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Total Synthesis of 13β-Allylgonanes. III[1]

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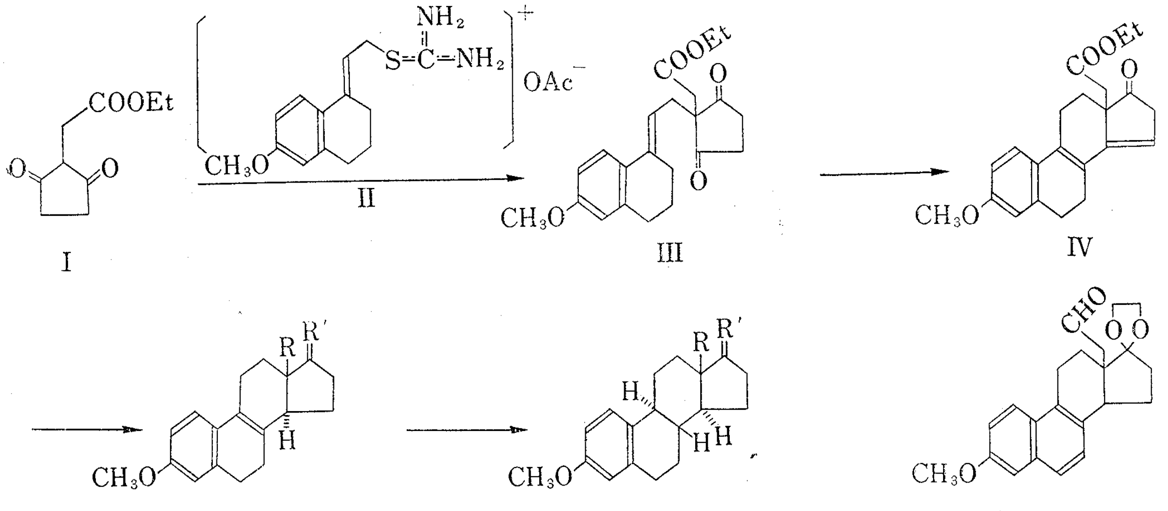
The improved method for synthesizing gonanes having the allyl group at C-13 was examined. Potassium salt of 2-ethoxycarbonylmethylcyclopentane-1,3-dione (I) was choosen as a starting material and the ethoxycarbonylmethyl group was converted into the allyl group after the steroid skeleton was formed.

We report here an improved synthesis of 13β-allylgonanes including *dl*-17α-ethynyl-17β-hydroxy-13β-allylgon-4-en-3-one.[3] Because the angular allyl group is susceptible to reducing agents, we tried to introduce it as late as possible.

Condensation of the potassium salt of 2-ethoxycarbonylmethylcyclopentane-1,3-dione (I)[4] with the isothiuronium salt (II)[5] in methanol gave 3-methoxy-13β-ethoxycarbonylmethyl-8,14-secogona-1,3,5(10),9-tetraene-14,17-dione (III) in 28% yield, calculated on the basis of I.

Cyclization of III with hydrogen chloride in ethanol gave *dl*-3-methoxy-13β-ethoxycarbonylmethylgona-1,3,5(10),8,14-pentaen-17-one (IV) in 56% yield, λ_{max} nm (ε): 313 (27000).



I II III IV XII

V : $R=CH_2COOEt, R'=O$

VI : $R=CH_2COOEt, R'=<^{O}_{O}]$

VII : $R=CH_2CH_2OH, R'=<^{O}_{O}]$

VIII : $R=CH_2CH_2OH, R'=<^{O}_{O}]$

IX : $R=CH_2CHO, R'=<^{O}_{O}]$

X : $R=CH_2CH=CH_2, R'=<^{O}_{O}]$

XI : $R=CH_2CH=CH_2, R'=O$

Chart 1

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[1] Part II: K. Yoshioka, G. Goto, K. Hiraga, and T. Miki, *Chem. Pharm. Bull.* (Tokyo), **21**, 2202 (1973).

[2] Location: *Juso-Nishino-cho, Higashiyodogawa-ku, Osaka.*

[3] Part I: K. Yoshioka, T. Asako, G. Goto, K. Hiraga, and T. Miki, *Chem. Pharm. Bull.* (Tokyo), **21**, 2195 (1973).

[4] S. Seto, H. Sugiyama, S. Takenaka, and H. Watanabe, *J. Chem. Soc.*, **1969**, 1625.

