Acetylation of IV (101 mg) with Ac_2O (2 ml) and pyridine (5 ml) at room temperature overnight followed by usual work-up furnished a heptaacetate (117 mg) which was purified by ether–*n*-hexane (amorphous). *Anal.* Calcd. for $C_{46}H_{64}O_{20}$: C, 58.96; H, 6.89. Found: C, 58.77; H, 6.63. PMR ($CDCl_3$) τ: 8.95 (3H, s), 8.74 (3H, s), 8.01, 7.94, 7.90 (totally 21H, all s).

Steviolbioside (IV) from Stevioside (I)——A mixture of I (200 mg) in aq. 10% KOH (5 ml) was heated at 100° for one hour. After cooling, the reaction mixture was acidified with glacial acetic acid and a product was crystallized from MeOH to give IV (75 mg), mp 184—185°. IR ν_{max}^{KBr} cm^{-1}: 3450 (br) (OH), 1700 (COOH), 895 ($\rangle C=CH_2$). In lit.[6]: mp 188—192° (corr.), IR ν_{max} μ: 3.65—4.25 (carboxyl-hydroxyl), 5.92, 6.03 (w) (carboxyl).

Acknowledgement The authors would like to express their sincere thankness to the Hōansha for the research grant.

[Chem. Pharm. Bull.
20(11)2502—2506(1972)]

UDC 547.567.057

Synthetic Studies on Anthracyclinones. XII.[1] Synthesis of 8-Ethyl-1,6,11-trihydroxynaphthacenequinone

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(Received June 9, 1972)

8-Ethyl-1,6,11-trihydroxynaphthacenequinone (I)[3] is the important substance known as bisanhydro-γ-rhodomycinone[4] or bisanhydrodecarbomethoxy-ε-rhodomycinone[5] and is considered to be a potential starting material for the synthesis of bisanhydrodaunomycinone (II).[6]

In the course of the synthetic studies of II, it was needed for the present authors to prepare a considerable amount of I by a rather simple procedure involving a explicit characterization of the intermediates.

Compound (I) was first synthesized by Brockmann, *et al.*[3] starting from Friedel–Crafts condensation of 3-hydroxyphthalic anhydride (III) with 7-ethyl-1-naphthol[3b] (IV) and with 6-ethyl-1-naphthol (V) without separation or characterization of the isomeric condensed products.

Recently, there has been clarified[7] the behavior of the condensation of III or 3-methoxyphthalic anhydride (VI) with α-naphthol. According to the result, the condensation of V

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[1] Part XI: Z. Horii, S. Fujita, Y. Ozaki, M. Hanaoka, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **20**, 827 (1972).

[2] Location: *6-1-1, Toneyama, Toyonaka, Osaka.*

[3] *a*) H. Brockmann and R. Zunker, *Tetrahedron Letters*, **1966**, 45; *b*) H. Brockmann, R. Zunker, and H. Brockmann Jr., *Ann.*, **696**, 145 (1966).

[4] H. Brockmann, P. Boldt, and J. Niemeyer, *Chem. Ber.*, **96**, 1356 (1963).

[5] H. Brockmann and H. Brockamnn Jr., *Chem. Ber.*, **94**, 2681 (1961).

[6] F. Arcamone, G. Franceschi, P. Orezzi, G. Cassinelli, W. Barbieri, and R. Mondelli, *J. Am. Chem. Soc.*, **86**, 5334 (1964); F. Arcamone, G. Franceschi, P. Orezzi, S. Penco, and R. Mondelli, *Tetrahedron Letters*, **1968**, 3349; R.H. Iwamoto, P. Lim, and N.S. Bhacca, *ibid.*, **1968**, 3891; F. Arcamone, G. Cassinelli, G. Franceschi, R. Mondelli, P. Orezzi, and S. Penco, *Gazz. Chim. Ital.*, **100**, 949 (1970).

