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139. Zen-ichi Horii, Toyoshi Katagi, Yasumitsu Tamura, and Teiji Tanaka : Synthetic Studies on Sorigenins. I. Syntheses of γ-Lactones of 1-Methoxy-3-hydroxymethyl-2-naphthoic Acid and 3-Hydroxymethyl-4-methoxy-2-naphthoic Acid.

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α- and β-Sorigenin are aglycons of α- and β-sorinin, which were isolated from the bark of *Rhamnus japonica* MAXIM. by Z. Nikuni[1] in 1938. H. Schmid, Z. Nikuni and coworkers[2] assigned the structural formulae 3-hydroxymethyl-6-methoxy-1,8-dihydroxy-2-naphthoic acid γ-lactone (I, R-OCH_3) and 3-hydroxymethyl-1,8-dihydroxy-2-naphthoic acid γ-lactone (I, R=H) to α- and β-sorigenin, respectively, but their syntheses have not yet been accomplished. So the syntheses of α- and β-sorigenin were undertaken to verify and support their structural formulae as assigned by them. The present report describes the preparations of 1-hydroxy-3-hydroxymethyl-2-naphthoic acid γ-lactone (VII) and its methyl ether (VIII) carried out as an exploratory experiment.

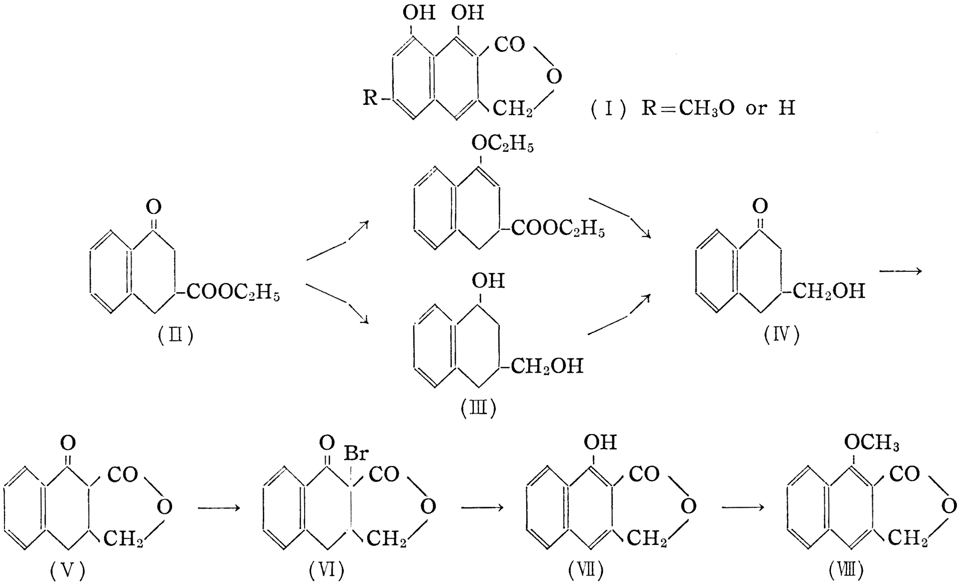

Chart 1.

[*1] Toneyama, Toyonaka-shi, Osaka (堀井善一, 加多木豊之, 田村恭光, 田中悌二).
1) Z. Nikuni : J. Agr. Chem. Soc. Japan, **14**, 352 (1938).
2) R.G. Haber, Z. Nikuni, H. Schmid, K. Yagi : Helv. Chim. Acta, **39**, 1654 (1956).

