mp 109-112° (amorphous powder, reprecipitated from ether solution with hexane). Found: C 67.00; H 6.74%. $C_{20}H_{24}O_6$. Calculated: C 66.65; H 6.71%.

From (VII) we obtained isogibberellin A_3 (X) in 58% yield, mp 153-160° (reprecipitated from ether solution with hexane); cf. [12].

From (VIII) we obtained 19-noracid (XII) in 62% yield, mp 108-110° (amorphous powder, reprecipitated from ether solution with hexane). The treatment of (XII) with CH_2N_2 gave the liquid methyl ester (XIIa).

Isomerization of (II) and (IV). A. To a solution of 100 mg of (II) in 3 ml of abs. THF was added a solution of 5 mg of $Pd(OAc)_2$ in 2 ml of abs. ether. After 16 h an additional 5 mg of $Pd(OAc)_2$ was added and the solution was let stand for 24 h at 18-20°. Based on the TLC and PMR spectral data, (II) remained completely unchanged. A similar experiment with (IV) gave the same result.

B. To a solution of 200 mg of (II) in 10 ml of abs. THF under argon was added a saturated solution of 5 mg of $Pd(Ph_3)_4$ in abs. ether and the mixture was kept for 15 min at ~ 20°, evaporated, and the residue was chromatographed on a preparative plate in the system: 4:2:1 benzene–ether–MeCN. From the zones with R_f 0.25 we isolated 12 mg of the starting (II). From the zones with R_f 0.17, after repeated purification in the same system, we obtained 163 mg of (VII) as an amorphous powder with mp 131-134°.

The same experiment was run with 220 mg of (IV). From the zones with R_f 0.45 we isolated by preparative TLC 15 mg of (IV), and from the zones with R_f 0.32 we isolated 148 mg of the iso ester (VI) with mp 98-106° (foam).

3-O-Formylgibberellin A_3 (XIII). To a solution of 6.92 g (20 mmoles) of (I) in 25 ml of abs. pyridine at 0-2° was added in 10 min 10 ml of acetic formic anhydride [15] and after 24 h the mixture was poured on a

TABLE 1. PMR Spectra of Obtained Compounds

Compound	δ, ppm										
	C^{18}	C^{9}	C^{5}	C^{3}	C^{17}	C^{3}	C^{1}	O^{3}	ArOMe	OCH_2CO	Ar
(IV) *	1,25 s (3H)	2,73 d (1H)	3,23 d (1H)	3,57 d (1H)	4,87 (1H) 5,12 (1H)	5,92 d. d (1H)	6,26 d (1H)	3,37 s (3H)	3,78 s (3H)	5,25 s (2H)	6,86 (2H) 7,72 (2H)
(VI) *	1,32 s (3H)	2,67 d (1H)	3,10 m (1H)	3,58 d (1H)	4,89 (1H) 5,04 (1H)	4,70 t (1H)	5,67 m (1H)	3,37 s (3H)	3,78 s (3H)	5,24 s (2H)	6,88 (2H) 7,76 (2H)
(VII)†	1,24 s (3H)	2,67 d (1H)	3,25 m (1H)	4,19 d (1H)	4,90 (1H) 5,04 (1H)	4,63 t (1H)	5,72 m (1H)	–	3,80 s (3H)	5,25 s (2H)	6,90 (2H) 7,76 (2H)
(VIII) *	1,31 s (3H)	2,60 ‡ d (1H)	3,02 m (1H)	3,31 d (1H)	4,90 (1H) 5,04 (1H)	0,63 m (1H)	5,21 *m (1H)	3,56 s (3H)	3,79 s (3H)	5,24 ‡ (2H)	6,86 (2H) 7,78 (2H)
(XI) †	1,27 s (3H)	2,67 d (1H)	3,25 m (1H)	3,56 d (1H)	4,88 (1H) 5,04 (1H)	4,63 t (1H)	5,67 m (1H)	3,41 s (3H)	–	–	–
(XII) *	1,26 s (3H)	2,60 ‡ d (1H)	3,02 m (1H)	3,31 d (1H)	4,91 (1H) 5,06 (1H)	0,60 m (1H)	5,21 m (1H)	3,56 s (3H)	–	–	–
(XIIa) *	1,27 s (3H)	2,55 ‡ (1H)	3,05 m (1H)	3,35 m (1H)	4,91 (1H) 5,05 (1H)	0,63 m (1H)	5,19 m (1H)	3,55 s (3H)	3,65 s (3H, 7-COOMe)		
(XIII)†	1,15 s (3H)	2,71 d (1H)	3,23 d (1H)	5,35 d (1H)	4,85 (1H) 5,19 (1H)	5,87 d. d (1H)	6,57 d (1H)	8,22 s (1H)	–	–	–
(XIV) †	1,14 s (3H)	2,79 d (1H)	3,25 d (1H)	5,35 d (1H)	5,01 (1H) 5,17 (1H)	5,87 d. d (1H)	6,57 d (1H)	8,22 s (1H)	8,02 s (1H, 13-OCHO)		
(XVa) *	1,26 s (3H)	2,61 d (1H)	2,85 m (1H)	5,30 d. d (1H)	4,87 (1H) 5,00 (1H)	5,98 d. d (1H)	5,54 m (1H)	–	5,54 s (3H, 19-COOMe) 3,61 s (3H, 7-COOMe)		
(XVIIa)*	2,17 s (3H)	3,37 s (1H)	–	m (1H) ‡	4,95 (1H) 5,09 (1H)	6,85–7,15 m (3H) ‡		–	2,64 t (1H, 9β-H) 3,57 s (3H, 7-COOMe)		
(XVIII)†	1,16 s (3H)	2,55 d (1H)	3,17 m (1H)	5,32 d (1H)	4,97 (1H) 5,15 (1H)	4,84 t (1H)	5,81 m (1H)	8,18 s (1H)	–	–	–

