EVALUATION OF CEREAL CROP RESIDUES: INFLUENCE OF SPECIES, VARIETY AND ENVIRONMENT ON NUTRITIVE VALUE

ODA Research Project X0093

Final Report

APPENDIX

BRITISH SOCIETY OF ANIMAL PRODUCTION

ABSTRACT FOR WINTER MEETING

Title:

FEEDING SORGHUM STOVER TO ETHIOPIAN SHEEP : EFFECT OF CHOPPING AND AMOUNT OFFERED ON GROWTH, INTAKE AND SELECTION

Name and address of author to present paper

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Please tick as appropriate

Theatre		President's Prize	YES	✓	BSAP	YES	✓	Main author title: Prof		Dr		Mr	✓
Poster	✓	Candidate	NO		Member	NO.		Mrs		Miss		Ms	

Following hand-harvesting of sorghum grain (non bird-resistant variety Dinkamash) in mid-November, the stover (straw) was hand-cut from the field in mid-January and stored indoors until feeding in May. Forty eight Menz Highland rams of 17.2 kg initial weight (M) and ca.15 months old were fed 113 g dry matter (DM) cottonseed cake per day (d) and ad libitum stover over 56 d; salt licks were also provided. Using a 2 x 2 factorial arrangement of treatments, stover, either in the long form or chopped (Alvan Blanch Maxi Chaff Cutter) was offered at 25 or 50 g DM per kg M.d. There were four groups, each of three rams, per treatment. Ram live-weight gain (g/d) was improved, both by chopping the stover ($P<0.05$; 43.2, 58.1, s.e. 3.98) and offering more ($P<0.001$; 38.2, 63.2, s.e. 3.98); stover form and amount offered did not interact ($P>0.05$). Stover intake (kg DM/group.d) was improved by both chopping the stover ($P<0.05$; 1.11, 1.34, s.e. 0.06) and offering more ($P<0.001$; 1.03, 1.42, s.e. 0.06); form and amount did not interact ($P>0.05$). Rams selected for leaf and sheath, and against stem. The proportion of offered stover left uneaten ranged from 0.11 (chopped 25) to 0.52 (long 50). The data offer strategies for feeding stover to alleviate dry-season feed shortages and also generating residues for other purposes e.g fuel

• • • Please see notes overleaf • • •

BRITISH SOCIETY OF ANIMAL PRODUCTION

ABSTRACT FOR WINTER MEETING

Title:

FEEDING SORGHUM STOVER TO ETHIOPIAN GOATS AND SHEEP : EFFECT OF AMOUNT OFFERED ON GROWTH, INTAKE AND SELECTION

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Please tick as appropriate

Theatre	
Poster	✓

President's Prize Candidate	YES	
	NO	✓

BSAP Member	YES	✓
	NO	

Main author title

Prof		Dr		Mr	✓
Mrs		Miss		Ms	

Twenty four male goats initial weight MJ 15.5 kg) and 24 rams 17.0 kg M) were individually-fed 150 g cottonseed cake per day (d) and minerals, and offered 25, 50 or 75 g sorghum (bird-resistant variety Seredo) stover straw) per kg M.d in a 2 x 3 factorial experiment over 75 d, following a preliminary period of 21 d. Stover was offered in chopped form (Alvan Blanch 'Maxi' Chaff Cutter . Live-weight gain (g/d) of sheep was higher than goats (P<0.001; 48.2, 21.5, s.e. 4.51); there was no interaction between species and amount of stover offered Growth rates increased with increasing amount of stover offered (P<0.001; 19.5, 39.8, 47.9, s.e. 5.84). Stover intake (g DM/d) was higher for sheep than goats (P<0.001; 475, 428, s.e. 24.9 and there was no interaction of species with amount of stover offered. Stover intake increased with increasing amount of stover offered (P<0.001; 315, 487, 563, s.e. 14.6). The proportion of offered stover remaining uneaten increased with increasing amounts offered: sheep, 0.05, 0.31, 0.49; goats, 0.16, 0.41 and 0.53. The proportions of leaf and leaf sheath in uneaten stover decreased with decreasing amounts of stover offered. data indicate that both goats and sheep are capable of selective feeding, leading to increased intake and growth, when they are offered increasing ad libitum amounts of chopped sorghum stover.

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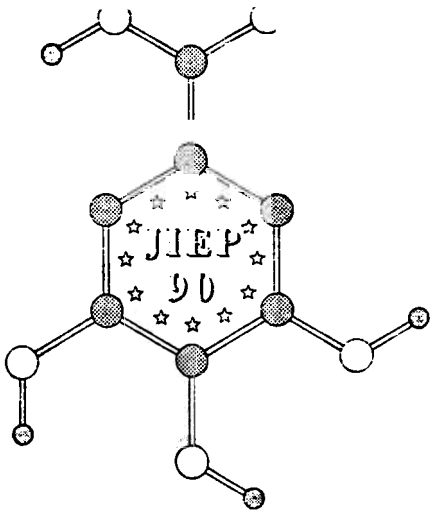

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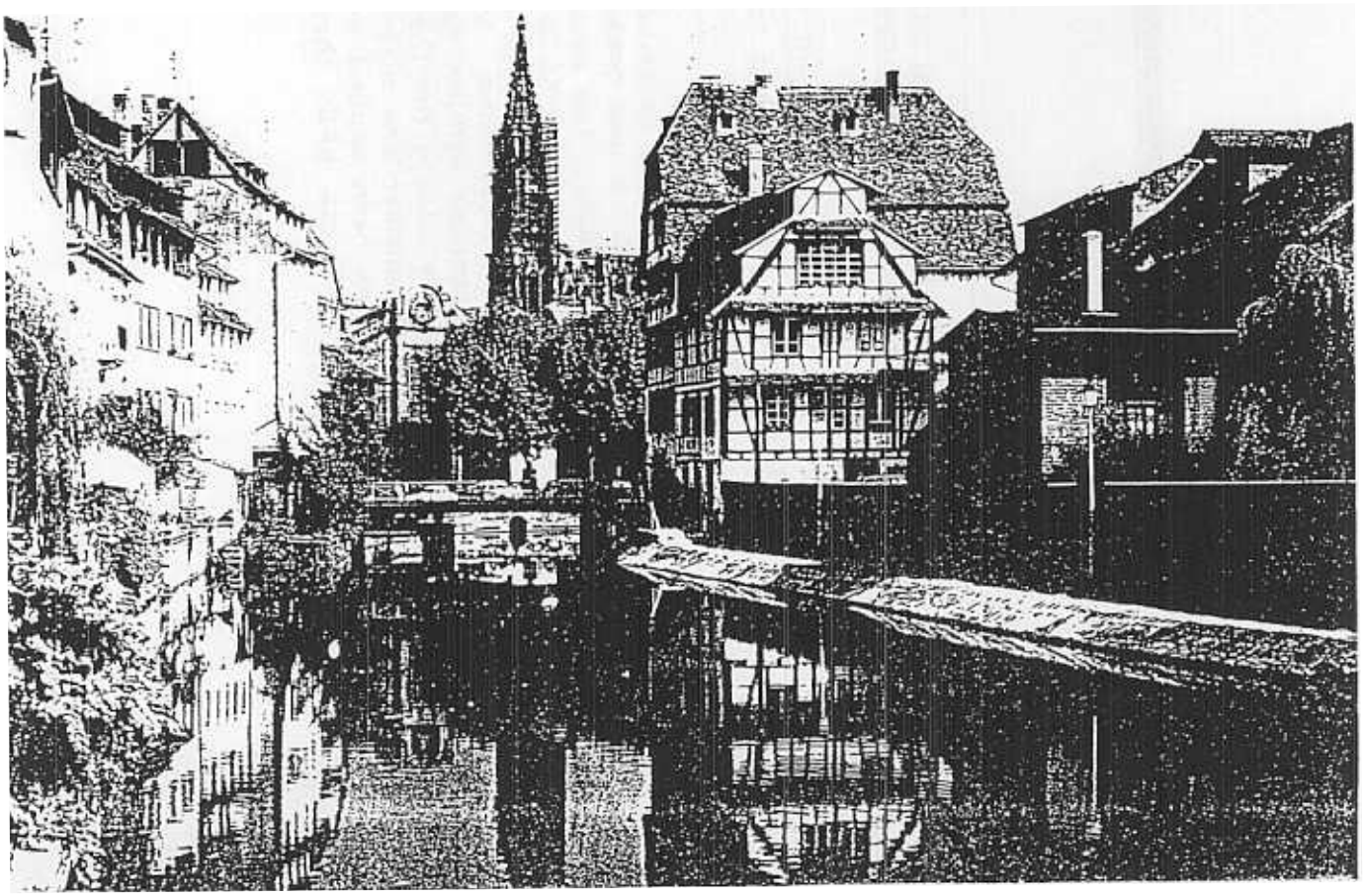

Strasbourg - La Petite France

AN IMPROVED POST-COLUMN DERIVATIZATION PROCEDURE USING SHIFT REAGENTS FOR THE UV-VIS SPECTROSCOPY OF PHENOLIC COMPOUNDS IN PLANT EXTRACTS

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A previously published procedure (Hostettmann et al., J. Chromatogr. 283, 1984, 137) was modified. A new commercially available solvent mixing chamber (Lee Visco-Jet Micro mixer, Lee Products) was used to introduce the shift reagents. It has a series of 36 spin chambers and an internal volume of 10 ul. This mixing system causes hardly any loss of resolution even in complex chromatographic separations. In addition, it was found necessary to adjust the pH of the column effluent to ca. 3.5 before adding the $AlCl_3$ reagent and to ca. 7.0 before adding the H_3BO_3 reagent. These pH adjustments were achieved with another Lee mixer.
This method has been applied to mixtures of standard compounds (flavonoids) and to plant extracts. HPLC chromatograms and UV-Vis spectra are shown.

Cluster analysis of HPLC and other chemical data to describe varietal differences between sorghum crop residues and their responses to different sites

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ABSTRACT

Phenolic compounds from 24 sorghum varieties grown at several sites were analysed by HPLC and the data subjected to cluster analysis. It was found that environment had the greatest effects on phenolic composition However there were also clear varietal differences. Most varieties gave strong environment x genotype interactions however, the phenolic composition of two bird-resistant BR) varieties, X/35:24 and Ikinyaruka, was more stable in different environments than the other varieties tested These two varieties were at the higher end of *in vitro* digestibilities within this group of 24 varieties

Differences between bird- and non bird-resistant varieties were clearly expressed in leaves at some sites, but not at others Abreeding strategy is suggested for selecting BR-varieties with improved digestibilities

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Tannins - Their Biochemistry and Nutritional Properties

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TANNINS - THEIR BIOCHEMISTRY AND NUTRITIONAL PROPERTIES

1. Introduction

This review collates information on tannins from different areas of research. The aim is to present the various factors contributing to the biosynthesis of tannins, to describe the variety of their chemical structures and their interactions with other macromolecules. This information is important in an agricultural context: the production of tanniniferous plants and their utilization by animals. A survey [1 was shown that 80% of woody perennial dicots and 15% of annual and herbaceous perennial dicots contain tannins. Plants with high levels of tannins (e.g. browse plants) are especially important in many developing countries as potential protein sources for animals.

This review will not describe techniques for isolating, characterizing or quantifying tannins as these have been covered elsewhere [2,3]. We wish instead to provide an update on different types of chemical structures and on nutritional effects of tannins. Recognising the wide range of tannin structures that exists between plants, the reader will appreciate the complexity of their nutritional effects.

Recent studies on the interactions of tannins with other nutrients (proteins, polysaccharides) will be presented which has led to some interesting hypotheses relevant to animal nutrition. Although the literature abounds with information about negative effects of tannins on nutrition, a few important experiments will be discussed in which

tannins have produced positive effects. It is for these reasons that the study of tannins is an exciting topic in animal nutrition.

2. Definition of tannins

Plant extracts have been used for centuries to produce leather from hide during the tanning process [4]. Our understanding of what constitutes a tannin has therefore been influenced by early research on natural products. The active components of the tanning process were named tannins and defined as 'compounds able to convert hide into leather'. The transformation of hide into leather results from tannins crosslinking neighbouring collagen (protein) strands. However, the definition of tannins is regularly modified in the light of new research findings. These have revealed that all tannins are polyphenolic compounds which are synthesized in many plants. It was realized that these polyphenols not only bound strongly with hide proteins but also with many other proteins and also with polysaccharides, nucleic acids, steroids, alkaloids and saponins [5]. Such interactions are obvious when the complexes between tannins and these compounds precipitate out from solution. However, tannins also form soluble complexes with some of the above compounds which have often been overlooked [6]. If the bonds in such complexes are strong, profound physiological or nutritional effects can result from the consumption of tannin-rich foods.

Traditionally, tannins have been divided into two groups: the 'condensed' and 'hydrolysable' tannins 4]. The 'condensed' tannins are made up of flavan-3-ols linked via carbon-carbon bonds, e.g. compounds

(1 and 2). They are also called proanthocyanidins for the reason that on treatment with alcoholic acid, coloured anthocyanidin compounds are produced 7]. 'Hydrolysable' tannins are polyesters of gallic acid, hexahydroxydiphenic acid and/or their derivatives and glucose or quinic acid compounds 3, 4, 5, 6 [8]. However, within the last 10 years many new compounds have been identified, which do not fit into either of these two categories, yet they show tannin-like properties. Whilst it would seem that the 'condensed' tannins are the most widely distributed tannins in plants, the picture is not yet complete and we must wait for their distribution to be recorded more fully.

One attempt to describe the properties of those polyphenols which behaved as tannins stipulated that the polyphenols must be water-soluble compounds with molecular weights of between 500 and 3000 Daltons [4]. However, in-depth studies of the interactions between tannins and proteins have revealed great variability in the binding strengths with seemingly similar tannins.

It will be seen from the above that the definition of a tannin is problematical. For the purposes of this paper, we will define a tannin as a polyphenol capable of complexing with proteins, polysaccharides and saponins (many of these tannins also bind of course other macro-molecules).

3. Biosynthesis of tannins

3.1. Tannins based on gallic acid

The biosynthesis of these tannins has not yet been elucidated. A recent review by Haslam [5] succinctly summarises the known facts.

Gallic acid may be synthesised by either of three routes all of which originate from quinic acid. Subsequent esterification to glucose produces β-penta-O-galloyl-D-glucose. This compound seems to represent a biosynthetic 'watershed' in the plant kingdom from which many different tannin compounds are derived either by depsidic linkages (gallotannins) or by oxidative coupling between further gallic acid units (ellagitannins) [9]. Not much is known about the enzymology of these reactions but biosynthetic schemes have been proposed that link precursors and end-products in a logical manner [5, 10]

3.2. Tannins based on flavanols

Far more is known about the biosynthesis and enzymology of flavonoids. All enzymes necessary for the formation of flavanols have been described and these are the immediate precursors of oligoflavanol tannins.

Two precursors are necessary for flavonoid synthesis, acetate and phenylalanine, which originate from carbohydrates and proteins respectively [11 (Scheme 1). Whilst the A-ring carbons (see compound 1 are derived from three acetate units , the B and C ring carbons come from phenylalanine. A chalcone compound forms the first intermediate, followed by a flavanone and then a dihydroflavonol. A flavan-3,4-diol is one of the immediate precursors of oligomeric flavanols. The other precursor is usually a flavanol, but other suitable compounds can also participate as the nucleophile. No enzymes have yet been isolated which govern these condensation steps. Controversy has surrounded the nature of the reactive intermediate derived from flavan-3,4-diol. A flav-3-en-3-ol has been suggested (compound 7) [12]. However, the

available evidence tends to favour a quinone methide intermediate, which may be enzyme mediated [12]. This intermediate has a strongly electrophilic carbon at C-4 and readily condenses with many nucleophiles.

Porter 13] discussed the fact that the upper and lower flavanoid units often differ within oligoflavanoids. This suggests that these units are synthesised by different metabolic routes. Two distinct metabolic pools may provide the electrophilic (chain elongating; T, M, J-units) and the nucleophilic units (chain terminating; B-units) (Scheme 2)

Roux and Ferreira [14] were able to interpret the relative ratios between tannin regio-isomers, which were obtained by in vitro synthesis. They considered the relative stabilities of potential electrophiles and nucleophiles as chain elongating and terminating units respectively (Schemes 3 and 4). From these deliberations, it follows that the relative ratios of 4 → 8) to (4 → 6) oligocatechin regio-isomers (e.g. compounds 1 and 2) are 10 : 1, whereas for oligofisetinidins they are 4 : 1. In some plants (e.g. Schinopsis sp), the same ratios were detected in vivo as were obtained by synthesis in vitro. However, in other plants (e.g. wattle) significantly different ratios were found. They hypothesised that the condensation reactions leading to tannins were under enzymatic control in 'the metabolically active wattle bark which also contains chlorophyll', but that the condensation reactions in the heartwood of Schinopsis and Rhus sp. were the product of an ageing process which was probably not under strict enzymatic control. Th enzymes are responsible for the final structures of flavanoid tannins in most living tissues is apparent from the fact, that plants using the

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5. Chemical structures of tannins

5.1. Tannins based on flavanols

Views on the nutritional effects of tannins are mixed and sometimes confused. Most reports conclude that tannins have negative effects on animal nutrition (see Sections 8 and 9.). However, there is good evidence that some tannins have beneficial effects. An objective for future research will be to link particular tannin structures with particular nutritional effects. This is a distant goal. For the time being we need to be aware of the variety and complexity of tannin structures and their different nutritional effects. Good compilations of tannin structures and their plant sources have been provided [5, 12, 29, 30]. Some general rules governing tannin structures based on research to date are set out below.

Porter's review [12] covered the literature up to 1986 on flavan-3-ols, flavan-4-ols, flavan-3,4-diols. Many of the newly identified flavan-3-ol oligomers also contain other molecules which are not flavanols. We therefore propose to use a term first coined by Roux' group [31-34] which is more general than 'condensed' tannins, namely 'oligomeric flavanoids'. The assumption is that some of the newly included oligomers will also fit the definitions of tannins just as well as the 'condensed' tannins.

5.1.1. Nomenclature

Two different nomenclature systems are in use for naming oligoflavan-3-ols. The IUPAC system is widely used by chemists and provides a systematic approach to the naming of chemical structures. However, the IUPAC rules are rather awkward when applied to flavanoids

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The C to A ring links of higher oligomers have been investigated in great detail. Three types of building blocks arise from C to A ring links. 'Linear' oligomers result from 4 → 8 carbon-carbon links between three or more monomers [40] (e.g. compound 10). On the other hand, if three monomers are linked so that the middle unit (M-unit) is bonded *via* 4 → 6 and 4 → 8 links [13] (e.g. compound 11), 'angular' oligomers result [41]. If four or more monomers are linked so that there is one central unit (J-unit) surrounded by three monomers, all of which are 4 → 6 and 4 → 8 linked, then 'branched' oligomers are formed [40] (e.g. compound 12).