The compound (VII) and (VIII) were successively synthesized through 3-hydroxymethyl-3,4-dihydro-1(2*H*)-naphthalenone (IV) as shown in Chart 1. Finding, however, that the intermediates for syntheses of sorigenins, corresponding to (IV), can not be prepared by this method, the partial reductions of 1-methoxy-2,3-naphthalenedicarboxylic acid derivatives were investigated to explore an alternative route to (VIII). Thus, it was found that reduction of 1-methoxy-2,3-naphthalenedicarboxylic anhydride (XIV) with zinc and conc. hydrochloric acid and reduction of the halfester (XXI), prepared by alcoholysis of (XIV), with lithium aluminium hydride gave a mixture of (VIII) and its isomer, 3-hydroxymethyl-4-methoxy-2-naphthoic acid γ-lactone (XV), while reduction of halfesters, (XVIII) and (XX), prepared by alkaline partial hydrolysis of diethyl 1-hydroxy-2,3-naphthalenedicarboxylate (XI) and diethyl 1-methoxy-2,3-naphthalenedicarboxylate (XII), with lithium aluminium hydride gave only (XV).

Compound (IV) was prepared by reduction of the enol ether of ethyl 4-oxo-1,2,3,4-tetrahydro-2-naphthoate (II) with lithium aluminium hydride according to the method of van Tamelen,[3] or by manganese dioxide oxidation[4] of 1-hydroxy-1,2,3,4-tetrahydro-3-naphthalenemethanol (III) which was obtained by reduction of (II) with lithium aluminium hydride. Compound (IV) was subjected to ester condensation with diethyl carbonate in the presence of sodium hydride. The reaction product was simultaneously lactonized to provide 1-oxo-3-hydroxymethyl-1,2,3,4-tetrahydro-2-naphthoic acid γ-lactone (V) in 79% yield. Bromination with bromine in chloroform followed by dehydrobromination with 2,4,6-collidine converted (V) to (VII) (43%), which gave (VIII) by the action of diazomethane.

Compound (XI) was prepared starting from (II). Condensation of (II) with diethyl carbonate in the presence of sodium hydride gave the diester (IX) (60%), which was converted to (XI) by bromination and subsequent dehydrobromination in 95% over all yield. Methylation of (XI) with methyl iodide and potassium carbonate in acetone yielded (XII) (80%), which was hydrolyzed with an ethanolic potassium hydroxide solution to 1-methoxy-2,3-naphthalenedicaboxylic acid (XIII) in 59% yield. Treatment of the dicarboxylic acid (XIII) with acetyl chloride gave the corresponding anhydride (XIV) in 60% yield. When (XIV) was reduced with zinc and conc. hydrochloric acid in a mixture of glacial acetic acid and dioxane, and the crude product was chromatographed on an alumina column, two lactones of m.p. 138° and 168° were isolated. Both lactones were transformed to the same compound, 1-methoxy-2,3-naphthalenedimethanol (XVI) on lithium aluminium hydride reduction. The lactone of m.p. 138° was identified with a sample of (VIII) prepared by the method indicated in Chart 1. It follows, therefore, that the lactone of m.p. 168° would be 3-hydroxymethyl-4-methoxy-2-naphthoic acid γ-lactone (XV).

The halfester (XVIII) was prepared in 50% yield by hydrolysis of (XI) with a 50% aqueous ethanolic potassium hydroxide solution at room temperature. A previous attempt to hydrolyze (XI) with an anhydrous ethanolic potassium hydroxide (two equivalent moles) solution or the same solution containing a few drops of water resulted in the formation of 4-hydroxy-2-naphthoic acid (XVII) at boiling temperature, or the recovery of the diester (XI) at reaction temperature below 50°. Reduction of the halfester (XVIII) with lithium aluminium hydride in a mixture of ether and tetrahydrofuran at $-5\sim0^\circ$ gave an unpurifiable lactone, which was treated with diazomethane to give the lactone of m.p. 168°. This lactone was identical with a sample of (XV), one of the reduction products of (XIV) with zinc and conc. hydrochloric acid, by a mixed melting point determination and comparison of their infrared spectra. Reduction of the halfester (XX), prepared by partial hydrolysis of (XII) with an ethanolic potassium hydroxide (one equi-

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[3] E.E. van Tamelen, J. McNary, F.A. Lornitzo : J. Am. Chem. Soc., **79**, 1231 (1959).

