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, (ε=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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[1] H. Mitsuhashi and Y. Shimizu, *Chem. Pharm. Bull.* (Tokyo), 7, 649 (1959); *idem, ibid.*, **7**, 949 (1959); *idem, ibid.*, **8**, 565 (1960); *idem, ibid.*, **8**, 738 (1960); *idem, ibid.*, **10**, 719 (1962); *idem, ibid.*, **10**, 725 (1962).

[2] K. Hayashi and H. Mitsuhashi, The 90th Annual Meeting of the Pharmaceutical Society of Japan, Abstract Papers, Sapporo, **II**, 215 (1970).

[3] H. Mitsuhashi, Y. Shimizu, T. Nomura, T. Yamada, and E. Yamada, *Chem. Pharm. Bull.* (Tokyo), **11**, 1198 (1963).

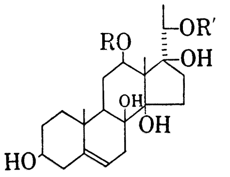
[4] H. Mitsuhashi and Y. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **10**, 433 (1962).

[5] Y. Shimizu and H. Mitsuhashi, *Tetrahedron*, **24**, 4143 (1968).

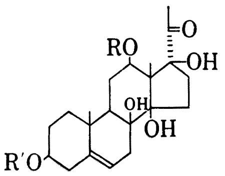
[6] All NMR spectra were taken in $CDCl_3$.

and ikemaic acid⁷⁾ (VII), $C_7H_{12}O_2$, m/e: 128 (M^+), 113 (M^+-CH_3), 83 (M^+-CO_2H), UV λ_{max}^{MeOH}: 221 nm, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3630, 1698, 1640 (conjugated double bond), gas liquid chromatography (t_R, 7.2, 8.4 min).⁸⁾ These two peaks are likely to be geometric isomers of ikemaic acid. The confirmation of this problem is on the way. Deacylmetaplexigenin was identified by mixed melting point with authentic specimen. Acetylation of caudatin with acetic anhydride in pyridine at room temperature gave monoacetate (IVa), $C_{30}H_{44}O_8$ m/e; 532 (M^+), 489, 472, IR ν_{max}^{neat} cm^{-1}: 1730, 1710, 1240.

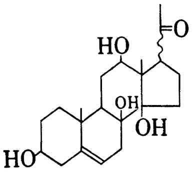
The NMR signal due to a proton on C_{12} of caudatin (IV) appears at δ 4.52 (J=9 and 6.5 Hz) as quartet. From these it is concluded that caudatin (IV) is the ester of deacylmetaplexigenin (III) with ikemaic acid (VII), and the ester linkage is located at 12β-hydroxyl group of deacylmetaplexigenin (III).⁹⁾



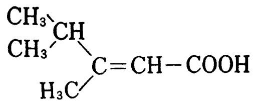
I : R=R'=H
II : R, R'= { nicotinoyl, cinnamoyl }



III : R=R'=H
IV : R=ikemaoyl
R'=H
IVa : R=ikemaoyl
R'=acetyl



V : $C_{17\alpha}$–H
VI : $C_{17\beta}$–H



$$(CH_3)_2CH(H_3C)C{=}CH{-}COOH$$

VII

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7) H. Mitshuhashi and Y. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **8**, 318 (1960).

8) 25% DEGS. 2 m Glass Column. Column temperature 180°. Injection port temperature 200°. Detector temperature 250°. Detector, FID. Carrier gas, N_2.

9) J.E. Bridgeman, P.C. Cherry, A.S. Cleggy, J.M. Evans, Sir Ewart R.H. Jones, A. Kasal, V. Kumar, G.D. Meakins, Y. Morisawa (Mrs.), E.E. Richards, and P.D. Woodgate, *J. Chem. Soc.* (*C*), **1970**, 250.