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

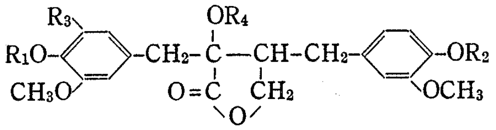
In previous paper[1] we proposed that structures of tracheloside (I) and nortracheloside(II) are to be 4,8′-dihydroxy-3,3′, 4′-trimethoxy-lignan-olid(9,9′)-4-β-D-glucopyranoside and 4,4′,8′-trihydroxy-3,3′-dimethoxy-lignan-olid(9,9′)-4-β-D-glucopyranoside, respectively, from the mass spectral measurements of their related derivatives.

In this case, we reported the relative abundances of fragment peaks due to benzyl cations were particularly significant and the change of the fragment intensity due to benzyl cations was observed between III and IV.

But recently we found that the peak of higher intensity and the presence of the metastable ion due to benzyl cation could be observed only from benzyl group attached to C-8′ having tertiary hydroxy group in the mass spectrum of di-O-methyl hydroxythujaplicatin methyl ether(V) whose structure is already established.

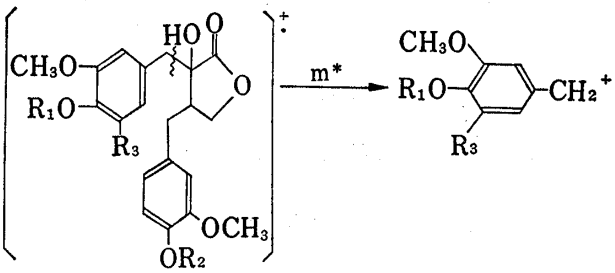
This fact suggested that the previous fragmentation pathways[1] for interpretation of the change of fragment intensity were wrong.

Therefore, it is reasonable for the benzyl peak of higher intensity to be interpreted as shwon in Chart 2.



I: R_1=glucosyl, $R_2=CH_3$, $R_3=H$, $R_4=H$
II: R_1=glucosyl, $R_2=H$, $R_3=H$, $R_4=H$
III: $R_1=C_2H_5$, $R_2=CH_3$, $R_3=H$, $R_4=H$
IV: $R_1=CH_3$, $R_2=C_2H_5$, $R_3=H$, $R_4=H$
V: $R_1=CH_3$, $R_2=CH_3$, $R_3=OCH_3$, $R_4=H$
VI: $R_1=CH_3$, $R_2=CH_3$, $R_3=H$, $R_4=CH_3CO$
VII: $R_1=C_2H_5$ $R_2=CH_3$, $R_3=H$, $R_4=CH_3CO$

Chart 1



$R_1=C_2H_5$, $R_2=CH_3$, $R_3=H$, *m/e* 416	$R_1=C_2H_5$, $R_3=H$, *m/e* 165
$R_1=CH_3$, $R_2=C_2H_5$, $R_3=H$, *m/e* 416	$R_1=CH_3$, $R_3=H$, *m/e* 151
$R_1=CH_3$, $R_2=CH_3$, $R_3=OCH_3$, *m/e* 432	$R_1=CH_3$, $R_3=OCH_3$, *m/e* 181

Chart 2

Moreover the fragmentation pathways of acetyl derivatives, VI, $C_{24}H_{28}O_7$, mp 101—102°, and VII, $C_{25}H_{30}O_7$, mp 121—123°, were as shown in Chart 3. The presence of the metastable ion appropriate to a transition is denoted by *m**.

These fragmentation pathways were sufficiently supported from that of helianthoidin which has piperonyl ester at tertiary hydroxy group.[2]

So the attached position of D-glucose in I and II should be changed to 4′-position from 4-position.

Thus, I and II were correctly 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, respectively.

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[1] S. Nishibe, S. Hisada and I. Inagaki, *Chem. Pharm. Bull.* (Tokyo), **19**, 866 (1971).
[2] R.S. Burden, L. Crombie and D.A. Whiting, *J. Chem. Soc.* (*C*), **1969**, 693.

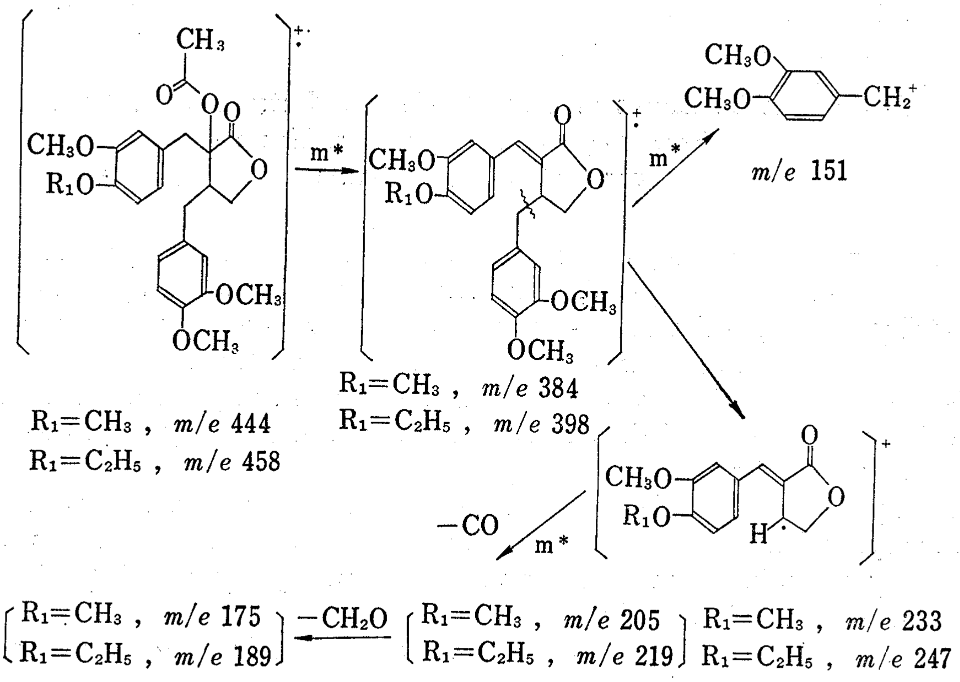

Chart 3

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Novel Ring Expansions of Pyrrolo-pyrimidines to Pyrimido-pyrimidines

We report two novel conversions of pyrrolo-pyrimidines into pyrimido-pyrimidines involving reduction-induced and nucleophile-induced ring expansions.

Method A

Stirring 1,3-dimethyl-5-nitroso-6-phenylpyrrolo[2,3-*d*]pyrimidine-2,4(1H, 3H)-diones (Ia, Ib and Ic) under mild reflux with excess potassium pyrosulfite ($K_2S_2O_5$) in dimethylformamide (DMF) for 1 hr followed by cooling caused 1,3-dimethyl-5-hydroxy-7-phenylpyrimido[4,5-*d*] pyrimidine-2,4(1H, 3H)-diones (IIa, IIb and IIc)[1] (mp>320° for all) to separate (52%, 60% and 48%). To our knowledge, the reaction seems to be the first example in which $K_2S_2O_5$ was successfully introduced into preparative organic chemistry. Treatment of Ia with sodium

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[1] F. Yoneda and M. Higuchi, *Chem. Commun.*, **1972**, 402.