dehydrated olefines, XV and XVI, in a ratio of about 2.3:1 on the basis of gas-liquid chromatographic analysis.[*6] However, a reverse ratio of XV to XVI (1:2.2), favourable to attaining the present object, was obtained by refluxing the mixture in benzene in the presence of *p*-toluenesulfonic acid.10) Osmium tetroxide hydroxylation of the thus obtained mixture gave four *cis*-glycols, XVII, m.p. 183~185°, XVIII, m.p. 181~183°, XIX, m.p. 205~207°, and XX, m.p. 196~197°, which were separated on alumina. The ratio of the combined yield of the first two glycols, originated from the Δ^{17}-compound (XV), to that of the last two, originated from the isomeric Δ^{16}-derivative (XVI), was about 1:1.8. This ratio agrees well with the above mentioned gas chromatographic result.

Both glycols, XIX and XX, underwent periodic acid oxidation and gave the same oily keto aldehyde (XXII), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2700, 1715, showing the original diols were epimeric. Ring closure of this crude keto aldehyde was effected by refluxing it in xylene containing triethylamine acetate to give the expected steroids, *dl*-3α-acetoxy-5β-pregna-9(11),16-dien-20-one (XXIV), m.p. 153~155°, UV λ_{max}^{EtOH} mμ (ε): 206 (4880), 238 (6960), IR $\nu_{max}^{CS_2}$ cm^{-1}: 1725, 1660. The infrared and ultraviolet spectra of this compound are identical with those of an authentic sample of the natural steroid.11) Finally, the other two epimeric glycols, XVII and XVIII, were cleaved in the same manner to give the same oily keto aldehyde (XXI), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2680, 1715, which was then cyclized to *dl*-16-acetyl-5β-androsta-9(11),16-dien-3α-ol acetate (XXIII), m.p. 116~117°, UV λ_{max}^{EtOH} mμ (ε): 206 (4730), 238 (9690), IR $\nu_{max}^{CS_2}$ cm^{-1}: 1728, 1660.

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[*6] Gas-liquid chromatographic analysis was carried out by Dr. N. Ikekawa (Institute of Physical and Chemical Research, Tokyo). We express our thanks for this courtesy and for the valuable discussion on the result.

10) cf. L. Velluz, G. Amiard, R. Heymes, B. Goffinet: Bull. Soc. chim. France, 2166 (1961).

11) S.A. Szpilfogel, V. Gerris: Rec. Trav. Chem., **74**, 1462 (1955).

UDC 581.19:582.288

Synthesis of Rubrofusarin Dimethyl Ether

Rubrofusarin was isolated first by Raistrick, *et al.*1) as orange red crystals, m.p. 214.5~215.5°, from *Fusarium culmorum* (W.G. Smith) Sacc. and some related *Fusarium* spp.

The structure of rubrofusarin (XII) was established by Stout and Dreyer2) in X-ray analysis, and almost the same time by Tanaka and Tamura3) by chemical reactions.

In the present study, the synthesis of rubrofusarin dimethyl ether has been carried out by the following scheme:

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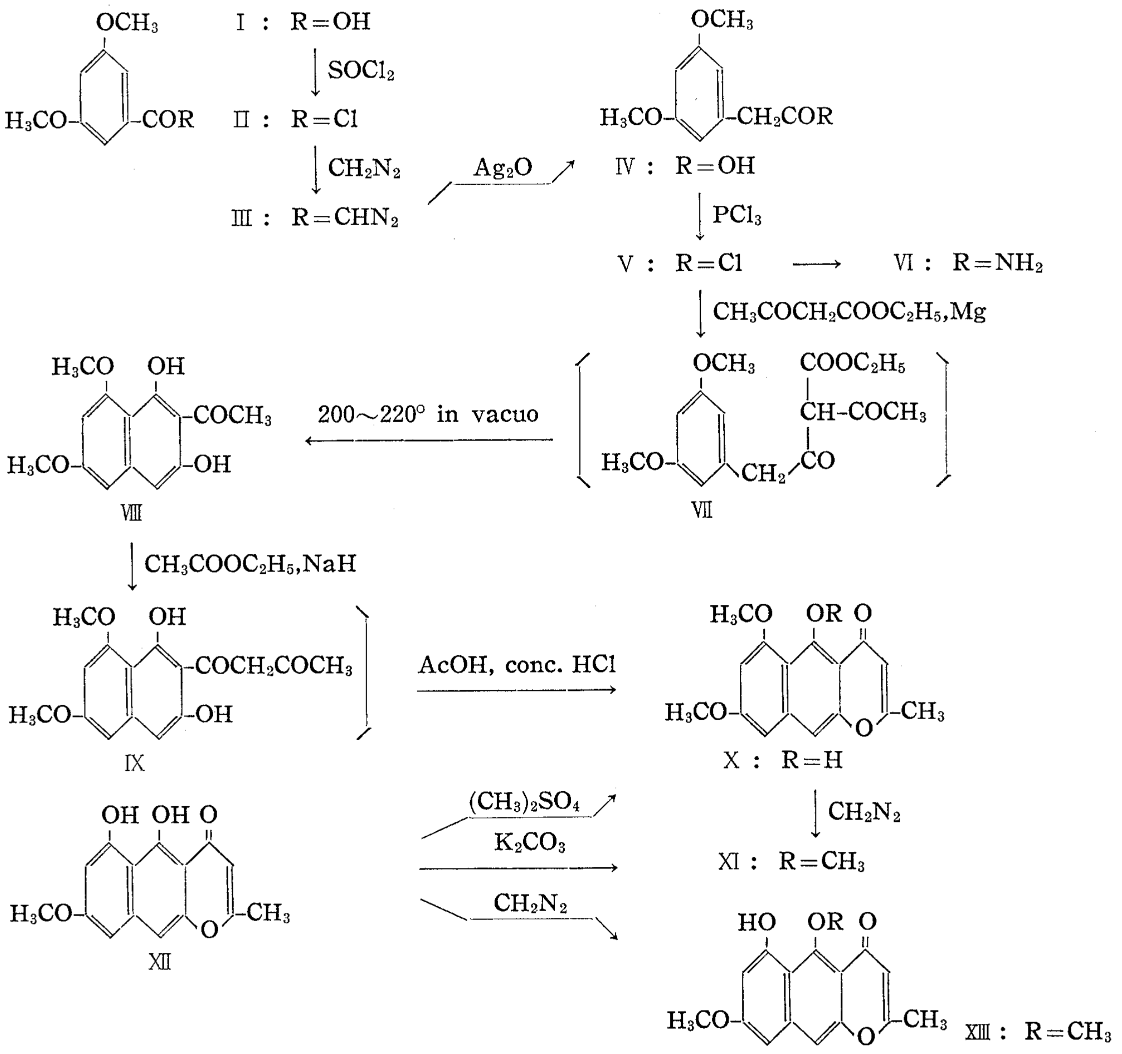
1) J.N. Ashley, B.C. Hobbs, H. Raistrick: Biochem. J., **31**, 385 (1937).

2) G.H. Stout, D.L. Dreyer, L.H. Jensen: Chem. & Ind. (London), 289 (1961); Acta Cryst., **15**, 451 (1962).

3) H. Tanaka, T. Tamura, Y. Ohne, N. Ogawa: Tetrahedron Letters, No. 4, 151 (1961); Agr. Biol. Chem., **27**, 48 (1963).



3,5-Dimethoxybenzoyl chloride[4] (II), m.p. 30~32°, was subjected to the Arndt-Eistert reaction to obtain a diazoketone (III), m.p. 71~72°, which was converted into 3,5-dimethoxyphenyl acetic acid[5] (IV), m.p. 100~101°, by the action of silver oxide. The acid chloride[5] (V) which was characterized as the acid amide (VI), m.p. 126~127°, (*Anal.* Calcd. for $C_{10}H_{13}O_3N$: C, 61.54; H, 6.66; N, 7.18. Found: C, 61.99; H, 6.70; N, 7.13), was reacted with ethyl acetoacetate and magnesium in abs. benzene by the Spassow reaction to yield ethyl 2-(3,5-dimethoxyphenylacetyl)acetoacetate (VII).