The oligomers described above are linked *via* single carbon-carbon bonds between monomers. However, another type of linkage (A-type) is often encountered (e.g. compound 13) where the C and A rings are doubly linked through (C2–O–C7) and (C4 → C8) [12]

A few representative examples of natural compounds follow below in order to illustrate these structural principles. The reader is referred to Porter [12] for a more complete list. Linear dimeric and trimeric oligomers of (4 → 8) linked catechin and epicatechin are widespread. Tetrameric and pentameric oligomers containing epicatechin as T- and M-units coupled to catechin as B-unit have been found in sorghum seeds [42]. The highest oligomers that have so far been isolated and identified are linear hexamers of (–)-epicatechin [43]. Pure oligocatechins or oligoepicatechins (*syn*. procyanidins) have been found in some 38 species [12, 20, 44, 45]. Although most had (4 → 8) linkages, some had a very high proportion of (4 → 6) linkages [15].

A dimeric prodelphinidin (gallocatechin-(4 → 8)-epigallocatechin) has been isolated from *Ribes sanguineum* [46]. Flowers of *Trifolium*

repens are unique in having oligomers consisting only of gallocatechins and/or epigallocatechins (syn. prodelphinidins) [20]. Only a few other pure oligoflavanols are known. These are dimers of afzelechin, prosopins and fisetinidols [12].

The vast majority of oligoflavan-3-ols contain a mixture of monomers in which either of the following monomers (afzelechin, gallocatechin, guibourtinidol, fisetinidol or robinetinidol) form top, middle or junction units (T-, M-, or J-units; Scheme 2) and catechin or epicatechin usually form the bottom (B- units [12].

A-type links have been found in dimers between afzelechin and catechins. In higher oligomers (up to the pentamer), they have been found in oligo-epicatechins. These contained only one A-link per molecule which may be due to steric constraints or because other oligomers have not yet been identified

5.1.3. Molecular weights

Average chain lengths of flavanoid tannins range from two flavan-3-ol units in barley seeds to 20 or 25 in Lotus pedunculatus roots and sainfoin leaves. For most samples of the same plant species the ratios of delphinidin to cyanidin, formed by oxidising the tannins, were quite similar [44, 45, 47]. However, tannins from Lotus corniculatus leaves and roots yielded extremely variable ratios between samples which may be due to genetic variability [20].

Average molecular weights of tannins obtained from these plant samples tended to be similar ranging between 2000 and 4000 Daltons, with the exception of Trifolium repens flowers (M_n = ca. 3000, [47]; M_n = 2050, [20]), and sainfoin leaves (M_n = ca. 5700-9400; [47], M_n = 2100,

20]). The authors could not explain the large discrepancy between the sainfoin samples. It would be interesting to know whether these variable molecular weights are caused by seasonal or cultivar differences

5.1.4. Phlobatannins

In this section other classes of oligoflavanoids are presented underlining the chemical diversities that can be found amongst tannins and showing how widespread the carbon-carbon bonds are between different types of flavanoids. The reaction of oligoflavan-3-ols in strong mineral acids yields red insoluble polyphenols, the so-called 'phlobaphenes' or 'tanners' reds'. Their structural identities are not known. While investigating such acid induced changes, Roux and co-workers discovered a new group of tannins, which they named phlobatannins [33, 34, 48-50]. The authors suggested that the tanners' reds may be a mixture of phlobatannins, red anthocyanidins and some self-condensation products. It should be noted however, that whilst the tanners' reds were formed in the presence of oxygen, the phlobatannins were synthesized under nitrogen. Phlobatannins are thought to arise via C-ring opening followed by rearrangement. The reaction may involve a quinone methide intermediate [50] (compound 14). Several phlobatannin compounds are known consisting of flavanoid 'dimers' and 'trimers' with three or four fused rings (compounds 15 and 16)

Phlobatannins with the molecular weight of a flavanoid 'dimer 'have now also been found in nature. They were isolated from the heartwoods of Guibourtia coleosperma (false mopane) and Baikiaea plurijuga (Rhodesian teak) [33, 34].

5.1.5. Flavanol glycosides

It is somewhat surprising that monomeric flavan-3-ol glycosides are relatively rarely detected in plants. Several combinations of catechin, epicatechin, epiafzelechin with glucose, arabinose, apiose, xylose or allose have been identified [12]. 6C- and 8C-glucosides of a flavanol dimer, catechin-(4 α→ 8)-catechin, were found by Kashiwada et al. [51 in medicinal rhubarb together with a 7-O-analogue. The identification of glycosylated oligoflavanols may be the first step towards resolving the longstanding question of the nature of insoluble tannins [52, 53] Insolubility of these tannins may (i stem from their large molecular size, (ii be due to the formation of a large number of hydrogen bonds with polysaccharides, or (iii arise from covalent linkages to the polysaccharides. C-13 n.m.r. studies of oligoflavanols by Porter et al. and Shen et al. [53] clearly revealed carbohydrate signals in what regarded as highly purified preparations. The ratio of glucosyl to flavanoid residues was as high as 1 in the Pinus and Picea sp. tannins, but it was much smaller for the quince tannins. Glucosyl units in quince tannins were probably attached at the terminal epicatechin-3-O-positions. The same attachment positions were observed for allose in epicatechin oligomers [55]. However, glucosyl residues in Pinus and Picea tannins must have been attached to the phenolic hydroxyl groups [54]. The exact glucosyl-positions could not be determined due to similar labilities of the glucosidic and interflavanoid bonds!

5.1.6. Flavanol-gallates

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hydroxy benzylalcohol derivatives in large amounts 77] and also synthesise novel tannins. These have building block units consisting of β-D-glucose and 3,4,5-trihydroxybenzylalcohol (compound 30). Castamollissin (compound 31 77] contains a benzylaldehyde derivative and may be an intermediate in the biosynthesis of these benzylalcohol derivatives. Gallic acid is esterified at either the glucose moiety (castamollissin; compound 31 or at the benzylalcohol moiety (cretanin; compound 32). Chestanin and isochestanin may be envisaged as the dimers of two oxidatively coupled cretanins. Oxidative coupling between cretanin and gallic acid leads to chesnatin or isochesnatin.

It may well be that these compounds are only the first representatives of a new class of tannins yet to be explored further.

6. Interactions of tannins with other molecules

6.1. Conformations of tannins

In the previous sections we have illustrated the primary structure of tannins. However, in order to understand the phenomenon of tannins binding with other molecules, one also needs to appreciate their secondary and tertiary structures, i.e. their conformations. These three-dimensional structures have been investigated using X-ray crystallography, nuclear magnetic resonance (n.m.r.) and computer models. Although X-ray crystallography is accredited with providing the final proof of structures, conformations in the solid, densely packed state are not necessarily the same as in solution 79]. For solution studies, n.m.r. is a highly valuable tool as it provides information on primary and secondary structures. If ^{1}H n.m.r.-spectra exhibit

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different sources bind polyphenols to varying degrees [105, 108]. Cellulose - in contrast to starches - adsorbs polyphenols on its surfaces [97].

7. Effects of tannins on digestion

7.1. Do tannins bind to enzymes or substrates?

Digestion of feeds may be affected by tannins complexing with protein substrates and/or with digestive enzymes. Mole and Waterman [109] investigating the proteolysis of BSA by trypsin at pH 7.5 concluded that tannic acid deprived trypsin of substrate rather than acting directly on the enzyme. Similarly, Blytt *et al.* [110] reported that tannins from sorghum seeds (oligocatechins) and from quebracho (oligofisetinidins) hardly inhibited crude alkaline phosphatase and 5'-nucleotide phosphodiesterase. They therefore proposed that any anti-nutritional effects of tannins would be due to substrate (protein) complexation.

It would however be premature to draw firm conclusions from this limited number of experiments, as the interactions are highly protein and tannin specific. In addition, Mole and Waterman [6] pointed out how very different proteolytic rates were obtained depending on the substrate proteins and the complexation conditions.

An *in vivo* study by Griffiths and Moseley [111 pointed to direct enzyme inhibition. Trypsin activity in the gut was determined using a synthetic substrate. This activity was lower in rats fed high-tannin field beans, but polyvinylpyrrolidone (PVP) extracts of the gut resulted in similar activities being measured on straw and tannin diets, presumably because PVP bound the tannins thus freeing the enzymes

The answer to the question whether proteolysis by trypsin in the presence of tannins is substrate or enzyme inhibited is not quite as clear-cut because the experiments are not directly comparable: firstly the proteins (BSA and bean protein), secondly the tannins (purified tannic acid and unpurified bean tannins) were different in these experiments. It is possible that under the experimental conditions of and Waterman [109] tannins bound preferrentially to the substrate and under the conditions of Griffith and Moseley's [111 experiment they bound preferrentially to the enzyme. Results from in vivo deer experiments also demonstrated a reduction in protein digestibility [112], the extent of which could be predicted from the protein precipitating capacity of tannins. Whatever the mechanism, it would appear that proteolysis is reduced by tannins [100, 109-111

Lipid metabolism on the other hand exhibits a different response to tannins. Whilst in vitro studies with purified lipase, alkaline phosphatase and 5'-nucleotide phosphodiesterase showed a depression of enzyme activities due to tannins [100, 110], crude fractions in which enzymes were associated with phospholipids were hardly affected [110]. Lipase activity was also not changed and occasionally even enhanced in rat trials [100, 111]. As a result, the digestion of substrate lipids was not negatively affected by tannins [100]. These results are rather interesting as they may explain some aspects of the altered lipid metabolism observed when animals are fed tanniniferous feeds (Section 8).

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may explain the following observation. Sainfoin tannins did not protect red clover proteins from degradation in the rumen (see section 8. when the two diets were mixed [115].

Free soluble phenolics may therefore be more detrimental to animals than many tannins [112]. They certainly seem to be better deterrents to Quelea birds than did the oligo-catechins of sorghum seeds [116] This view has also been expressed by Singleton [117] who stated that a significant nutritional drag on animals is observed when phenols exceed 1 to 5% of the diet. However, this range will be higher for phenols of low solubility which would probably include tannins rendered insoluble through complex formation.

pH does not only govern protein complexation by tannins, acid pH values are possibly also important in breaking down some tannins in the

For example, it has been shown that 4 → 8 carbon-carbon linkages are much more susceptible to acid cleavage than 4 → 6 links [118]. Tannins having 4 → 8 links may therefore potentially be more toxic to animals as they will release more phenolic monomers which in turn may be absorbed by the animal and will have to be detoxified.

8. Nutritional Effects of Tannins

Studies on the effects of tannins on animal nutrition have involved a wide range of plants and covered a wide variety of wildlife species. In the vast majority of cases there has been little or no characterisation of the tannins present in the feedstuffs used. Even measurements of total tannins or polyphenols presented are equivocal in

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but have adapted to and accepted it in their feed [125]. Levels of tannic acid and some other tannins in diets have been associated with decreased dry matter intakes in chickens, rats and cattle [126-128]. However, the effects of tannin levels in the diet may also be quite negligible or indeed they may even enhance intake [127, 129]. Some of these results may be due to tannins affecting other dietary components present in the feed.

Effects of tannins on voluntary intake may also reflect any toxicity. Several studies support the assumption that the oligo-flavanol tannins [130] of Sericea may be responsible for its apparently low palatability [131, 132]. The following example illustrates a typical case in which the different structural types of tannins were completely disregarded. In this study with calves, gallotannins were added to alfalfa hay diets to bring its tannin content equal to that of Sericea lespedeza [133] which contains oligo-flavanol tannins. The addition of gallotannins did not affect the intakes of alfalfa hay compared with non-tannin containing diets, but the intakes of alfalfa hay plus gallotannins were higher than the intakes of Sericea. However, increasing levels of oak browse (contains a mixture of tannins, the relative proportions of which change with leaf development [134]) in alfalfa based diets resulted in reduced voluntary intake by goats [135]. Given a choice of browse and stocking rate allowing, goats eating blackbrush (Colegyne ramosissima) twigs will select low tannin containing older growth compared with high tannin current season's growth [136]. However, tannin levels of older growth may only appear to be lower due to an increase in molecular weights

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may therefore be more important than tannins in defending plants against ruminants [139]

9. Effects of tannins on Different Animal Species and Insects

9.1. Herbivorous Insects

The role of tannins as defense agents of plants has been strongly questioned following studies on insects [140]. Although there are experiments which show tannins as effective insect deterrents, equally there are those in which no effects were observed [124, 141]. For example, phenolics reported to confer resistance to sorghum against insect attack are used as nutrients by a tree locust [142] resulting in increased growth rate and survival. This, of course, may reflect selective adaptation.

Tree species selected as host by saturniid larvae were rich in phenolic components and low in alkaloids [143]. Studies with two closely related papilionid species showed that when Papilio polyxenes caterpillers (a species restricted to tannin-free Umbelliferae) were given tannins, large numbers of lesions were found in the gut. On the other hand when the same tannins were given to Papilio glaucus caterpillers (a species which feeds on tanniniferous trees) only one small lesion was found [144]. Feeny [145] suggested that the decreased binding between proteins and tannins at alkaline pH may exert a selection pressure for higher gut pH in herbivorous insects where the mid-gut pH is around 9.2.

Insects may also protect themselves against dietary tannins in other ways. It has been suggested that tannins may be adsorbed on to

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leucine, these effects were even more marked when raw kidney bean diets were fed [164]. However, it was not established whether compounds other than tannins could have caused these effects in soya or kidney beans.

Histopathological effects in chicks receiving sal seed (Shorea robusta) meal or tannic acid containing diets include decreases in blood haemoglobin, red and white cell counts; hydropic degeneration of the liver and intestinal villi and necrosis of the kidney tubules [165, 166]. Conversely chicks and hens given HT sorghum grain diets for 33 and 84 days respectively showed no histopathological lesions in any section of the intestinal tract [167]. The metabolic fate of dietary tannic acid was studied by Potter and Fuller [168]. They found that it was apparently hydrolysed to gallic acid and a large part of this was O-methylated and excreted as 4-O-methylgallic acid. Decarboxylation of gallic acid accounted for another urinary metabolite - pyrogallol.

Other detrimental production responses have also been associated with tannin intake. Decreases in egg production have been reported in hens receiving diets containing 1% tannic acid with further reductions when diets contained 2% tannic acid [169]. HT containing horse beans (oligo-flavanols) depressed egg weights and reduced the laying rate of hens [170] and an inverse relationship between egg weight laid per day and tannin content of the diet has also been found [171] Egg yolk mottling and discolouration was observed with diets containing 2% tannic acid [169] and egg taint has been related to the tannin content of rape seed meal used in the diets [172]. This latter effect appeared to be a result of inhibition of liver microsomal trimethylamine oxidase by the dietary tannins.

9.3. Small Mammals

An extensive literature exists on rat feeding trials with sorghum grains of different tannin content [173]. Tannins in diets of rabbits rats and mice have been shown to reduce growth rate, protein and amino acid utilisation and to increase faecal nitrogen excretion [129, 174-178]. Reductions in amino acid digestibilities were greatest for proline, glycine and glutamic acid [174]. In rats receiving diets containing raw field beans or raw soyabeans as protein sources there was significant impairment in the ability of the small intestine to transport amino acids or sugars [179, 180]. This was postulated to be a result of tannin content of the feeds. Food intake was depressed in rats fed tannic acid at 4, 5 and 8% levels in the diet [126]. Other workers have reported increased feed consumption of rats receiving diets containing 3.2 or 6.4% tannic acid in diets [129]. Positive and negative effects were found on feed intake of rabbits receiving tannin containing birch twigs or isolated tannins of birch twig polyphenol extracts, catechin or tannic acid in their diets [176]. Mitjavala et al. [129] also found significant growth depression with increasing levels of tannic acid in the diet and FER was halved at levels of 6.4% tannic acid. The main reason for weight reduction appeared to be a considerably reduced deposition of fat. In rats receiving diets containing 10% of HT field bean testa, intestinal activities of α-amylase and trypsin were significantly lower than in animals receiving diets containing 10% of LT field bean testa, whereas lipase activity was considerably higher with the HT diet [181]. These results were confirmed by Horigome et al. [100] after feeding 1% black locust tannins to rats

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9.4. Pigs

Although field beans (Vicia faba L. have frequently been used in pig diets the nutritional response has generally been less than that expected from the nutrient composition of the beans [188]. The nature of the anti-nutritive factor(s) is not known but field beans can contain 0-3.5% tannins in their dry matter [189]. In vitro assessment of the protein quality of different varieties of field beans [190] showed that the presence of tannins in the seed was associated with a significant reduction in the availability of methionine. In practical studies where a LT containing bean was compared with a "standard" tannin containing bean in fistulated pigs, more dietary nitrogen was digested and absorbed on the LT diet (69.4 v 64.7). However, in a subsequent experiment the same author found little difference in incremental daily nitrogen retention between LT and HT bean containing diets [188].

Sorghum grain has also been used to some extent in pig diets. Twelve varieties of sorghum grain grown under the same conditions were fed in low protein diets to pigs [191]. Highest digestion co-efficients were obtained for the varieties with yellow or red seedcoat colours and yellow endosperm and lowest co-efficients for varieties with brown seedcoats and white endosperm. Oligo-flavanol tannin contents of the sorghums varied between 0.21 and 0.65%. Other workers [192-194] also found that feeding HT containing sorghum grains usually resulted in poorer performance, particularly feed conversion efficiency, compared with LT varieties. In a study where two HT (3.7%) sorghum hybrids and two LT (0.9%) hybrids were fed to pigs, the digestibility of dry matter, gross energy and nitrogen were lower with the HT varieties but there was no reduction in nitrogen utilisation [193]. Caution is needed when

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whereas phenolics in Acacia seyal may have beneficial effects by increasing rumen microbial utilisation of recycled endogenous nitrogen [222]. Increased levels of shinnery oak in an alfalfa based diet resulted in decreases in organic matter, crude protein, and fibre digestibilities and increases in faecal nitrogen, and decreases in urinary nitrogen 138]. Zelter et al. [229] treated a variety of proteins with chestnut tannins which resulted in reduction in proteolysis of these proteins as measured in an in vitro rumen system. Other work in vivo confirmed these findings. For example, soyabean meal was treated with 10% taratannin (compound 6) and fed to lambs [230]. Compared with similar diets containing untanned soyabean meal, average daily gains, efficiency of feed utilisation, nitrogen balance and the efficiency of nitrogen utilisation were all increased on the treated soyabean meal diet, presumably as a result of higher protein flows to the duodenum.

