The reaction proceeds also in dry ethanol at room temperature and is catalized by sodium ethoxide.

Nicotinamide and isonicotinamide also add to the nitrone in dry ethanol to give the expected 1:1 adduct. The structure of the adduct was confirmed by elemental analysis (shown in the Table) and the following spectral evidences. The infrared (IR) spectrum of (I-d) (KBr disk) exhibits strong absorptions at 3350 and 3210 cm^{-1} (NH and OH), and two characteristic absorptions of secondary amide at 1526 and 1216 cm^{-1}. The nuclear magnetic resonance (NMR) spectrum of (I-d) (in DMSO-d_6 with tetramethylsilane as an internal reference) shows a broad singlet at τ 1.88 (1H, CHO), a singlet at 1.62 (1H, OH), a broad doublet at 1.69 (1H, NH), and a triplet at 5.76 (1H, Pri–C<u>H</u>–NHCO).

Many runs carried out on both aromatic and cyclic nitrones, which have no α-cyano group, failed to give the similar adduct.

The studies on the additional chemical and physical properties of the adduct, and the reaction of other amides with nitrones are now being in progress.

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Structures of Tracheloside and Nortracheloside from *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai

During our investigation on the constituents of the stems of *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai (Apocynaceae), three lignan glucosides, arctiin (I), matairesinoside (II) and tracheloside have hitherto been isolated.[1,2]

In addition, we have isolated a new lignan glucoside named nortracheloside from the ethyl acetate-soluble fraction of the methanol extracts by silica gel column chromatography.

This paper deals with the structures of tracheloside and nortracheloside.

In a previous paper, we suggested the structure of tracheloside as IX or X.[2] We have now proposed X for tracheloside and XI for nortracheloside.

XI, $C_{26}H_{32}O_{12}\cdot H_2O$, mp 95—100°, was obtained as a white powder from chloroform–ethanol, $[\alpha]_D^{19}$ −47.9 (c=1.02, EtOH), UV λ_{max}^{EtOH} mμ (log ε):229 sh (4.07), 282 (3.70), $\lambda_{max}^{EtOH+NaOH}$ mμ: 247, 284, 298, IR ν_{max}^{KBr} cm^{-1}: 1770 (C=O), 1605, 1515 (aromatic C=C).

On hydrolysis with dil. H_2SO_4, XI gave D-glucose and amorphous nortrachelogenin (XIII) which was already isolated from the ether-soluble fraction and elucidated to be 4,4′,8′-trihydroxy-3,3′-dimethoxy-lignan-olid(9,9′).[3]

On methylation with excess diazomethane, XI gave X, $C_{27}H_{34}O_{12}\cdot 1/2H_2O$, mp 168—170°. Enzymatic hydrolysis of X with β-glucosidase gave D-glucose and trachelogenin (XII). Hence, XI is mono-glucoside of XIII.

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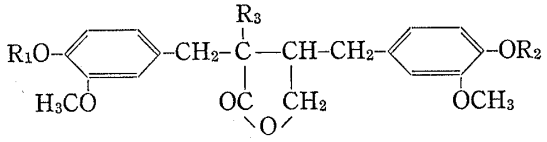
1) I. Inagaki, S. Hisada and S. Nishibe, *Chem. Pharm. Bull.* (Tokyo), **16**, 2307 (1968).
2) I. Inagaki, S. Hisada and S. Nishibe, *Phytochemistry*, **10**, 211 (1971).
3) S. Nishibe, S. Hisada and I. Inagaki, *Phytochemistry*, in press.