On vacuum distillation of VII, 2-acetyl-6,8-dimethoxy-1,3-naphthalenediol (VIII), yellow prisms, m.p. 194°, was afforded (Yield: 16.5%, calcd. from IV) (*Anal.* Calcd. for $C_{14}H_{14}O_5$: C, 64.12; H, 5.34. Found: C, 64.20; H, 5.31. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ $\mathrm{cm^{-1}}$: 3320 (OH); 1650 (C=O)), which gave a dark green color with ferric chloride and dark red color with Gibbs' reagent.

The naphthalene derivative (VIII) was subjected to the Claisen condensation with ethyl acetate using sodium hydride to yield 2-acetoacetyl-6,8-dimetoxy-1,3-naphthalenediol (IX) which was cyclized by the action of acetic acid and hydrochloric acid to afford 2-methyl-5-hydroxy-6,8-dimethoxy-4*H*-naphtho[2,3-*b*]pyran-4-one (X), orange yellow needles, m.p. 213° (*Anal.* Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.89. Found: C, 67.08; H, 4.81) giving a green

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[4] J.C. Roberts, *et al.*: J. Chem. Soc., **1955**, 2784; *Ibid.*, **1962**, 2063.

[5] F. Mauthner: J. prakt. Chem. (2), **110**, 127 (1925); A.J. Birch, *et al.*: Austral. J. Chem., 8, 529 (1955).

color with ferric chloride and indigo color with Gibbs' reagent (Yield, 90% from IX, and 38.7% from VIII).

This compound was proved to be identical with a monomethyl ether of rubrofusarin, m.p. 215°, which was yielded as a byproduct when rubrofusarin was converted into dimethyl ether by the action of dimethyl sulfate and potassium carbonate.

Another monomethyl ether (XIII), m.p. 203~204°,[6] was formed on methylation of rubrofusarin with diazomethane, which gave no ferric chloride reaction and exhibited a blue Gibbs' reaction.

The compound (X) was methylated with diazomethane to furnish 2-methyl-5,6,8-trimethoxy-4*H*-naphtho[2,3-*b*]pyran-4-one (XI), colorless needles, m.p. 186~187° (*Anal.* Calcd. for $C_{17}H_{16}O_5$: C, 68.00; H, 5.33. Found : C, 68.08; H, 5.31). IR : ν_{max}^{KBr} 1650 cm^{-1} (C=O). (Yield, 47.6% from X). This compound was proved to be identical with the dimethyl ether of natural rubrofusarin, m.p. 186~187°, by a mixed fusion (mixed m.p. 186~187°), comparison of infrared spectra (KBr) and thin layer chromatography.

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[6] J.C. Roberts, *et al.* : J. Chem. Soc., **1962**, 40.

UDC 547.661.1

Structure of Lyoniresinol (Dimethoxyisolariciresinol)

The skeleton and the position of free phenolic hydroxyl groups of lyoniside (I)[1a,b,c] and lyoniresinol (II), m.p. 170.7~171°, $[\alpha]_D^{22}$ +68.4° (c=2.01, Me_2CO) were determined by degradation as shown in Chart 1.

4-Ethoxy-4′-nitro-3,5-dimethoxyazobenzene (III), m.p. 106.6°, (*Anal.* Calcd. for $C_{16}H_{17}O_5N_3$: C, 58.00; H, 5.17; N, 12.68. Found : C, 58.01; H, 5.10; N, 12.77) was obtained from lyoniside (I) and proved to be identical with the authentic specimen synthesized from pyrogallol 1,3-dimethyl ether.

4-Ethoxy-3,5-dimethoxyphthalic acid (IV) derived from I, m.p. 185~185.5° (*Anal.* Calcd. for $C_{12}H_{14}O_7$: C, 53.33; H, 5.22. Found : C, 53.43; H, 5.33) was established on admixture with authentic specimen, m.p. 189°,[2] giving no depression of melting point.

Two γ-lactones[1a,c] were obtained by oxidation of V to give the following physical properties : resinolide (VI) (γ-lactone-A in previous papers), m.p. 194°, $[\alpha]_D^{16.7}$ −94.2°

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[1] *a*) M. Yasue, Y. Kato : Yakugaku Zasshi, **80**, 1013 (1960); *b*) *Idem* : This Bulletin, 8, 844 (1960); *c*) *Idem* : Yakugaku Zasshi, **81**, 526, 529 (1961).

[2] R.H.F. Manske, A.E. Ledingham, H.L. Holmes : Can. J. Research, **23B**, 100 (1945).