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 : $\nu_{\max}^{\mathrm{KBr}}$ 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).

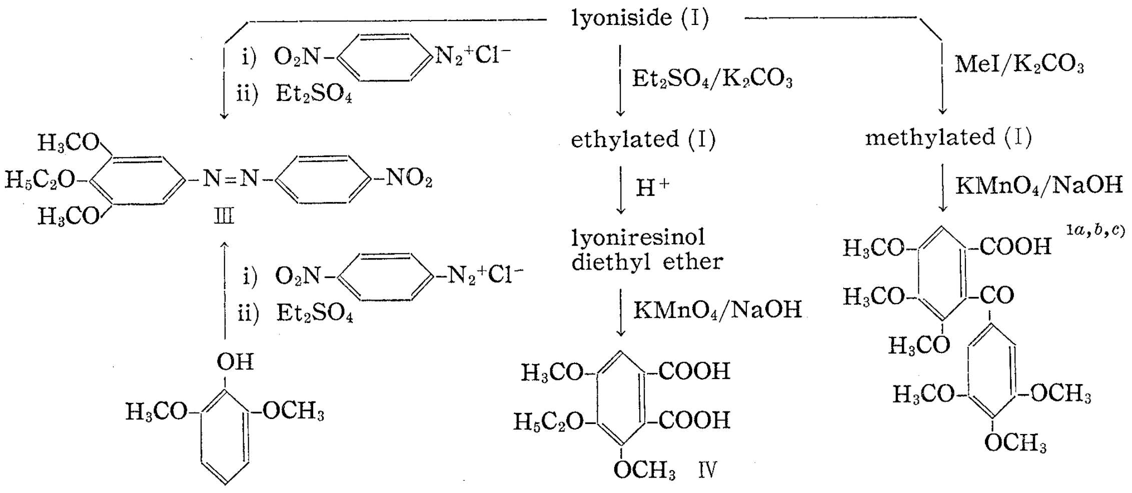


Chart 1.

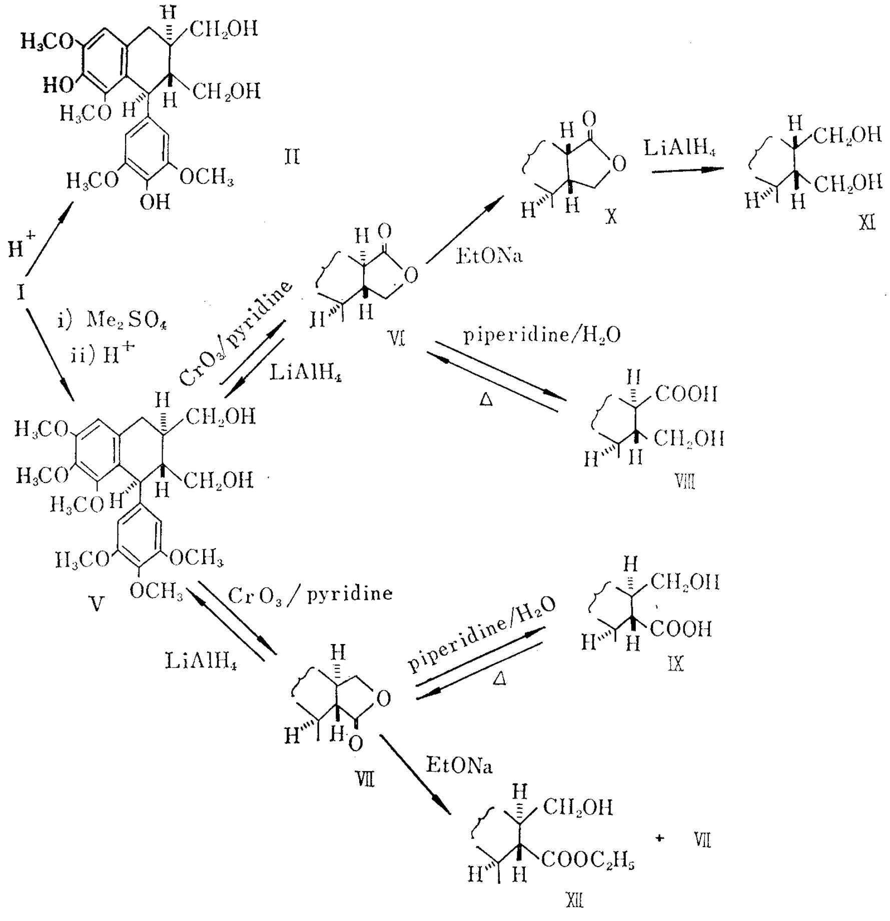


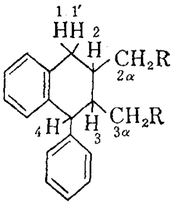
Chart 2.

