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PROANTHOCYANIDINS OF *SALACIA CHINENSIS* LINN.

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Recent years have witnessed a considerable increase in our knowledge of proanthocyanidins. Besides a large number of leucoanthocyanidins, combinations of one leucoanthocyanidin with catechin,[1-6] epicatechin[7-9] or gallocatechin[6] resulting in the formation of C_{30}, C_{45} and higher molecular forms[10] have been recorded. Instances of a leucoanthocyanidin condensing with itself to form a dimer have also been reported recently. Lewak[11] isolated a leucocyanidin dimer from the leaves of *Crataegus oxyacantha*. Rangaswami and Venkateswarlu[12] isolated another leucocyanidin dimer from the bark of *Rhododendron grande*, and Drewes et al.[6] found a dimer of leucofisetinidin in the bark of *Acacia mearnsii*. Herein we record the occurrence of leucopelargonidin (I) in monomeric, dimeric (two forms) and tetrameric states in the same plant source. This has been noticed in a drug known as *Saptarangi* in Sanskrit which is used in Indian indigeneous medicine as an oral anti-diabetic. Botanically it consists of the roots of *Salacia chinensis* Linn.

Both the roots and stems of the plant were examined separately. The proanthocyanidins were obtained by the usual methods. The powdered plant material was exhausted with benzene and ether. From the marc, proanthocyanidins were extracted with cold acetone, warm acetone, cold rectified spirit and warm rectified spirit in succession.

Each solvent-free residue was extracted with cold ethyl acetate and then with cold methanol. The ethyl acetate solution was concentrated at a low temperature and diluted with petroleum ether and the methanol extract after concentration was diluted with ether. The precipitate obtained in each case was subjected to repeated purification by solution and reprecipitation with the same solvents as before. Each product was examined for identity by boiling with 6% alc. hydrochloric acid and studying the flavylium salt by standard methods. The acid hydrolysates were also examined for the presence of catechin or epicatechin by extraction with ethyl acetate and examination of this extract by paper chromatography. In all the cases neither catechin nor epicatechin was present and pelargonidin was the only flavylium salt produced. Each proanthocyanidin fraction was characterised by conversion into the acetate (pyridine-acetic anhydride at 38° for 48 hr.) and into the methyl ethers. For the methylation the reagents employed were dimethyl sulphate and potassium carbonate; acetone was used as solvent in the case of the monomer and dimers, and acetone-methanol in the case of the tetramer. The degree of polymerization of the proanthocyanidin was assessed by quantitative periodate titrations of the methyl ethers[13]. Consumption of ca 1 mole periodate per C_{15}-trimethyl ether was taken as evidence for the presence of the monomeric form, of ca 0.5 mole as evidence for a dimer and ca 0.25 mole as evidence for a tetramer. One of the proanthocyanidins did not consume periodate at all (absence of free glycol grouping). In this case the molecular weight was determined by the Rast method. The result agreed with a dimeric structure.
The properties of the substances mentioned above are given in Table 1.

The monomer was the predominant constituent of the ethyl acetate-soluble portion of the cold acetone extract of the roots of the plant (see also ref. 14). The dimer with free glycol grouping was obtained mainly from the ethyl acetate-solubles of the hot acetone extract of the roots and the dimer without free glycol grouping from the ethyl acetate-solubles of both the cold and warm alcohol extracts of the stem of the plant. The tetramer was present in the methanol-soluble portion of both the cold and warm alcohol extracts of the roots.

Of the several possible modes of linking between two leucoanthocyanidin units to yield a dimer with free glycol grouping the most probable is the one involving the alcoholic hydroxyl at position 4 of one unit and the highly reactive hydrogen at position 8 of the other (see fig. II). Presumably the tetramer is formed by a repetition of this process with two further monomeric units (see fig. IV). In the case of the dimer without free glycol grouping one hydroxyl of the glycol in each monomeric constituent should be involved; this would lead to a C-O-C link. The most probable structure is C_4-O-C_4 (see fig. III) (cf. ref.11).