[5] C.H. Kuo, D. Taule, and N.L. Wendler, *Angew. Chem.*, **77**, 1142 (1965).

Partial hydrogenation of IV over Raney nickel catalyst in dioxane at atmospheric pressure gave the gonatetraen-17-one (V) in 41% yield, λ_{max} nm (ε): 280 (16000). V was changed to the acetal (VI) with ethylene glycol and *p*-toluenesulfonic acid in benzene in 60% yield. Reduction of VI with lithium aluminum hydride in ether at room temperature gave the 13-(2′-hydroxyethyl) compound (VII) in 97% yield.

Attempts to convert the primary alcohol of VII into aldehyde by oxidation with chromium trioxide–pyridine complex and with pyridine–sulfur trioxide complex in dimethyl sulfoxide,[6] yielded only the 6,7-dehydroaldehyde (XII), ν_{max} cm^{-1}: 1710, λ_{max} nm (ε): 231 (58000), 267, 277 (5350), 288, 322, 337.

Reduction of VII with potassium in liq. ammonia and tetrahydrofuran gave the 13-(2′-hydroxyethyl)-gonatriene (VIII) in 74% yield, λ_{max} nm (ε): 278 (2000), 286 (1800).

Oxidation of VIII with chromium trioxide–pyridine complex at 5° gave the aldehyde (IX) in 67% yield, ν_{max} cm^{-1}: 1700. IX was subjected to a Wittig reaction with triphenylphosphonium methylide in dimethyl sulfoxide,[7] followed by acid treatment to give the 13β-allylgonane (XI) in 91% yield, mp 117—118°. The compound thus obtained was identical in all respects with a sample obtained previously.[3] The total yield of XI from the secodione (III) by the present method was about 6%.

