Communications to the Editor

Chem. Pharm. Bull.
30(2) 766—769 (1982)

CASUARIIN, STACHYURIN AND STRICTININ, NEW ELLAGITANNINS FROM *CASUARINA STRICTA* AND *STACHYURUS PRAECOX*

Takuo Okuda,* Takashi Yoshida, Mariko Ashida
and Kazufumi Yazaki
Faculty of Pharmaceutical Sciences, Okayama University,
Tsushima, Okayama 700, Japan

Three new ellagitannins, casuariin (**5**), stachyurin (**6**) and strictinin (**7**) have been isolated from *Casuarina stricta*, and their structures elucidated. Of these, **5** and **6** were found to be *C*-glucosidic tannins. All of the ellagitannins (**1-7**) isolated from *C. stricta* have been found also in *Stachyurus praecox*.

KEYWORDS —— *Casuarina stricta*; Casuarinaceae; *Stachyurus praecox*; Stachyuraceae; tannin; ellagitannin; *C*-glucosidic tannin; isolation; structure elucidation; ^{1}H and ^{13}C NMR spectra

Plants of *Casuarina* species have been used as the astringents in Pacific islands, and are regarded as rich tannin resources. Besides casuarinin (**1**), casuarictin (**2**), pedunculagin (**3**) and tellimagrandin-I (**4**),$^{1)}$ three new ellagitannins, which we have named casuariin (**5**), stachyurin (**6**) and strictinin (**7**), have been isolated from the leaves of *Casuarina stricta* Ait. (Casuarinaceae). Five of these seven tannins, **1-3**, **6** and **7** have also been isolated from the leaves of *Stachyurus praecox* Sieb. et Zucc. (Stachyuraceae) whose fruit was used in Japan as a substitute for Chinese gall. The other two tannins, **4** and **5** were also detected in *S. praecox* by high-performance liquid chromatography (normal and reversed phase).

The aqueous acetone homogenate of the leaves was partitioned between AcOEt and water. The water layer yielded casuariin and stachyurin by droplet countercurrent chromatography (*n*-BuOH-*n*-PrOH-H_2O 2:1:3, ascending method), followed by column chromatography on Sephadex LH-20 and cellulose. Strictinin was isolated from the AcOEt layer in an analogous way.

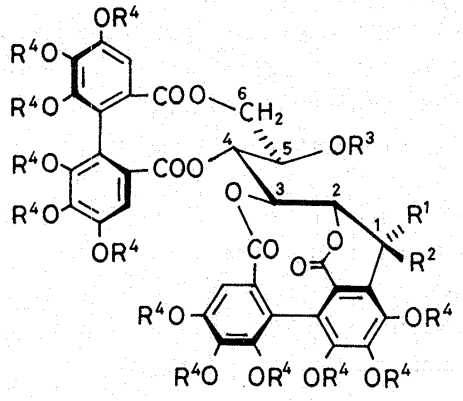
Casuariin (**5**) was obtained as a pale yellow amorphous powder, $C_{34}H_{24}O_{22}\cdot 5H_2O$, $[\alpha]_D$ +162° (c=0.5, MeOH), UV λ_{max}^{EtOH} nm (log ε) 213 (4.70), 233 (4.74), 257 (infl.) (4.50). The ^{1}H nuclear magnetic resonance (NMR) analysis (Table I) indicated that 5 could be degalloylated casuarinin, and this structure has been confirmed by direct comparison with a specimen$^{1)}$ prepared by hydrolysis of **1** with tannase.

Stachyurin (**6**) was isolated as an off-white amorphous powder, $C_{41}H_{28}O_{26}\cdot 5H_2O$, $[\alpha]_D$ +39° (c=0.4, MeOH), UV λ_{max}^{MeOH} nm (log ε) 221 (4.88), 267 (sh.) (4.53). The absence of the hemiacetal carbon signal of sugar at the region of δ 90-100 in the

Table I. ^{1}H NMR Spectra of **1**, **2**, **5**, **6** and **7** (90 MHz, acetone-d_6)[a]

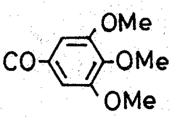
	HHDP[b] (1H each, s)	Galloyl (2H, s)	Glucose (*J*, Hz) H-1	H-2	H-3	H-4	H-5	H-6	H-6'
1	6.78, 6.56 6.50	7.12	5.64d (5)	4.67dd (2,5)	5.45–5.33			4.18dd (3,13)	4.06d (13)
5	6.67, 6.53 6.43		5.66d (5)	4.75dd (5,3)	5.44t (3)	5.02dd (3,9)	4.11dd (9,3)	4.65dd (3,12)	3.84d (12)
6[c]	6.82, 6.55 6.50	7.14	4.93d (2)	4.86t (2)	4.98t (2)	5.62dd (2,9)	5.36dd (9,3)	4.84dd (3,13)	4.02d (13)
7	6.72, 6.61	7.21	5.76d (7)	3.73dd (7,9)	3.84t (9)	4.91t (9)	4.11dd (9,6)	5.22dd (6,14)	3.79d (14)
2	6.68, 6.55 6.47, 6.38	7.18	6.21d (8)	5.18dd (8,9)	5.48t (9)	5.18t (9)	4.50dd (9,6)	5.30dd (6,14)	3.88d (14)

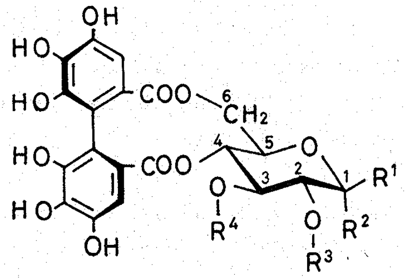
a) Chemical shifts are given in δ-values (ppm) from TMS as internal standard. Assignments were aided by appropriate double resonance experiments.
b) Hexahydroxydiphenoyl.
c) Recorded on 200 MHz instrument.