[7] 3-Methoxy-2-(1-hydroxy-2-naphthoyl)benzoic acid or 2-hydroxy-6-(1-hydroxy-2-naphthoyl)benzoic acid has been shown to be the main product in the Friedel–Crafts condensation between VI or III and α-naphthol. Z. Horii, H. Hakusui, T. Momose, and E. Yoshino, *Chem. Pharm. Bull.* (Tokyo), **16**, 1251 (1968).

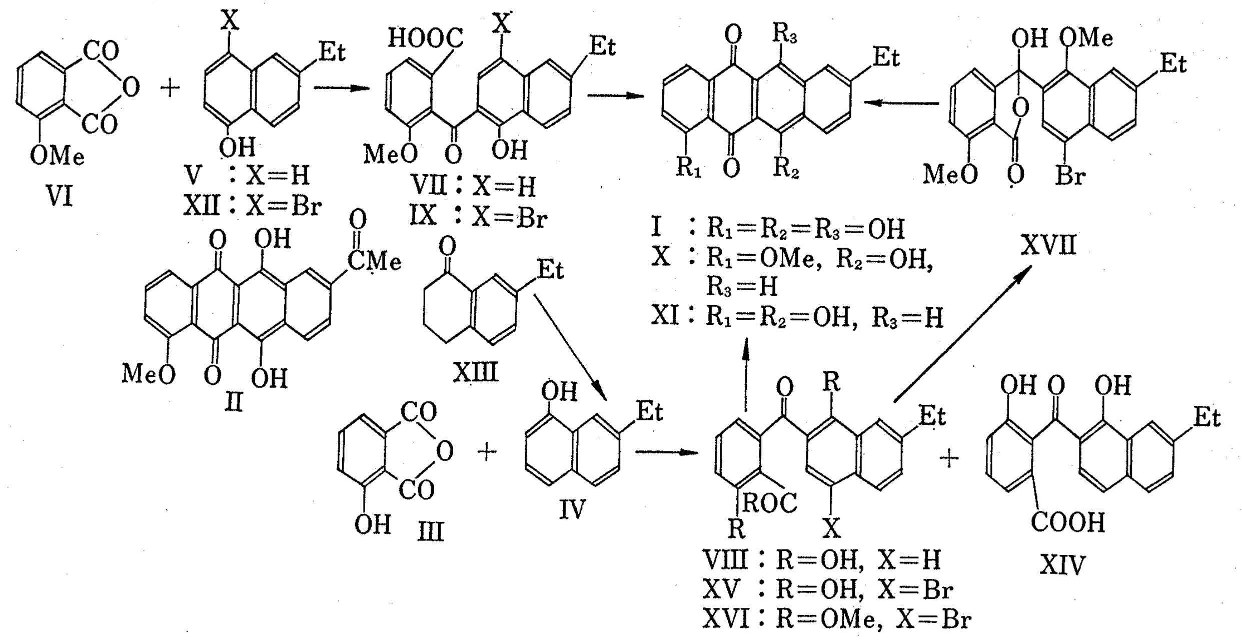

Chart 1

with VI or that of III with IV would result in the predominant formation of 3-methoxy-2-(6-ethyl-1-hydroxy-2-naphthoyl)benzoic acid (VII) or 2-hydroxy-6-(7-ethyl-1-hydroxy-2-naphthoyl)benzoic acid (VIII). On the basis of this expectation, compound (I) was synthesized by two pathways as described below.