[4] D.L. Turner : *Ibid.*, **76**, 5175 (1954); W.J. Gensler, F. Johnson, A.D.B. Sloan : *Ibid.*, **82**, 6074 (1960).

valent mole) solution containing a few drops of water in 89% yield, with lithium aluminium hydride also afforded the lactone (XV), while the same reduction of the halfester (XXI), prepared by boiling (XIV) with ethanol in 97% yield, gave both lactones of (XV) and (VIII) after chromatography on alumina column. From the behavior of lithium aluminium hydride towards the halfesters, it would be concluded[5] that the halfester (XX) and (XVIII) are 3-ethoxycarbonyl-4-methoxy-2-naphthoic acid and 3-ethoxycarbonyl-4-hydroxy-2-naphthoic acid, respectively, and (XXI), having a fairly broad range of melting point, is consisted of (XX) and 1-methoxy-3-ethoxycarbonyl-2-naphthoic acid.

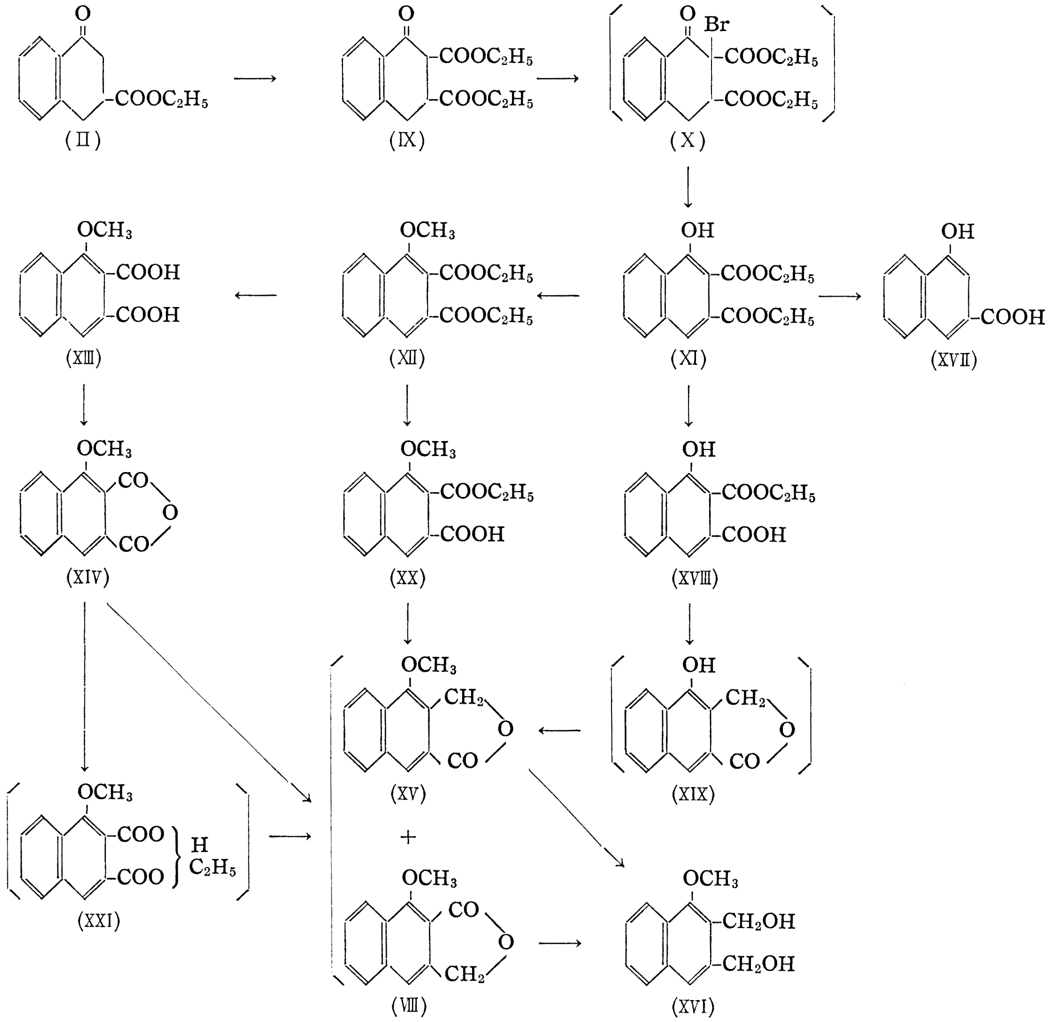

Chart 2.