In animals receiving mixed roughage: concentrate diets, any potential effects of a HT containing component are frequently offset by the other dietary constituents present. A number of HT containing concentrate sources have been used to limited extents in ruminant rations with little or no reduction in the overall nutritional value of the diet. Feedlot diets containing up to 10% peanut skins did not affect steer performance, but feedlot heifer performance was depressed when 20% peanut skins were included in the diets [231]. On the other hand the effects of oligoflavanol- and gallic acid based tannins in sal seed meal are such that it has been recommended that its use in livestock rations should be discontinued [232]. In animals receiving all roughage diets (grazers, browsers and mixed feeders) the overall

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Treatments to Overcome Anti-nut tional Effects of Tannins

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Research at Purdue University has shown conclusively that many herbivores respond to tannins in feed by producing special salivary proteins [250, 251]. Many of these proteins have a great affinity for different tannins which has been attributed to their primary and secondary structures. They consist largely of proline, glycine and glutamate and are characterised by a virtual absence of aromatic and sulphur containing amino acids. This means they are almost devoid of essential amino acids and represent no great dietary loss to the producer. These proteins have a highly flexible and open conformation which promotes strong interaction with tannins. Decreased intestinal digestibility of proline, glycine and glutamate (the major components of PRP's) observed in certain digestion studies [174, 195] suggest that tannin:PRP complexes are not digested in the intestinal tract. Synthesis of proline rich proteins in rats has been induced by oligoflavanols and gallotannins. In humans, PRPs are constitutive and account for about 70% of parotid saliva [251 - this may explain our preference for foods with astringent tastes. PRPs have been found in deer, sheep, cattle, hares, rabbits, rats, mice, monkeys, humans, koala bears and ringtail opposums. However, the tannin affinity of PRPs from these sources varied greatly. PRPs from deer, bound much more strongly than those from sheep or cattle [251] Tannin feeding of hamsters has no effect on salivary glands and PRP's are not produced [250], perhaps explaining, at least in part, the higher susceptibility of hamsters to tannins.

The rumen microflora is extremely adaptable to changes in dietary nutrient supply. Although there is little or no direct evidence of the effects of tannins on rumen microbes, it seems probable that some

adaptation can occu He found adj to changes in chemical tanni inhibi of diges on mo ly than they di to the br feeds The abrupt oduc de ti ted salseed meal to the tions of da ry cows esulted educed ntake tl rumina and indigesti [22 ye adual in oducti of rying evel of salseed meal di the fects ruminants bi trans ti may to nut absorpti the area the small intestines whereas with monogastr herb secondary substance may be absorbed und gested exampl pl typhyl de ti l typhy de ted the faeces ruminants but in the ine rabbits and hares Detoxi tanni tanni oducts has been extensi ly ewed [ ] When tann i oduced ctly the tomach of ts gall and 4 O methy galla exc ed i the 86 The end-products togethe with smal ts of O methy pyrogal ol observed when gall aci wa fed togethe with amounts O methy pyroga The same nd-p oducts ound the chicks tanni gall ds 68 Othe rk have shown imila end products and concluded 11 54 tha tann absorbed th ough the gas inte inal ract and detoxi ed i the inal ds acting as surfactants apparently al bind to tannins They ai the of tannins via the faeces 00

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species nutritional effects have been studied in detail but the characterisation of the tannins present has been poor. Thus there is a clear need for closer interdisciplinary research between animal nutritionists and chemists.

Further confusion arises from attempts to extrapolate observed nutritional effects between animal species. Beneficial effects of tannins on bloat prevention and better nutrient utilisation have been observed in ruminants under certain circumstances but in general and also with most other species anti-nutritional effects result from the presence of high tannin contents of feeds. However, if the tannin to protein ratios are favourable, then the anti-nutritional effects may not be too great. Natural adaptation to high tannin feeds does occur and may vary between species. Some animals, such as deer, regulate dietary intake thus not overloading the body's detoxification mechanism. Other species produce proline-rich-proteins which bind to the tannins rendering them inocuous. These proline-rich-proteins represent no drain on essential amino acids of the body thus the animal detoxifies the tannins at what is probably a minimal nutritional cost.

In developing countries tanniniferous feeds such as browse plants, crop residues and other agricultural by-products are extremely important economically and maximum usage of these can only be achieved on a fuller understanding of tannin chemistry and biochemistry. Indeed tanniniferous plants may also become more important in those parts of the world where, as a result of environmental pollution, lower input farming may have to be practised in the future.

REFERENCES

[1 Bate-Smith, E. C. and Metcalf, C. R., J. Linn. Soc. Botany, 55 (1957) 669-

Mangan, J. L., Nutr. Res. Rev., 1 (1988) 209-231.

Mueller-Harvey, I., Anim. Feed Sci. Technol., (1989), (in press).

Haslam, E., 'Vegetable tannins', In Conn, E. E. (ed.), The Biochemistry of Plants (Vol. 7), Academic Press, London and New York, 1981, pp. 527-556.

[5] Haslam, E., 'Hydroxybenzoic acid and the enigma of gallic acid, In Conn, E. E. (ed.), Chapter 7, The Shikimic Acid Pathway, Recent Advances in Phytochemistry (Vol. 20), Plenum Press, New York, 1986, pp. 163-200.

Mole, S. and Waterman, P. G., J. Chem. Ecol., 11 (1985) 1323-1332.

Porter, L. J., Hrstich, L. N. and Chan, B. G., Phytochem., 25 (1986) 223-230.

Haslam, E. and Lilley, T. H., 'New Polyphenols for Old Tannins' In Van Sumere, C. F. and Lea, P. J. (eds.), Annual Proceedings of the Phytochemical Society of Europe, (Vol. 25), Clarendon Press, Oxford, 1985, pp. 237-256.

Beart, J. E., Lilley, T. H. and Haslam, E., Phytochem., 24 (1985) 33-38

[10] Yoshida, T., Okuda, T., Memon, M. U. and Shingu, T., J. Chem. Soc. Perkin Trans. I (1985) 315-321.

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Steenkamp, J. A., Steynberg, J. P., Brandt, E. V., Ferreira, D. and Roux, D. G., J. Chem. Soc., Chem. Commun., (1985) 1678-1679.

Young, D. A., Cronje, A., Botes, A. L., Ferreira, D. and Roux, D. G., J. Chem. Soc. Perkin Trans. I (1985) 2521-2527.

Steynberg, J. P., Young, D. A., Burger, J. F. W., Ferreira, D and Roux, D. G., J. Chem. Soc., Chem. Commun. (1986) 1013-1015.

[51 Kashiwada, Y., Nonaka, G-I. and Nishioka, I., Chem. Pharm. Bull., 34 (1986) 3208-3222.

[52] Reed, J. D., J. Range Manage., 39 (1986) 5-7.

Shen, Z., Haslam, E. and [in part] Falshaw, C. P., Begley, M. J. Phytochem., 25 (1986) 2629-2635

Porter, L. J., Foo, L. Y. and Furneaux, R. H., Phytochem., 24 (1985) 567-569.

Hwang, T-H., Kashiwada, Y., Nonaka, G-I. and Nishioka, I., Phytochem., 28 (1989) 891-896.

[56] Sun, D., Zhao, Z., Wong, H. and Foo, L. Y., Phytochem., 27 (1988) 579-583.

[57] Ayoub, S. M. H., Fitoter., (1983) 183-187

Ayoub, S. M. H., Int. J. Crude Drug Res., 23 (1985) 87-90.

Wagner, H., Ann. Proc. Phytochem. Soc. Europe, 25 (1985) 409-425

Mueller-Harvey, I., McAllan, A. B., Theodorou, M. K. and Beever, D. E., 'Phenolics in fibrous crop residues and plants and their effects on the digestion and utilization of carbohydrates and proteins in ruminants'. In Plant Breeding and the Nutritive Value of Crop Residues. Proceedings of a workshop held at ILCA, Addis Ababa, Ethiopia, 7-10 December 1987, pp. 97-132.

Self, R., Eagles, J., Galletti, G. C., Mueller-Harvey, I Hartley, R. D., Lea, A. G. H., Magnolato, D., Richli, U., Gujer R. and Haslam, E., Biomed. Mass Spectrom., 13 (1986) 449-468.

[62] Sastry, G. P., Baruah, J. N. and Rao, P. R., Ind. J. Chem., 1 (1963) 542-543.

Bhanu, K. U., Rajadurai, S. and Nayudamma, Y., Aust. J. Chem., 17 (1964) 803-809.

Goodwin, A. J. and Nursten, H. E., J. Soc. Leath. Technol. Chem., 57 (1973) 166-172.

Yazaki, K., Shida, S. and Okuda, T., Phytochem., 28 (1989) 607-609

Viviers, P. M., Young, D. A., Botha, J. J., Ferreira, D., Roux, D. G. and Hull, W. E., J. Chem. Soc. Perkin Trans. I (1982) 535-540.

Foo, L. Y., J. Chem. Soc., Chem. Commun., (1986) 675-677.

[68] Young, D. A., Ferreira, D. and Roux, D. G., J. Chem. Soc. Perkin Trans. I (1983) 2031-2035.

[69] Brown, B. R., Stuart, I. A. and Tyrrell, A. W., J. Chem. Soc. Perkin Trans. I (1984) 2563-2572.

Nonaka, G-I. and Nishioka, I., Chem. Pharm. Bull., 28 (1980) 3145-3149.

Saini, K. S. and Ghosal, S., Phytochem., 23 (1984) 2415-2421.

Steynberg, J. P., Ferreira, D. and Roux, D. G., J. Chem. Soc. Perkin Trans. I (1987) 1705-1712.

Nonaka, G-I., Nishimura, H. and Nishioka, I., J. Chem. Soc. Perkin Trans. I (1985) 163-172.

maru shima Nonaka Mihashi and shioka Chem Pha Bull 36 88

shi Ishimatsu Nonaka G- Mihash Iwase and shioka Chem Pharm Bul 36 988

Okuda Hatano Kaneda shizaki and Shingu Phytochem 98 3-2

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Okuda Yoshida Hatano eda Shingu and Chem Pha Bul 86 5-408

McManus, J. P., Davis, K. G., Lilley, T. H. and Haslam, E., J Chem. Soc., Chem. Commun., (1981) 309-311.

Hagerman, A. E. and Robbins, C. T., J. Chem. Ecol., 13 (1987) 1243-1259.

[91 Artz, W. E., Bishop, P. D., Dunker, A. K., Schanus, E. G. and Swanson, B. G., J. Agric. Food Chem., 35 (1987) 417-421.

Hagerman, A. E. and Butler, L. G., J. Agric. Food Chem., 26 (1978) 809-812.

Watanabe, T., Mori, T., Tosa, T. and Chibata, I., J. Chromatogr., 207 (1981 13-20

Watanabe, T., Mori, T., Tosa, T. and Chibata, I., Agric. Biol. Chem., 45 (1981) 1001-1003.

Jones, W. T. and Mangan, J. L., J. Sci. Food Agric., 28 (1977) 126-136.

Martin, J. S. and Martin, M. M., J. Chem. Ecol., 9 (1983) 285-294

[97] Haslam, E. and Lilley, T. H., 'Interationcs of natural phenols with macromolecules'. In Cody V., Middleton, E. Jr. and Harborne, J. B. (eds.), Plant Flavonoids in Biology and Medicine: Biochemical, Pharmacological, and Structure - Activity Relationships, Alan R. Liss, Inc., New York, 1986, pp. 53-65.

Martin, R., Lilley, T. H., Bailey, N. A., Falshaw, C. P., Haslam, E., Magnolato, D. and Begley, M. J., J. Chem. Soc., Chem. Commun., (1986) 105-106.

Martin, R., Lilley, T. H., Falshaw, C. P., Haslam, E., Begley, M. J. and Magnolato, D., Phytochem., 26 (1987) 273-279.

[100] Horigome, T., Kumar, R. and Okamoto, K., Brit. J. Nutr., 60 (1988) 275-285.

101 Asquith, T. N., Uhlig, J., Mehansho, H., Putman, L., Carlson, D. M. and Butler, L. G., J. Agric. Food Chem., 35 (1987) 331-334

[102] Butler, L. G., Riedl, D. J., Lebryk, D. G. and Blytt, H. J., J. Amer. Oil Chem. Soc., 61 (1984) 916-920.

[103] Hagerman, A. E. and Butler, L. G., J. Biol. Chem., 256 (1981) 4494-4497.

[104] McManus, J. P., Davis, K. G., Beart, J. E., Gaffney, S. H., Lilley, T. H. and Haslam, E., J. Chem. Soc. Perkin Trans. II (1985) 1429-1438

[105] Davis, A. B. and Hoseney, R. C., Cereal Chem., 56 (1979) 310-314.

[106] Gaffney, S. H., Martin, R., Lilley, T. H., Haslam, E. and Magnolato, D., J. Chem. Soc., Chem. Commun., (1986) 107-109.

[107] Ozawa, T., Lilley, T. H. and Haslam, E., Phytochem., 26 (1987) 2937-2942.

[108] Deshpande, S. S. and Salunkhe, D. K., J. Food Sci., 47 (1982) 2080-2083.

[109] Mole, S. and Waterman, P. G., Phytochem., 26 (1987) 99-102.

[110] Blytt, H. J., Guscar, T. K. and Butler, L. G., J. Chem. Ecol., 14 (1988) 1455-1465.

[111 Griffiths, D. W. and Moseley, G., J. Sci. Food Agric., 31 (1980) 255-259.

[112] Robbins, C. T., Hanley, T. A., Hagerman, A. E., Hjelford, O., Baker, D. L., Schwartz, C. C. and Mantz, W. W., Ecology, 68 (1987) 98-107.

[113] Hahn, D. H., Rooney, L. W. and Earp, C. F., Cereal Foods World, 29 (1984) 776-779.

114 Ford, C. W., Aust. J. Agric. Res., 29 (1978) 963-974

[115] Beever, D. E. and Siddons, R. C., 'Digestion and metabolism in the grazing ruminant'. In Millingan, L. P., Grovum, W. L. and Dobson, A. (eds.), Control of Digestion and Metablism in Ruminants, Prentice-Hall, New Jersey, USA, 1985, pp. 479-497.

[116 Oberthur, E. E., Nicholson, R. L. and Butler, L. G., J. Agric. Food Chem., 31 (1983) 660-662.

117 Singleton, V. L., Adv. Food Res., 27 (1981) 149-242.

118] Hemingway, R. W., McGraw, G. W., Karchesy, J. J., Foo, L. Y. and Porter, L. J., J. Appl. Polym. Sci.: Appl. Polym. Symp., 37 (1983) 967-977

[119] Butler, L. G., Rogler, J. C., Mehansho, H. and Carlson, D. M., In Cody, V., Middleton, E. Jr., Harborne, J. B. and Berety, A. (eds.), Plant Flavonoids in Biology and Medicine II: Biochemical Cellular and Medicinal Properties., A. R. Liss Inc., 1986, pp. 141-157

[120] Kumar, R. and Singh, M., J. Agric. Food Chem., 32 (1984) 447-453.

121] McLeod, M. N., Nutr. Absts. Revs., 44 (1974) 803-815

[122] Price, M. L. and Butler, L. G., Purdue Univ. Agr. Exptl. Sta. Bull., No 272 (1980).

123] Waterman, P. G., 'Food acquisition and processing as a function of plant chemistry', Chapter 8, In Chivers, D. J., Wood, B. A. and Bilsborough, A. (eds.), Food Acquisition and Processing by Primates, Plenum Press, New York, 1984, pp. 177-211.

[124] Waterman, P. G., In Cody, V., Middleton, E. Jr., Harborne, J. B. and Beretz (eds.), Plant Flavonoids in Biology and Medicine II: Biochemical, Cellular and Medicinal Properties, Alan R. Liss, Inc., 1988, 77-91.

Arnold, G. W., de Boer, E. S. and Boundy, C. A. P., Aust. J. Agric. Res., 31 (1980) 571-587

[126] Glick, Z. and Joslyn, M. A., J. Nutr., 100 (1970) 509-515.

[127] Pal, R. N., Daniel, S. J. and Murty, V. N., Ind. J. Anim. Sci., 43 (1973) 267-271.

Vohra, P., Kratzer, F. H. and Joslyn, M. A., Poult. Sci., 45 (1966) 135-141.

[129] Mitjavala, S., Carrera, G. and Derache, R., Annls. Nutr. Aliment., 25 (1971) 297-310

[130] Sarkar, S. K., Howarth, R. E. and Goplen, B. P., Crop Sci., 16 (1976) 543-546

Donnelly, E., Agron. J., 46 (1954) 96-97.

[132] Wilkins, H. L., Bates, R. P., Henson, P. L., Lindahl, I. L. and Davis, R. E., Agron. J., 45 (1953) 335-336.

133] Hawkins, G. E. Jr., J. Dairy Sci., 38 (1955) 237-243.

[134] Scalbert, A. and Haslam, E., Phytochem., 26 (1987) 3191-3195.

[135] Nastis, A. S. and Malechek, J. C., J. Anim. Sci., 53 (1981) 283-290.

[136] Provenza, F. D. and Malechek, J. C., J. Appl. Ecol., 21 (1984) 831-841.

[137] McCabe, S. M. and Barry, T. N., J. Agric. Sci. (Cambridge), 111 (1988) 1-9.

[138] Villena, F., Pfister, J. A., San Martin, F. and James, L. F., J. Anim. Sci., 66 [Supplement 1 (1988) 347.

[139] Robbins, C. T., Mole, S., Hagerman, A. E. and Hanley, T. A., Ecol., 68 (1987) 1606-1615.

Martin, J. S., Martin, M. M. and Bernays, E. A., J. Chem. Ecol., 13 (1987) 605-621.

[141 Bernays, E. A., Ecol. Entomol., 6 (1981 353-360.

[142] Bernays, E. A. and Woodhead, S., Science, 216 (1982) 201-203.

[143] Janzen, D. H. and Waterman, P. G., Biol. J. Linnean Soc., 21 (1984) 439-454.

[144] Steinly, B. A. and Berenbaum, M., Entomol. Experent. Applic., 39 (1985) 3-9.

[145] Feeny, P. P., Phytochem., 8 (1969) 2119-2126

[146] Chang, S. I. and Fuller, H. L., Poult. Sci., 43 (1964) 30-36.

Connor, J. K., Hurwood, I. S., Burton, H. W. and Fuelling, D. E., Aust. J. Exptl. Agric. Husb., 9 (1969) 497-

Fuller, H. L., Potter, D. K. and Brown, A. R., University of Georgia Agric. Exptl. Stat. Bull. N.S., 176 (1966) 5-14.

[149] Gous, R. M., Kuypel, M. A. and Dennison, C., S.A.J. Anim. Sci., 12 (1982) 39-44.

[150] Lacassagne, L., Francesch, M., Carre, B. and Melcion, J. P., Anim. Feed Sci. Technol., 20 (1988) 59-68

[151 Rostagno, H. D., Featherston, W. R. and Rogler, J. C., Poult. Sci., 52 (1973) 765-772.

[152] Rostagno, H. D., Rogler, J. C. and Featherston, W. R., Poult. Sci., 52 (1973) 772-778.

Stephenson, E. L., York, J. O., Bragg, D. B. and Ivy, C. A., Poult. Sci., 50 (1971 581-584.