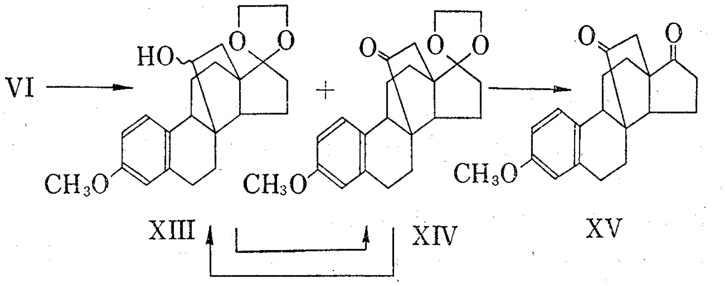

Chart 2

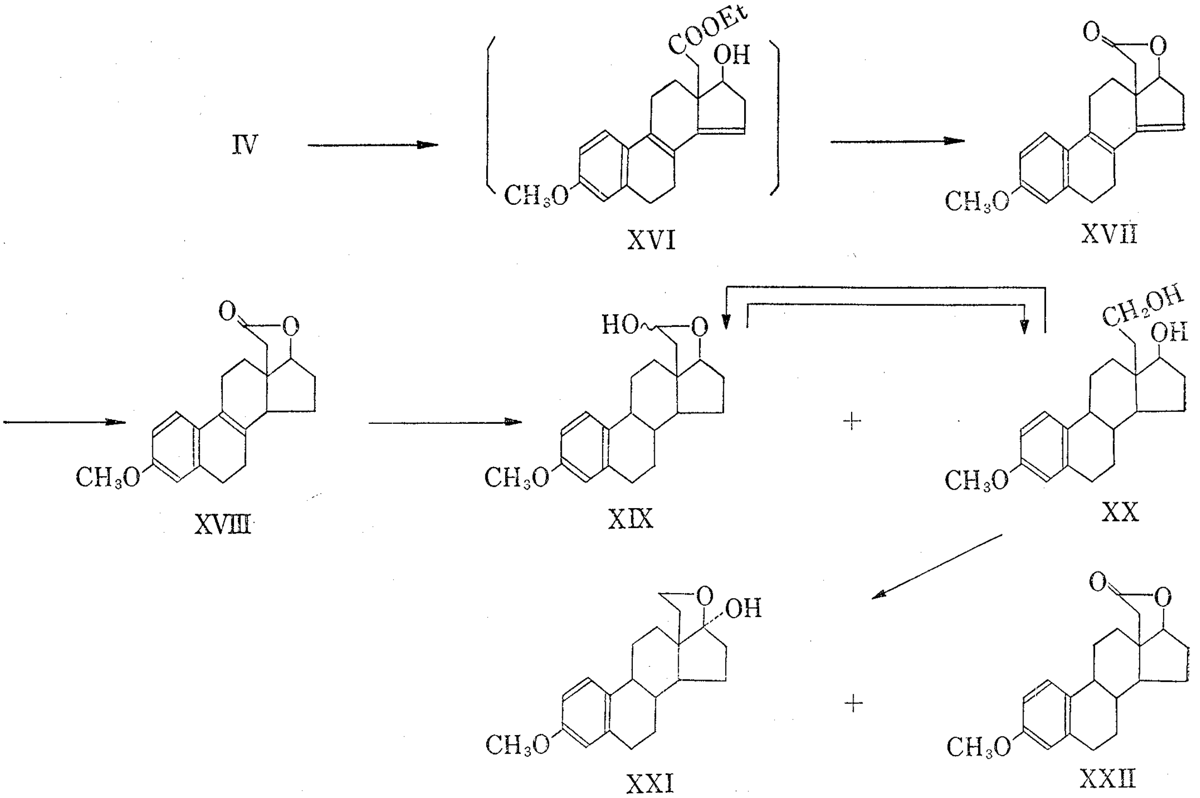

Chart 3

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[6] J.R. Parikh and W. von E. Doering, *J. Am. Chem. Soc.*, **89**, 5506 (1967).

[7] M. Hanack and H.M. Ensslin, *Ann.* **713**, 49 (1968).

Some anomalous observations in this series of reactions are described below. In an attempt to prepare VIII, VI was treated with potassium in liq. ammonia and tetrahydrofuran prior to reduction of the ester at C-18, to give a mixture of XIII and XIV. Oxidation of XIII with chromium trioxide–pyridine complex gave XIV, which was reduced with lithium aluminum hydride to regenerate XIII. Deacetalization of XIV with acid yielded the 17,2′-diketone (XV). The configuration of the hydrogen at C-9 was assumed to be a thermodynamically more stable α. The mechanism of this anomalous cyclization seems analogous to the reaction reported by Stork, *et al.*,8) namely an anion generated at C-8 reacted with the ester at the side chain prior to protonation.

As stated above, the yield of the selectively hydrogenated compound (V) from IV could not be raised above 41% when this procedure was employed. It seems to us that the reason for this relatively low yield might lie in the instability of IV. Attempts to prepare the 17β-hydroxy compound (XVI) by treatment of IV with sodium borohydride in tetrahydrofuran and methanol gave only the 2′→17β lactone (XVII) in 64% yield, ν_{max} cm^{-1}: 1760.

We examined the possibility of preparing the 13β-allylgonanes using XVII as an intermediate. Partial hydrogenation of XVII in the presence of Raney nickel in dioxane gave the gonatetraene lactone (XVIII) in 81% yield. This lactone was treated with potassium in liq. ammonia to give a mixture of the 17β,2′-diol (XX) and the 17β,2′-hemiacetal (XIX). XIX was smoothly reduced by lithium aluminum hydride to XX. Attempts to oxidize the primary hydroxy group of XX selectively by treatment with pyridine–sulfur trioxide complex in dimethyl sulfoxide,6) gave only XIX and treatment with chromium trioxide–pyridine complex yielded a mixture of the 2′→17β lactone (XXII) and the hemiacetal (XXI). Since the steric requirements of the partially oxidized compound apparently caused formation of a lactone or a hemiacetal, these approaches to formation of an allyl group at C-13 by a Wittig reaction were not investigated further.

Experimental

3-Methoxy-13-ethoxycarbonylmethyl-8,14-secogona-1,3,5(10),9-tetraene-14,17-dione (III)——A solution of K salt of I4) (20.7 g) in MeOH (200 ml) was refluxed with the isothiuronium salt5) (II) (30.0 g) for 1 hr. The reaction mixture was poured into H_2O and extracted with ether. The ether layer was washed with H_2O, dried and evaporated. The resulting yellow oil (20 g) was chromatographed on silica gel (500 g). Elution with benzene–ether (10: 1) gave a slightly yellow oil. Yield 12.0 g (28%). IR ν_{max}^{liq} cm^{-1}: 1720 (C=O), 1200 (ester). NMR ($CDCl_3$) δ: 1.18 (3H, triplet, J=6 Hz, $CH_2\underline{CH}_3$), 3.74 (3H, singlet, OCH_3), 4.00 (2H, quartet, J=6 Hz, $O\underline{CH}_2CH_3$), 5.64 (1H, quartet, J=8 Hz, –CH=C), 6.5—7.4 (3H, multiplet, arom. H). Mass Spectrum $C_{22}H_{26}O_5$ (370.43) *m/e*: 370 (M^+). UV λ_{max}^{EtOH} nm (ε): 267 (15700).

