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Condensed Tannins: (4β→8;2β→O→7)-Linked Procyanidins in *Arachis hypogea* L.

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Mature, red peanut skins contain about 17% by weight of procyanidins. Nearly 50% of these compounds are low molecular weight oligomers that are soluble in ethyl acetate. The flavan-3-ols catechin and epicatechin are present in a ratio of 9 to 1 but in low concentration. Among the dimeric procyanidins, epicatechin-(4β→8;2β→O→7)-catechin dominates, with smaller proportions of epicatechin-(4β→8;-2β→O→7)-epicatechin and very small proportions of epicatechin-(4β→8)-catechin. Higher oligomers that are soluble in ethyl acetate contain both the (4β→8 or →6) and (4β→8;2β→O→7) interflavanoid bonds. The water-soluble polymeric procyanidins are predominately 2,3-*cis*-procyanidins linked by (4β→8 or →6) bonds that are terminated with the 2,3-*trans*-flavan-3-ol catechin. Water-soluble polymeric procyanidins from flaked and pelletized peanut skins have comparatively low number-average molecular weights (about 2200 as the peracetate) and low dispersitivities (about 1.8). These polymers have excellent potential for use in cold-setting adhesive applications.

INTRODUCTION

The skins of mature peanuts (*Arachis hypogea* L.) contain condensed tannins of the procyanidin class, but little is known of their structure (Stansbury et al., 1950; Sanders, 1977; Sanders and Mixon 1978). These tannins are credited with fungistatic properties inhibiting the development of *Aspergillus parasiticus* (Lansden, 1982; Sanders and Mixon, 1978). Approximately 40 000 dry tons of peanut skins is produced annually in the United States, and their high protein (about 17%) and fat (about 5%) contents have prompted their use as animal feeds. How-

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ever, the presence of condensed tannins interferes with protein digestibility in feed supplements for cattle and pigs. In poultry feeds, high tannin content is considered to be responsible for decreased feed intake, reduced protein digestibility, and a marked increase in leg deformities (Galloway, 1983).

A recent development in room-temperature curing phenolic resins is to use a condensed tannin resorcinol adduct produced from southern pine bark to replace over 60% of the resorcinol requirement (Hemingway and Kreibich, 1984; Kreibich and Hemingway, 1985). This suggests that it might be possible to similarly extract peanut skins to produce a reactive phenolic polymer for resin manufacture. The extracted skins, which would no longer contain objectionable tannin contents, could then be used as animal feeds. To evaluate this possibility it is necessary to determine the amounts, structures, and molecular weight distributions of condensed tannins and related procyanidins extractable from mature peanut skins.

EXPERIMENTAL SECTION

Proton and carbon NMR spectra were recorded on a Varian FT-80A and a Bruker AM 400 spectrometer. Fast atom bombardment (FAB) mass spectra were obtained using a Varian CH-7 mass spectrometer modified to accept an Ion Tech, Ltd., saddle field ion source. Xenon was used as the primary atom beam, with the saddle field ion source operating at 7 keV. Optical rotations were measured in acetone with a Jasco 181 polarimeter. Ultraviolet and visible spectra were recorded with a Perkin-Elmer Lambda-3 spectrometer.

Two-dimensional cellulose TLC was done on Schleicher and Schuell F-1440 plates (10 × 10 cm) developed in the first dimension with (TBA) *tert*-butyl alcohol–acetic acid–water (3:1:1, v/v/v) and in the second dimension with 6% acetic acid. Plates were sprayed with either vanillin–hydrochloric acid, diazotized sulfanilic acid, or ferric chloride–potassium ferricyanide. Anthocyanidins were separated on Whatman 3M sheets developed with Forestal solvent (acetic acid–water–HCl, 30:10:3, v/v/v). Silica gel TLC was done with Baker Flex-IBF sheets developed with chloroform–methanol–acetic acid–water (85:15:10:3, v/v/v/v) for phenols and with benzene–acetone (8:2 or 9:1, v/v) for peracetate derivatives. Some of the sheets were sprayed with diazotized sulfanilic acid; others were sprayed with formalin–H_2SO_4 and heated. Preparative TLC of peracetates was done on thick (0.75-mm) Baker-7G silica gel plates developed with benzene–acetone (8:2, v/v).