	R^1	R^2	R^3	R^4
1	H	OH	gall	H
5	H	OH	H	H
6	OH	H	gall	H
8	OH	H	gall(Me)$_3$	Me
9	OAc	H	gall(Me)$_3$	Me

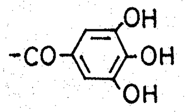
gall(Me)$_3$ =





	R^1	R^2	R^3	R^4
2	O-gall	H	(S)-HHDP	
3	H, OH		(S)-HHDP	
4	H, OH		gall	gall
7	O-gall	H	H	H
10	H, OH		H	H

gall =



(S)-HHDP =

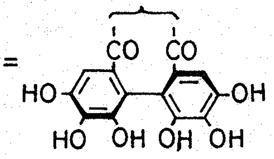


Chart 1

^{13}C NMR spectrum, and the ^{1}H NMR spectrum (Table I) suggest that stachyurin is a *C*-glucosidic ellagitannin which is closely related to **1**. The distinguishing feature of the ^{1}H NMR spectrum of **6** is the doublet (J=2 Hz) due to H-1, which resonates at a higher field (δ 4.93) than that in **1** (δ 5.64, d, J=5 Hz). Methylation of **6** with diazomethane yielded a pentadecamethyl derivative (**8**), $C_{56}H_{58}O_{26}$, M^+ *m/z* 1146, which gave a monoacetate (**9**), $C_{58}H_{60}O_{27}$, M^+ *m/z* 1188. The ^{1}H NMR spectrum of **9** exhibited the H-1 signal as a broad singlet at δ 6.18, which shifted downfield by *ca.* 1 ppm from that of **8**. These data indicate that the hydroxyl group at C-1 in **6** is free, and also that the dihedral angle between H-1 and H-2 is approximately 90°. Stachyurin is therefore presumed to be an epimer at C-1 of casuarinin (**1**), and this assumption was confirmed as follows. Casuarinin (**1**) was epimerized in boiling water as in the epimerization[2)] of castalagin, and the product which was isolated by column chromatography on cellulose from a mixture with unchanged **1** (*ca.* 1:1) was identified as **6**. Based on these data, stachyurin is represented by the formula **6**.

Strictinin (**7**) forms an off-white amorphous powder, $C_{27}H_{22}O_{18}\cdot 3H_2O$, $[\alpha]_D$ $-3°$ (c=0.4, MeOH), UV λ_{max}^{MeOH} nm (log ε) 218 (4.78), 267 (4.44). Comparison of the ^{1}H NMR spectrum with that of casuarictin (**2**) (Table I) indicates that **7** is an ellagitannin in which the hydroxyl groups at C-1, 4 and 6 of the glucopyranose are esterified by a hexahydroxydiphenoyl group and a galloyl group. Enzymic hydrolysis of **7** with tannase yielded 4,6-*O*-(*S*)-hexahydroxydiphenoyl-glucose (**10**),[3,4)] $[\alpha]_D$ +44° (c=0.5, EtOH) and gallic acid. The β-linkage of the galloyl group at C-1 of **7** was deduced from the coupling constant (J=7 Hz), based on the *C1* conformation of the glucopyranose indicated by the ^{1}H NMR spectrum. Therefore, the structure of strictinin is 1-*O*-galloyl-4,6-*O*-(*S*)-hexahydroxydiphenoyl-β-D-glucose (**7**).

A possible biogenetic precursor of **1**, **5** and **6** may be coexisiting pedunculagin (**3**), as they could be formed from **3** through the cleavage of the glucopyranose ring upon the formation of the *C*-glucosidic linkage as illustrated in Chart 2.

It is remarkable that these seven tannins with their distinct structures constitute tannin resources produced by two plants which stand far apart from each other taxonomically.

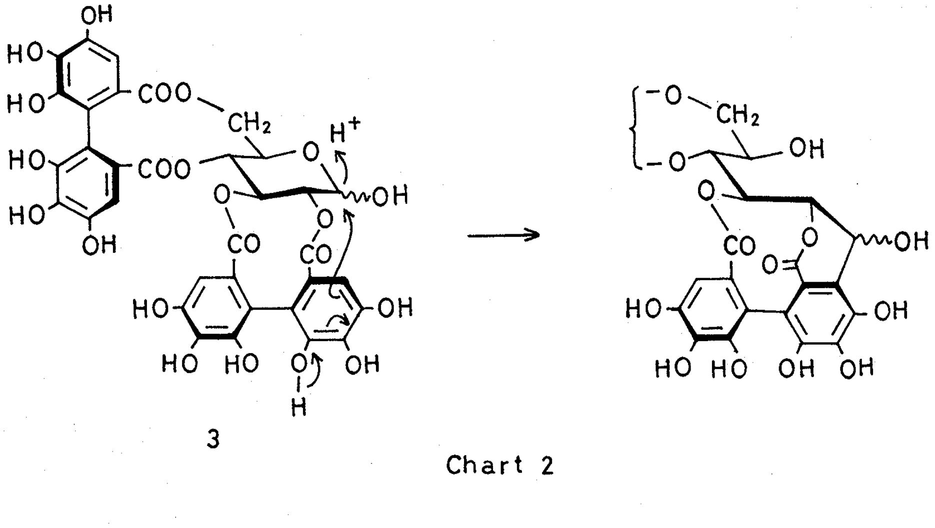


Chart 2

ACKNOWLEDGEMENT We wish to thank Prof. T. Fujita and Assoc. Prof. Y. Takeda, Faculty of Pharmaceutical Sciences, Tokushima University, for the 200 MHz NMR spectra.

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(Received January 13, 1982)