***dl*-3-Methoxy-13β-ethoxycarbonylmethylgona-1,3,5(10),8,14-pentaen-17-one (IV)**——A solution of III (10.0 g) in 10% EtOH–HCl (150 ml) was refluxed for 5 min. The reaction mixture was poured into H_2O and extracted with ether. The organic layer was washed successively with aq. $NaHCO_3$ and H_2O, then dried and evaporated. The residual oil (9.5 g) was chromatographed on silica gel (200 g). Elution with benzene–ether (10: 1) gave a colorless oil. Yield 5.3 g (55.7%). IR ν_{max}^{liq} cm^{-1}: 1720—1740 (C=O), 1250 (ester). NMR ($CDCl_3$) δ: 1.20 (3H, triplet, J=7 Hz, $CH_2\underline{CH}_3$), 3.80 (3H, singlet, OCH_3), 4.06 (2H, quartet, J=7 Hz, $-O\underline{CH}_2CH_3$), 5.95 (1H, triplet, J=2 Hz, C_{15}-H), 6.65—7.30 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 313 (27000).

***dl*-3-Methoxy-13β-ethoxycarbonylmethylgona-1,3,5(10),8-tetraen-17-one (V)**——A mixture of IV (5.3 g) and Raney–Ni (15 g, wet) in dioxane (300 ml) was shaken under a stream of hydrogen at atmospheric pressure. After absorption of *ca.* 350 ml of hydrogen, the catalyst was filtered off. The filtrate was concentrated under reduced pressure to give crude crystals. Yield 2.2 g (41.2%). Recrystallization from ether gave colorless scales, mp 112—114°. *Anal.* Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.62; H, 7.12. IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O), 1240 (ester). NMR ($CDCl_3$) δ: 1.21 (3H, triplet, J=7 Hz, $CH_2\underline{CH}_3$), 3.78 (3H, singlet, OCH_3), 4.08 (2H, quartet, J=7 Hz), $O\underline{CH}_2CH_3$, 6.64—7.20 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 280 (16000).

***dl*-17,17-Ethylenedioxy-3-methoxy-13β-ethoxycarbonylmethylgona-1,3,5(10),8-tetraene (VI)**——A mixture of V (4.8 g), ethyleneglycol (20 ml) and *p*-TsOH (250 ml) in benzene (300 ml) was refluxed for 20 hr,

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8) G. Stork, P. Rosen, N. Goldman, R.V. Coombs, and J. Tsuji, *J. Am. Chem. Soc.*, **87**, 275 (1965).

with H_2O being removed by a water separator. After cooling, H_2O was added to the mixture. The benzene layer which separated was washed with H_2O, then dried and evaporated to give crystals. Yield 3.2 g (59.0%). Recrystallization from ether gave colorless columns, mp 138—141°. *Anal.* Calcd. for $C_{24}H_{30}O_5$: C, 72.33; H, 7.59. Found: C, 72.28; H, 7.60. IR ν_{max}^{KBr} cm^{-1}: 1735 (C=O), 1140 (ester). NMR ($CDCl_3$) δ: 1.11 (3H, triplet, $J=6$ Hz, $CH_2\underline{CH_3}$), 3.75 (3H, singlet, OCH_3), 3.90 (4H, broad singlet, $-OCH_2CH_2O-$), 4.02 (2H, quartet, $J=6$ Hz, $O\underline{CH_2}CH_3$), 6.60—7.20 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 280 (15500).

***dl*-17,17-Ethylenedioxy-3-methoxy-13*β*-(2′-hydroxyethyl)gona-1,3,5(10),8-tetraene (VII)**——To a solution of VI (3.0 g) in ether (200 ml), $LiAlH_4$ (1.0 g) was added and the mixture was stirred at room temperature for 30 min. After removal of excess $LiAlH_4$ with AcOEt, the mixture was poured into H_2O and the ether layer which separated was washed with H_2O and dried. Evaporation of ether gave crystals. Yield 2.6 g (97.0%). Recrystallization from ether gave colorless columns, mp 135—137°. *Anal.* Calcd. for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.28; H, 7.90. IR ν_{max}^{KBr} cm^{-1}: 3500 (OH). UV λ_{max}^{EtOH} nm (ε): 272 (15000).