I: R_1=glucose, R_2=CH_3, R_3=H
II: R_1=glucose, R_2=H, R_3=H
III: R_1=H, R_2=CH_3, R_3=H
IV: R_1=H, R_2=H, R_3=H
V: R_1=CH_3, R_2=CH_3, R_3=H
VI: R_1=C_2H_5, R_2=CH_3, R_3=H
VII: R_1=CH_3, R_2=C_2H_5, R_3=H
VIII: R_1=C_2H_5, R_2=C_2H_5, R_3=H
IX: R_1=glucose, R_2=CH_3, R_3=OH
X: R_1=CH_3, R_2=glucose, R_3=OH
XI: R_1=H, R_2=glucose, R_3=OH
XII: R_1=CH_3, R_2=H, R_3=OH
XIII: R_1=H, R_2=H, R_3=OH
XIV: R_1=CH_3, R_2=CH_3, R_3=OH
XV: R_1=CH_3, R_2=C_2H_5, R_3=OH
XVI: R_1=C_2H_5, R_2=CH_3, R_3=OH
XVII: R_1=C_2H_5, R_2=C_2H_5, R_3=OH

Chart 1

In order to determine the attached possition of D-glucose in X and XI, we prepared XII, methyltrachelogenin (XIV) and ethyltrachelogenin (XV) from X, ethylmethylnortrachelogenin (XVI) and diethylnortrachelogenin (XVII) from XI.

These derivatives were amorphous and gave crystalline hydroxy-acids on treatment with 1N NaOH as follows ; hydroxy-acids of XII, $C_{21}H_{26}O_8$, mp 149—150°, XIV, $C_{22}H_{28}O_8$, mp 97—99°, XV, $C_{23}H_{30}O_8$, mp 114—115°, XVI, $C_{23}H_{30}O_8$, mp 115—116.5°, XVII, $C_{24}H_{32}O_8$, mp 113—114.5°.

Also we prepared arctigenin (III), $C_{21}H_{24}O_6$, mp 101—102°, methylarctigenin (V), $C_{22}H_{26}O_6$, mp 126—127°, and ethylarctigenin (VI), amorphous, from I, matairesinol (IV), $C_{20}H_{22}O_6$, mp 117—119°, ethylmethylmatairesinol (VII), $C_{23}H_{28}O_6$, mp 97—99°, and diethylmatairesinol (VIII), $C_{24}H_{30}O_6$, mp 95—96°, from II.

Mass spectra of III, IV, V, VI, VII, VIII, XII, XIV, XV, XVI and XVII were measured and discussed.

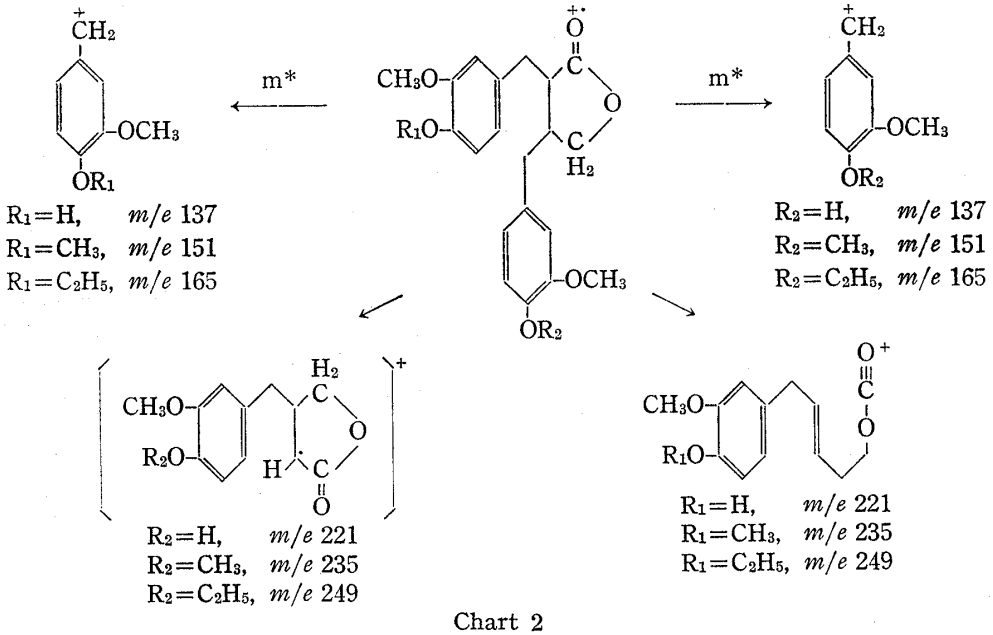


Chart 2

The relative abundances of fragment peaks due to benzyl cations were particulaly significant. These peakes could be interpreted as shown in Chart 2 and 3. The presence of the metastable ion appropriate to a transition is denoted by m*. The peaks due to benzyl cations were as shown in Fig. 1. The peak of *m/e* 151 which was higher intensity than that of *m/e* 165 could be observed in both of VI and VII.

