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APOCYNACEAE

COMPARATIVE EXAMINATION ON CONSTITUENTS OF SEVERAL *TRACHELOSPERMUM* SPECIES

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Abstract—The stem constituents of several *Trachelospermum* species were investigated. All species except *T. difforme* contain a series of four lignan glucosides. Dambonitol was found in all species investigated.

DURING an investigation of the stem constituents of *Trachelospermum asiaticum* Nakai var. *intermedium* Nakai, four lignan glucosides were isolated, namely arctiin, tracheloside, matairesinoside and nortracheloside.[1-3] The structures of matairesinoside, tracheloside and nortracheloside[2,3] were shown to be 4,4′-dihydroxy-3,3′-dimethoxy-lignan-olid(9,9′)-4′-β-D-glucopyranoside, 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. Dambonitol (1,3-di-*o*-methyl-*myo*inositol), $C_8H_{16}O_6$, m.p. 209–210°, was also isolated.[4]

In this paper a brief comparative examination of several *Trachelospermum* species for lignan glucosides and dambonitol is described.

The plant materials collected were: *T. asiaticum* Nakai var. *intermedium* Nakai in April 1968 at Kushimoto (Japan); *T. liukiuense* Hatusima in January 1970 at Yakushima; *T foetidum* Nakai in August 1969 at Ogasawara; *T. jasminoides* Lemaire var. *pubescens* Makino in August 1969 at Kumamoto; *T. jasminoides* Lemaire in August 1970 at Wuusau (Taiwan); *T. gracilipes* Hooker in August 1970 at Wuusau; and *T. difforme* A. Gray in August 1970 in Mississippi (U.S.A.).

The results are as shown in Table 1. All Asiatic species are chemically almost alike, but

TABLE 1. CONSTITUENTS OF *Trachelospermum* SPECIES

Trachelospermum species	Constituents A	B	C	D	E
T. asiaticum var *intermedium*	+	+	+	+	+
T. liukiuense	+	+	+	(+)	+
T. foetidum	+	(+)	(+)	(+)	+
T. jasminoides var. *pubescens*	(+)	(+)	(+)	(+)	+
T jasminoides	(+)	(+)	(+)	(+)	+
T. gracilipes	(+)	(+)	(+)	(+)	+
T. difforme	(−)	(−)	(−)	(−)	(+)

In order of decreasing R_f value (A–D)· A—Arctiin, B—Tracheloside; C—Matairesinoside; D—Nortracheloside. Plate: Kieselgel G, Solvent system: $CHCl_3$–EtOH = 4:1, Color reag.: 10% H_2SO_4; E = Dambonitol. Plate: Kieselgel G, Solvent system $CHCl_3$–MeOH = 2.1, *n*-BuOH $(CH_3)_2CO$: H_2O = 4·5.1. Color reag.: 10% H_2SO_4. (+)—TLC spot, (−)—No spot; +—Isolated.

[1] I. INAGAKI, S. HISADA and S. NISHIBE, *Chem. Pharm. Bull Tokyo* **16,** 2307 (1968)
[2] I. INAGAKI, S. HISADA and S NISHIBE, *Phytochem* **10,** 211 (1971).
[3] S. NISHIBE, S. HISADA and I. INAGAKI, *Chem. Pharm Bull Tokyo* **19,** 866 (1971)
[4] S NISHIBE, S. HISADA and I. INAGAKI, to be published.

the four lignan glucosides are absent from *T. difforme*, the only known North American species.[5]

Schneider[5] and Pichon[6] proposed on morphological grounds exclusion of *T. difforme* from the genus *Trachelospermum*. The chemical differences of *T. difforme* appear to agree with this proposal.

EXPERIMENTAL

The stems (100 g and upwards) were extracted with MeOH, the solution evaporated to small volume and diluted with H_2O. After extraction with light petroleum and Et_2O, the aqueous layer was extracted with $CHCl_3$. The residue was concentrated to syrup and extracted with EtOAc. Then syrup was extracted with $CHCl_3$–MeOH (2:1).

The extracts with $CHCl_3$ and EtOAc were chromatographed on silica gel and eluted by $CHCl_3$–EtOH (4:1) for examination of lignan glucosides. The extract with $CHCl_3$–MeOH was chromatographed on activated charcoal and eluted by EtOH–H_2O (1:99) for examination of dambonitol.

The results are given in Table 1.

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[5] C. SCHNEIDER, *Plantae Wilsonianae*, III, 336 (1916).
[6] M. PICHON, *Bulletin du Musèum*, XX, 190 (1948).

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ARISTOLOCHIACEAE

ANTHOCYANINS OF *ASARUM ASAROIDES*

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Abstract—Four anthocyanins in the flower of *Asarum asaroides* have been identified as peonidin 3-gentiobioside and cyanidin 3-gentiobioside acylated separately with *p*-coumaric and caffeic acids.

Asarum asaroides (Morren et Decaisne) Makino, blooms in May and the flowers are dark purple; no anthocyanins have been reported before in this family.[1] Four anthocyanins were isolated from the flowers by paper chromatography. Two of them liberated *p*-coumaric acid on saponification with NaOH, and caffeic acid was obtained from the other two. The $E_{acyl\ peak}/E_{vis.\ max}$ ratio (see Table 1) suggests that each pigment contains one moiety of either of *p*-coumaric and caffeic acids. Complete and partial acid hydrolysis of the deacylated anthocyanins showed that they were the 3-diglucosides of cyanidin and peonidin. Aglycones were identified by spectral and chromatographic comparison with the authentic specimens by alkaline fusion and H_2O_2 oxidation. Finally, the deacylated anthocyanins yielded gentiobiose by H_2O_2 degradation.

[1] J. B. HARBORNE, in *Comparative Biochemistry of the Flavonoids*, p. 126, Academic Press, London (1967).