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SHORT COMMUNICATION

LIGNAN GLYCOSIDES OF *TRACHELOSPERMUM ASIATICUM* VAR. *INTERMEDIUM*

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Abstract—Matairesinol-4′-β-D-glucoside (matairesinoside) and tracheloside have been isolated from the stem of *Trachelospermum asiaticum var. intermedium*. The structure of tracheloside is discussed.

IN A PREVIOUS paper, arctiin(I) was reported as one of the constituents of *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai.[1] In addition, two lignan glycosides were obtained from the stem. One of glycosides, matairesinoside (II), was isolated by silica gel column chromatography of chloroform extracts after elution of the arctiin fraction. II was recrystallized from ethyl acetate to give a white powder, m.p. 93°; $[\alpha]_D^{12}$-46·0 (ethanol). (Found: C, 57·64; H, 6·41. $C_{26}H_{32}O_{11} \cdot H_2O$ required: C, 57·98; H, 6·36%.) On hydrolysis with dil. H_2SO_4, II gave matairesinol(IV), m.p. 117–119°; (found: C, 67·23; H, 6·15; calc. for $C_{20}H_{22}O_6$: C, 67·02; H, 6·19%) and glucose. On methylation with excess diazomethane, II gave I; therefore II is matairesinol-4′-β-D-glucoside.*

After extraction with chloroform, the mother liquor was evaporated to syrup and extracted with ethyl acetate. Second glycoside(III) was separated by crystallization from the ethyl acetate extracts. III, m.p. 168–170°; $[\alpha]_D^{20}$-60·0 (ethanol); ν_{max}^{KBr} 3450 (hydroxyl), 1770(lactone), 1610, 1590, 1515(aromatic C=C) cm^{-1}, was identified as tracheloside by i.r. spectrum, TLC and mixed melting point with an authentic sample, m.p. 168–171°.[2] The molecular formula for III was reported as $C_{36}H_{50}O_{18}$ by T. Takano *et al.*[2] but methyltrachelogenin was shown[3] to be identical with methylarctigenin(V) derived from arctigenin(VI),[1] hence the formula of III was doubtful.

We have found that the molecular formula of III is $C_{27}H_{34}O_{12}$. (Found: C, 57·90; H, 6·35. $C_{27}H_{34}O_{12} \cdot 1/2H_2O$ required: C, 57·95; H, 6·31%.)† On hydrolysis with dil. H_2SO_4, III gave an aglycone(VII) and glucose. VII, although chromatographically pure, could not be crystallized. On treatment with N NaOH, VII gave an hydroxy-acid, m.p. 149–150°. (Found: C, 62·19; H, 6·55. $C_{21}H_{26}O_8$ required: C, 62·06; H, 6·45%.) Alkaline $KMnO_4$ oxidation of VII gave 3,4-dimethoxybenzoic acid. The i.r. spectrum of VII had peaks at 1775 cm^{-1} (lactone) and 3560 cm^{-1} (hydroxyl groups). The NMR spectrum of VII

* Presented at the 89th Annual Meeting of the Pharmaceutical Society of Japan, Nagoya, April 1969. Authors proposed the structure independently, later knew the isolation of same glucoside from Forsythia species was reported by H. THIEME *et al. Pharmazie* **23**, 519 (1968).

† Presented at the Tokai Branch Meeting of the Pharmaceutical Society of Japan, Gifu, November 1969

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

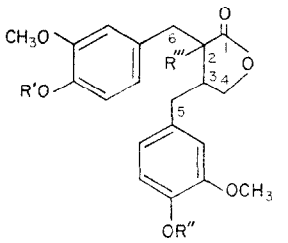
[2] M. MIYAZAKI, H. WATANABE and T. TAKANO, *Yakugaku Zasshi* **78**, 879 (1958).