1) Synthesis of I from VI and V

Compound (VII) was obtained, as expected, in 27% yield by condensation of VI with V in the presence of anhydrous aluminum chloride. Bromination of VII with bromine gave 3-methoxy-2-(4-bromo-6-ethyl-1-hydroxy-2-naphthoyl)benzoic acid (IX) in 80% yield. The position of methoxyl in VII and the location of bromine in IX were confirmed as follows. Compound VII was cyclized to 8-ethyl-11-hydroxy-1-methoxynaphthacenequinone (X) in 19% yield. Demethylation of X with boron tribromide gave 8-ethyl-1,11-dihydroxynaphthacenequinone (XI) in 92% yield. Compound (XI) showed non-chelated quinone-carbonyl band at 1664 cm^{-1} in its infrared (IR) spectrum, confirming the arrangement of hydroxyl in XI and accordingly the structure of VII. Compound (IX) was also obtained in 27% yield by Friedel–Crafts condensation between VI and 4-bromo-6-ethyl-1-naphthol (XII)[8] in the presence of aluminum chloride, confirming the structure IX. Cyclization of IX gave I in 78% yield.

2) Synthesis of I from III and IV

Compound (IV) was obtained in 69% yield by bromination[9] of 7-ethyl-1-tetralone (XIII)[8] with bromine followed by dehydrobromination.[10] The Friedel-Crafts condensation of III with IV in the presence of boric anhydride gave VIII and 3-hydroxy-2-(7-ethyl-1-hydroxy-2-naphthoyl)benzoic acid (XIV) in 24% and 1% yield, respectively. Separation of isomeric two products was effected by differential extraction with 2% sodium carbonate solution. Compound (VIII) was brominated with bromine to the bromo-derivative (XV) in 90%yield.

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[8] Z. Horii, S. Yamamura, H. Hakusui, T. Nishikado, and T. Momose, *Chem. Pharm. Bull.* (Tokyo), **16**, 2456 (1968).

[9] The procedure is essentially the same as that reported for preparation of 2-bromo-6-methyl-1-tetralone (L.F. Fieser and J.T. Dunn, *J. Am. Chem. Soc.*, **58**, 572 (1936)).

[10] The procedure is essentially the same as that reported for preparation of 7-bromo-1-naphthol (J.S. Franzen and S.B. Binkley, *J. Org. Chem.*, **24**, 992 (1959)).

Because of the difficutly of the cyclization of salicylic acid types (VIII, XV) under the condition successful in cyclization of *o*-anisic acid types,[7] XV was methylated with dimethyl sulfate to the permethylate (XVI) in 69% yield. Hydrolysis of XVI with potassium hydroxide gave the corresponding acid (XVII) in 78% yield. The IR absorptions of XVII at 1775 cm^{-1} (C=O) and 3337 cm^{-1} (OH) showed its lactol structure.

Cyclization of XVII gave I in 84% yield. Direct cyclization of XVI was also found to give I. Compound (I) from XVI or XVII was identical with that from IX.

Since the starting material IV could be prepared in good yield and in a large quantity, the procedure 2 was found to be a useful method for preparation of I.

Experimental[11]

3-Methoxy-2-(6-ethyl-1-hydroxy-2-naphthoyl)benzoic Acid (VII)——A mixture of 3-methoxyphthalic anhydride (VI, 8.7 g), 6-ethyl-1-naphthol (V, 6.7 g) and dry $CHCl_2CHCl_2$ (70 ml) was heated up to 100° until a clear solution resulted, and then cooled to 40°. To this was added 10.4 g of pulverized anhyd. $AlCl_3$ in one portion, and the temperature was maintained at 150—155° for 1 hr. The reaction mixture was poured onto a mixture of cracked ice and conc. HCl, and the solid was crushed and treated with conc. HCl and AcOEt one after the other to destroy the complex. The AcOEt layer was washed twice with H_2O and shaken repeatedly with satd. $NaHCO_3$ until the last alkaline layer afforded no precipitates on acidification. From the alkaline extract deposited precipitates of Na salt of VII on standing. The Na salt was dissolved in H_2O, and the solution was acidified with dil. HCl to give pale yellow precipitates, recrystallization of which from MeOH gave 2.6 g of VII, mp 227—228°. *Anal.* Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 72.19; H, 5.08. IR ν_{max}^{KBr} cm^{-1}: 3413 (OH), 1686 (C=O), 1626 sh, 1608, 1582 sh (arom.).