Column chromatography was done on Sephadex LH-20 eluted with ethanol or ethanol–water (1:1, v/v) solvents for the separation of oligomeric procyanidins in the ethyl acetate soluble fractions. Water-soluble polymeric procyanidins were purified of carbohydrates by chromatography on Sephadex LH-20 by eluting first with methanol–water (1:1, v/v) and then with acetone–water (1:1, v/v) (Czochanska et al., 1980; Foo and Porter, 1980). Separations were monitored by cellulose TLC developed with 6% acetic acid.

Flavan-3-ols were further separated and purified by reversed-phase HPLC on a Gilson chromatograph fitted with a 9.4-mm i.d. Supelco LC-8 column eluted with methanol–water in gradients. Gel permeation chromatography of polymeric procyanidin peracetates was accomplished on a Waters Associates unit fitted with a series of Microstyragel columns (10^4, 10^3, and 500 Å) and eluted with chloroform. Number-average molecular weights of peracetate derivatives by vapor pressure osmometry and elemental analyses were performed by Galbraith Laboratories.

Extraction Conditions. Two samples of peanut skins, a freshly prepared flake and a pelletized product, were supplied by Associates Research Management Inc. These two products were each extracted with acetone–water (1:1, v/v) for 2 h at room temperature, and the extracts were filtered through shark skin. The insoluble residue was extracted a second time under the same conditions, and the extracts were combined. Acetone was removed from the filtrate by evaporation at reduced pressure and 35–40 °C. The aqueous suspension was extracted five times with equal volumes of ethyl acetate. The residual water-soluble product was freeze dried to obtain a light tan powder. Samples (5 g) of the water-soluble product were separated into polymeric procyanidins and carbohydrates by chromatography on Sephadex LH-20. The two fractions were freeze dried and weighed. Samples of the flaked and pelletized skins before and after extraction were dried 24 h at 105 °C to determine moisture contents.

Fractionation of Ethyl Acetate Soluble Products. Samples of the ethyl acetate soluble products (3–5 g) were separated on Sephadex LH-20 columns (2.5 cm × 90 cm) by elution with ethanol and collection of 15-mL fractions (150 tubes). Material remaining on the column was eluted with acetone–water (1:1, v/v). Fractions eluted with ethanol, containing flavan-3-ols or groups of oligomeric procyanidins, were combined and rechromatographed on Sephadex LH-20 columns (1.0 cm × 90 cm) by eluting with ethanol–water (1:1, v/v) or ethanol.

Catechin (1) and Epicatechin (2). Fractions 17–21 (47 mg from 2 g) were combined and cochromatographed with authentic (+)-catechin and (−)-epicatechin on two-dimensional cellulose TLC and reversed-phase HPLC. Comparisons of the relative peak areas of HPLC chromatograms were used to estimate the relative proportions of the two compounds in the extracts.

Epicatechin-(4β→8)-catechin (3). Fractions 25–30 (54 mg from 2 g) were combined and cochromatographed with the authentic compound by two-dimensional cellulose TLC and by reversed-phase HPLC.

Epicatechin-(4β→8;2β→*O*→7)-catechin (4). The combined fractions 41–56 (247 mg from 2 g) were still a mixture, but repeated separation on Sephadex LH-20 gave 4 as a single compound. A sample of this isolate was added to 5% HCl in 2-butanol (5 mL) and heated under reflux for 1 h. The anthocyanidins produced were separated by paper chromatography, and the R_f values were compared with authentic anthocyanidins. Visible absorbtion spectra for products eluted from the paper with 5% HCl in ethanol were recorded in this solvent. The phenol (2 mg) was combined with phloroglucinol (2 mg) or benzenethiol (2 drops) in ethanol (5 mL) containing acetic acid (3 drops) and the resultant mixture heated in a sealed vial at 105 °C for 3 and 24 h, and the products were examined by two-dimensional cellulose TLC. An ^{1}H NMR (2D COSY) spectrum of 4 was obtained in methanol-d_4, and ^{13}C NMR spectra were obtained in acetone-d_6 + D_2O and methanol-d_4. The FAB mass spectrum of 4 was obtained using a glycerol matrix. Compound 4 was acetylated (acetic anhydride–pyridine, 1:1, v/v) and purified by preparative silica gel TLC. ^{1}H NMR spectra of the product were recorded in acetone-d_6 and $CDCl_3$.