***dl*-17,17-Ethylenedioxy-3-methoxy-13*β*-(2′-hydroxyethyl)gona-1,3,5(10)-triene (VIII)**——To a solution of VII (1.2 g) in tetrahydrofuran (150 ml) and liq. NH_3 (300 ml), K (2.4 g) was added portionwise at $-50°$ and the mixture was stirred for 30 min. After addition of NH_4Cl (1.0 g) NH_3 was allowed to evaporate and the residue was partitioned between H_2O and ether. The ether layer was washed with H_2O and dried. The solvent was evaporated to give a colorless oil. Yield 0.9 g (74.3%). IR ν_{max}^{liq} cm^{-1}: 3400 (OH). UV λ_{max}^{EtOH} nm (ε): 278 (2000), 286 (1800). Mass Spectrum *m/e*: 356 (M^+), 311 ($M^+-CH_2CH_2OH$).

***dl*-17,17-Ethylenedioxy-3-methoxy-13*β*-(2′-oxoethyl)gona-1,3,5(10)-triene (IX)**——A solution of XIII (900 mg) in pyridine (10 ml) was added to CrO_3–pyridine complex, which had been prepared under ice-cooling from 900 mg of CrO_3 and 9 ml of pyridine. The reaction mixture was allowed to stand at 5° for 12 hr then was poured into H_2O and extracted with ether. The ether layer was washed with H_2O, dried and evaporated to give crystals. Yield 600 mg (67.0%). Recrystallization from ether gave colorless columns, mp 137—139°. *Anal.* Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.37; H, 7.31. IR ν_{max}^{KBr} cm^{-1}: 1710 (CHO). NMR ($CDCl_3$) δ: 3.76 (3H, singlet, OCH_3), 3.92 (4H, broad singlet, $-OCH_2CH_2O-$), 6.5—7.3 (3H, multiplet, arom. H), 9.93 (1H, triplet, $J=2$ Hz, CHO). UV λ_{max}^{EtOH} nm (ε): 278 (2000), 286 (1800).

***dl*-17,17-Ethylenedioxy-3-methoxy-13*β*-allylgona-1,3,5(10)triene (X)**——A mixture of IX (500 mg), methyltriphenylphosphonium bromide (1.12 g) and *t*-BuOK (336 mg) in DMSO (10 ml) was stirred under N_2 gas at room temperature for 10 hr. The reaction mixture was poured into H_2O and extracted with ether. The ether layer was washed with H_2O, dried and evaporated. The resulting residue was purified by preparative thin-layer chromatography (TLC) (Kieselgel GF_{254}, Merk, benzene 10: AcOEt 1) to give crystals. Yield 450 mg (90.5%). Recrystallization from ether gave plates, mp 94—97°. *Anal.* Calcd. for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.16; H, 7.38. IR ν_{max}^{KBr} cm^{-1}: 3060, 1630, 900 (allyl). NMR ($CDCl_3$) δ: 3.74 (4H, singlet, $-OCH_2CH_2O-$), 3.90 (3H, singlet, OCH_3), 4.80—5.20 (2H, multiplet, $CH_2=C$), 5.70—6.35 (1H, multiplet, $C=CH$), 6.52—7.33 (3H, multiplet, arom. H).

***dl*-3-Methoxy-13*β*-allylgona-1,3,5(10)-trien-17-one (XI)**——XI (400 mg) in tetrahydrofuran (20 ml) and MeOH (20 ml) was treated with conc. HCl (0.5 ml) at room temperature for 1 hr. The reaction mixture was poured into H_2O and extracted with ether. The ether layer was washed with aqueous $NaHCO_3$ solution and H_2O, then dried and evaporated to give crystals. Yield 350 mg (100%). Recrystallization from ether–*n*-hexane gave needles, mp 117—118°. *Anal.* Calcd. for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.55; H, 8.56. IR ν_{max}^{KBr} cm^{-1}: 1725 (C=O), 3080, 1630, 860 (allyl). NMR ($CDCl_3$) δ: 3.73 (3H, singlet, OCH_3), 4.85—5.10 (2H, multiplet, $C=CH_2$), 5.40—5.80 (1H, multiplet, $CH=C$), 6.6—7.2 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 278 (2000), 286 (1850). Mass Spectrum *m/e*: 310 (M^+). This compound was identical with a sample prepared previously.[3)]