[3] H. WATANABE and T. TAKANO, *Yakugaku Zasshi* **78**, 882 (1958).

showed signals assigned to aromatic protons (δ 6·6–7·0 ppm, unresolved multiplet, 6H), phenoxyl protons (δ 5·83 ppm, singlet, 1H, quenched by deuterium exchange), C-4 protons (δ 4·08 ppm, doublet, 2H), methoxyl protons (δ 3·95 ppm, singlet, 9H), C-3,5,6 protons (δ 2·4–3·3 ppm, multiplet, 5H) and hydroxyl proton (δ 2·53 ppm, singlet, 1H, quenched by deuterium). The Gibbs test was negative. Methylation of VII with diazomethane yielded an amorphous methyl ester of the aglycone(VIII), which on treatment with N NaOH gave a hydroxy-acid, m.p. 97–99°; mass spectrum *m/e* 402 (M^+-H_2O), 151 (dimethoxybenzyl). (Found: C, 63·08; H, 6·85. $C_{22}H_{28}O_8$ required: C, 62·84; H, 6·71%). The i.r. spectrum of VIII was not identical with that of methyltrachelogenin.[3] The NMR spectrum of VIII indicated all the phenolic hydroxyls were methylated. The hydroxyl group resisting acetylation was presumed to be tertiary and attached to C-2 or C-3 of lactone ring. Further evidence of the absence of hydroxyl group attached to the benzylic carbons was provided by the lack of a colour reaction with *N*-chloro-*p*-benzoquinoneimide.[4]

TABLE 1. U.V. SPECTRA OF LIGNAN DERIVATIVES

Compounds	λ_{max}^{EtOH} nm	$\lambda_{max}^{EtOH+NaOH}$ nm
I	280	no shift
II	281	297
III	280	no shift
IV	283	298
VI	282	302
V	281	no shift
VII	282	297
VIII	281	no shift



I: R′ = glucosyl, R″ = CH_3, R‴ = H
II: R′ = glucosyl, R″ = R‴ = H
III: a R′ = glucosyl, R″ = CH_3, R‴ = OH
b R′ = CH_3, R″ = glucosyl, R‴ = OH
IV: R′ = R″ = R‴ = H
V: R′ = R″ = CH_3, R‴ = H
VI: R′ = R‴ = H, R″ = CH_3
VII: a R′ = H, R″ = CH_3, R‴ = OH
b R′ = CH_3, R″ = H, R‴ = OH
VIII: R′ = R″ = CH_3, R‴ = OH

In the NMR spectra of VII and VIII both hydrogens of the methylene at C-4 appear as doublet signals at δ 4·08 ppm with separation of 6·0 c/s. The methylene at C-4 of IV, V and VI, on the other hand, give a multiplet in the range δ 4·0–4·4 ppm, δ 4·1–4·4 ppm and δ 3·9–4·4 ppm, respectively. The methylene at C-4 of hydroxythujaplicatin methyl ether, di-*O*-methylhydroxythujaplicatin methyl ether[5] and alcohol of helianthoidin,[6] all having a hydroxyl group attached to C-2, appear as doublet signals at δ 4·05 ppm, δ 4·07 ppm and δ 4·02 ppm with a separation of 6·0 c/s, respectively. The NMR spectra of VII and VIII thus clearly suggest a hydroxyl group attached to C-2 of the lactone ring. VIII should be 2-hydroxy-2,3-bis(3,4-dimethoxybenzyl)-butyrolactone. The u.v. spectra of lignan derivatives

[4] J. GIERER, *Acta Chem. Scand.* **8**, 1319 (1954).
[5] H. MACLEAN and K. MURAKAMI, *Can. J. Chem.* **44**, 1827 (1966).
[6] R. S. BURDEN, L. CROMBIE and D. A. WHITING, *J. Chem. Soc.* **5**, 693 (1969).

are as shown in Table 1. The NMR spectrum of acetylated III showed the presence of four acetoxyls (δ 2·01 and 2·05 ppm), attached to the glucosyl group. These results suggest two possible structures for both VII and III; VIIa or VIIb and IIIa or IIIb respectively. Both the co-occurence of III with I and II and from the biogenetic point of view, III probably have the structure IIIa.

Chemical proof of the structure IIIa and the configuration of the tertiary hydroxy group are being carried out.

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[7] D. A. WHITING, personal communication (1970).