Epicatechin-(4β→8;2β→*O*→7)-epicatechin (5). Fractions 57–65 (101 mg from 2 g) were combined and rechromatographed on Sephadex LH-20 by eluting with ethanol–water. Thiolysis products and phloroglucinol adducts were prepared and analyzed as described above. The phenol remained an impure isolate as evidenced by ^{13}C NMR. The isolate was acetylated (acetic anhydride–

Table I. Extract Yields from Flaked and Pelletized Peanut Skins

	% of o.d. tissue wt	
	flaked	pelletized
acetone–water extr	20.8	23.5
ethyl acetate sol	7.8	10.4
water sol	13.0	13.1
tannin	7.0	9.2
carbohydrate	6.0	3.9
moisture content	12.3	9.7
extr residue	67.6	65.6

pyridine) and purified by preparative silica gel TLC. ^1H NMR spectra of the isolate were recorded in acetone-d_6 and $CDCl_3$.

Higher Ethyl Acetate Soluble Oligomers. A number of minor constituents evident on cellulose TLC plates were obtained only as mixtures of compounds in low yield, so their structures have not been determined. Separation of the ethyl acetate soluble material (2 g) on Sephadex LH-20 by elution with ethanol retains large proportions of the extract on the column. This fraction (870 mg) was recovered by elution with acetone–water (1:1, v/v).

Water-Soluble Polymeric Procyanidins. The polymeric procyanidins isolated from either the flake or pelletized products (15 mg each) were added to 5% HCl in 2-butanol and heated under reflux for 1.5 h. The anthocyanidins were separated by paper chromatography as described above, and the absorbance at 545 nm was compared for products from the two isolates after dilution to equal volume. Each polymeric procyanidin (5 mg) was dissolved in ethanol (1 mL) to which benzenethiol (2 drops) and acetic acid (3 drops) were added. The vials were sealed and heated overnight at 105 °C after which the products were examined by two-dimensional cellulose TLC. Each polymeric procyanidin (5 mg) was also combined with phloroglucinol (5 mg) and the resultant mixture added to ethanol (1 mL) containing acetic acid (3 drops). The sealed vials were heated at 105 °C overnight and products examined by two-dimensional cellulose TLC. Each polymeric procyanidin sample (275 mg) was dissolved in acetone-d_6 + D_2O (1:1, v/v) and its ^{13}C NMR spectrum recorded.

Water-soluble polymeric procyanidin isolates were acetylated (acetic anhydride–pyridine, 1:1) and the products worked up by precipitation from ice–water, solution in chloroform, and a second precipitation from *n*-hexane. The off-white amorphous powders were examined for molecular weight distribution by gel permeation chromatography, number-average molecular weight by vapor pressure osmometry, and elemental composition.

RESULTS AND DISCUSSION

Over 20% of the dry weight of peanut skins (either as the flaked or pelletized product) was soluble in acetone–water, and approximately 40% of the extract was soluble in ethyl acetate (Table I). Two-dimensional cellulose TLC showed that the ethyl acetate soluble fraction was a complex mixture of compounds (Figure 1). Separations on Sephadex LH-20 provided a small amount of a flavan-3-ol fraction that was shown to consist of catechin (1) and epicatechin (2) in a ratio of 9:1 by HPLC. A small amount of the dimeric procyanidin epicatechin-(4β→8)-catechin (3) was also obtained from the ethyl acetate soluble fraction.

Two major constituents (4 and 5) of the ethyl acetate soluble material had comparatively low R_f values in the acetic acid dimension and gave strong vanillin–hydrochloric acid reactions. These two components proved to be particularly difficult to separate and purify on Sephadex

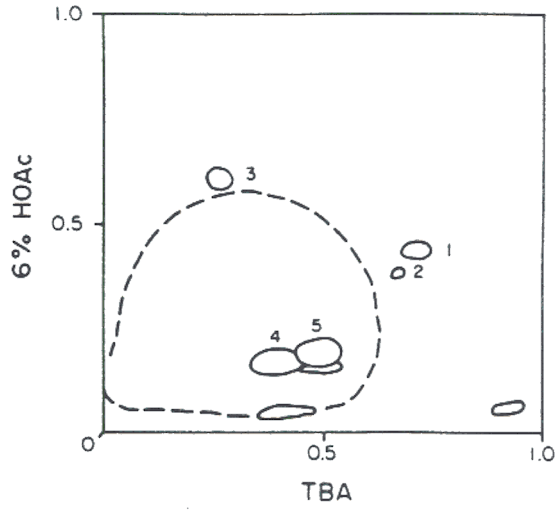

Figure 1. Two-dimensional cellulose TLC of ethyl acetate soluble fraction from peanut skins.