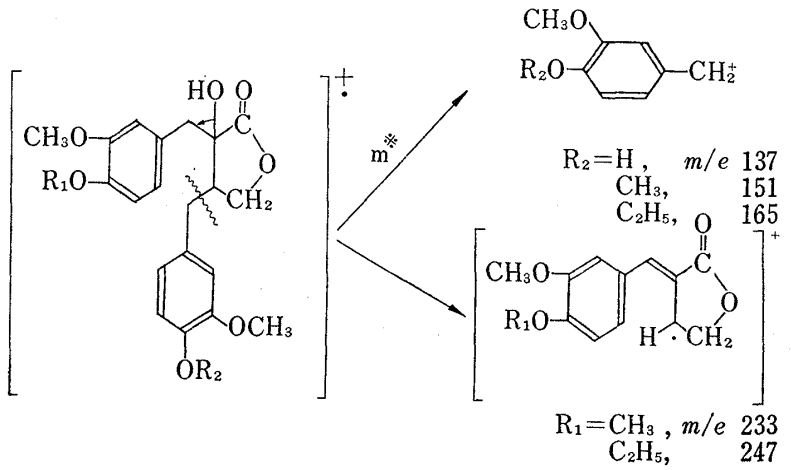


Chart 3

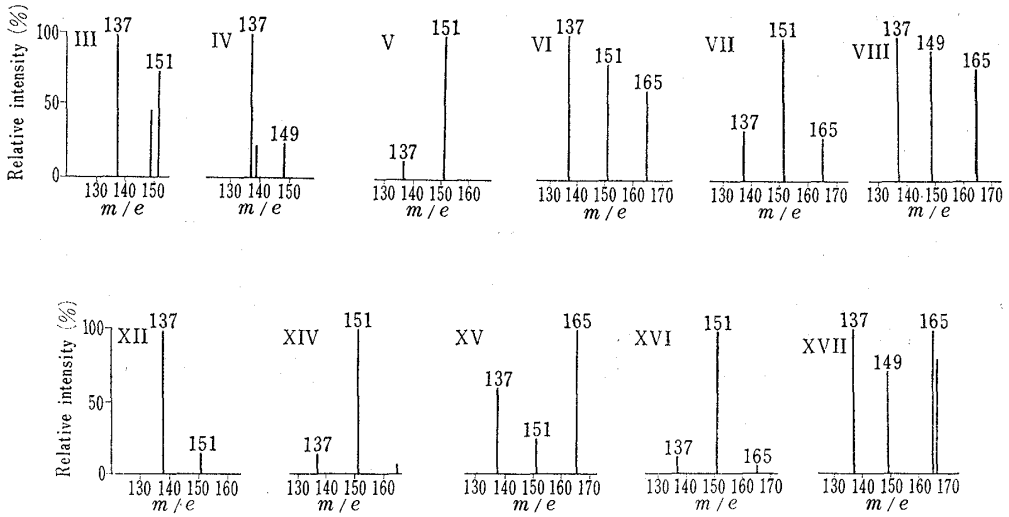


Fig. 1

However, the conversion of the intensity was occured between XV and XVI. The ions at *m/e* 151 (24%) in XV, *m/e* 165 (6%) in XVI and *m/e* 151 (16%) in XII could not be associated with any of the observable metastable ions. As the results, structures XV, XVI and XII are supported.

Thus, X and XI were established to be 4,8′-dihydroxy-3,3′,4′-trimethoxy-lignan-olid (9,9′)-4-β-D-glucopyranoside and 4,4′,8′-trihydroxy-3,3′-dimethoxy-lignan-olid (9,9′)-4-β-D-glucopyranoside by the nomenclature of Freudenberg and Weinges,[4] respectively.

The configuration of tertiary hydroxy group of X and XI is under investigation.

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