result in decomposition of the product. Two or three intermediates, whose structures have not been determined yet, have been obtained. The mechanism of this reaction is now under investigation.

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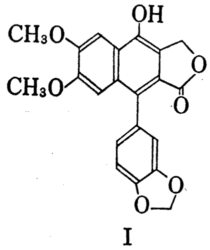
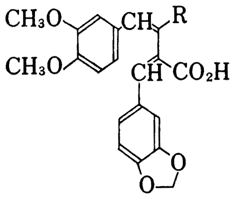
Biogenetic-Type Transformation of α-[α-(Hydroxymethyl)-3,4-dimethoxystyryl]-3,4-methylenedioxycinnamic Acid γ-Lactone into Diphyllin

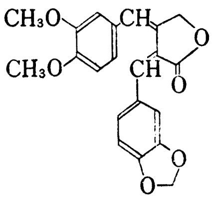
In the preceding paper,[1] we have described the structure and synthesis of diphyllin (I). Recently, Lin, *et al.*[2] have reported that taiwanin A coexisted together with taiwanin C and E in a plant and that an acetone solution of taiwanin A, after standing in the light, gave taiwanin C and E. Accordingly, we assumed that dibenzylidenebutyrolactone derivatives[2,3] could be a biogenetic precursor[4] of 1-aryl-4-hydroxy-2,3-naphthalide type lignans.[5]

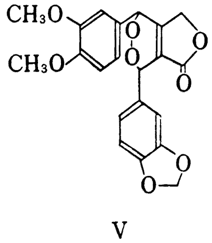
In this communication, we wish to report the biogenetic-type transformation of α-[α-(hydroxymethyl)-3,4-dimethoxystyryl]-3,4-methylenedioxycinnamic acid γ-lactone (IV)[6] into diphyllin (I) *via* photosensitized oxygenation.[7]

The Stobbe condensation of veratrole with diethyl piperonylidenesuccinate[8] gave the half ester (II)[6] (77%), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, 1705, which was reduced on lithium aluminum diethoxyhydride[9] to give the alcohol (III)[6] (44%), IR ν_{max}^{Nujol} cm^{-1}: 3370, 1685, and subsequent treatment with *p*-toluenesulfonic acid gave the lactone (IV)[6] IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750. A solution of the lactone (IV)[6] and Rose Bengal in acetone, through which dry oxygen was bubbled,


I


II : R=$CO_2C_2H_5$
III : R=CH_2OH


IV


V

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was irradiated for 30 min, with a 100 watt high-pressure mercury lamp enclosed in a Pyrex well. Preparative thin-layer chromatography of the crude product on silica gel gave diphyllin (I) (5%), mp 286—289°, which was identical with an authentic sample.

This photooxidative reaction is thought to proceed by a cyclic peroxide (V) formed by 1,4-addition of oxygen, by analogy to the reaction with cyclic diene.[7]

This method exemplifies a potentially important synthetic process of 1-aryl-4-hydroxy-2,3-naphthalide type lignans.

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The Structure of Caudatin

The structures of a number of polyoxypregnane derivatives isolated from *Cynanchum caudatum* MAX., a plant of Asclepiadaceae family, have been reported.[1] In addition to the previously described substances, we have newly isolated polyoxypregnane-derivatives condurango ester F (II),[2] caudatin (IV), isolineolon (V),[3] lineolon (VI),[4] deacylmetaplexigenin (III),[3] and sarcostin (I),[4,5] as aglycones of the glycosides.

The evidence establishing structure IV for the new compound caudatin is reported in the present communication. The molecular formula of $C_{28}H_{42}O_7$ (M^+ at *m/e* 490), (*Anal.* Calcd. for $C_{28}H_{42}O_7$: C, 68.54; H, 8.63. Found: C, 68.47; H, 8.70) was given for caudatin, mp 158—160/190—195° (double melting point), $[\alpha]_D^{20}+20.8°$ ($c=0.5$, $CHCl_3$). Caudatin (IV) exhibits the following spectroscopic properties, ultraviolet spectrum (UV) λ_{max}^{MeOH} 221 nm, ($\varepsilon=15900$) ($\alpha\beta$-unsaturated ester), infrared spectrum (IR) $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715, 1680 (shoulder), 1645 (conjugated double bond), 1170 ($\alpha\beta$-unsaturated ester). The nuclear magnetic resonance (NMR) spectrum of IV indicates the presence of two olefinic protons (δ 5.32, broad singlet; δ 5.5, singlet), a methylketone (δ 2.15, singlet), a vinyl methyl (δ 2.1, 3H, singlet), a geminal dimethyl (δ 1.05, 6H, doublet), and two angular methyls (δ 1.12, 3H, singlet; δ 1.4, 3H, singlet).[6] The mass spectrum suggests the presence of a ikemaoyl (3,4-dimethyl-2-pentenoyl) group, *m/e*: 362 ($M^+-C_7H_{12}O_2$), 111 ($C_7H_{11}O$), and methylketone, 447 (M^+-COCH_3), 43 ($COCH_3$).

Alkali hydrolysis of IV with 5% methanolic potassium hydroxide yields deacylmetaplexigenin (III) $C_{21}H_{32}O_6$ (M^+ at *m/e* 380), mp 217—220°, IR ν_{max}^{Nujol}: 1710 cm^{-1} (methylketone),

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