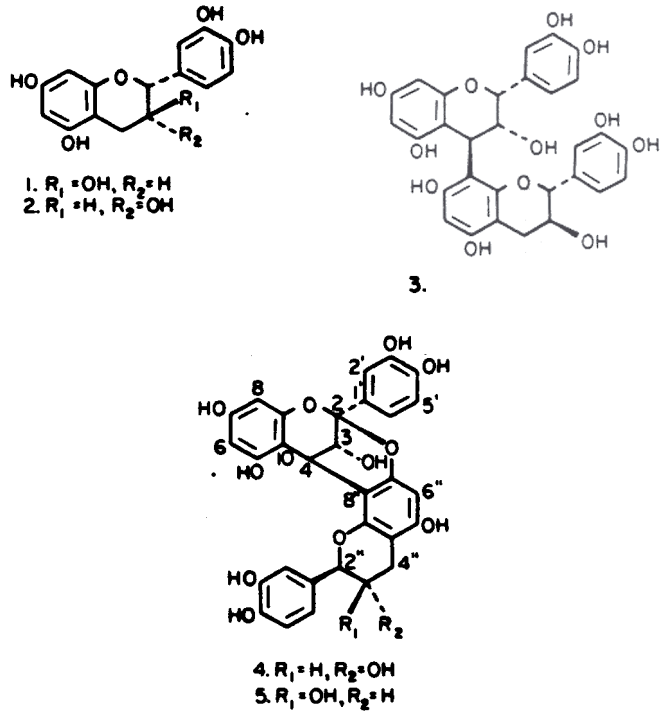

Figure 2. Compounds isolated.

LH-20 and gave nearly identical R_f values on cellulose or silica gel TLC plates developed with a number of different solvents. Compound 4 was finally purified by repeated chromatography on Sephadex LH-20 by elution with ethanol.

Reaction of 4 with HCl in 2-butanol gave an anthocyanidin with an R_f value slightly higher than that for cyanidin chloride with Forestal solvent, but it had a similar absorbance maximum (545 nm) in 5% HCl–ethanol. Acid-catalyzed cleavage with benzenethiol or phloroglucinol as the nucleophile showed that the compound was resistant to cleavage. Under severe conditions, mostly unidentified products and only small amounts of epicatechin-4-phenyl sulfide or epicatechin-4-phloroglucinol were obtained. A FAB mass spectrum of 4 showed the MH^+ parent ion at m/z 577.

These data suggested that 4 is a (4β→8;2β→*O*→7) doubly linked procyanidin dimer. This conclusion was supported by the distinctive ^{13}C NMR spectrum that,