[154] Kratzer, F. H., Singleton, V. L., Kadirvel, R. and Rayudu, G. V. N., Poult. Sci., 54 (1975) 2124-2127

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ng and ru EEC 80 pp 5-

Booth and Soc Ex Med 128

68 -8

[183] Mitjavala, S., Saint Blanquat, G. de and Derache, R., Nutr. Metabol., 15 (1973) 163-170

[184] Panda, N. C., Sahu, B. K., Panda, S. K. and Rao, A. G., Ind. J. Nutr. Dietet. 18 (1981 97-101.

[185] Roy, S. N. and Mukherjee, S., Ind. J. Biochem. Biophys., 16 (1979) 93-97.

[186] Booth, A. N., Morse, M. S., Robbins, O. J., Emerson, O. H., Jones, F. T., and De Eds, F., J. Biol. Chem., 234 (1959) 3014-3016.

[187] Camp, B. J., Steel, E. and Dollahite, J. W., Amer. J. Vet. Res., 28 (1967) 290-292.

[188] Fowler, V. R., In Bond, D. A. (ed.), Vicia faba, Feeding Value, Processing and Viruses. EEC., Brussels, 1980, pp. 31-43

Carbrera, A. and Martin, A., J. Agric. Sci., 106 (1986) 377-382.

Ford, J. E. and Hewitt, D., Brit. J. Nutr., 41 (1979) 341-352.

[191 Noland, P. R., Sharp, R. N., Campbell, D. R., Johnson, X. B. and York, J. O., J. Anim. Sci., 40 (1975) pp. 180 [abs.]

Almond, M., Smith, W. C., Savage, G. P. and Lawrence, T. L., J. Anim. Prod., 29 (1979) 143-150

[193] Cousins, B. W., Tanksley, T. D., Knabe, D. A. and Zebrowska, T. J. Anim. Sci., 53 (1981 1524-1537.

Myer, R. O. and Gorbet, D. W., Anim. Feed Sci. Technol., 12 (1985) 179-186.

[195] Mitaru, B. N., Reichert, R. D. and Blair, R., J. Nutr., 114 (1984) 1787-1796.

Mitaru, B. N., Reichart, R. D. and Blair, R., J. Anim. Sci., 58 (1984) 1211-1215

[197] Knabe, D. A., Tanksley, T. D. Jr. and Hesby, J. H., J. Anim. 49 (1979) 134-

[198] Albrecht, J. E., Clawson, A. J., Ulberg, L. C. and Smith, F. H., J. Anim. Sci., 27 (1968) 976-

[199] Smith, H. A., Amer. J. Path., 33 (1957) 353-

[200] Clawson, A. J. and Smith, F. H., J. Nutr., 89 (1966) 640-647.

[201 Skutches, C. L., Herman, D. L. and Smith, F., J. Nutr., 104 (1974) 415-423.

[202] Clawson, A. J., Smith, F. H., Osborne, J. C. and Barrick, E. R. J. Anim. Sci., 20 (1961) 547-552.

[203] Hale, F. and Lyman, C. M., J. Anim. Sci., 16 (1957) 364-369.

[204 Braham, J. E., Jarquin, R., Bressani, R., Gonzalez, J. M. and Elias, L. G., J. Nutr., 93 (1967) 241-248.

[205] Skutches, C. L., Herman, D. L. and Smith, F., J. Nutr., 103 (1973) 851-855.

[206] Withers, W. A. and Brewster, J. F., J. Biol. Chem., 15 (1913) 161-165.

[207] Reid, C. S. W., 'Limitations to the productivity of the herbage-fed ruminant that arise from the diet'. Chapter 33 In Butler, G. W. and Bailey, R. W. (eds.), Chemistry and Biochemistry of Herbage, Academic Press, New York, 1973, pp. 215-262.

[208] Kornegay, E. T., Clawson, A. J., Smith, F. H. and Barrick, E. R. J. Anim. Sci., 20 (1961 597-602.

[209] Sharma, M. P., Smith, F. H. and Clawson, A. J., J. Nutr., 88 (1966) 434-438.

[210] Buitrago, J. A., Clawson, A. J. and Smith, F. H., J. Anim. Sci., 31 (1970) 554-558.

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[239] Singh, K. and Arora, S. P., Ind. J. Dairy Sci., 33 (1980) 310-315

[240] Reichart, R. D., Fleming, S. E. and Schwab, D. J., J. Agric. Food Chem., 28 (1980) 824-829.

[241 Daiber, K. H. and Taylor, J. R. N., J. Agric. Food Chem., 30 (1982) 70-72.

[242] Goldstein, J. L. and Swain, T., Phytochem., 4 (1965) 185-192

[243] Dollahite, J. W., Pigeon, R. R. and Camp, B. J., Am. J. Vet. Res., 23 (1962) 1264-1267.

[244] Armstrong, W. E., Featherston, W. R. and Rogler, J. C., Poult. Sci., 52 (1973) 1592-1599.

[245] Booth, A. N., Robbins, J. J. and De Eds, F., J. Nutr., 75 (1961 104-106.

[246] Rayudu, G. V. N., Kedirvel, R. R., Vohra, P. and Kratzer, F. H., Poult. Sci., 49 (1970) 957-960

[247 Sinha, R. P. and Nath, K., Ind. J. Anim. Sci., 52 (1982) 1165-1169.

[248] Hill, G. M., Utley, P. R. and Newton, G. L., J. Anim. Sci., 64 (1987) 1-7

[249] Mehansho, H., Hagerman, A., Clements, S., Butler, L. G., Rogler, J. and Carlson, D. M., Proc. Natl. Acad. Sci. USA, 80 (1983) 3948-3952.

[250] Mehansho, H., Butler, L. G. and Carlson, D. M., Ann. Rev. Nutr. 7 (1987) 423-440.

[251 Butler, L. G. and Mole, S. Proceedings of the 14th International Conference of Groupe Polyphenols, Narbonne, France 1988, pp. 111-114

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[224 Thomson, D. J., Beever, D. E., Harrison, D. G., Hill, I. W. and Osbourn, D. F., Proc. Nutr. Soc., 3 (1971) 14A.

[225] Waghorn, G. C., John, A., Jones, W. T. and Shelton, I. D., Proc. N. Z. Soc. Anim. Prod., 47 (1987) 25-30.

[226] Waghorn, G. C., Ulyatt, M. J., John, A. and Fisher, M. T., Brit. J. Nutr., 57 (1987) 115-126.

[227] Barry, T. N. and Duncan, S. J., Brit. J. Nutr., 51 (1984) 485-491.

[228] Barry, T. N. and Manley, T. R., Brit. J. Nutr., 51 (1984) 492-504.

[229] Zelter, S. Z., Leroy, F. and Tissier, J. P., Annls Biolog. Anim. Biochim. Biophys., 10 (1970) 123-141.

[230] Driedger, A. and Hatfield, E. E., J. Anim. Sci., 34 (1972) 465-468.

[231] McBrayer, A. C., Utley, P. R., Lowry, R. S. and McCormick, W. C., J. Anim. Sci., 56 (1983) 173-183.

[232] Negi, S. S., Anim. Feed Sci. Technol., 7 (1982) 161-183.

[233] Barry, T. N., Manley, T. R. and Duncan, S. J., Brit. J. Nutr., 55 (1986) 123-137

[234] Reed, C. S. W. and Johns, A. T., N.Z.J. Sci. Technol., 38A (1957) 908-917.

[235] Jones, W. T., Lyttleton, J. W. and Clarke, R. T. J., N.Z.J Agric. Res., 13 (1970) 149-

[236] Kendall, W. A., Crop Sci., 6 (1966) 487-489.

[237] Purchas, K. W. and Keogh, R. G., Proc. N.Z. Soc. Anim. Prod., 44 (1984) 219-221

[238] Chibber, D. A. K., Mertz, E. T. and Axtell, J. D., J. Agric. Food Chem., 26 (1978) 679-683.

Table 1: Flavan-3-ol units found in naturally occurring oligo-flavanols [12]

Monomeric flavan-3-ol	Oligomeric flavan-3-ol	Substitution pattern						
		3	5	7	8	3′	4′	5′
catechin	procyanidin	OH	OH	OH	H	OH	OH	H
gallocatechin	prodelphinidin	OH	OH	OH	H	OH	OH	OH
guibourtinidol	proguibourtinidol	OH	H	OH	H	H	OH	H
fisetinidol	profisetinidin	OH	H	OH	H	OH	OH	H
robinetinidol	prorobinetinidin	OH	H	OH	H	OH	OH	OH
prosopin	promelacacinidin	OH	H	OH	OH	OH	OH	H

Table 2: Naturally occurring gallic acid (GA) esters of flavan-3-ols

Compound	Plant source	Reference
3-O-GA esters of:		
(+)-catechin		see [12]
(-)-epicatechin		see [12]
(-)-epigallocatechin		see [12]
7-O-GA esters of:		
(+)-catechin		see [12]
(-)-epicatechin	Acacia nilotica bark & fruit	see [57,58]
(+)-gallocatechin		see [12]
3'-O-GA ester and 4'-O- GA ester of:		
(+)-catechin	A. nilotica leaves; A. gerrardi bark	see [61,260
3,5-di-O-GA esters of:		
(-)-epicatechin		see [12]
(-)-epigallocatechin		see [12]
5,7-di-O- GA esters of:		
(-)-epigallocatechin	A. nilotica bark & fruit	see [57,58]
3',7-di-O-GA esters and 4',7-di-O-GA esters of:		
(+)-catechin	A. gerrardi bark	see [260]
5 (or 7), 3'(or 4') -di-O-GA esters of:		
(+)-catechin	A. nilotica leaves	see [61
4',5-di-O-GA esters of:		
(+)-gallocatechin	A. nilotica fruit	see [59]

Captions to schemes:

Scheme 1: An illustration of the biosynthesis of oligoflavanols using the example of propelargonidins [11].

Scheme 2: An example of oligoflavanol building units: top (T); middle (M); junction (J) and bottom (B)-units [13].

Scheme 3: Relative stabilities of potential electrophiles [14].

Scheme 4: Relative stabilities of potential nucleophiles [14].

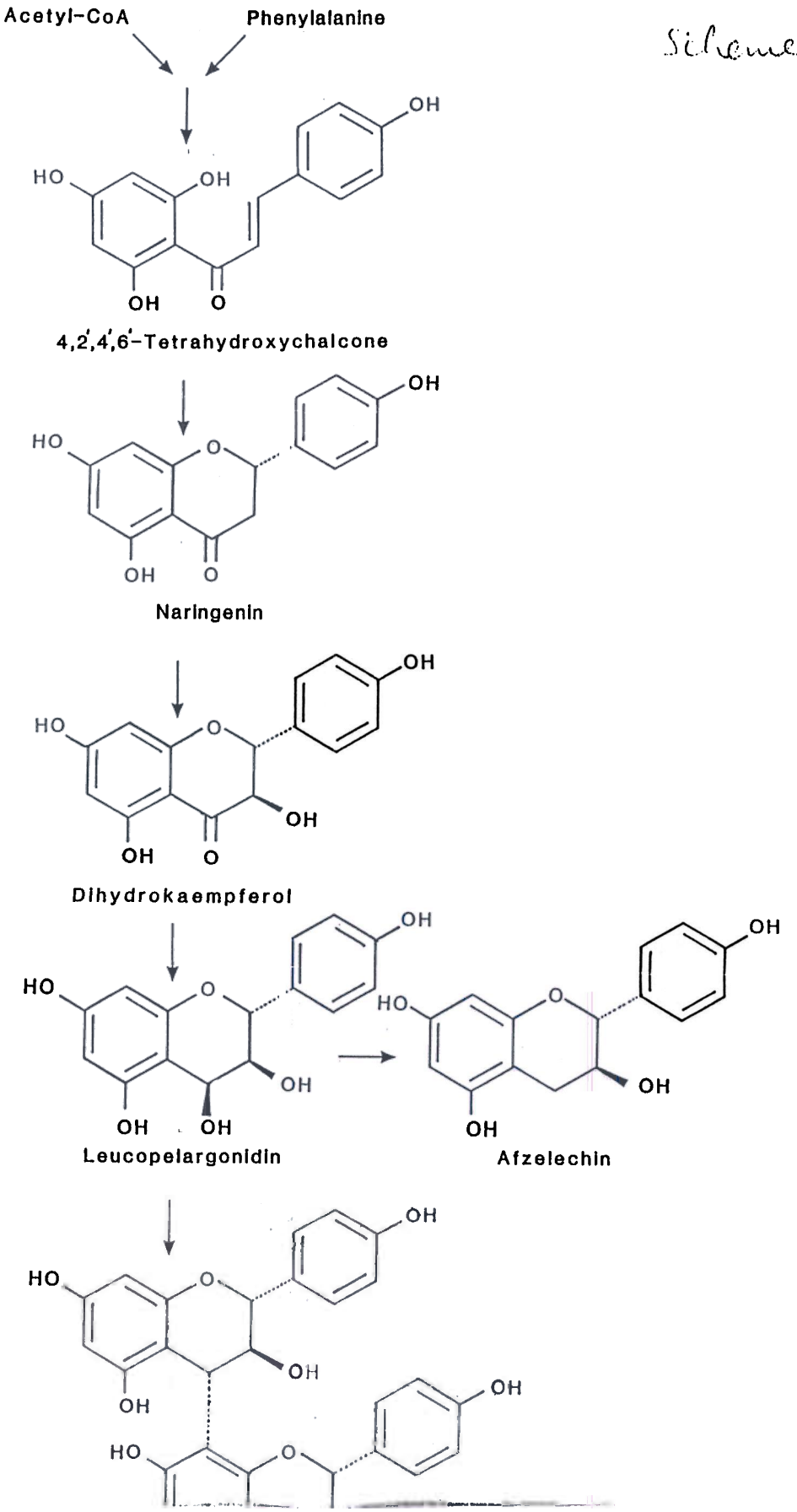
Scheme 5: Examples of two nomenclature systems when applied to a flavanol pentamer.

Scheme 6: Proposed biosynthetic pathways leading to gallotannins and ellagitannins [5].

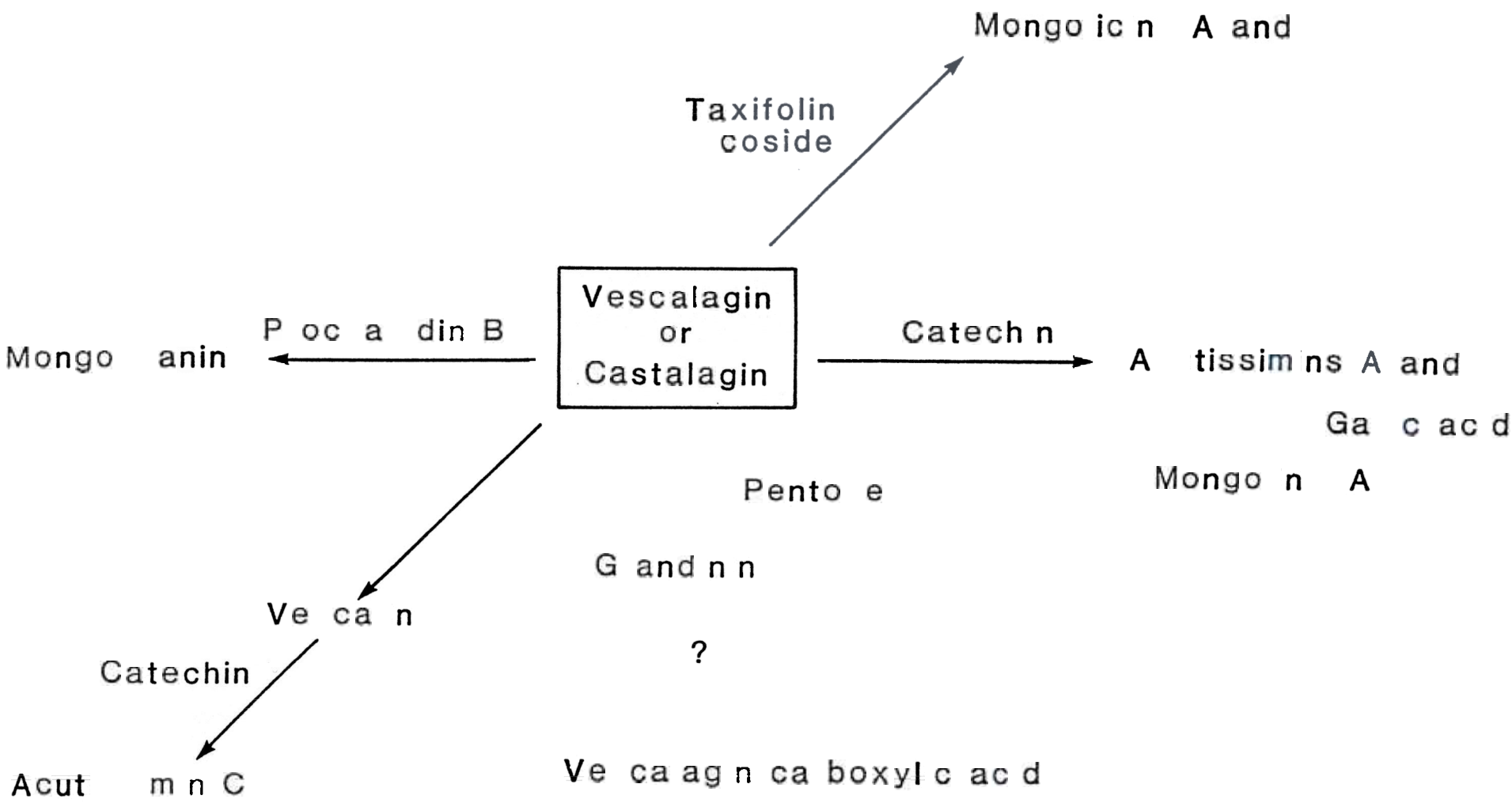
Scheme 7: A hypothetical biosynthetic scheme linking ellagitannins containing glucopyranose and open chain glucose cores with flavanoellagitannins.

Scheme 8: A hypothetical biosynthetic scheme linking vescalagin or castalagin with flavano- and flavonoellagitannins.