Experimental

1-Hydroxy-1,2,3,4-tetrahydro-3-naphthalenemethanol (III)——To a solution of 1 g. of ethyl 4-oxo-1,2,3,4-tetrahydro-2-naphthoate (II) in anhyd. Et_2O was added a suspension of 0.2 g. of $LiAlH_4$ in anhyd. Et_2O at room temperature during a period of 45 min. Water was added cautiously to decompose excess of $LiAlH_4$ followed by addition of 10% H_2SO_4. The whole mixture was extracted

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5) E. E. Eliel, A. W. Burgstahler, D. E. Rivard, L. Haefele : J. Am. Chem. Soc., **77**, 5092 (1955).

with Et_2O and the Et_2O solution was washed with water and dried over Na_2SO_4. Evaporation of Et_2O gave 0.62 g. of colorless crystals of m.p. 109~112°, which was raised to 114~115° by recrystallization from EtOH. *Anal.* Calcd. for $C_{11}H_{13}O_2$: C, 74.13; H, 7.92. Found : C, 74.34; H, 7.86.

3-Hydroxymethyl-3,4-dihydro-1(2*H*)-naphthalenone (IV)——i) Prepared by the method of van Tamelen.[3]

ii) A mixture of 104 mg. of (III), 1 g. of MnO_2 and 10 cc. of anhyd. benzene was refluxed under stirring for 1.5 hr. The reaction mixture was filtered and MnO_2 filtrated was well washed with benzene. The filtrate and washing were combined and the solvents were evaporated to give 60 mg. of the crude (IV). The 2,4-dinitrophenylhydrazone showed m.p. 240°(decomp.), which was identical with that of the authentic sample prepared above in i) and was not depressed on admixture with it.

1-Oxo-3-hydroxymethyl-1,2,3,4-tetrahydro-2-naphthoic Acid γ-Lactone (V)——To a suspension of 0.3 g. of NaH in 20 cc. of anhyd. benzene was added slowly a solution of 1 g. of (IV) in 20 cc. of anhyd. benzene and the mixture was stirred for 20 min. Then, a solution of 2 g. of freshly distilled diethyl carbonate in 20 cc. of anhyd. benzene was added dropwise. After the addition was completed, the reaction mixture was refluxed for further 4 hr. and then cooled in an ice-water bath followed by the addition of EtOH to destroy excess of NaH. To this reaction mixture was added 10% HCl and the benzene layer separated was extracted with 5% NaOH. The alkaline solution was acidified with 10% HCl under ice-cooling and the precipitated crude (V) was washed with water to give 0.9 g. (79%) of pale brown crystals, m.p. 124~126°. An analytical sample (m.p. 129°) was obtained by recrystallization from EtOH or benzene. *Anal.* Calcd. for $C_{12}H_{10}O_3$: C, 71.29; H, 4.99. Found : C, 71.11; H, 5.23. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 1776, 1674.

When the reaction was carried out by refluxing in toluene solution, lower yields of (V) were obtained.

1-Oxo-2-bromo-3-hydroxymethyl-1,2,3,4-tetrahydro-2-naphthoic Acid γ-Lactone (VI)——A solution of 390 mg. of Br_2 in 5 cc. of $CHCl_3$ was added dropwise to a cold solution of 500 mg. of (V) in 10 cc. of $CHCl_3$ and was stirred for 2 hr. The reaction mixture was washed successively with water, saturated $NaHCO_3$ solution, $NaHSO_3$ solution and water, dried and evaporated. The oily residue was crystallized from Et_2O and then iso-PrOH to yield 515 mg. (74%) of the bromide (VI), m.p. 114~116°. An analytical sample (m.p. 116°) was prepared by several recrystallizations from iso-PrOH. *Anal.* Calcd. for $C_{12}H_9O_3Br$: C, 51.27; H, 3.23. Found : C, 51.48: H, 3.12.