The alkaline solution separated from the crystalline Na salt was shaken with AcOEt (50 ml × 2), filtered and acidified with dil. HCl to give 4.1 g of pale greenish yellow precipitates, which were chromatographed on silica gel (260 g) in $CHCl_3$. The earlier fraction gave 0.65 g of the second crop of VII. Total yield: 26.8%. The product was proved to be free from its isomer by GLC analysis of its permethylate which was prepared by methylation of VII with methyl iodide in the presence of potassium carbonate in dry acetone.

3-Methoxy-2-(4-bromo-6-ethyl-1-hydroxy-2-naphthoyl)benzoic Acid (IX)——a) From Condensation of VI with 4-Bromo-6-ethyl-1-naphtol (XII): The condensation between VI (1.17 g) and XII (1.10 g) was carried out, in a similar manner to that for VII in boiling $CHCl_2CHCl_2$ (20 ml) in the presence of anhyd. $AlCl_3$ (1.32 g). By purification of the product *via* Na salt was obtained 520 mg (27.5%) of IX as pale greenish yellow crystals (from MeOH), mp 224—225°. This compound showed a positive $FeCl_3$ test (green in EtOH). *Anal.* Calcd. for $C_{21}H_{17}O_5Br \cdot CH_3OH$: C, 57.27; H, 4.59; Br, 17.32. Found: C, 57.52; H, 4.53; Br, 17.51. IR ν_{max}^{KBr} cm^{-1}: 3378 (OH), 1706 (C=O), 1692 (C=O), 1610, 1605 (arom.).

b) By Bromination of VII: To an ice-cooled and stirred solution of VII (1.80 g) in $CHCl_3$ (10 ml) was added a solution of Br_2 (0.87 g) in $CHCl_3$ (20 ml) over a period of 1 hr. After an additional 3 hr's stirring at room temperature, the reaction mixture was concentrated and diluted with CCl_4 (10 ml) to give 1.75 g (79.5%) of IX as yellow crystals, mp 218—220°. This compound was identical with the sample synthesized in a).

8-Ethyl-11-hydroxy-1-methoxynaphthacenequinone (X)——To a solution of H_3BO_3 (4.0 g) in H_2SO_4 (40 ml) was added VII (0.4 g) at room temperature, and the mixture was heated with stirring at 70—90° for 2 min, at 90—110° for 3 min and at 120—130° for 3 min, then poured onto cracked ice. The deposited dark red precipitates were collected, washed with H_2O, then with satd. $NaHCO_3$ and again with H_2O, and dried. The crude quinone was extracted with $CHCl_3$ by Soxhlet extractor to give 80 mg of orange red crystals, which were sublimed at 190—200°/2 mmHg to give 70 mg (18.7%) of X as orange red needles (from benzene), mp 206—208°. *Anal.* Calcd. for $C_{21}H_{16}O_4$: C, 75.89; H, 4.85. Found: C, 75.90: H, 4.84. IR ν_{max}^{KBr} cm^{-1}: 1663 (C=O), 1616, 1577 (arom.).

8-Ethyl-1,11-dihydroxynaphthacenequinone (XI)——A cooled solution of X (40 mg) in dry CH_2Cl_2 (20 ml) was mixed, at −60°, with a cooled solution of BBr_3 (320 mg) (10 molar equivalents) in dry CH_2Cl_2 (7 ml), and the mixture was allowed to warm up to room temperature and then stood for 2 hr, and poured onto cracked ice. The mixture was extracted with AcOEt, and the extract was washed with satd. $NaHCO_3$ and with H_2O, then dried and evaporated. The resulting orange red residue was sublimed at 200—210°/2 mmHg to give 37 mg (91.5%) of orange red crystals (from benzene), mp 211—213°. *Anal.* Calcd. for $C_{20}H_{14}O_4$: C, 75.46; H, 4.43. Found: C, 75.25; H, 4.39. IR ν_{max}^{KBr} cm^{-1}: 1664 (C=O), 1610, 1595, 1572 (arom.).