* In deuterochloroform.

† In d_6-acetone.

‡ Partial overlapping with adjacent signals.

TABLE 2. Infrared and Mass Spectra of Gibberellin A_3 Derivatives

Compound	ν, cm^{-1}	m/e	
		M+	ions
(IV) *	3590, 3060, 1770, 1740, 1695, 1600, 1175, 1100, 895	508 w	490, 476, 448, 432 w, 135 main
(VI) *	3490, 3080, 1768, 1735, 1690, 1600, 1180, 1120, 980, 900	508 w	490, 477, 432, 359 w, 135 main
(VII) *	3450, 3080, 1770 (sh), 1740, 1695, 1605, 1120, 985, 910	494 w	476, 432, 328, 297 w-m, 135 main
(VIII) *	3530, 3050, 1735, 1690, 1605, 1110, 930, 905	464 w	418 w, 135 main
(XI) *	3430, 3270, 3080, 1765, 1705, 1665, 1100, 960, 905	360 m	239 main
(XII) †	3610, 3060, 1705, 1665, 1190, 1110, 965, 905	316 m	284, 239main136
(XIIa)†	3600, 3060, 1740, 1665, 1190, 960, 905	330 m	298, 264, 239main 136
(XIII) *	3515, 3200–3100, 1770, 1735, 1720, 1660, 1160, 895	–	–
(XIV) *	3200, 3090, 3010, 1755, 1745, 1720, 1660, 1195, 1155, 905	–	–
(XV) *	3350–3200, 3075, 3040. 3025, 1705–1690, 1665 (sh), 1610, 905	330(0,53)	315(0,35), 312(0,40), 297(0,25), 284(0,80), 269(0,90), 251(0,38), 239(1,00)
(XVa) †	3610, 3085, 3040, 3015, 1725, 1715 (sh), 1165, 1605, 895	358(0,94)	343(0,29), 326(0,13), 298(0,25), 293(0,75), 239(1,00)
(XVIIIa) *	3480, 3080, 1765, 1740, 1665, 1190, 1100, 965, 905	388 w	370, 342, 329, 324, 298, 239

* IR spectrum as KBr pellets.

† IR spectrum in $CHCl_3$ solution.

mixture of 300 ml of ice and 300 ml of conc. HCl. The obtained precipitate was filtered, washed with water, dried in the air, and chromatographed on a column packed with 200 g of silica gel. Elution with a 75:25 benzene–EA mixture gave 1.05 g (13%) of diformate (XIV) with mp 193-196° (crystals from CH_2Cl_2–hexane). Elution with benzene–EA mixtures (55:45 and 50:50) gave 6.353 g (85%) of 3-monoformate (XIII) with mp 238-242° (crystals from EA–cyclohexane). Found: C 64.23; H 6.07%. $C_{20}H_{22}O_7$. Calculated: C 64.13; H 5.93%.