Schema 1


Acetyl-CoA
Phenylalanine
4,2',4',6'-Tetrahydroxychalcone
Naringenin
Dihydrokaempferol
Leucopelargonidin
Afzelechin

Scheme 8


Mongo ic n A and
Taxifolin coside
Vescalagin or Castalagin
P oc a din B
Mongo anin
Catech n
A tissim ns A and
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Pento e
G and n n
Ve ca n
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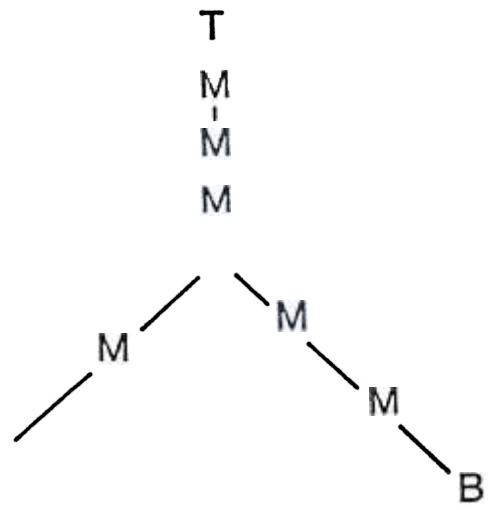
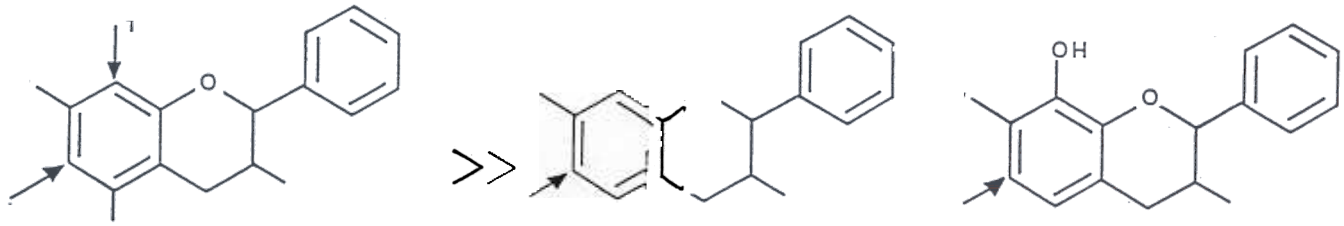
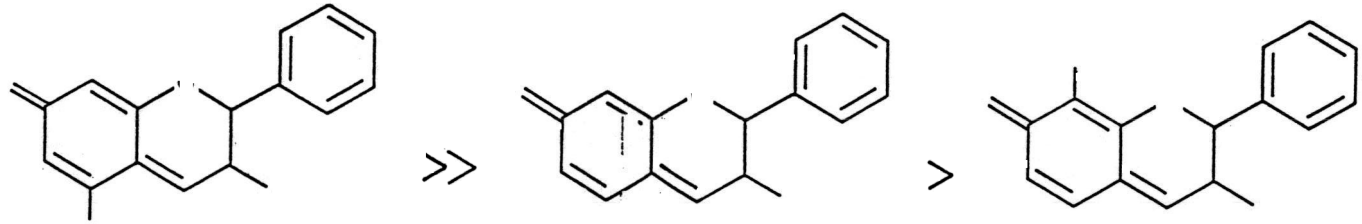
Catechin
Acut m n C
Ve ca ag n ca boxyl c ac d

Scheme 2





Scheme 4



Scheme 3

Scheme 5

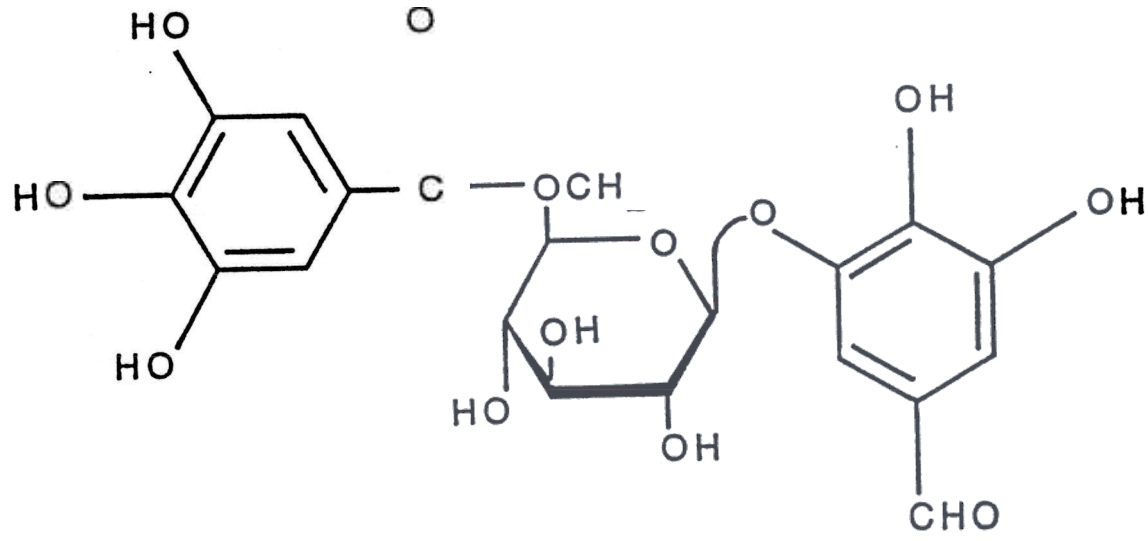
Nomenclature based on IUPAC system [35]

(2R, 3S)-2,3-trans-6-[(2S, 3R, 4S)-2,3-trans-3,4-cis-flavan-3,3′,4′, 7-tetraol-4-yl]-8-{(2S, 3R, 4R)-2,3-trans-3,4-trans-6,8-bi[(2S, 3R, 4R)-2,3-trans-3,4-trans-flavan-3,3′,4′,7-tetraol-4-yl]-flavan-3,3′,4′, 7-tetraol-4-yl}-flavan-3,3′,4′,5, 7- pentaol.

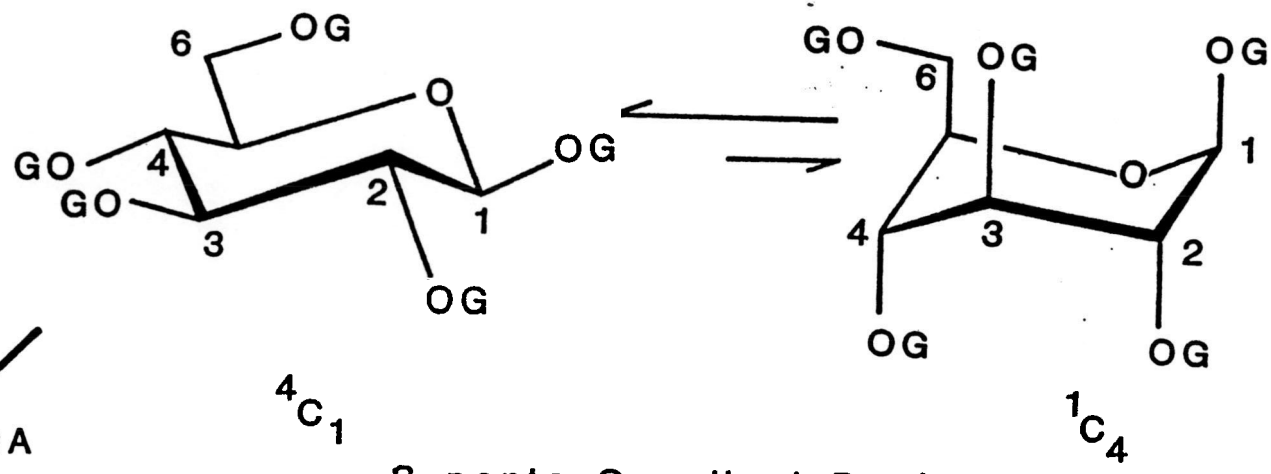
New proposed nomenclature [15]

(+)-fisetinidol (4β → 8), (+)-fisetinidol (4β → 6)-(+)-fisetinidol (4β → 8), (+)-fisetinidol (4α → 6)-(+)-catechin

Compound 3



Scheme 6



$^4C_1$ $^1C_4$

β-penta O-galloyl-D glucose

GOH

2A

addition of gallic acid as m depsides

'GALLOTANNINS'

2B

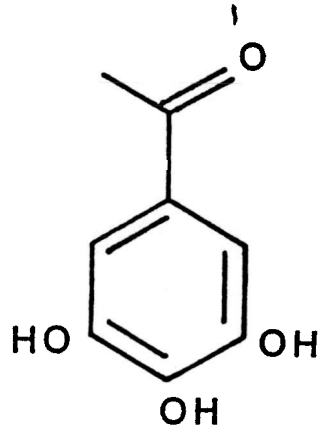
oxidative coupling of vicinal galloyl ester groups

2C

4 6
2 3

or

1-6
3 6
2 4

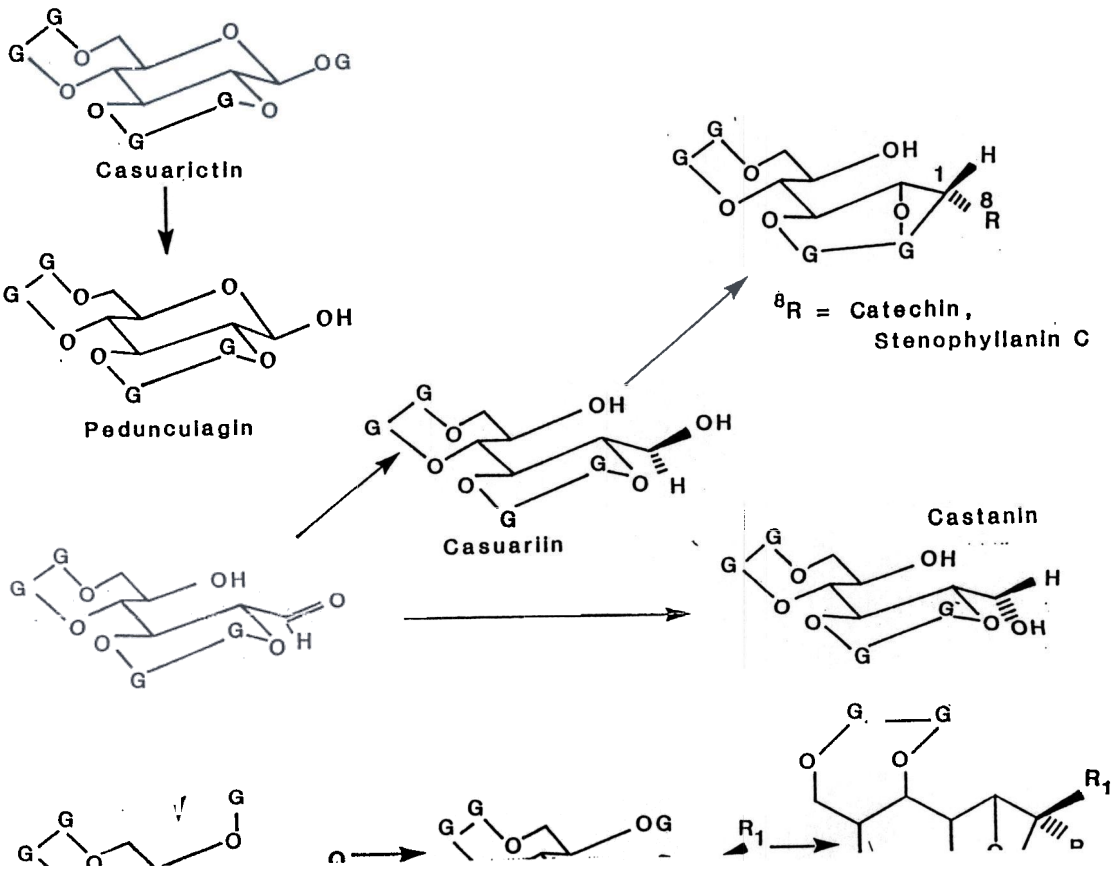


= G

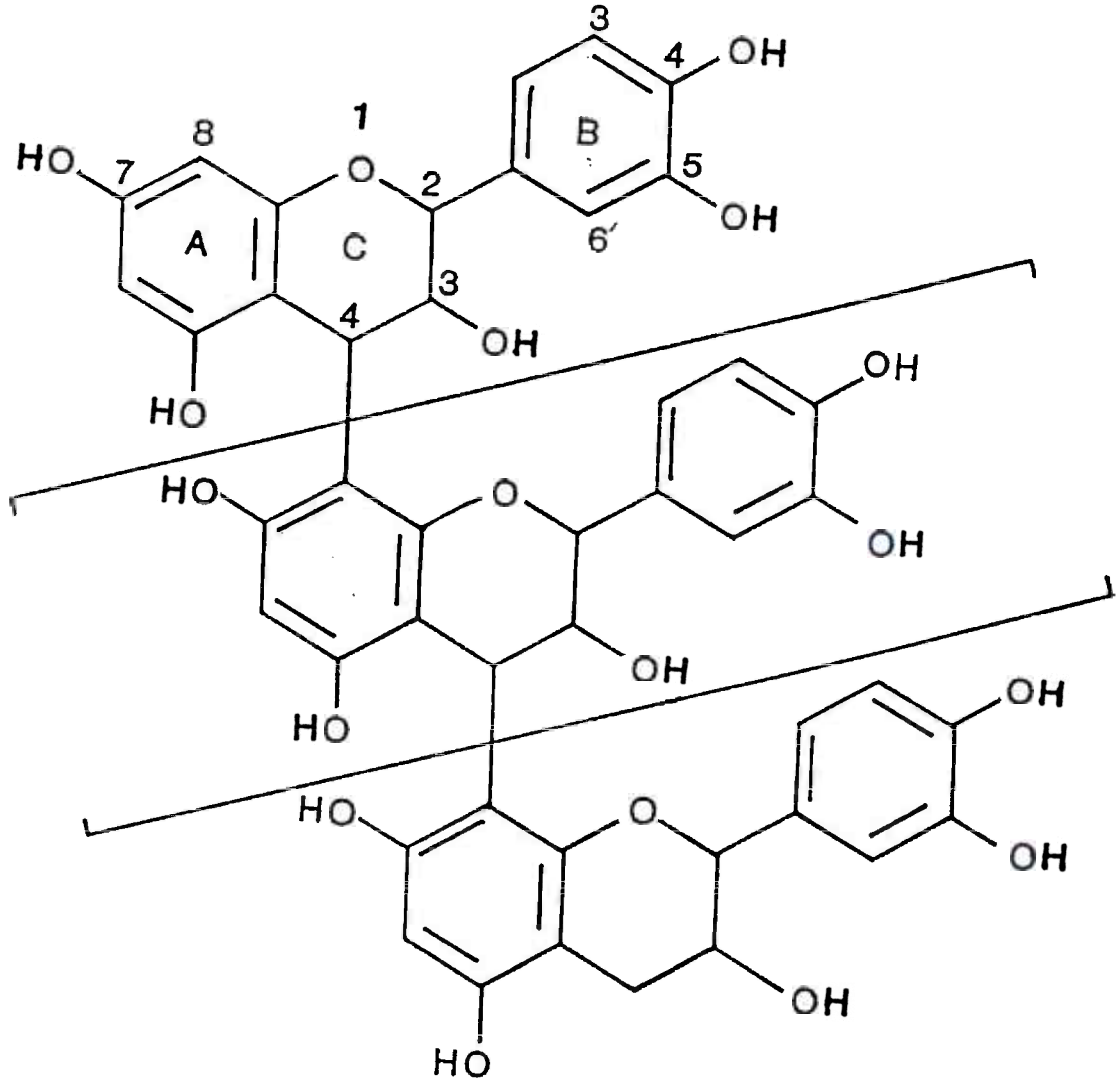
oxidative oligomerisation

'ELLAGITANNINS'