***dl*-17,17-Ethylenedioxy-3-methoxy-13*β*-(2′-oxoethyl)gona-1,3,5(10),6,8-pentaene (XII)**——A solution of VIII (250 mg) in pyridine (2.5 ml) was added to CrO_3–pyridine complex (prepared from 250 mg of CrO_3 and 2.5 ml of pyridine) under ice-cooling. The reaction mixture was allowed to stand at room temperature for 2 days, then was poured into H_2O and extracted with ether. The ether layer was washed, dried and evaporated. The residue was purified by preparative TLC (benzene 10: AcOEt 1). Yield 62 mg. Recrystallization from ether gave colorless crystals, mp 184—188°. *Anal.* Calcd. for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86. Found: C, 74.96; H, 6.89. IR ν_{max}^{KBr} cm^{-1}: 1710 (CHO). NMR ($CDCl_3$) δ: 3.88 (3H, singlet, OCH_3), 3.95 (4H, multiplet, $-OCH_2CH_2O-$), 6.5—7.9 (5H, multiplet, arom. H). 9.94 (1H, triplet, $J=3$ Hz, CHO). UV λ_{max}^{EtOH} nm (ε): 231 (58000), 267, 277 (5350), 288, 322, 337. Mass Spectrum *m/e*: 352 (M^+), 308 (M^+-CH_2CHO).

Reduction of VI with K and liq. NH_3——VI (750 mg) was reduced with K (1.5 g) and liq. NH_3 (150 ml) in tetrahydrofuran (70 ml) as described above for the preparation of VIII. Two products (XIII, 280 mg; XIV, 200 mg) were separated by TLC (benzene 2: AcOEt 1).

XIII: Needles, mp 144—147° (from ether). *Anal.* Calcd. for $C_{22}H_{24}O_4$: C, 74.13; H, 7.92. Found: C, 74.60; H, 7.91. IR ν_{max}^{KBr} cm^{-1}: 3500 (OH). NMR ($CDCl_3$) δ: 3.72 (3H, singlet, OCH_3), 3.87 (4H, multiplet, $-OCH_2CH_2O-$), 4.20—4.45 (1H, multiplet, CH-OH), 6.55—7.25 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm: 279, 287.

XIV: Columns, mp 140—141° (from ether). *Anal.* Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.58; H, 7.54. IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O). NMR ($CDCl_3$) δ: 3.74 (3H, singlet, OCH_3), 3.90 (3H, multiplet,

-OCH_2CH_2O-), 6.6—7.1 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 276 (1800), 281 (1650). Mass Spectrum *m/e*: 354 (M^+).

Oxidation of XIII with CrO_3-Pyridine Complex——XIII (100 mg) was oxidized with CrO_3-pyridine complex as described above for the preparation of XII. XIV was obtained (56 mg).

Reduction of XIV with $LiAlH_4$——A suspension of XIV (14 mg) and $LiAlH_4$ (10 mg) in ether (10 ml) was refluxed for 2 hr. The product showed the same *Rf* value (0.80) as XIII in TLC (benzene 5: AcOEt 1).

Preparation of XV——A solution of XIV (65 mg) in $CHCl_3$ (5 ml), acetone (5 ml) and conc. HCl (0.1 ml) was refluxed for 1 hr. The reaction mixture was poured into H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried and evaporated to give crystals (35 mg). mp 190—193° (from MeOH). *Anal.* Calcd. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 76.02; H, 7.06. IR ν_{max}^{KBr} cm^{-1}: 1720 (C=O). NMR ($CDCl_3$) δ: 3.75 (3H, singlet, OCH_3), 6.7—7.1 (3H, multiplet, arom. H).

***dl*-17β-Hydroxy-3-methoxygona-1,3,5(10),8,14-pentaenyl-13β-acetic Acid Lactone (XVII)**——To a solution of IV (2.5 g) in tetrahydrofuran (50 ml) and MeOH (50 ml), $NaBH_4$ was added portionwise with stirring under ice-cooling. The reaction mixture was poured into H_2O and extracted with ether. The ether layer was washed with H_2O, dried and evaporated to give crystals. Yield 1.4 g (64%), columns (from ether), mp 160—163°. *Anal.* Calcd. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.94; H, 6.62. IR ν_{max}^{KBr} cm^{-1}: 1760 (5-membered ring lactone). NMR ($CDCl_3$) δ: 3.80 (3H, singlet, OCH_3), 4.90 (1H, double doublet, J=5 Hz, C_{17}-H), 5.51 (1H, triplet, J=3 Hz, C_{15}-H), 6.63—7.35 (3H, multiplet, arom. H). UV λ_{max}^{EtOH}nm (ε): 310 (27000).

