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SHORT COMMUNICATION

THE ETHER-SOLUBLE LIGNANS OF *TRACHELOSPERMUM ASIATICUM* VAR. *INTERMEDIUM*

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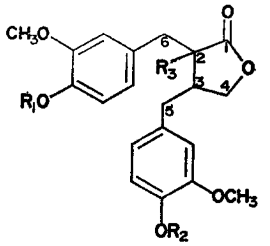
Abstract—Matairesinol (I), arctigenin (II), trachelogenin (III) and a new lignan, *nortrachelogenin* (IV), have been isolated from stems of *Trachelospermum asiaticum* var. *intermedium*. The structure of IV has been proposed.

IN THIS paper the ether-soluble lignans of stems of *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai are investigated.

The ether-soluble lignans were separated to 10% Na_2CO_3-soluble fraction A and 10% NaOH-soluble fraction B. Fractions A and B were chromatographed on silica gel and eluted with chloroform–ethylacetate mixture, respectively. Compounds I and IV were isolated from fraction A. Compounds II and III were isolated from fraction B.

(I) m.p. 117–119°, (II) m.p. 101–102°, and (III) amorphous, were identified as matairesinol (I), arctigenin (II) and trachelogenin (III),* respectively, by comparison with aglycones of lignan glucosides isolated from the stems of the title plant.[1,2]



I : $R_1 = H$, $R_2 = H$, $R_3 = H$
II : $R_1 = H$, $R_2 = CH_3$, $R_3 = H$
IV : $R_1 = H$, $R_2 = H$, $R_3 = OH$
III : $R_1 = H$, $R_2 = CH_3$, $R_3 = OH$
V : $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = H$
VI : $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = OH$
VIII : $R_1 = C_2H_5$, $R_2 = C_2H_5$, $R_3 = H$
VII : $R_1 = C_2H_5$, $R_2 = C_2H_5$, $R_3 = OH$

Both of I and II gave methylarctigenin (V) with excess diazomethane. III was further confirmed by conversion into hydroxy-acid, m.p. 149–150°, which was identical with trachelogenic acid. IV, $[\alpha]_D^{17}$-16·8 (ethanol), although chromatographically pure, could not be crystallized. The IR spectrum of IV in chloroform had absorptions at 1780 cm^{-1}, due to lactone and 3520 cm^{-1}, due to hydroxyl groups.

Methylation of IV with diazomethane gave methyltrachelogenin (VI), whose structure was proposed in previous paper.[2] Ethylation of IV with diazoethane yielded glassy ethyl ester (VII), which on the treatment with 1 N sodium hydroxide solution gave hydroxy-acid, m.p. 113–114·5°; ν_{max}^{KBr} 3420 (hydroxyl), 1705 (carboxyl), 1605, 1590, 1515 (aromatic C=C)

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* The authors proposed the possible structure as (III) (see Ref. 2).

[1] I. INAGAKI, S. HISADA and S. NISHIBE, *Chem. Pharm. Bull.* **16**, 2307 (1968).

[2] I. INAGAKI, S. HISADA and S. NISHIBE, *Phytochem.* **10**, 211 (1971).

cm^{-1}. (Mass spectrum calc. for $C_{24}H_{30}O_7$ (M^+-H_2O): 430·1991. Obsd.: 430·1975; calc. for $C_{10}H_{13}O_2$ [3-methoxy-4-ethoxy-benzyl]: 165·0915. Obsd.: 165·0913; Found: C, 64·05; H, 7·14. $C_{24}H_{32}O_8$ required: C, 64·27; H, 7·19%.)

Diethyl-ester (VIII) of I, m.p. 95–96° (Lit.[3] m.p. 97–98°), was prepared for comparison with VII. Hydroxy-acid of VIII had m.p. 123–124°; ν_{max}^{KBr} 3380 (hydroxyl), 1690 (carboxyl), 1605, 1590, 1515 (aromatic C=C), cm^{-1}. (Mass spectrum calc. for $C_{24}H_{30}O_6$ (M^+-H_2O): 414·2042. Obsd.: 414·2067; calc. for $C_{10}H_{13}O_2$ [3-methoxy-4-ethoxy-benzyl]: 165·0915. Obsd.: 165·0915; Found: C, 66·50; H, 7·43. $C_{24}H_{32}O_7$ required: C, 66·65; H, 7·46%.)

The mass spectral fragmentations of VII were similar to those of VIII and showed the increase of 16 mass units due to an extra hydroxyl group.

The NMR spectrum of VII showed signals assigned to aromatic protons (δ 6·4–6·9 ppm, unresolved multiplet, 6H), C-4 protons (δ 4·04 ppm, doublet, 2H), methoxyl protons (δ 3·87 ppm, singlet, 6H), ethoxyl protons (CH_3–δ 1·43 ppm, triplet, $J = 7{\cdot}5$ c/s, 6H; —CH_2–δ 3·95 ppm, quartet, $J = 7{\cdot}5$ c/s, 4H), C-3,5,6 protons (δ 2·3–3·2 ppm, multiplet, 5H) and hydroxyl proton (δ 2·63 ppm, singlet, 1H, quenched by deuterium).

Alkaline permanganate oxidation of VII gave only 3-methoxy-4-ethoxybenzoic acid.

The UV and IR spectral data for these lignans are as shown in Table 1 and Fig. 1.

TABLE 1. UV SPECTRA OF LIGNANS

Compounds	λ_{max}^{EtOH} nm (log ϵ)	$\lambda_{max}^{EtOH+NaOH}$ nm
I	283 (3·74)	298
II	282 (3·74)	302
V	281 (3·70)	—
IV	283 (3 75)	297
III	282 (3·68)	297
VI	281 (3·73)	—

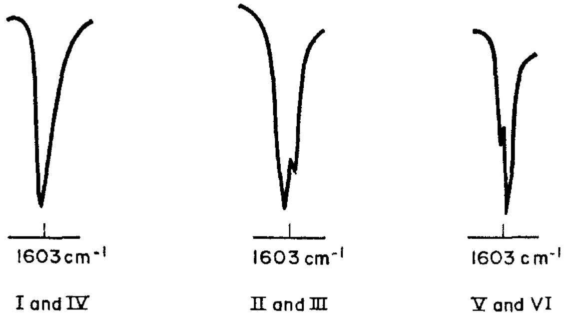

FIG. 1. ABSORPTION OF IR SPECTRA FOR AROMATIC C=C OF LIGNANS IN CHLOROFORM.

The spectrum λ_{max}^{EtOH} 283 nm and characteristic absorption of IR spectrum for aromatic C=C of IV clearly support the structure closely related with I.

From the above results, the authors propose 2-hydroxy-2,3-bis (3-methoxy-4-hydroxy-benzyl)-butyrolactone for IV and name nortrachelogenin.

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[3] R. D. HAWORTH and T. RICHARDSON, *J. Chem. Soc.* 633 (1935).