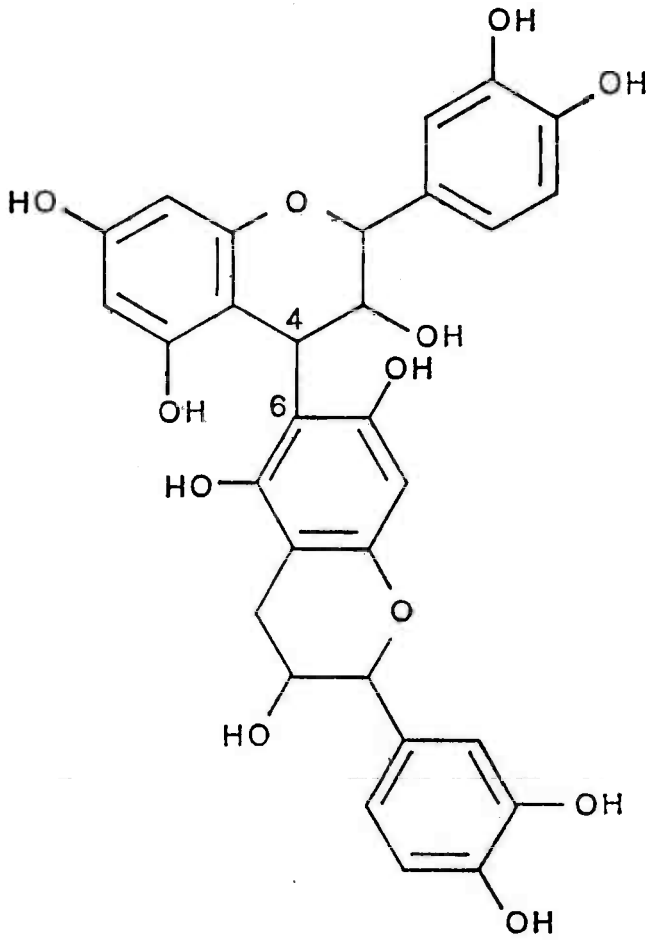
Scheme 7


Casuarictin
Pedunculagin
Casuariin
Castanin
8R = Catechin,
Stenophyllanin C

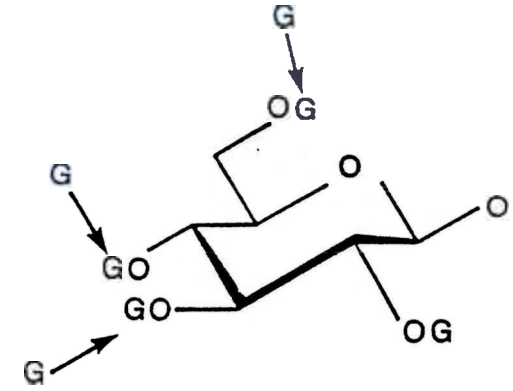
Compound

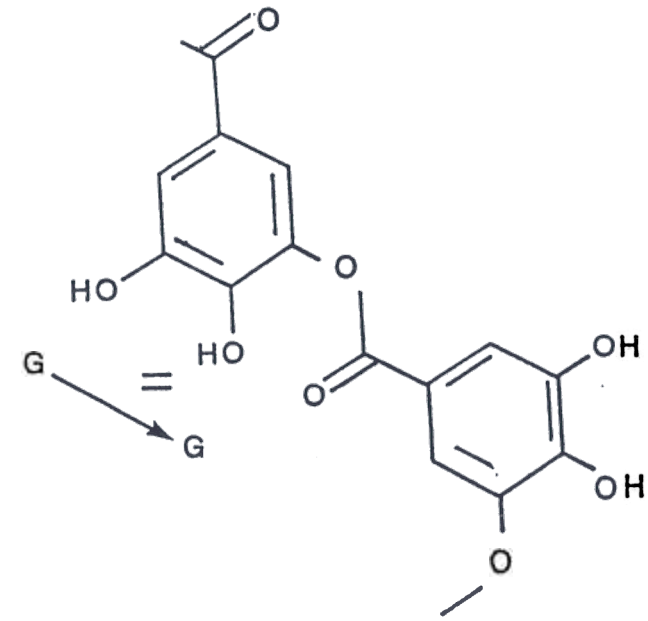


Compound 2



Compound 3



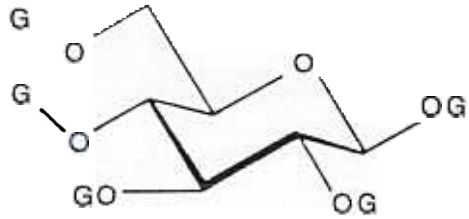


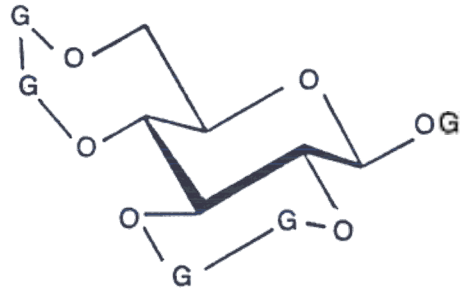
Compound (4): Tellimagrandin II

Compound (5): Casuarictin

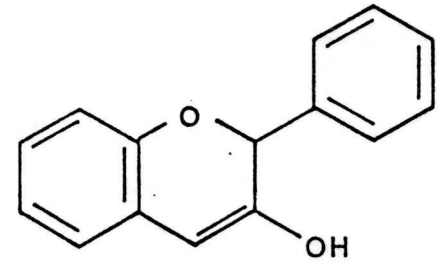
Compound (7): Flav-3-en-3-ol

Compound 4

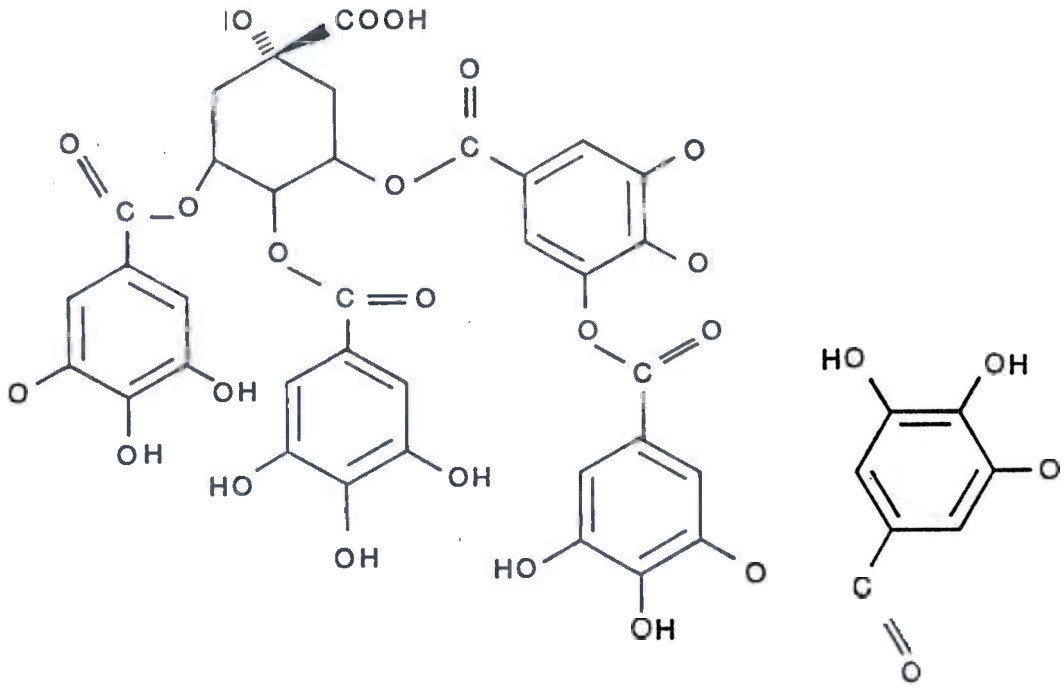




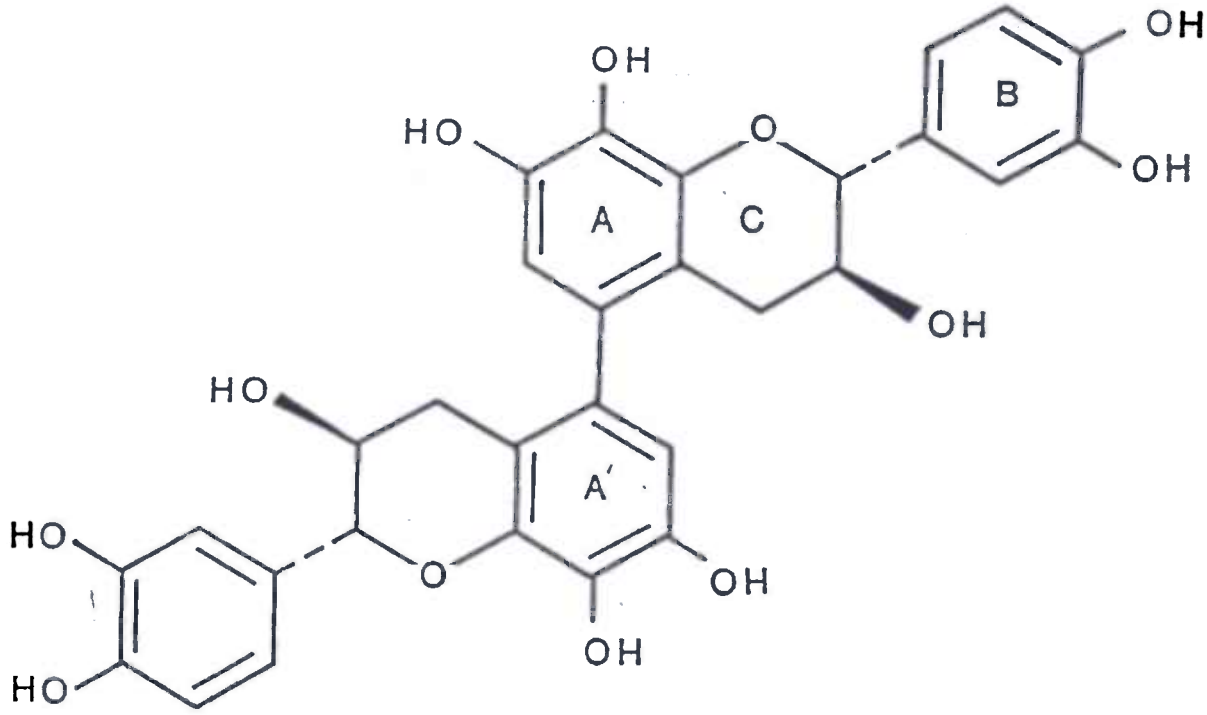
compo d 7



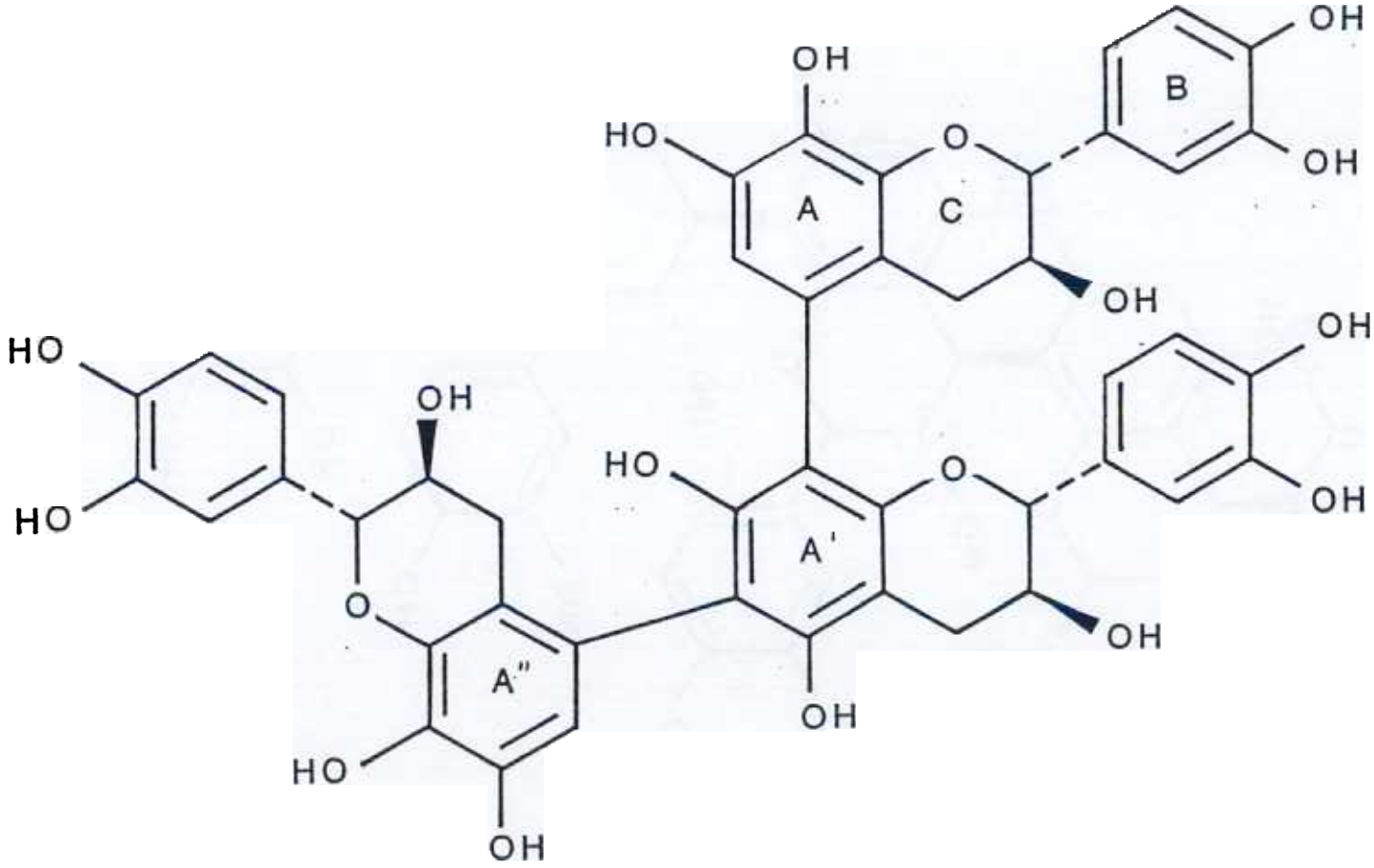
Compound 6



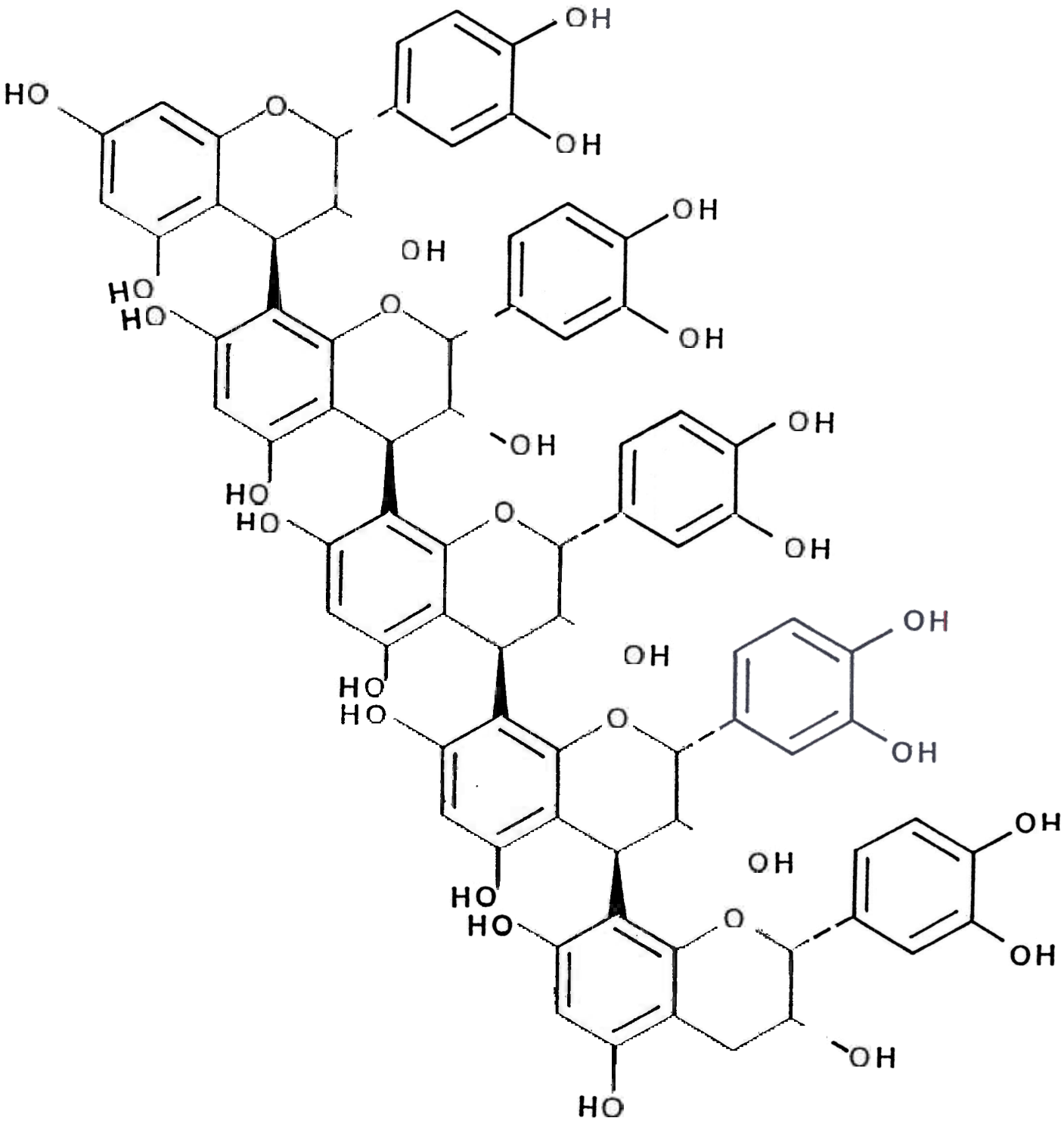
