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On the Constituents of *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai

As one of the constituents of *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai (Apocynaceae), Japanese name "Teikakazura," tracheloside (I′) was already reported by T. Takano, *et al.*[1] Recently we obtained several glycosides through silica gel column chromatography of chloroform extracts of the stem. One of the glycosides, mp 174°, IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 3400 (broad OH), 1773 (C=O), 1593, 1513 (aromatic C=C), was shown to be identical with tracheloside from infrared spectrum, thin-layer chromatography and mixed fusion.

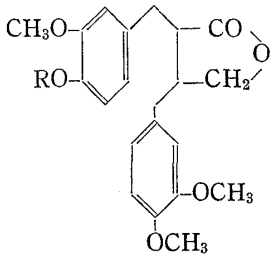
Another component of these glycosides was recrystallized from ethyl acetate containing a small amount of water to give white crystalline powder.

This compound showed mp 112°, $[\alpha]_D^{27}$ −51.5 (c=2.0 in EtOH), UV $\lambda_{\max}^{\text{EtOH}}$ mμ (log ε): 230 (4.26), 280 (3.63), IR $\nu_{\max}^{\text{KBr}}$ cm^{-1}: 1780 (C=O), 1593, 1510 (aromatic C=C), NMR ($CDCl_3$) δ: 6.48—6.99 (6H, multiplet, aromatic H), 3.71, 3.79, 3.82 (9H, 3 singlet, 3 CH_3O-), (*Anal.* Calcd. for $C_{27}H_{34}O_{11}\cdot H_2O$[2]: C, 58.69; H, 6.57. Found: C, 58.63; H, 6.55) and no depression with arctiin[3] (I) which was isolated from *Arctium lappa* L. and recrystallized from ethyl acetate containing a small amount of water. The ultraviolet, infrared, nuclear magnetic resonance (UV, IR, NMR) spectra and *Rf* value on thin-layer chromatography (TLC) (Merck silica gel G, $CHCl_3$–EtOH=8:2) were identical with those of arctiin.

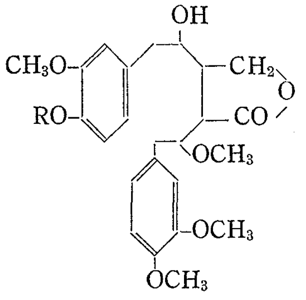
It is the first example and a very interesting fact that arctiin which is at present only known in specific species of Compositae[4] has also been found in Apocynaceae.

Moreover, in the comparison of methyltrachelogenin (II′) with the methylate of arctigenin (II) and dimethylmatairesinol (III), respectively by IR, TLC and mixed fusion, it was found that they are all the same compounds.

Therefore, the structure of methyltrachelogenin[5] (II′) should be corrected to be represented by dimethylmatairesinol or arctigenin methyl ether (III).



I: R=$C_6H_{11}O_5$
II: R=H
III: R=CH_3



I′: R=$C_{12}H_{21}O_{10}$
II′: R=CH_3
(Formulas by Takano)

Studies on the other glycosides are in progress.

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[1] M. Miyazaki, H. Watanabe, and T. Takano, *Yakugaku Zasshi*, **78**, 879, 882 (1958).

[2] The molecular formula $C_{30}H_{40}O_{12}$ in Abstracts of papers of the 88th Annual Meeting of the Pharmaceutical Society of Japan, Tokyo, April 1968, p. 217. should be corrected.

[3] T. Omaki, *Yakugaku Zasshi*, **55**, 816 (1935); **56**, 982, 985 (1936).

[4] R. Hänsel, H. Schulz, and Ch. Leuckert, *Z. Naturforsch.*, **19b**, 727 (1964).

[5] T. Takano, *Yakugaku Zasshi*, **79**, 443, 447 (1959).

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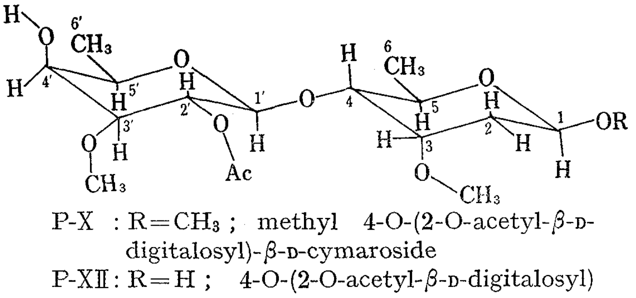
A New Acetylbiose from Steroidal Glycosides of "Pei-Wujiapi"

In continuation of our study on the chemical constituents of "Pei–Wujiapi"[1,2] (Asclepiadaceae), two new compounds (P-X and P-XII) were obtained from steroidal glycoside H_1[1] or total glycosides fraction by mild acidic hydrolysis. The isolation of these compounds from hydrolysis mixture was carried out by column chromatography on silica gel developed with ethyl acetate.

P-X, $C_{17}H_{30}O_9$, mp 171°, colorless needles (from AcOEt), $[\alpha]_D^{23}$ $-25.5°$ (c=1.10 pyridine), IR ν_{max}^{KBr} cm^{-1}: 3550, 1750, 1240, gave monoacetate, mp 116°, $[\alpha]_D^{23}$ $-22.4°$ (c=0.98 pyridine), IR ν_{max}^{KBr} cm^{-1}: 1750, 1240 with Ac_2O in pyridine at room temperature.

P-XII, $C_{16}H_{28}O_9$, mp 177°, colorless needles (from AcOEt-hexane), $[\alpha]_D^{21}$ $-55.7°$ (c=0.47 pyridine), IR ν_{max}^{KBr} cm^{-1}: 1745, 1240, showed positive color reaction with aniline hydrogen phthalate, NH_3–$AgNO_3$ (Tollens' R), xanthohydrol, *p*-nitrophenylhydrazine but negative with $NaIO_4$–benzidine.



P-X : R=CH_3 ; methyl 4-O-(2-O-acetyl-β-D-digitalosyl)-β-D-cymaroside
P-XII : R=H ; 4-O-(2-O-acetyl-β-D-digitalosyl)-D-cymarose

When P-X was treated with 0.4 N KOH under the gas flow of N_2 at 50° for 2 hr, deacetyl P-X, $C_{15}H_{28}O_8$, mp 116°, $[\alpha]_D^{21}$ $-6.7°$ (c=0.75 pyridine), IR ν_{max}^{Nujol} cm^{-1}: 3500, was formed. The formation of D-cymarose and D-digitalose from deacetyl P-X was revealed by gas liquid-chromatography (GLC)[3] and thin-layer chromatography (TLC)[3] of the hydrolysate of deacetyl P-X with 0.05 N H_2SO_4 refluxed on water bath for 30 min. The optical rotation of each sugars were measured on the samples which were collected by preparative TLC.

When P-XII was refluxed with anhydrous 0.05 N HCl–MeOH for 30 min, P-X was produced with other by-products. On the other hand, when P-X was heated with 0.05 N H_2SO_4 for 15 min, P-XII was formed. From these facts it was elucidated that P-X was methyl glycoside of P-XII and formed from the glycosides of Pei–Wujiapi by methanolic acid-hydrolysis.

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1) S. Sakuma, S. Kawanishi, J. Shoji and S. Shibata, *Chem. Pharm. Bull.* (Tokyo), **15**, 720 (1967).
2) S. Sakuma, S. Kawanishi, J. Shoji and S. Shibata, *Chem. Pharm. Bull.* (Tokyo), **16**, 326 (1968).
3) S. Sakuma, S. Kawanishi and J. Shoji, *Shoyakugaku Zasshi*, **22**, 23 (1968).

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