***dl*-17β-Hydroxy-3-methoxygona-1,3,5(10),8-tetraenyl-13β-acetic Acid Lactone (XVIII)**——XVII (1.1 g) was partially hydrogenated with Raney Ni (wet 5.5 g) in dioxane (100 ml) in the same manner as the preparation of V. Yield 900 mg, pale yellow crystals (from AcOEt-ether), mp 157-159°. *Anal.* Calcd. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.27; H, 6.65. IR ν_{max}^{EtOH} cm^{-1}: 1760 (5-membered ring lactone). NMR ($CDCl_3$) δ:3.76 (3H, singlet, OCH_3), 4.63 (1H, double doublet, J=3 Hz, C_{17}-H), 6.60—7.20 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 279 (14300).

Reduction of XVIII with K and Liq. NH_3——XVIII (800 mg) was reduced with K (1.7 g) and liq. NH_3 (100 ml) in tetrahydrofuran (50 ml) as described above for the preparation of VIII. Two products, XIX (310 mg) and XX (315 mg) were separated by preparative TLC (benzene 2: AcOEt 1).

XIX: Columns, mp 140—150° (from ether). IR ν_{max}^{liq} cm^{-1}: 3400 (OH). UV λ_{max}^{EtOH} nm: 280, 289. NMR ($CDCl_3$) δ: 3.72 (3H, singlet, OCH_3), 4.40 (1H, broad singlet, -CH_2-O), 5.53 (1H, broad singlet, -OCH-O), 6.5—7.2 (3H, multiplet, arom. H).

XX: Needles, mp 231—233° (from $CHCl_3$-MeOH). *Anal.* Calcd. for $C_{20}H_{28}O_3$: C, 75.91; H, 8.92. Found: C, 76.19; H, 8.76. IR ν_{max}^{KBr} cm^{-1}: 3100—3300 (OH). NMR ($CDCl_3$) δ: 3.66 (3H, singlet, OCH_3), 3.55 (3H, multiplet, CH_2OH and C_{17}-H), 6.5—7.2 (3H, multiplet, arom. H). UV λ_{max}^{EtOH} nm (ε): 279 (1930), 287 (1830). Mass Spectrum (316.42) *m/e*: 316 (M^+), 298 (M^+-H_2O).

Oxidation of XX——1) Oxidation with CrO_3-Pyridine Complex: XX (100 mg) was oxidized with CrO_3-pyridine complex as described above for the preparation of XII. Two products were separated by preparative TLC (benzene 2: AcOEt 1).

XXI: Yield 15 mg, columns, mp 137—140°. IR ν_{max}^{KBr} cm^{-1}: 3320, 1100 (OH). Mass Spectrum $C_{20}H_{26}O_3$ (314.41) *m/e*: 314 (M^+), 296 (M^+-H_2O).

XXII: Yield 12 mg, needles, mp 160—165°. IR ν_{max}^{KBr} cm^{-1}: 1760 (5-membered ring lactone). Mass Spectrum $C_{20}H_{24}O_3$ (312.39) *m/e*: 312 (M^+), 284 (M^+-CO).

2) Oxidation with SO_3-Pyridine Complex in DMSO: A mixture of XX (75 mg), SO_3-pyridine complex (100 mg), DMSO (8 ml) and triethylamine (200 mg) was stirred at room temperature for 1 hr. The reaction mixture was poured into H_2O and extracted with ether. The ether layer was washed with H_2O, dried and evaporated to give crystals (35 mg), which had IR and NMR spectra and mixed melting point identical with those of XIX described above.

Reduction of XIX with $LiAlH_4$: A suspension of XIX (50 mg) and $LiAlH_4$ (20 mg) in dry ether (5 ml) was refluxed for 3 hr. The reaction mixture was poured into H_2O, and the ether layer was separated and washed with H_2O, then dried. Evaporation of the solvent gave crystals (28 mg), which had IR spectrum, *Rf* value (TLC) and mixed melting point identical with those of XX.

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