when recorded in methanol-d_4, showed (δ, from methanol at 49.0 ppm) the following: 28.8 (C4″), 29.2 (C4), 67.7 (C3″), 68.0 (C3), 84.4 (C2″), 96.7 (C8 + C6″), 98.2 (C6), 100.4 (C10′), 103.2 (C2), 104.1 (C10), 106.8 (C8′). The two catechol B rings appeared at δ 115.7 (3C), 116.4, 119.9, 120.7, 130.6, 132. 3 with COH carbons at δ 145.6, 146.3, and 146.7 (2C). Six A-ring COR carbons appeared from 151.3 to 158.1 ppm. These data are similar to those for epicatechin-(4β→8;2β→*O*→7)-epicatechin with the exception of the C2″ signal at 84.4 ppm, which in **4** is significantly downfield (Schilling et al., 1973; Jacques et al., 1974; Nonaka et al., 1983). The C2″ chemical shift at 84.4 ppm suggested that compound **4** is the dimeric procyanidin A-1 or epicatechin-(4β→8;2β→*O*→7)-catechin. A two-dimensional ^{1}H NMR (COSY) of the free phenol and one-dimensional spectra of the peracetate derivative confirmed this structure. The COSY spectrum of **4** showed (δ from Me_4Si) the following: 6.80–7.14 (6 H, m, B-ring ArH), 6.09 (1 H, s, H6″), 6.08 (1 H, d, J = 2.1 Hz, H8), 5.90 (1 H, d, J = 2.1 Hz, H8), 4.74 (1 H, d, $J_{2'',3''}$ = 7.7 Hz, H2″), 4.24 (1 H, d, $J_{3,4}$ = 3.5 Hz, H3), 4.15 (1 H, m, H3″), 4.07 (1 H, d, $J_{3,4}$ = 3.5 Hz, H4), 2.93 (1 H, q, $J_{4''a,4''b}$ = 16.5 Hz, $J_{4''b,3''}$ = 8.3 Hz, H4″b), 2.58 (1 H, q, $J_{4''a,4''b}$ = 16.5 Hz, $J_{4''a,3''}$ = 5.5 Hz, H4″a). The $J_{2'',3''}$ coupling of 7.7 Hz clearly established the lower flavanoid unit of **4** as the 2″,3″-trans isomer, i.e. catechin. ^{1}H NMR of the peracetate when recorded in $CDCl_3$ showed (δ from Me_4Si) the following: 7.2–7.7 (6 H, m, B-ring ArH), 6.87 (1 H, d, J_{meta} = 2.2 Hz, H6), 6.53 (1 H, s, H6″), 6.50 (1H, d, J_{meta} = 2.2 Hz, H8), 5.32 (1 H, d, $J_{3,4}$ = 3.9 Hz, H3), 5.32 (2 H, s + s, H2″ + H3″), 4.70 (1 H, d, $J_{3,4}$ = 3.9 Hz, H4), 2.65 (2 H, m, H4″a + H4″b). The approximately equal chemical shifts for H2″ and H3″ precluded seeing $J_{2'',3''}$ coupling. However, when the spectrum was recorded in acetone-d_6, the H3, H2″, and H3″ signals appeared as a group of one triplet and two doublets with the signal for H3 as a sharp doublet at δ 5.46 with $J_{3,4}$ = 4.1 Hz. The H2″ proton was at δ 5.39 and H3″ at δ 5.57, and these showed a $J_{2'',3''}$ of 5.8 Hz. The assignment of this structure was also supported by the strong levorotation of the peracetate, $[\alpha]_D$ −100°, *c* 0.1% acetone, lit. −92° (Weinges et al., 1968). This compound is comparatively rare, having been found previously only in cranberries (Weinges et al., 1968).

Compound **5** resisted purification, but after repeated separations on Sephadex LH-20, it was isolated with only small amounts of **4** as an impurity. Degradation reaction products were similar to those obtained from **4**. The ^{13}C NMR spectrum of **5** was also similar to that of **4**, the most obvious difference being the prominent signals at 66.0 and 81.1 ppm. These data suggested that compound **5** is the dimeric procyanidin A-2, epicatechin-(4β→8;2β→*O*→7)-epicatechin (Schilling et al., 1973; Jacques et al., 1973; Jacques et al., 1974; Nonaka et al., 1983). Compound **5** was finally purified as the peracetate derivative. The ^{1}H NMR spectrum of the peracetate recorded in $CDCl_3$ showed (δ from Me_4Si) the following: 7.20–7.70 (6 H, m, B-ring ArH), 6.77 (1 H, d, J_{meta} = 2 Hz, H6), 6.48 (1 H, s, H6″), 6.45 (1 H, d, J_{meta} = 2 Hz, H8), 5.30 (1 H, br s, H3″), 5.22 (1 H, s, H2″), 5.25 (1 H, d, $J_{3,4}$ = 4 Hz, H3), 4.57 (1 H, d, $J_{3,4}$ = 4 Hz, H4), 2.80 (2 H, m, H4″a and H4″b). These chemical shifts are nearly identical with those reported by Jacques et al. (1973). Insignificant coupling for $J_{2'',3''}$ establishes that the lower flavan unit is the 2″,3″-cis isomer. Dreiding models show considerable strain on the heterocyclic ring and justify the $J_{3,4}$ coupling constant of about 4 Hz for both **4** and **5**. Compound **5** is also present in tannin extracts from horse chestnut, avocado, and cinnamon (Jacques et al., 1974; Nonaka et al., 1983).