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11) Melting points and boiling points are uncorrected. Organic extracts were dried over anhyd. Na_2SO_4. The nuclear magnetic resonance (NMR) spectra were measured at 60 Mc with tetramethylsilane as internal reference.

7-Ethyl-1-naphthol[3b] **(IV)**——To an ice-cooled and stirred solution of 7-ethyl-3,4-dihydro-1(2H)-naphthalenone[8] (XIII, 53 g) in CS_2 (300 ml) was added a solution of Br_2 (55 g) in CS_2 (150 ml) over a period of 1.5 hr. After the addition was complete, the mixture was stirred at room temperature for an additional 1 hr, and evaporated. The resulting pale brown oil (82 g) was refluxed for 4 hr with LiCl (39 g) in DMF (500 ml) under N_2. After evaporation of DMF, H_2O (300 ml) was added, and the mixture was extracted with benzene (100 ml × 3). The extract was washed with H_2O and evaporated. The resulting brown oil was distilled *in vacuo* to give colorless crystals (49 g) which showed a positive Beilstein test. In order to remove the bromine from partially brominated naphthol mixture, the crystals were shaken with Raney nickel (5.0 g) and KOH (2.7 g) in MeOH (200 ml) under H_2 stream at room temperature for 5 hr. The catalyst was removed and the filtrate was evaporated. To the residue was added H_2O (300 ml), and the mixture was acidified with conc. HCl. The resulting mixture was extracted with benzene (100 ml × 3). The extract was washed with H_2O and evaporated to give 42 g of pale brown oil, which was distilled *in vacuo* to give 36 g (69.4%) of IV as colorless crystals (bp 135—142°/3 mmHg), mp 60—61° (lit.[3b] mp: 62°). These needles showed a negative Beilstein test.

2-Hydroxy-6-(7-ethyl-1-hydroxy-2-naphthoyl)benzoic Acid (VIII) and 3-Hydroxy-2-(7-ethyl-1-hydroxy-2-naphthoyl)benzoic Acid (XIV)——A pulverized mixture of 3-hydroxyphthalic anhydride (III, 26.7 g), IV (36.5 g) and B_2O_3 (59.7 g) was heated with stirring until a molten mixture resulted. The temperature was elevated up to 180° during 20 min and maintained at 180° for 20 min. The cooled mass was digested with hot H_2O and resulting black tarry material was taken in AcOEt (1 liter). The AcOEt layer was washed with H_2O and extracted with 2% Na_2CO_3 solution. A pH value of the extract was measured on every extraction. The extracts which indicated pH value between 5.0—8.0 were combined, shaken twice with AcOEt, filtered and acidified with dil. HCl to give 3-hydroxyphthalic acid. The extract which indicated pH value of 8.0—10.0 was treated as above to give 3-hydroxybenzoic acid. The extract which indicated pH value of 10.0—10.6 was treated as above to give 1.0 g of pale brown precipitates and was recrystallized from benzene to give 0.72 g (1.2%) of XIV as pale yellow crystals (from aq. MeOH), mp 231—233°. *Anal.* Calcd. for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.18; H, 4.93. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1682 (C=O), 1631 (C=O), 1610, 1590, 1560 (arom.).

When the extract indicated pH value of 10.6, the pH value did not change in spite of the further alkaline extraction. Then, the AcOEt layer was extracted with H_2O (80 ml × 58),[12] and the extract was washed with AcOEt and filtered. The filtrate was saturated with NaCl to afford pale brown precipitates of Na salt of VIII, which were collected, washed with satd. NaCl, and dried. Recrystallization from H_2O gave an analytical sample of Na salt, mp 203° (decomp.). *Anal.* Calcd. for $C_{20}H_{15}O_5Na \cdot 1\frac{1}{4}H_2O$: C, 63.07; H, 4.63. Found: C, 62.95; H, 4.85. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1630 sh, (C=O), 1573 broad (COO^-), 1586 (arom.).