1-Hydroxy-3-hydroxymethyl-2-naphthoic Acid γ-Lactone (VII)——A solution of 510 mg. of (VI) in 5 g. of 2,4,6-collidine was heated at 150° for 1 hr. The reaction mixture was taken up in AcOEt and the whole solution was washed successively with 10% HCl, water, saturated Na_2CO_3 solution and water. The AcOEt solution was dried over Na_2SO_4 and concentrated to give 330 mg. of the residue, which was purified by chromatography on alumina using benzene as eluent. The material eluted with benzene (210 mg. 57.3%) was recrystallized from EtOH to needles of the pure lactone (VII), m.p. 225~226°. *Anal.* Calcd. for $C_{12}H_8O_3$: C, 71.99: H, 4.03. Found : C, 72.11; H, 4,07. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 3388, 1724.

1-Methoxy-3-hydroxymethyl-2-naphthoic Acid γ-Lactone (VIII)——Excess of CH_2N_2 was passed through an ice-cooled suspension of 20 mg. of (VII) in Et_2O and the reaction mixture was allowed to stand in an ice-box for 4 days. Glacial AcOH was added to destroy an excess of CH_2N_2 and the reaction mixture was washed with water, saturated $NaHCO_3$ solution and then water, and dried over Na_2SO_4. The solvent was removed and the residue was recrystallized from benzene-petr. benzin giving colorless needles of m.p. 138°. *Anal.* Calcd. for $C_{13}H_{10}O_3$: C, 72.82; H, 4.71. Found : C, 73.22; H, 4.65. IR $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} : 1757.

Diethyl 1-Hydroxy-2,3-naphthalenedicarboxylate (XI)——A mixture of 37.5 g. of diethyl carbonate, 100 cc. of anhyd. benzene, 8.4 g. of NaH and 29.5 g. of (II) was heated under reflux for 3.5 hr. The reaction mixture was poured into ice-HCl and extracted with AcOEt. The AcOEt extract was washed with water, saturated $NaHCO_3$ solution and water successively, and dried over Na_2SO_4. After removing the solvent, the residue was distilled under reduced pressure, giving 24 g. (61%) of diethyl 1-oxo-1,2,3,4-tetrahydro-2,3-naphthalenedicaboxylate (IX) as slightly yellow viscous oil, b.p$_{0.2}$ 160°. IR $\nu_{\max}^{\text{oil}}$ cm^{-1} : 1730, 1686. With alcoholic $FeCl_3$ solution this compound gave a purple color. To a solution of 2 g. of (IX) in 30 cc. of $CHCl_3$ was added dropwise a solution of 1.62 g of Br_2 in 10 cc. of $CHCl_3$. Stirring was continued at room temperature for 1 hr. after the addition of Br_2. The reaction mixture was washed with water, saturated $NaHCO_3$ solution and then water, and dried over Na_2SO_4. Evaporation of $CHCl_3$ left 2.5 g. of the crude oily (X).

This crude (X) was heated with 10 g. of 2,4,6-collidine on a boiling water bath for 2 hr. After cooling, AcOEt and water were added to the reaction mixture. The AcOEt layer separated was washed with water, dil. HCl and then water and dried over Na_2SO_4. The solvent was removed and the residue was distilled under reduced pressure giving 1.9 g. (95%) of (XI), b.p$_{0.05}$ 163~164°. With alcoholic $FeCl_3$ solution this compound gave a blue color. *Anal.* Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found : C, 66.94; H, 5.60. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 3378, 1724, 1658.