Table II. Elemental Composition of Peanut Skin Polymeric Procyanidin Peracetates

	found		calcd	
	% C	% H	% C	% H
flaked skins				
1-stage purifcn	59.9	4.50		
2-stage purifcn	60.2	4.45		
pelletized skins				
1-stage purifcn	60.4	4.51		
2-stage purifcn	60.4	4.51		
linear (4β→8) linked tetramer ($C_{100}H_{88}O_{40}$)			60.2	4.51
tetramer with one (4β→8;2β→*O*→7) linkage ($C_{97}H_{86}O_{40}$)			61.6	4.55

The acetone–water-eluted higher oligomers from the Sephadex LH-20 column were recovered in a yield of 120 mg from 2 g of ethyl acetate soluble material. ^{13}C NMR spectra showed that this fraction consisted of higher molecular weight oligomers and suggested that it was made of compounds with both (4β→8 or →6) and (4β→8;2β→*O*→7) interflavanoid bonds in the ratio of 2.5 to 1 by integration of the C2, C3, and C4 carbon signals for the constituent monomer flavanoid units (Czochanska et al., 1980). Also, FAB MS showed the mixture (m/z) to be predominantly composed of trimers, one type with one (4β→8 or →6) linkage and one (4β→8;2β→*O*→7) linkage (MH^+ 865, $(M - H)^-$ 863) and the other with two (4β→8 or →6) linkages (MH^+ 867, $(M - H)^-$ 865). Similar oligomers have recently been reported from cinnamon (Nonaka et al., 1983).

The water-soluble polymeric procyanidins constituted 7–9% of the dry weight of peanut skins and were isolated as pale tan powders after purification from the carbohydrates. The ^{13}C NMR spectra indicated that these polymers were predominantly composed of procyanidin units with 2,3-cis chain extenders and 2,3-trans terminal units with a ratio of about 15:1 for (4β→8)/(4β→6) linkages to the (4β→8;2β→*O*→7) linkage. These observations were confirmed by degradation reactions. Treatment of the polymeric procyanidins with HCl in 2-butanol gave good yields of cyanidin chloride. Acid-catalyzed cleavage in the presence of benzenethiol or phloroglucinol gave good yields of epicatechin-4-phenyl sulfide and epicatechin-4-phloroglucinol, showing the 2,3-cis stereochemistry for the chain extender units and catechin from the terminal unit. Small amounts of epicatechin from the terminal unit and catechin-4-phenyl sulfide or catechin-4-phloroglucinol adducts were detected. There were also small amounts of unidentified products with chromatographic properties analogous to those obtained from the dimers **4** and **5** described above. On the basis of these results, the higher molecular weight procyanidins present in peanut skins are very similar to those from cinnamon bark. A few (4β→8;2β→*O*→7) linkages are interspersed with the more predominant (4β→8) and/or (4β→6) interflavanoid bonds, the main difference between the polymeric procyanidins of cinnamon and peanut skins being the 2,3-cis terminal units in cinnamon and 2,3-trans terminal units in peanut skin polymeric procyanidins (Nonaka et al., 1983). The polymeric procyanidins isolated from the flaked and pelletized products were essentially identical.

Samples of the water-soluble polymeric procyanidins were acetylated, and elemental compositions were determined because introduction of a (4β→8;2,3→*O*→7) linkage would significantly increase the carbon content of the peracetate derivative. These elemental analyses (Table II) also suggested that the polymers contained predominantly (4β→8 or →6) linkages. The number-average molecular weights of the water-soluble polymeric procyanidins

Table III. Molecular Weight Distribution of Peanut Skin Polymeric Procyanidins

	GPC			
	M_n	M_w	VPO M_n	dispersivity[a]
flaked skins				
1-stage purifcn	1803	3407	2206	1.70
2-stage purifcn	2123	3769	2013	1.82
pelletized skins				
1-stage purifcn	1701	3834	2176	1.98
2-stage purifcn	2120	3861	2284	1.75
average	1937	3718	2170	1.81

[a] Determined by average M_n by GPC and VPO and M_w by GPC. On the basis of a peracetate of a flavan unit (i.e. M_w = 500), this corresponds to a P_n of 3.9 and a P_w of 7.4. Because of the presence of some (4β→8;2β→O→7) linkages in the polymer, this underestimates the number of flavan units per number average of weight average chain.

were also determined by gel permeation chromatography and by vapor pressure osmometry of the peracetate derivatives. These analyses (Table III) showed that the molecular weights of peanut skin tannins are comparatively low and the molecular weight distributions is remarkably narrow in comparison with tannins from a broad spectrum of plants (Williams et al., 1982). Neither the elemental composition nor the molecular weight distribution was altered by a second purification of Sephadex LH-20. Furthermore, there was no significant difference in elemental composition or molecular weight distribution between water-soluble polymeric procyanidins isolated from the freshly prepared flaked or pelletized material.

Registry No. 1, 154-23-4; 2, 490-46-0; 3, 20315-25-7; 4, 103883-03-0; 5, 41743-41-3.

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