The Na salt was dissolved in H_2O, and the solution was filtered and acidified to give 12.5 g of pale yellow precipitates. Recrystallization from aq. MeOH gave 11.8 g of VIII as pale yellow needles, mp 206—212°. *Anal.* Calcd. for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found: C, 71.56; H, 4.61. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1664 (C=O), 1623 (C=O), 1600, 1592, 1575, 1548 (arom.).

The alkaline solution separated from crystalline Na salt was shaken twice with AcOEt, filtered, acidified with conc. HCl and extracted with AcOEt. The extract was wasehd with H_2O and evaporated to give 5.3 g of a brown solid, which was chromatographed on silica gel (106 g) in $CHCl_3$. The later fraction gave 3.0 g of the second crop of VIII. Total yield: 24.4%.

2-Hydroxy-6-(4-bromo-7-ethyl-1-hydroxy-2-naphthoyl)benzoic Acid (XV)——To an ice-cooled and stirred solution of VIII (50.4 g) in $CHCl_3$ (300 ml) was added a solution of Br_2 (24.0 g) in $CHCl_3$ (180 ml) over a period of 4 hr. After the addition was complete, the mixture was stirred at room temperature for an additional 1 hr. The deposited precipitates were collected, washed with $CHCl_3$ and then with H_2O and dried to give 55.5 g (89.5%) of XV as pale yellow crystals (from aq. MeOH), mp 222—228°. *Anal.* Calcd. for $C_{20}H_{15}O_5Br$: C, 57.85; H, 3.64. Found: C, 57.64; H, 3.60. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1661 (C=O), 1629 (C=O), 1605, 1600 (arom.).

Methyl 2-Methoxy-6-(4-bromo-7-ethyl-1-methoxy-2-naphthoyl)benzoate (XVI)——A mixture of XV (23.0 g), Me_2SO_4 (42.0 g), anhyd. K_2CO_3 (200 g) and dry acetone (500 ml) was refluxed with stirring for 6 hr. After evaporation of acetone, H_2O (600 ml) and aq. NH_3 were added to the residue. The mixture was extracted with benzene (100 ml × 3). The extract was washed with H_2O and evaporated. Resulting pale brown crystals were washed with MeOH to give 20.0 g of colorless crystals. Recrystallization from MeOH gave 17.5 g (69.2%) of XVI, mp 101.0—103.5°. *Anal.* Calcd. for $C_{23}H_{21}O_5Br$: C, 60.40; H, 4.63. Found: C, 60.54; H, 4.57. IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1733 (C=O), 1658 (C=O), 1585, 1546 (arom.).

2-Methoxy-6-(4-bromo-7-ethyl-1-methoxy-2-naphthoyl)benzoic Acid (XVII)——A mixture of XVI (20 g), MeOH (40 ml), H_2O (80 ml) and KOH (7.4 g) was refluxed for 8 hr. The mixture was diluted with H_2O (80 ml) and acidified to give 17 g of white precipitates, recrystallization of which from ether gave 14.6 g (77.7%) of XVII as white needles, mp 101.5—102.5°. *Anal.* Calcd. for $C_{22}H_{19}O_5Br$: C, 59.60; H, 4.32.

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[12] Owing to the salting effect, the sodium salt of VIII was found to be less soluble in 2% sodium carbonate solution than in ethyl acetate but soluble in plain water.

Found: C, 59.32; H, 4.42. IR ν_{max}^{KBr} cm^{-1}: 3337 (OH), 1755 (lactol), 1614, 1603, 1592 (arom.). NMR ($CDCl_3$) τ: 6.00 (6H, s, $OC\underline{H}_3 \times 2$), 7.21 (2H, q, $J=7$ Hz, $-C\underline{H}_2CH_3$), 8.68 (3H, t, $J=7$ Hz, $-CH_2C\underline{H}_3$).