Diethyl 1-Methoxy-2,3-naphthalenedicarboxylate (XII)——A mixture of 1.9 g. of (XI), 10 g. of MeI, 5 g, of anhyd. K_2CO_3 and 50 cc. of anhyd. Me_2CO was refluxed for 50 hr. A 0.5 cc. portion of MeI was added every 10 hr. during this period. After evaporation of Me_2CO, the residue was dissolved in water and extracted with benzene. The benzene extract was washed with 5% NaOH and water, dried over Na_2SO_4 and evaporated. The residue was distilled under reduced pressure, giving 1.5 g. (80%) of (XII), b.p$_{0.13}$ 164~166°. *Anal.* Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found : C, 67.89; H, 6.21. IR $\nu_{\max}^{\text{oil}}$ cm^{-1} : 1724.

1-Methoxy-2,3-naphthalenedicarboxylic Acid (XIII)——A solution of 350 mg. of (XII), and 230 mg. of KOH in 20 cc. of EtOH containing a few drops of water was heated under reflux for 10 hr. The reaction mixture was concentrated to dryness under reduced pressure. The residue was dissolved in water and washed with AcOEt. The aqueous solution was acidified with dil. HCl and extracted with AcOEt. The AcOEt extract was again extracted with saturated $NaHCO_3$ solution and the alkaline solution was acidified with dil. HCl followed by extraction with AcOEt. The extract was washed with water and dried. After removal of the solvent 176 mg. of solid was obtained. Recrystallization from AcOEt- petr. benzin gave 170 mg. (59%) of crystals, m.p. 197°. *Anal.* Calcd. for $C_{13}H_{10}O_5 \cdot \frac{1}{2}H_2O$: C, 61.17; H, 4.34. Found : C, 61.22; H, 4.40. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 2632, 1686.

1-Methoxy-2,3-naphthalenedicarboxylic Anhydride (XIV)——A suspension of 1 g. of (XIII) in AcCl was heated under reflux for 1.5 hr. Removing AcCl by distillation and recrystallization of the residue from benzene gave 550 mg. (60%) of colorless needles or plates, m.p. 197°. *Anal.* Calcd. for $C_{13}H_8O_4$: C, 68.42; H, 3.53. Found : C, 68.52; H, 3.55. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 1825, 1776.

Reduction of the Anhydride (XIV)——To a stirred mixture of 0.55 g. of (XIV), 5.5 cc. of dioxane, 1.8 g. of AcOH and 1.8 g. of conc. HCl, 0.9 g. of Zn dust was added in small portions. After the addition of Zn dust was completed, the mixture was heated on a boiling water bath for 11 hr. After removing the solvent under reduced pressure, the residual oil was taken up in AcOEt. The AcOEt solution was washed successively with water, saturated $NaHCO_3$ solution and water, and dried over Na_2SO_4. After evaporation of the solvent, the residue (390 mg.) was chromatographed through Al_2O_3 column using benzene-petr. benzin (10 : 2) as eluent giving two fractions. 1) From the first fraction, colorless needles of m.p. 138° were obtained on recrystallization from benzene-petr. benzin. This compound was shown to be identical with an authentic sample of 1-methoxy-3-hydroxymethyl-2-naphthoic acid γ-lacone (VIII) by mixed melting point and comparison of their infrared spectra. *Anal.* Calcd. for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found : C, 72.83; H, 4.72. IR $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} : 1757. 2) From the second fraction, colorless needles of 3-hydroxy-4-methoxy-2-naphthoic acid γ-lactone (XV), m.p. 168° were obtained on recrystallization from benzene-petr. benzin. *Anal.* Calcd. for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found : C, 72.75; H, 4.69. IR : $\nu_{\max}^{\text{CHCl}_3}$ 1757 cm^{-1}.

