Phytochemistry, 1972, Vol. 11, pp. 2333 to 2335. Pergamon Press. Printed in England.

SHORT COMMUNICATION

CATECHINS WITH (+)-EPI-CONFIGURATION IN NATURE

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(*Received* 10 *Febuary* 1972)

Key Word index—Palmae; (+)-epicatechin; (+)-epiafzelechin; proanthocyanidins.

Abstract—(+)-Epicatechin has been isolated from various species of Palmae and (+)-epiafzelechin from *Livinstona chinensis*. This is the first time that catechins with (+)-epi-configuration have been found in natural sources.

INTRODUCTION

WE HAVE recently reported[1] the presence of (+)-epicatechin among phenolic constituents of *Chamaerops humilis* (Palmae). This was the first time that (+)-epicatechin was unambiguously demonstrated to be present in natural sources. In the same plant, two new proanthocyanidins were found; procyanidin *C* and *D*, both resulting from the 4–8 linking of two molecules of (+)-epicatechin and epimeric at C_4. In order to establish whether (+)-epicatechin was also present in other species of Palmae, we have undertaken an extensive investigation on other members of this family.

The Palmae belong to the order of Principes and are a large family of tropical and equatorial woody shrubs or trees. It is estimated to contain 4000 or more species in 210 genera and six sub-families: Coryphoideae, Ceroxyloideae, Borassoideae, Lepidocaryoideae, Nipoideae and Phytelephantoideae. We here report the results on some species of the first two subfamilies.

RESULTS

The species examined are listed in Table 1. The yield of catechins varies from 0·4 g/kg to 0·8 g/kg of fresh plant, that of dimeric proanthocyanidins from 0·6 g/kg to 1·5 g/kg.

TABLE 1. OCCURRENCE OF CATECHINS AND PROANTHOCYANIDINS IN DIFFERENT PALMAE SPECIES

Subfamily	Species	Part	Catechins	Proanthocyanidins
Coryphoideae	*Chamaerops humilis*	(Drupes)	(+)-epicatechin, (+)-catechin	C,D
	Phoenix canariensis	(Leaves)	, (+)-catechin	D,C
	Livinstona chinensis	(Leaves)	, (+)-epicatechin	4 unidentified
Ceroxyloideae	*Butia capitata*	(Leaves)	, (+)-catechin	C
	Howea forsteriana	(Leaves)	, (+)-catechin	C + 1 unidentified
	Arcanthophoenix cunninghami	(Seeds)	, (+)-catechin	C + 1 unidentified

[1] F. DELLE MONACHE, F. FERRARI and G. B. MARINI-BETTOLO, *Gazz. Chim. Ital.* **101**, 387 (1971).

As previously found in *Chamaerops humilis*, the most abundant catechin (60–80%) was (+)-epicatechin; the other catechin present was (+)-catechin. Only in *Livingstona chinensis* was (+)-catechin absent. Apart from (+)-epicatechin, the other catechin (50%) surprisingly, was shown to be (+)-epiafzelechin, and therefore the possibility of epimerization of (+)-catechin to (+)-epicatechin can be eliminated.

With the exception of *Livinstona chinensis*, procyanidin *C* was found in all species. New proanthocyanidins, so far not identified, were found in *Howea forsteriana, Arcanthophoenix cunninghamii* and particularly in *Livinstona chinensis* and these will be more fully described in a forthcoming paper. *Chamaedorea elatior* (leaves) and *Cocos romanzoffiana* (seeds) contained only very small amount of substances reacting with the vanillin–HCl reagent and it was not possible to isolate them in sufficient quantity for identification.

DISCUSSION

It is well known that (+)-catechin and (−)-epicatechin are widely distributed in plants.[2,3] (+)-Afzelechin was found in *Eucalyptus calophylla*,[4] *Nothofagus fusca*,[5] and *Saxifraga ligulata*,[6] (−)-epiafzelechin in black tea[7] and in *Winstaria chinensis*.[8] Their optical antipodes were considered not to be present in nature.[2,9,10] Nevertheless it was reported[3] that (−)-catechin is present in several species of Acaciae, and (+)-epicatechin in 6 plants, but no references were given or could be found elsewhere. The finding of a small quantity of (+)-epicatechin in dried or long preserved samples of *Uncaria gambir*[11] may be considered as an artifact in the light of our present knowledge.