Compd 8



Compound 9



Compound 10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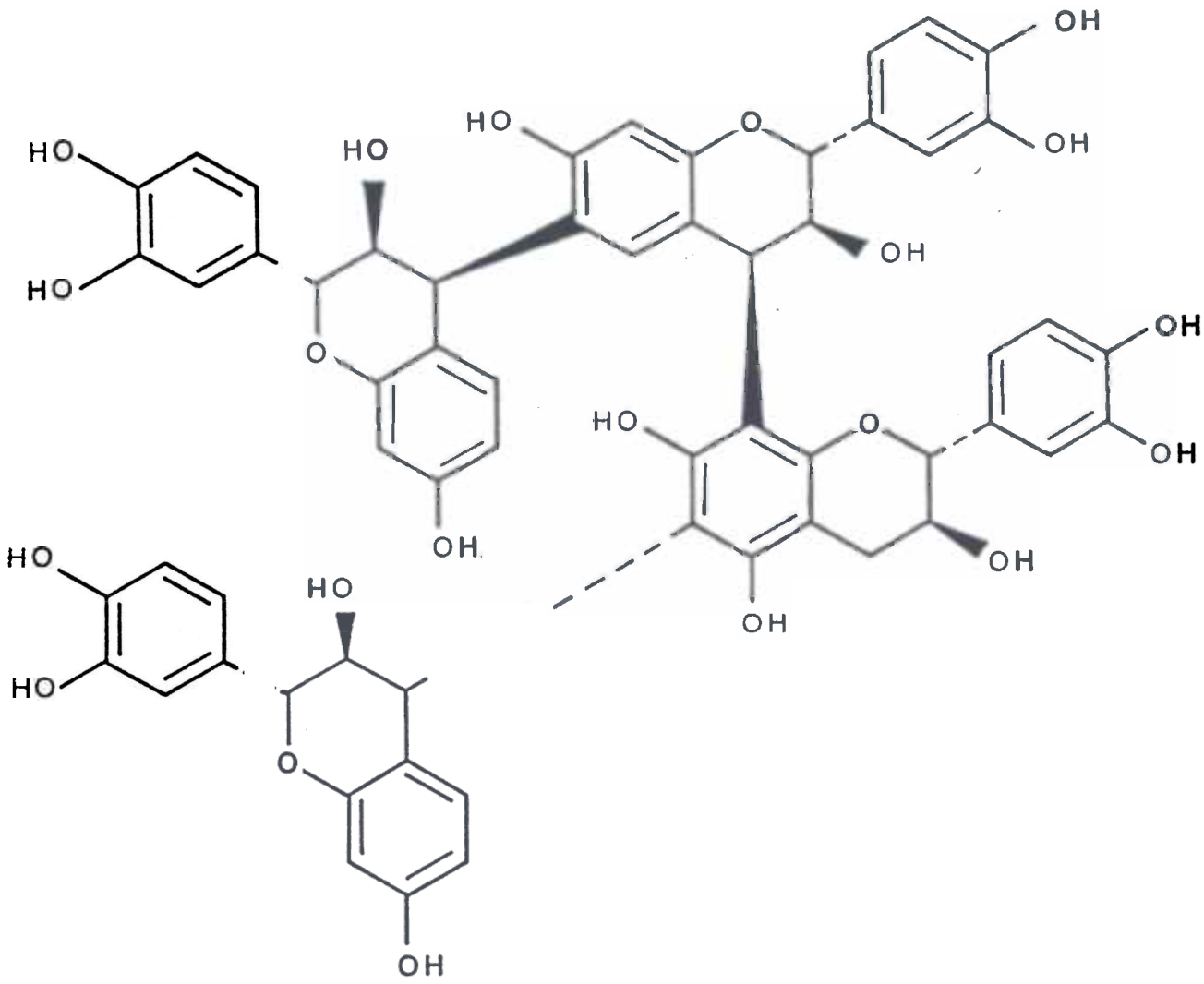
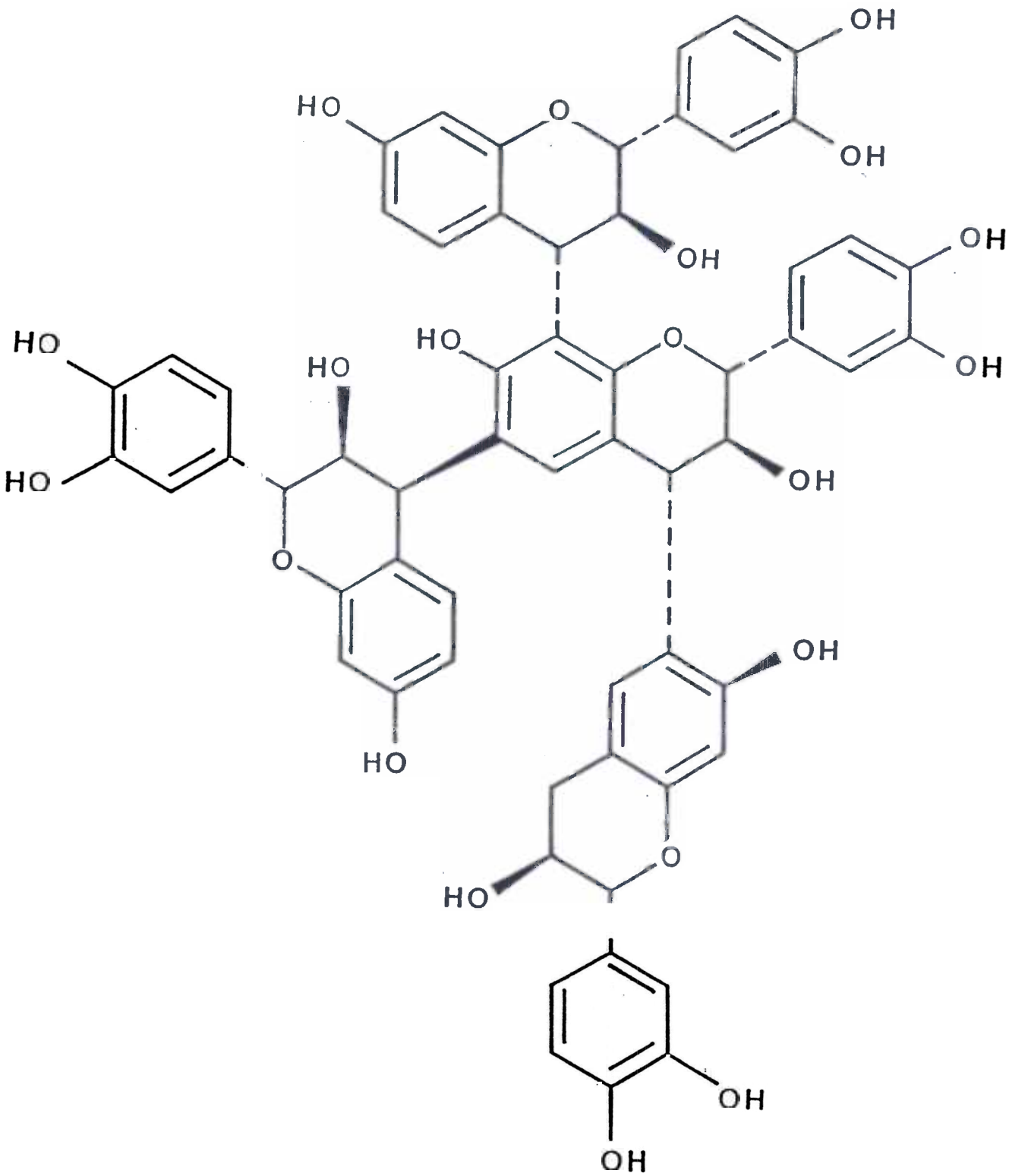
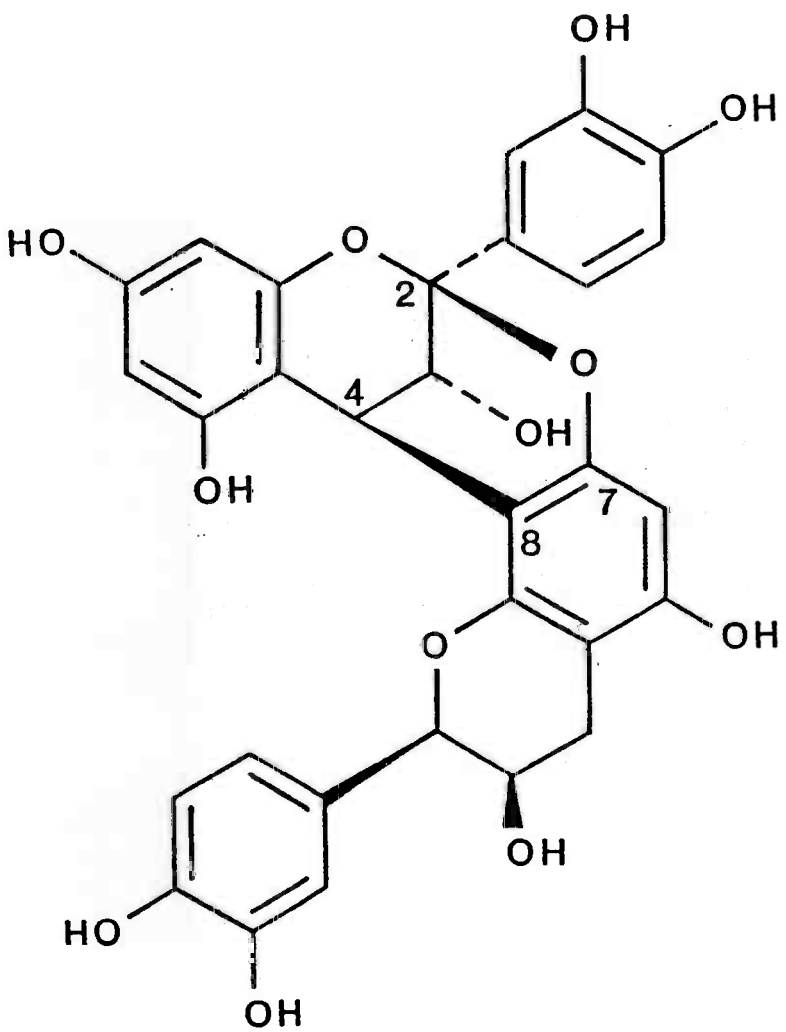
Compound d

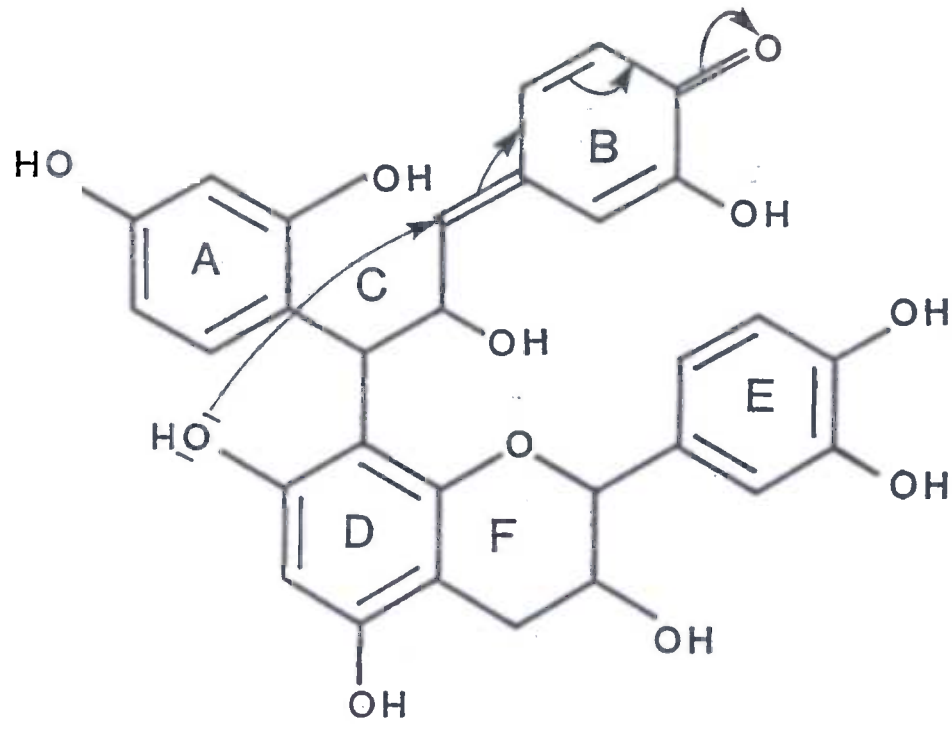


Compound 2



Compound 3




HO
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A
C
B
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HO
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D
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E
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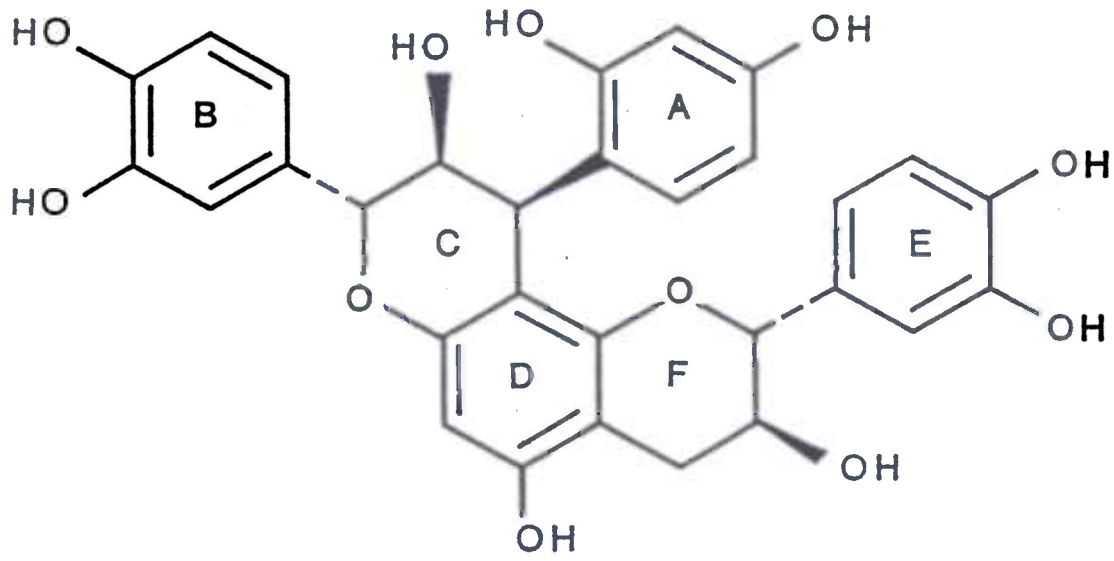
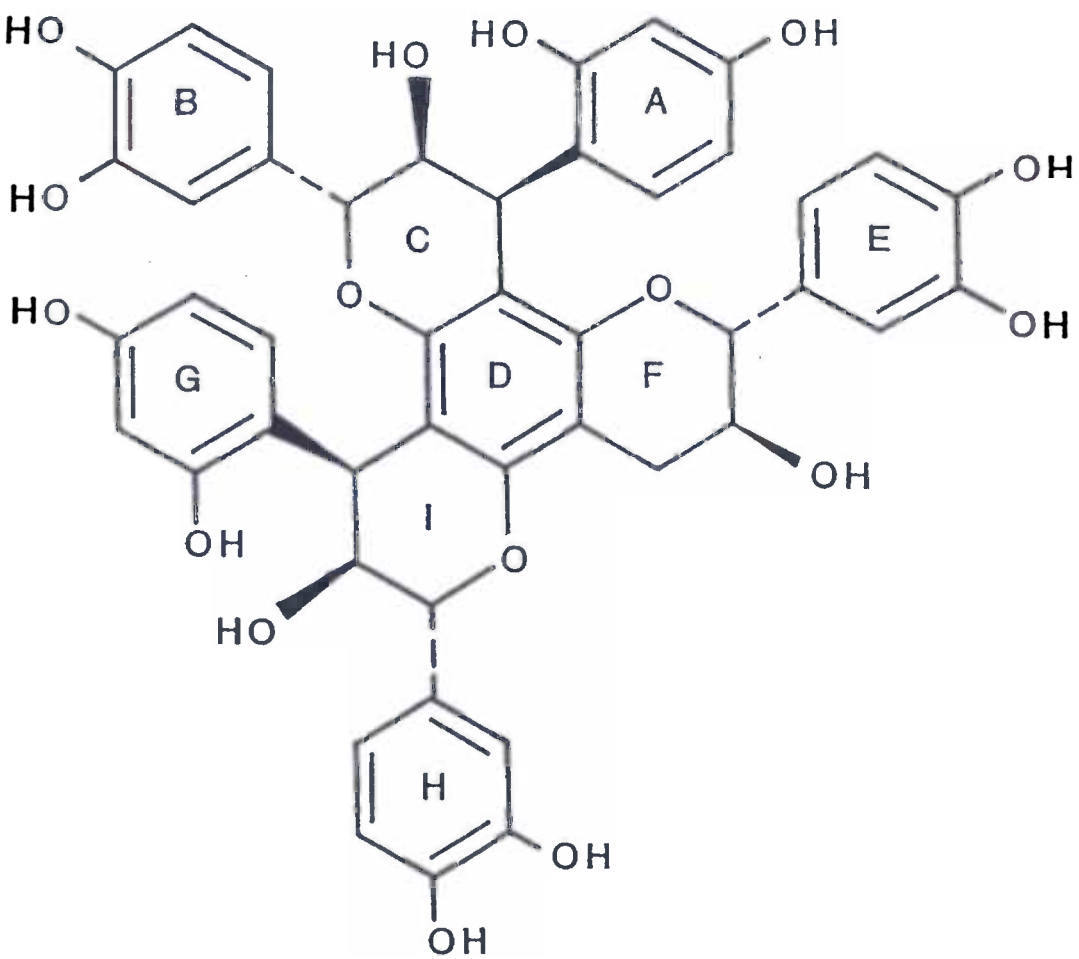
OH