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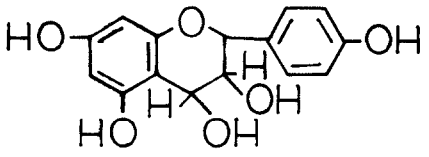

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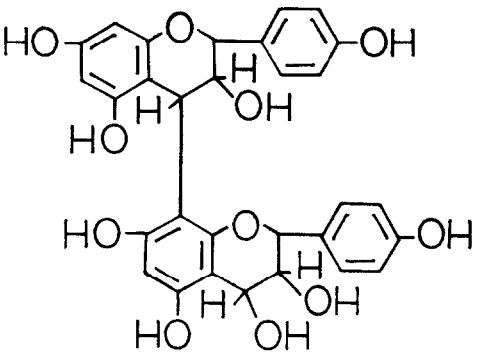

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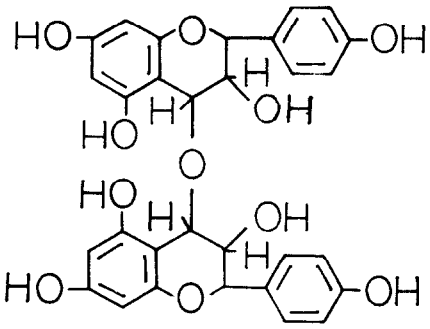

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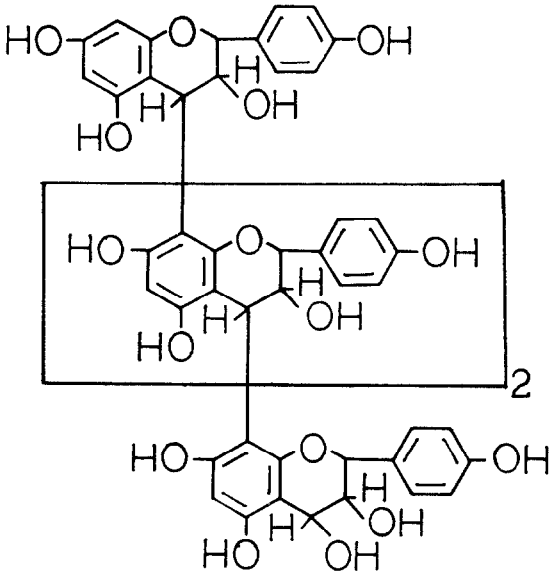

IV

TABLE I

Properties of the Proanthocyanidins of Salacia chinensis.

Substance	Description	Mol. formula	m.p.	$[\alpha]_D$
Leucopelargonidin Monomer	Colourless powder	$C_{15}H_{14}O_6,2H_2O$	220°(d)	+8.8° (Al)
" Pentaacetate	Colourless microcrystals	$C_{25}H_{24}O_{11}$	162-63°	+3.7° (Chf)
" Trimethyl ether	"	$C_{18}H_{20}O_6$	192-93°	+29.1° (Al)
Leucopelargonidin Dimer with free glycol grouping	Pale brown powder	$C_{30}H_{26}O_{11},3H_2O$	180-90°(d)	-
" Nonaacetate	Pale yellow powder	$C_{48}H_{44}O_{20}$	130-5° (sintering at 110°)	-22.2° (Chf)
" Hexamethylether	Colourless powder	$C_{36}H_{38}O_{11}$	135-9°	-27.2° (Chf)
Leucopelargonidin Dimer without free glycol grouping	Pale brown powder	$C_{30}H_{26}O_{11}$	180-95°(d)	-
" Octaacetate	Pale yellow powder	$C_{46}H_{42}O_{19}$	120-5°(d)	-27.7° (Chf)
" Hexamethylether	Colourless powder	$C_{36}H_{38}O_{11},H_2O$	130-5°(d)	-39.3° (Chf)
Leucopelargonidin Tetramer	Brownish red powder		above 330° (d)	-
" Heptadecaacetate	Colourless powder	$C_{94}H_{84}O_{38}$	148-60° (d)	-43.2° (Py)
" Dodecamethylether	Pale yellow powder	$C_{72}H_{74}O_{21},H_2O$	156-62° (d)	-16.8° (Py)

Al = Absolute Ethanol; Chf = Chloroform; Py = Pyridine

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