Alcoholysis of 1-Methoxy-2,3-naphthalenedicarboxylic Anhydride (XIV)——A suspension of 500 mg. of (XIV) in 20 cc. of absolute EtOH was heated under reflux for 20 hr. After evaporation of EtOH, the residue was dissolved in saturated $NaHCO_3$ solution and washed with AcOEt. The alkaline solution was acidified with dil. HCl, the deposited crystals were collected and washed. One recrystallization from benzene gave melting point of 137~167°. Further recrystallizations from the same solvent failed to give a sharp melting point. Yield was 570 mg. (97%). IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 1724 (shoulder), 1704. This material was used without further purification.

Reduction of (XXI) with $LiAlH_4$——A solution of 555 mg. of (XXI) in 20 cc. of anhyd. tetrahydrofuran was reduced using a suspension of 555 mg. of $LiAlH_4$ in 35 cc. of anhyd. Et_2O by the same procedure as described below for the preparation of (XV) from (XX). The crude product (370 mg.) was subjected to chromatography using Al_2O_3 and benzene-petr. benzin (10:3) as eluent giving two kinds of colorless needles, m.p. 168° and m.p. 138°. The former was assigned to (XV) and the latter to (VIII) by direct comparison with corresponding samples obtained by the reduction of (XIV).

3-Ethoxycarbonyl-4-methoxy-2-naphthoic Acid (XX)——A solution of 1 g. of (XII), 200 mg. of KOH, 3 drops of water in 10 cc. of EtOH was heated under reflux for 10 hr. After evaporation of EtOH, the residue was dissolved in a small amount of water and the aqueous solution was washed with AcOEt. The aqueous solution was acidified with dil. HCl under ice-cooling and the deposited product was washed with water. Recrystallization of the crude product from EtOH gave colorless needles of m.p. 175° (decomp.). *Anal.* Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found : C, 65.96; H, 5.10. IR $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} : 1724, 1695. $\nu_{\max}^{\text{Nujol}}$ cm^{-1} : 1724, 1684.

3-Ethoxycarbonyl-4-hydroxy-2-naphthoic Acid (XVIII)——To an ice-cooled solution of 220 mg. of KOH in 1.5 cc. of water was added a solution of 500 mg. of (XI) in 1.5 cc. of EtOH and the mixture was allowed to stand at room temperature for 45 hr. After evaporation of EtOH under reduced pressure, the residue was dissolved in a small amount of water and washed with AcOEt. The aqueous solution was acidified with dil. HCl. and extracted with AcOEt. The extract was shaken with saturated $NaHCO_3$ solution and the alkaline extract was again acidified with dil. HCl. The precipitate obtained was washed with water and recrystallized from benzene to give 225 mg. (50%) of colorless crystals, m.p. 173°. *Anal.* Calcd. for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found : C, 64.96;

H, 4.61. IR ν_{max}^{Nujol} cm^{-1}: 1692, 1658. The starting material (XI) (200 mg., 40%) was recovered from the AcOEt washing above.

4-Hydroxy-2-naphthoic Acid (XVII)——A solution of 500 mg. of (XI) and 400 mg. of KOH in 15 cc. of EtOH was heated under reflux for 8 hr. After evaporation of EtOH, the residue was dissolved in a small amount of water and washed with AcOEt. The aqueous solution was acidified with ice-HCl and extracted with AcOEt. The extract was shaken with saturated $NaHCO_3$ solution and the alkaline layer was again acidified with ice-HCl providing precipitate. The precipitate was washed with water and recrystallized from benzene to give 300 mg. of colorless pillars of m.p. 221°. This compound was shown to be identical with an authentic sample of (XVII), m.p. 220~222°, prepared by the method of Haworth, Jones, Way6) by mixed melting point and the infrared spectra. *Anal.* Calcd. for $C_{11}H_{18}O_3$: C, 70.21; H, 4.29. Found : C, 70.15; H, 4.16. IR ν_{max}^{Nujol} cm^{-1}: 2667 (broad), 1653.