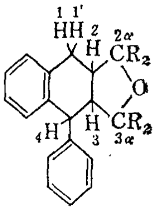
(c=2.20, $CHCl_3$), IR: $\nu_{max}^{CHCl_3}$ 1785 cm^{-1} (CO); retroresinolide (VII) (γ-lactone-B in previous papers), m.p. 153°, $[\alpha]_D^{17.4}$ $-72.6°$ (c=1.62, $CHCl_3$), IR: $\nu_{max}^{CHCl_3}$ 1791 cm^{-1} (CO).

Two hydroxy acids, resinolic acid (VIII) (hydroxy acid-A in previous papers[1a,c]), m.p. 184° and retroresinolic acid (IX) (hydroxy acid-B in previous papers[1a,c]), m.p. 173° were obtained respectively on treating the lactones (VI) and (VII) with piperidine in water. These hydoxy acids, VIII and IX were also obtained by the alkaline hydrolysis of the lactones (VI) and (VII), as described in the previous papers, and converted by heating

TABLE I. Chemical Shifts of Protons, p.p.m. (δ)a)

Compounds	$^{O}_{O}\!>\!CH_2$	4	2α, 3αc)	OCH_3	1, 1′ c)	2, 3c)
XIX			4.17	3.85	3.1	2.4
II			4.17	3.85, 3.72	3.17	2.55
V		4.97b) J =5.5 c.p.s.	4.11	3.88, 3.8, 3.67, 3.61	3.11	2.5
XIII		4.82	4.33~4.08	3.90, 3.84, 3.8, 3.74, 3.42	2.82	2.19
XIV		4.76b) J =4.2 c.p.s.	4.39~3.99	3.81, 3.73, 3.63, 3.59	3.12~2.95	2.77~2.74
XV		4.77	4.28~3.7	3.84, 3.8, 3.62	3.61~2.9	2.77~2.68
XVI	5.9	4.39b) J =8 c.p.s.	4.15	3.93, 3.68	3.13	2.48
XVII	5.9	4.78b) J =3.6 c.p.s.	4.5 ~3.98	3.91, 3.7	3.12	2.54
XVIII	5.96	4.55b) J =4.2 c.p.s.	4.27, 4.18, 4.09	3.97, 3.7	3.42~3.04	2.72~2.63
VI		4.15b) J =10.2 c.p.s.	4.32~4.06	3.89, 3.83, 3.8, 3.74, 3.18	3.13~2.98	2.46
VII		4.34b) J =9.6 c.p.s.	4.53~4.26	3.87, 3.8, 3.78, 3.74, 3.2	2.91	2.44





a) Spectra were determined in pyridine (II, V, XIII~XIX), $CHCl_3$ (VI) and $CDCl_3$ (VII), using tetramethylsilane as internal standard.
b) Doublet c) Multiplet

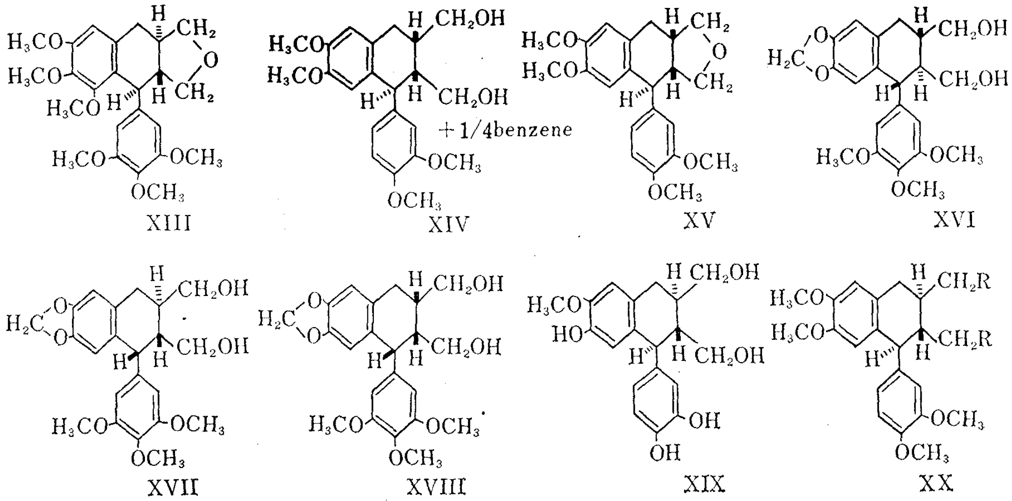


Chart 3.

into the corresponding lactones (VI) and (VIII) respectively. Reduction of these lactones (VI) and (VIII) with lithium aluminium hydride resulted the same diol, identified as V. On refluxing the compound (VI) with sodium ethoxide in ethanolic solution the lactone (X) named *epi*-resinolide, which was purified by silica gel chromatography to form colorless substance, was obtained (yield, 84%), IR : $\nu_{\max}^{\mathrm{CHCl_3}}$ 1774 cm^{-1} (CO).