8-Ethyl-1,6,11-trihydroxynaphthacenequinone (I) (Bisanhydro-γ-rhodomycinone or Bisanhydrodecarbomethoxy-ε-rhodomycinone)——a) From IX: A mixture of H_3BO_3 (44 g) and H_2SO_4 (440 ml) was heated until a clear solution resulted, and then cooled to room temperature. To this was added 3.84 g of IX, and the mixture was heated with stirring at 110—140° for 10 min and at 140—150° for 20 min. During the reaction period, initial dark brown color of the mixture turned into dark reddish violet. The mixture was poured onto cracked ice to give red precipitates, which were collected, washed with H_2O, then with satd. $NaHCO_3$ and again with H_2O, and dried to give 2.4 g of dark red solid which showed a positive Beilstein test. This solid was heated in glycerol (100 ml) at 200° to get suspension. After cooling to 100°, KOH (15 g) was added, and the temperature was maintained at 170—175° for 0.5 hr. The reaction mixture was poured onto cracked ice and acidified with conc. HCl to give dark red precipitates, which showed a negative Beilstein test. Three recrystallizations from benzene gave 2.35 g (78.4%) of I, mp 205—206° (lit.[3] mp 206°). *Anal.* Calcd. for $C_{20}H_{14}O_5$: C, 71.85; H, 4.22. Found: C, 71.84; H, 4.17. IR ν_{max}^{KBr} cm^{-1}: 1617 sh, 1592, 1581, 1561 sh, 1542 sh (arom.).

b) From XVII: A mixture of H_3BO_3 (16.7 g) and H_2SO_4 (167 ml) was heated with stirring until a clear solution resulted, and then cooled to 115°. To this was added 1.45 g of XVII, and the mixture was heated with stirring at 140—150° for 20 min, during which time, initial bluish violet color of the mixture turned into violet. The mixture was poured onto 500 g of cracked ice to give dark red precipitates, which were collected, washed with H_2O, then with satd. $NaHCO_3$, and again with H_2O, and dried to give 1.04 g of dark red crystals which showed a positive Beilstein test. Treatment of this crystals with KOH (6.1 g) in glycerol (34 ml) was carried out in a similar manner to that in a). The collected crystals (0.89 g, 84.0%) showed a negative Beilstein test and mp 204—206°. The sample was identical with that obtained in a).

c) From XVI: The cyclization of XVI (1.0 g) with H_2SO_4 (115 ml) in the presence of H_3BO_3 (11.5 g) was carried out in a similar manner to that in b). Resulting dark red crystals which indicated a positive Beilstein test were treated with KOH (4.1 g) in glycerol (27 ml) in a similar manner to that in a). The collected crystals (0.66 g, 89.0%) showed a negative Beilstein test. The sample was identical with that obtained in a).

〔Chem. Pharm. Bull.
20(11)2506—2510(1972)〕

UDC 547.92'457.1.04

Conversion of Steroid Saponins to the Corresponding Pregnane Glycosides

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(Received July 18, 1972)

The steroid sapogenins (spirostanols) (Ia—c) are well known[2] as the most important starting material for the convenient preparation and production of pregnan-3β-ol-20-one (IIa, b) and pregn-5-en-3β-ol-20-one (IIc), from which a variety of steroid compounds of medicinal importance are derived.

The spiroketal side chain at C-17 of I is degraded, through pseudomerization, oxidative cleavage of $\Delta^{20(22)}$ and hydrolysis of ester linkage, by the methods originally proposed by Marker and his collaborators.[2] A similar conversion of nitrogen analogs (spirosolane (IIIa) derivatives) of spirostanols has also been reported by Sato and his co-workers.[3]

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