3-Hydroxymethyl-4-methoxy-2-naphthoic Acid γ-Lactone (XV) i) Reduction of (XX) with LiAlH$_4$——To a solution of 425 mg. of (XX) in 20 cc. of anhyd. tetrahydrofuran was added at $-5\sim0°$ under stirring a suspension of 420 mg. of $LiAlH_4$ in 20 cc. of anhyd. Et_2O. After the addition was completed, the mixture was stirred at the same temperature for 6 hr. AcOEt was added to decompose excess of $LiAlH_4$ and the solvents were distilled off below 20°. The residue was poured into ice-dil. HCl and extracted with AcOEt. The extract was washed with water, saturated $NaHCO_3$ solution and then water, and dried over Na_2SO_4. After evaporation of the solvent, the residue was recrystallized from benzene to 173 mg. of colorless needles, m.p. 168°. *Anal.* Calcd. for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found : C, 72.99; H, 4.45.

ii) Reduction of (XVIII) with LiAlH$_4$——To a solution of 665 mg. of (XVIII) in 15 cc. of anhyd. tetrahydrofuran was added at $-5°\sim0$ under stirring a suspension of 665 mg. of $LiAlH_4$ in 50 cc. of anhyd. Et_2O. After the addition was completed, stirring was continued at the same temperature for 6 hr. AcOEt was added to destroy excess of $LiAlH_4$ and the solvents were distilled below 20°. The residue was poured into ice-dil. HCl and extracted with AcOEt. The extract was washed with water and saturated $NaHCO_3$ solution and then water, and dried over Na_2SO_4. After evaporation of the solvent, the oily residue (XIX) (88 mg.) was dissolved in an Et_2O solution containing a large excess of CH_2N_2 and allowed to stand for 3 days in an ice-box. After addition of AcOH to destroy the excess of CH_2N_2, the whole solution was washed successively with water, saturated $NaHCO_3$ and water, and dried over Na_2SO_4. The solvent was removed and the residue (90 mg.) was purified through Al_2O_3 column using benzene as eluent. Recrystallization of an eluted crystalline material from benzene gave colorless needles of m.p. 168°. This compound was identified with a sample of (XV) obtained by the reduction of (XIV) with Zn and conc. HCl by a mixed melting point determination and comparison of their infrared spectra.

1-Methoxy-2,3-naphthalenedimethanol (XVI) i) From (VIII)——A solution of 100 mg. of (VIII) in anhyd. Et_2O was added gradually to a stirred suspension of 140 mg. of $LiAlH_4$ in anhyd. Et_2O at room temperature. After the addition was completed, the mixture was heated under reflux for 3 hr. The reaction mixture was poured into ice-dil. H_2SO_4 and extracted with Et_2O. The Et_2O extract was washed with water, dried over Na_2SO_4 and the solvent was distilled off. The residual oil solidified on standing at room temperature. Recrystallization from benzene gave colorless needles or scales of m.p. 91°. *Anal.* Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found : C, 71.96; H, 6.47. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3571, 3367.

ii) From (XV)——Compound (XV) (100 mg.) was reduced by the same procedure as described in i) to give colorless crystals of m.p. 89°. *Anal.* Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found : C, 71.99; H, 6.32.

This compound was shown to be identical with a sample of (XVI) prepared by reduction of (VIII).

Summary

As an exploratory experiment on syntheses of sorigenins (I), 1-methoxy-3-hydroxymethyl-2-naphthoic acid γ-lactone (VIII) and 3-hydroxymethyl-4-methoxy-2-naphthoic acid γ-lactone (XV) were synthesized. Compound (VIII) was prepared from 3-hydroxymethyl-3,4-dihydro-1(2*H*)-naphthalenone (IV) as shown in Chart 1. Compound (XV) was prepared through reduction of 3-ethoxycarbonyl-4-hydroxy-2-naphthoic acid (XVIII) and its methyl ether (XX) with lithium aluminium hydride. Reductions of 1-methoxy-2,3-naphthalenedicarboxylic anhydride (XIV) and of the halfester prepared by alcoholysis of (XIV) with lithium aluminium hydride were found to give a mixture of (VIII) and (XV).

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6) R.D. Haworth, B. Jones, Y.M. Way : J. Chem. Soc., **1943**, 10.