The diol, *epi*-lyoniresinol dimethyl ether (XI), m.p. 176.8~177.2°, $[\alpha]_D^{15.7}$ +16.4° (c=1.83, $CHCl_3$) (*Anal.* Calcd. for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19. Found : C, 64.09; H, 7.25) was obtained from the compound (X) by reduction with lithium aluminium hydride. Above epimerization is corresponding to the conversion of α-conidendrin to β-conidendrin[3] and of α-conidendrin dimethyl ether to β-conidendrin dimethyl ether.[4]

An ethyl ester (XII) named ethyl retroresinolate, IR : $\nu_{\max}^{\mathrm{CHCl_3}}$ 1735 cm^{-1} (CO) (colorless glassy substance; yield, 37%) was obtained from VIII by refluxing with sodium ethoxide in ethanolic solution, where 43% of the starting material was recovered. This reaction is corresponding to the conversion of isodeoxypodophyllotoxin to methyl isodeoxypodophyllate[5] and of α-retrodendrin dimethyl ether to methyl α-retrodendrate dimethyl ether.[6]

It has now been concluded that the lactones (VI) and (VIII) have the same configuration, *trans*-(2,3)-*trans*-(3,4), and the constitutions of α-conidendrin type and α-retrodendrin[7] type, respectively.

The relation between carbonyl stretching frequencies and the configurations of the compounds (VI), (VIII) and (X) agrees with that of the lactones of podophyllotoxin type.[5] This conclusion was supported by the nuclear magnetic resonance spectra of the compounds (II), (V), anhydrolyoniresinol dimethyl ether (XIII), m.p. 142.9°, $[\alpha]_D^{16.3}$ −39.3° (c=1.46, $CHCl_3$), (XIV), (XV), (XVI), (XVII), (XVIII) and (XIX). In pyridine solution the compounds having *trans*-configuration at (2,3) showed a signal at about 2.5 p.p.m. (δ), and those having *trans*-configuration at (3,4) gave a signal at about 4.8 p.p.m., though there were some exceptions (Table I).

It would be concluded that lyoniresinol dimethyl ether (V) and isolariciresinol dimethyl ether (XX, R=OH) possess the same absolute configuration (2*R*:3*R*:4*S*), because the shifting of the optical rotation between V and of its anhydro compound (XIII) ($[\alpha]_D^{15.8}$ +49°[*1] → $[\alpha]_D^{16.3}$ −39.3°) is parallel with that of isolariciresinol dimethyl ether (XX, R=OH) and of its anhydro compound (XX, R=R=O) ($[\alpha]_D^{20}$ +15.8° → $[\alpha]_D^{20}$ −50°),[6] and is antipodal with that of the diol from isodeoxypodophyllotoxin (XVI) and of its anhydro compound ($[\alpha]_D^{20}$ −22.4° → $[\alpha]_D^{21}$ +30.7°).[6]

Free aglycone, lyoniresinol (II), m.p. 171° (*Anal.* Calcd. for $C_{22}H_{28}O_8$: C, 62.84; H, 6.71. Found : C, 62.81; H, 6.71) was also isolated from the wood of *Lyonia ovalifolia* var. *elliptica*.

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[*1] (c=2.4, $CHCl_3$).

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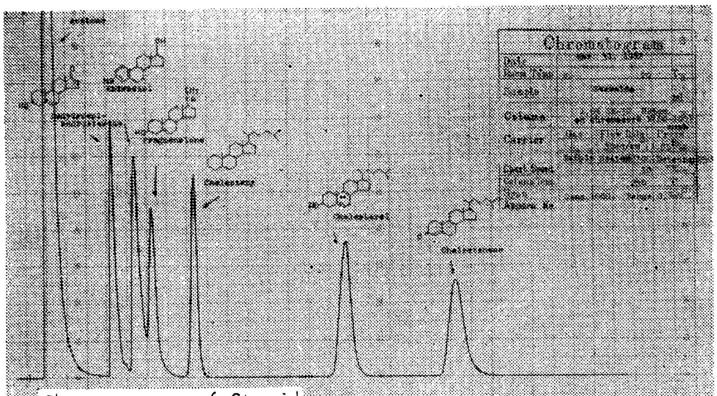

Chromatogram of Steroid