Therefore the finding of (+)-epicatechin and (+)-epiafzelechin in Palmae may be considered to be the first demonstration of the occurrence in fresh plants of catechins with (+)-epi-configuration.

TABLE 2. R_f VALUES OF CATECHINS AND THEIR DERIVATIVES ON TLC

Catechin	Free substance (*)	Fully *O*-methylated-derivative (†)	Fully-*O*-acetylated-derivative (†)	3-*O*-Acetyl-*n*-*O*-methyl-derivative (‡)
(+)-Catechin	0·36	0·32 (red)	0·40 (red)	0·47 (red)
(−)-Catechin	0·31	0·32 (red)	0·40 (red)	0·47 (red)
(+)-Epicatechin	0·25	0·36 (dark-green)	0·35 (red)	0·42 (green–violet)
(−)-Epicatechin	0·32	0·36 (dark-green)	0·35 (red)	0·42 (green–violet)
(+)-Afzelechin	0·38	0·50 (red-violet)	0·51 (red)	0·81 (lilac)
(−)-Afzelechin	0·30	0·57 (violet)	0·42 (red)	0·79 (lilac)

* Cellulose (Merck) with H_2O: vanillin–HCl reagent.
† Silica gel G (Merck), with benzene–acetone: 9–1: H_2SO_2–CH_2O (40%)–H_2O, 2:1:1 for 10 sec at 95°.
‡ Silica gel G (Merck) with benzene–acetone: 19–1: H_2SO_4–CH_2O (40%)–H_2O, 2:1:1 for 10 sec at 95°.

[2] T. A. GEISSMAN, in *The Chemistry of Flavonoid Compounds*, p. 197, Pergamon Press, Oxford (1962).
[3] F. M. DEAN, in *Naturally Occurring Oxygen Ring Compounds*, p. 427, Butterworth, London (1963).
[4] W. E. HILLIS and A. CARLE, *Austral. J. Chem.* **13**, 390 (1960).
[5] W. E. HILLIS and T. INOUE, *Phytochem.* **6**, 59 (1967).
[6] A. POCE-TUCCI, F. DELLE MONACHE and G. B. MARINI-BETTOLO, *Ann. Ist. Sup. Sanità* **5**, 555 (1969).
[7] M. MYERS, E. A. ROBERTS and D. W. RUSTIDGE, *Chem. & Ind.* 950 (1959).
[8] K. WEINGES, K. GÖRITZ and F. NADER, *Liebigs Ann. Chem.* **715**, 164 (1968).
[9] K. WEINGES, *Phytochem.* **3**, 263 (1964).
[10] K. WEINGES, W. BAHR, W. EBERTH and K. GÖRITZ, *Fortsch. Chem. Org. Natur.* **27**, 158. (1969).
[11] K. FREUDENBERG and L. PURRMAN, *Liebigs Ann. Chem.* **437**, 274 (1924).

EXPERIMENTAL

Extraction and purification. Fresh plant (0·5–1 kg) was extracted in a cool room at 5° with MeOH for 20–30 days. The low temperature was employed in order to prevent epimerization. The concentrated extracts (at 30–35° under low pressure) were fractionated on a silica gel column using EtOAc as eluant. Catechins were separated from proanthocyanidins and from substances that do not react with vanillin–HCl reagent.

Catechins. The catechins were separated on a cellulose column using H_2O as eluant. Derivatives were prepared in the usual manner, and the catechins were identified by direct comparison with authentic material by m. m.p., [α], NMR spectra, R_f values and colour reactions in TLC (Table 2). A sample of (+)-epiafzelechin was prepared by epimerisation of (+)-afzelechin with a 15% yield using the same methods for the preparation of (+)-epicatechin from (+)-catechin:[12] m.p. 239–242°, $[\alpha]_D^{25}$ +52 (*c* 0·9 in acetone); trimethyl (+)-epiafzelechin, m.p. 109–110° $[\alpha]_D^{26}$ +66 (*c* 0·7 in EtOH).

Proanthocyanidins. The proanthocyanidins were purified on a cellulose column as reported, in[1] and acetylated. Procyanidin *C* was identified on the basis of m.m.p., [α] and NMR spectrum in comparison with an authentic specimen from *Chamaerops humilis.*[1]

Acknowledgement—We are indebted to the Directors of the Orto Botanico of Rome and Palermo for having kindly supplied and determined the plants.

[12] W. MAYER and F. MERGER, *Liebigs Ann. Chem.* **644,** 65 (1961).