Dienedicarboxylic Acid (XV). Into a flask fitted with a sparger and a reflux condenser, connected to a scrubber containing $Ba(OH)_2$ solution, was charged a solution of 1.496 g (4 mmoles) of (XIII), 45 mg (0.2 mmole) of $Pd(OAc)_2$, and 786 mg (3 mmoles) of PPh_3 in 20 ml of abs. DMF. The mixture was heated rapidly in an argon stream until the CO_2 evolution began (85-90°), and then the temperature was gradually raised to 115° in 5 h until the CO_2 evolution ceased. The dark reaction mixture was poured on 300 ml of cracked ice, the obtained precipitate was filtered, and the filtrate was acidified to pH 2.5 and extracted with EA (6 ×75 ml). The extract was washed well with water to remove the DMF, dried over Na_2SO_4, evaporated, and the residue (1.1 g) was chromatographed on a column packed with 50 g of silica gel. Elution with $CHCl_3$–EA mixtures (85:15 and 80:20) gave 26 mg (2.3%) of epiallogibberoic acid (XVII) with mp 252-254° (crystals from CH_2Cl_2–hexane) (cf. [12], mp 244-245°). Mass spectrum: M^+ 284. The methyl ester (XVIIa) was obtained as an amorphous powder and was characterized via the spectra (see Tables 1 and 2). Ultraviolet spectrum (λ_{max}, nm, alcohol): 259, 265, and 274 (ε 240, 290, and 230). Elution with a 75:25 $CHCl_3$–EA mixture gave 151 mg (10.3%) of isogibberellin A_3 formate (XVIII) with mp 92-98° (amorphous powder, reprecipitated from EA solution with hexane); the methyl ester (XVIIIa) was obtained as a colorless solid foam with mp 76-79°. Elution with $CHCl_3$–EA mixtures (65:35 and 60:40) gave 608 mg (46%) of crystalline dicarboxylic acid (XV) with mp 189-191° (decompn.) (from CH_2Cl_2–acetone–hexane). Found: C 69.16; H 6.93%. $C_{19}H_{22}O_5$. Calculated: C 69.08; H 6.72%. Ultraviolet spectrum (λ_{max}, nm (alcohol)): 275.5(ε 3960). The treatment of (XV) with CH_2N_2 gave the dimethyl ester (XVa) as a colorless oil; λ_{max}, nm (alcohol): 276 (ε 4050).

Gibberellin A_5 (XVI). To a solution of 200 mg of (XV) in 40 ml of abs. CH_2Cl_2 was added a solution of 2.5 ml of CF_3COOH in 7.5 ml of abs. CH_2Cl_2, the mixture was left standing in the refrigerator at 0-5° for 3 days, the volatile products were vacuum-distilled, and the residue was chromatographed on a preparative plate covered with silica gel in the system: 92:8 $CHCl_3$–MeOH. From the zones with R_f 0.60 we isolated 92 mg (46%) of pure gibberellin A_5 (XVI) with mp 260-263° (from ether), $[\alpha]_D^{23}$ – 69.8° (C 0.8, alcohol) (cf. [13]; mp 260-261°, $[\alpha]_D$ – 77°). Infrared spectrum (KBr, ν, cm^{-1}): 3440, 1765, 1730, 1660, 1625, 895 and 700. The treatment of (XVI) with CH_2N_2 gave the methyl ester (XVIa) with mp 189-192° (from ether), which, when

analyzed by GLC on a one-piece glass capillary packed with 0.15% SE-30 (210°, N_2 flow rate 30 ml/min) coincided in its retention time with that of an authentic specimen (cf. [13]: mp 191-193°). From the zones with R_f 0.14 we isolated 89 mg (44.5%) of the starting (XV).

CONCLUSIONS

1. The regiospecific methylation of the allylic hydroxyl and isomerization of the double bond in ring A occur when the p-methoxyphenacyl ester of gibberellin A_3 is reacted with CH_2N_2 in the presence of $Pd(OAc)_2$.

2. Isomerization of the double bond in ring A is catalyzed by Pd^0.

3. The elimination of CO_2 from the 3-monoformate of gibberellin A_3, catalyzed by $Pd(OAc)_2$, leads to the formation of the gibberella-1(10), 2-diene system. This reaction was used to synthesize gibberellin A_5.

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