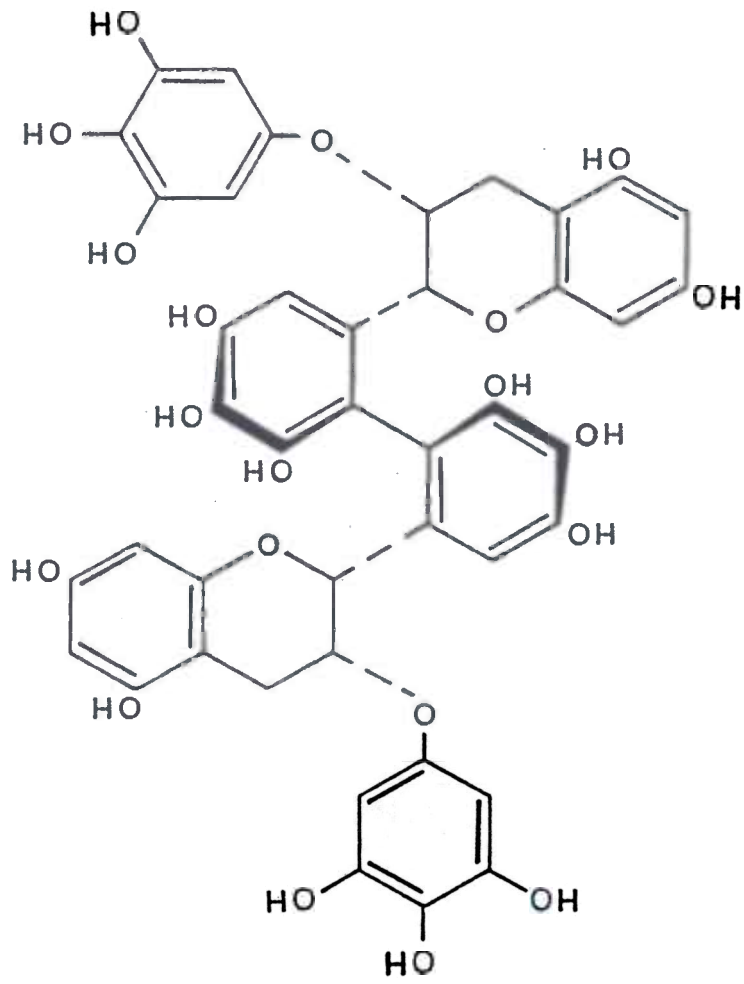
Compound 5



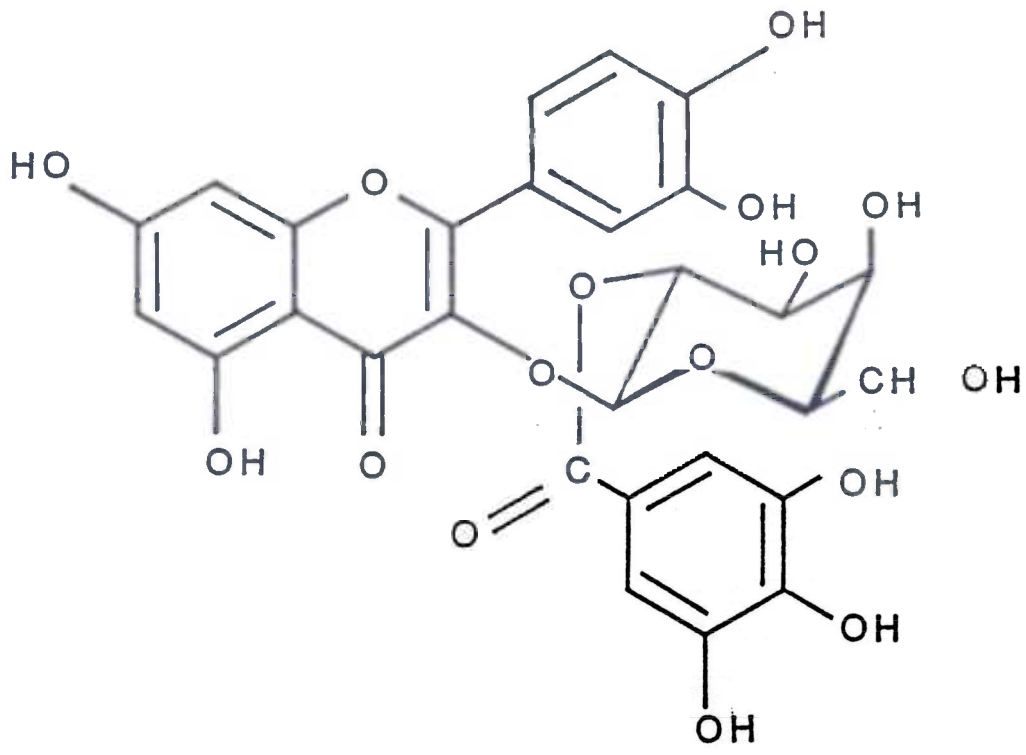
Compound 6



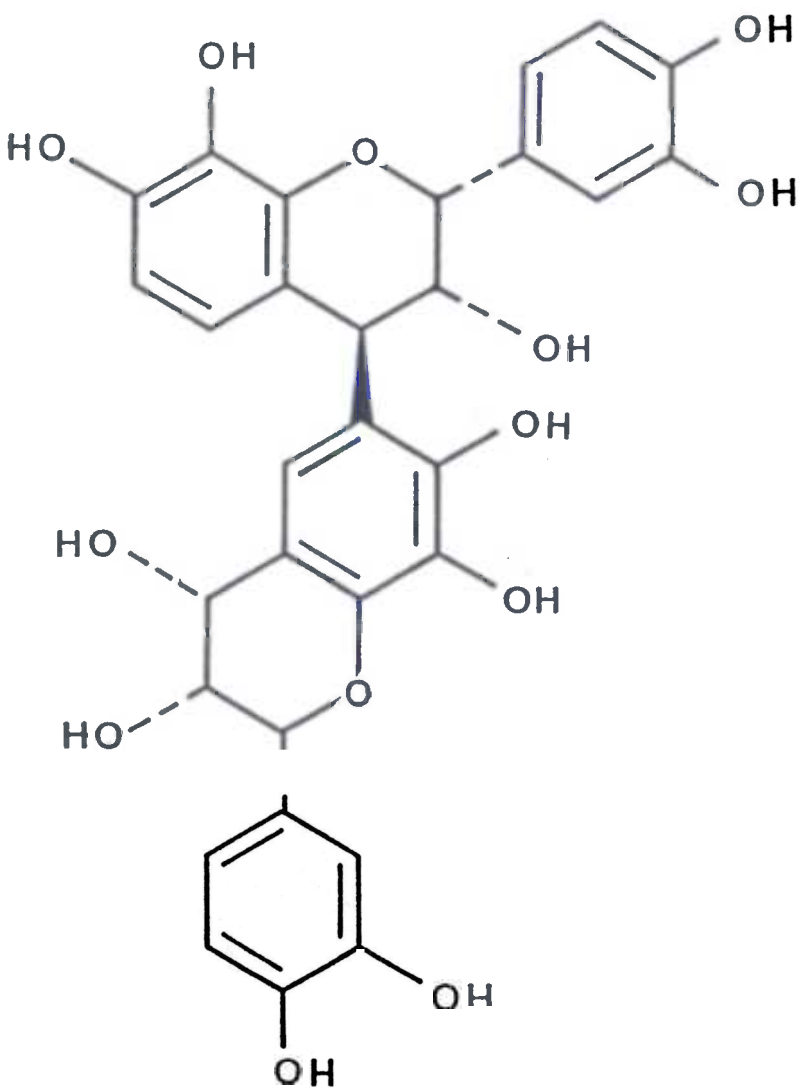
Comp d 7



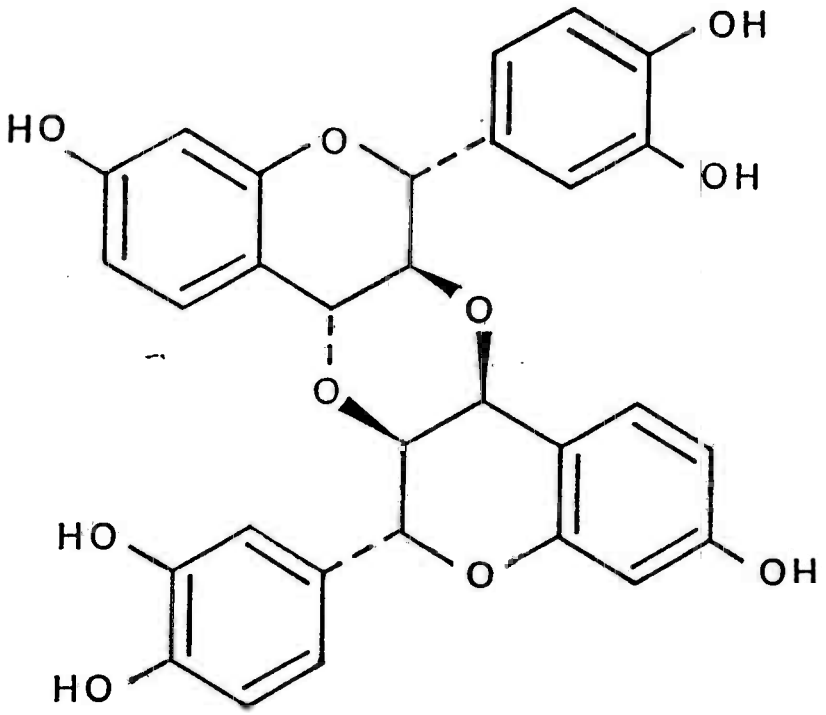
Compound 8

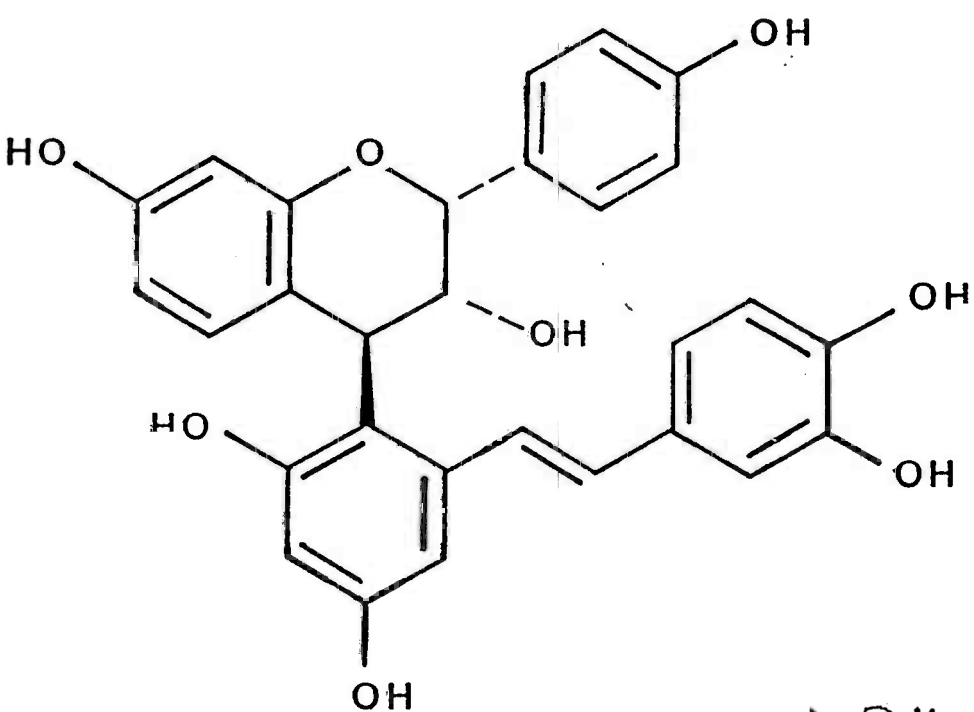


Compound 9



Compound 20





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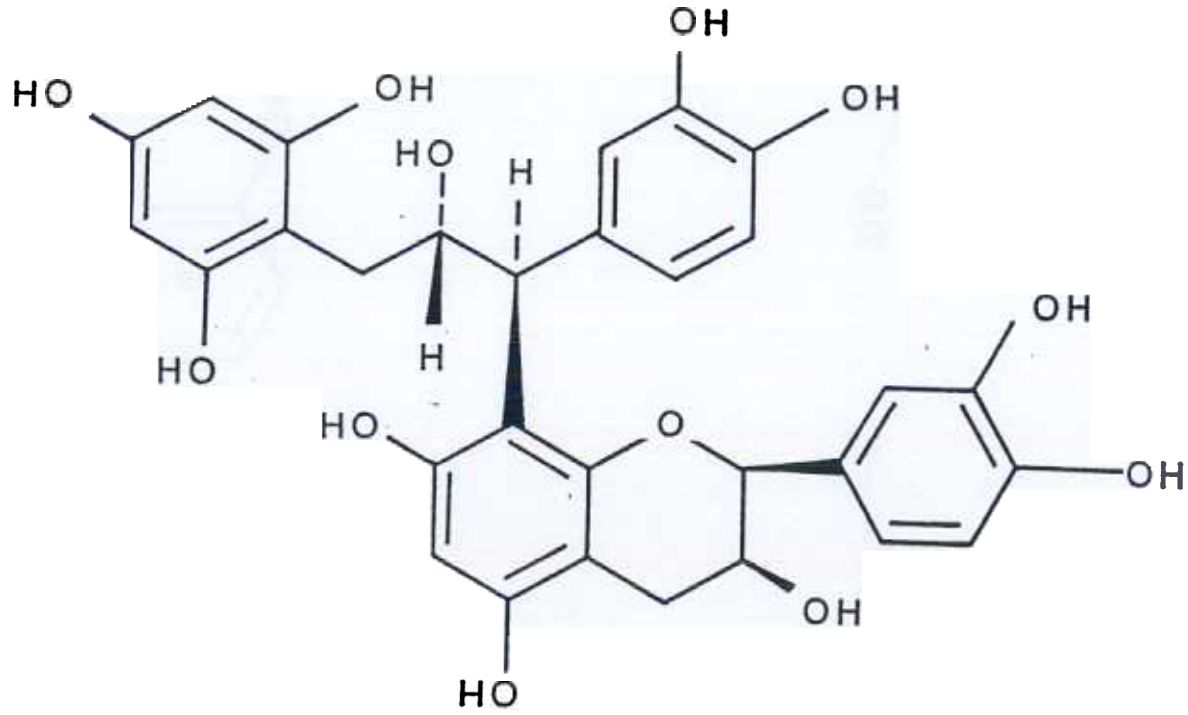
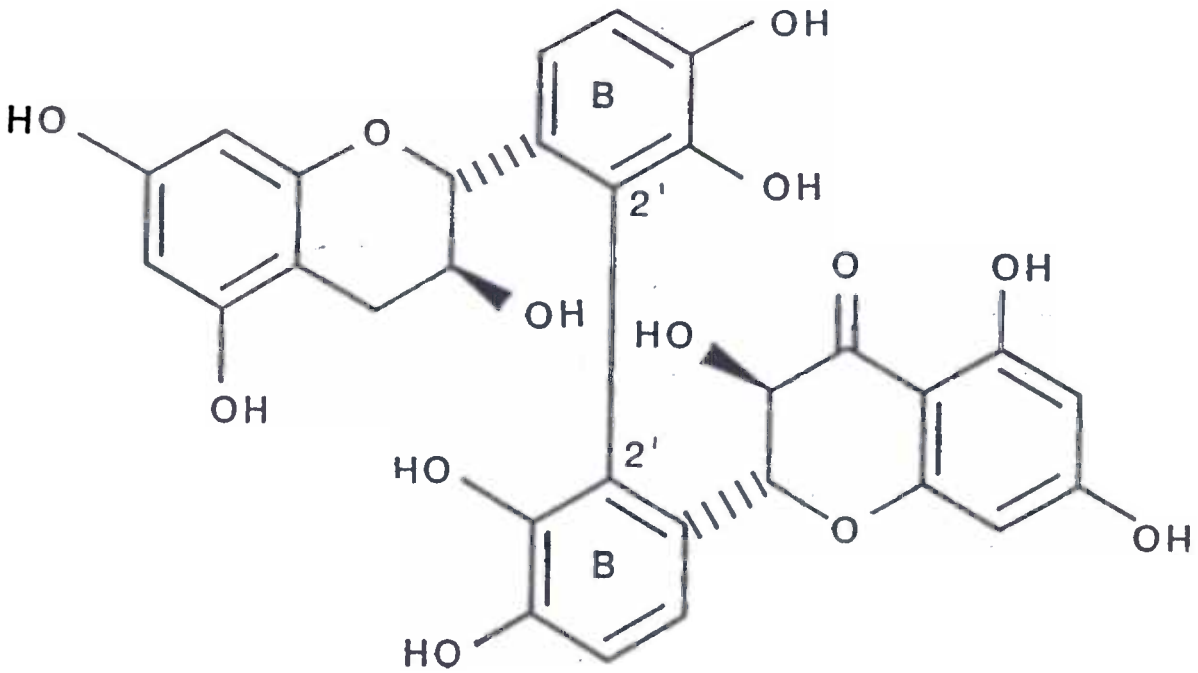
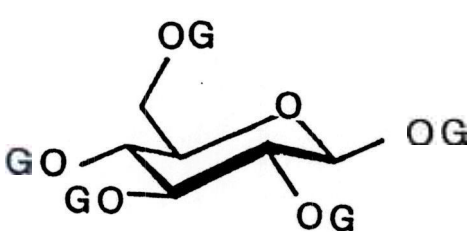
Compo d 2



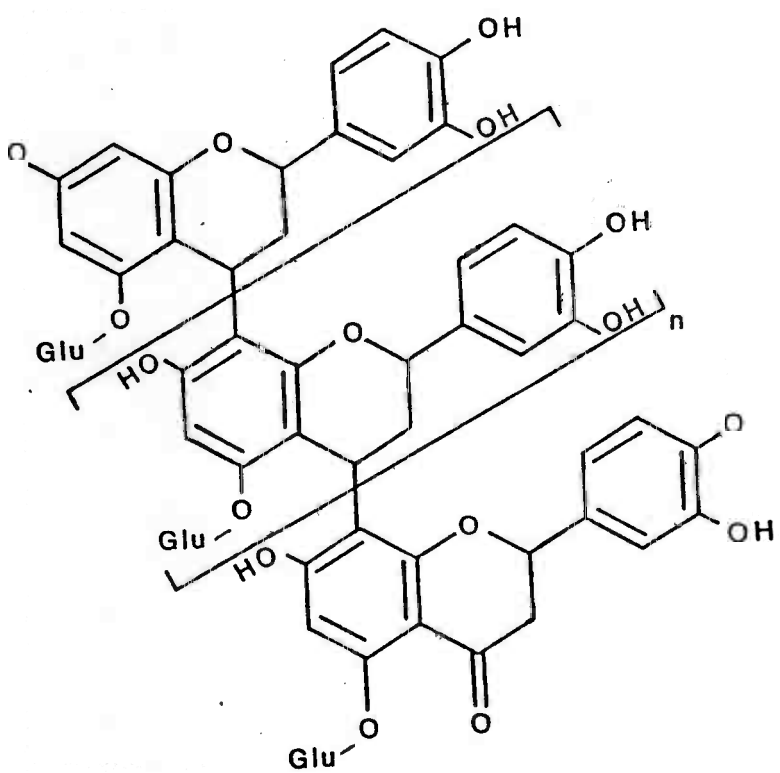
Compound 22



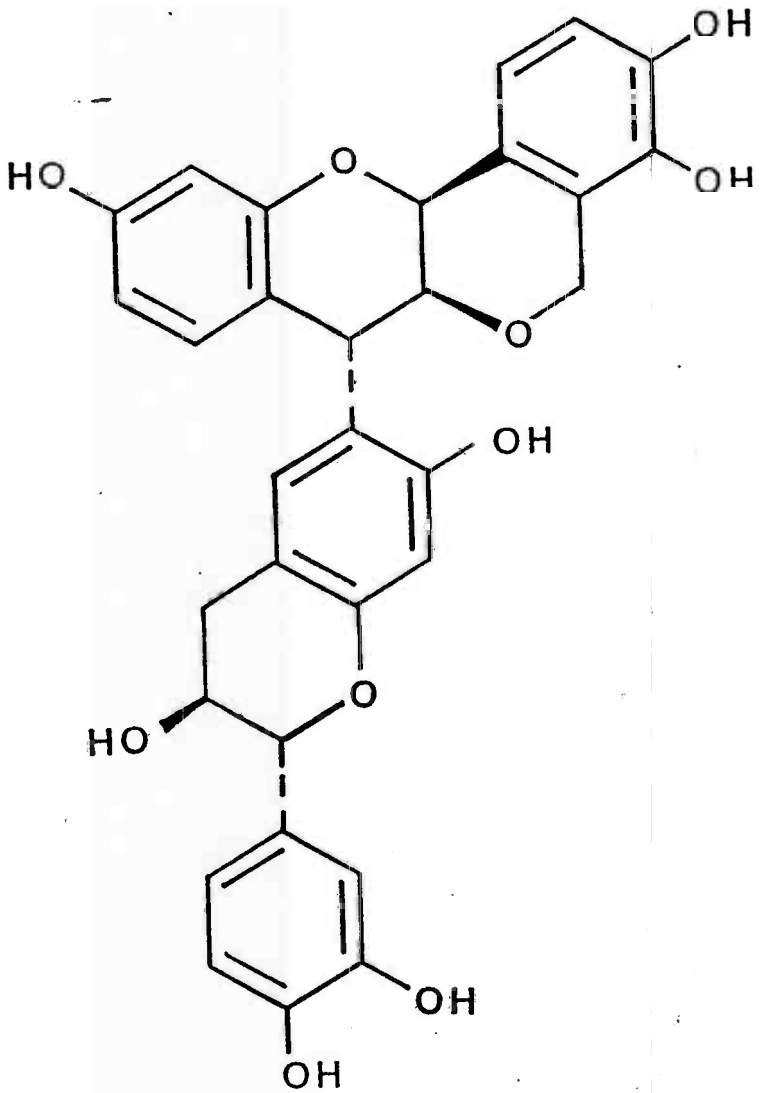


Comp d 26

Compound 23

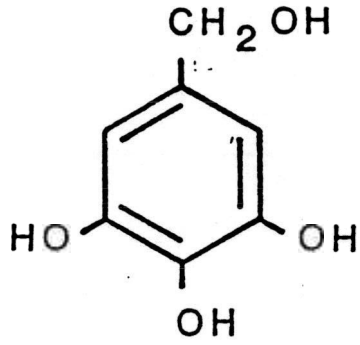


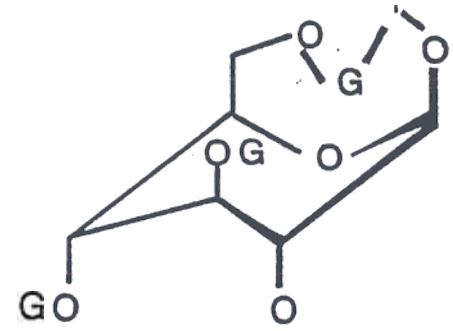
Compound 25.

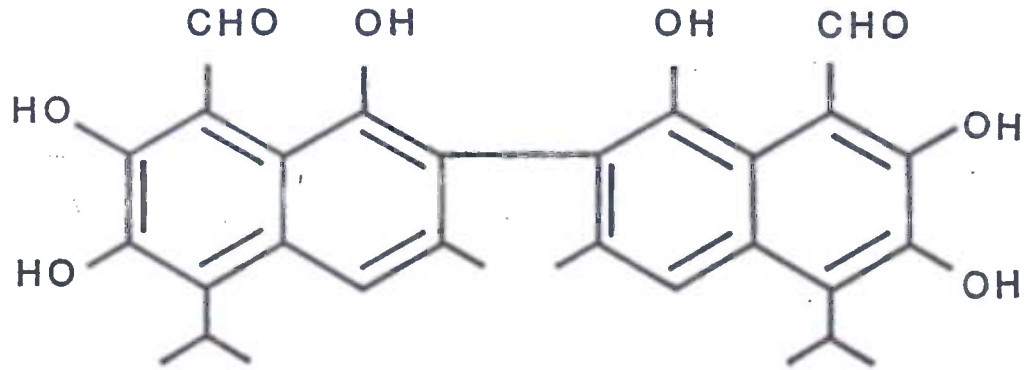


Compound (27): Davidiin

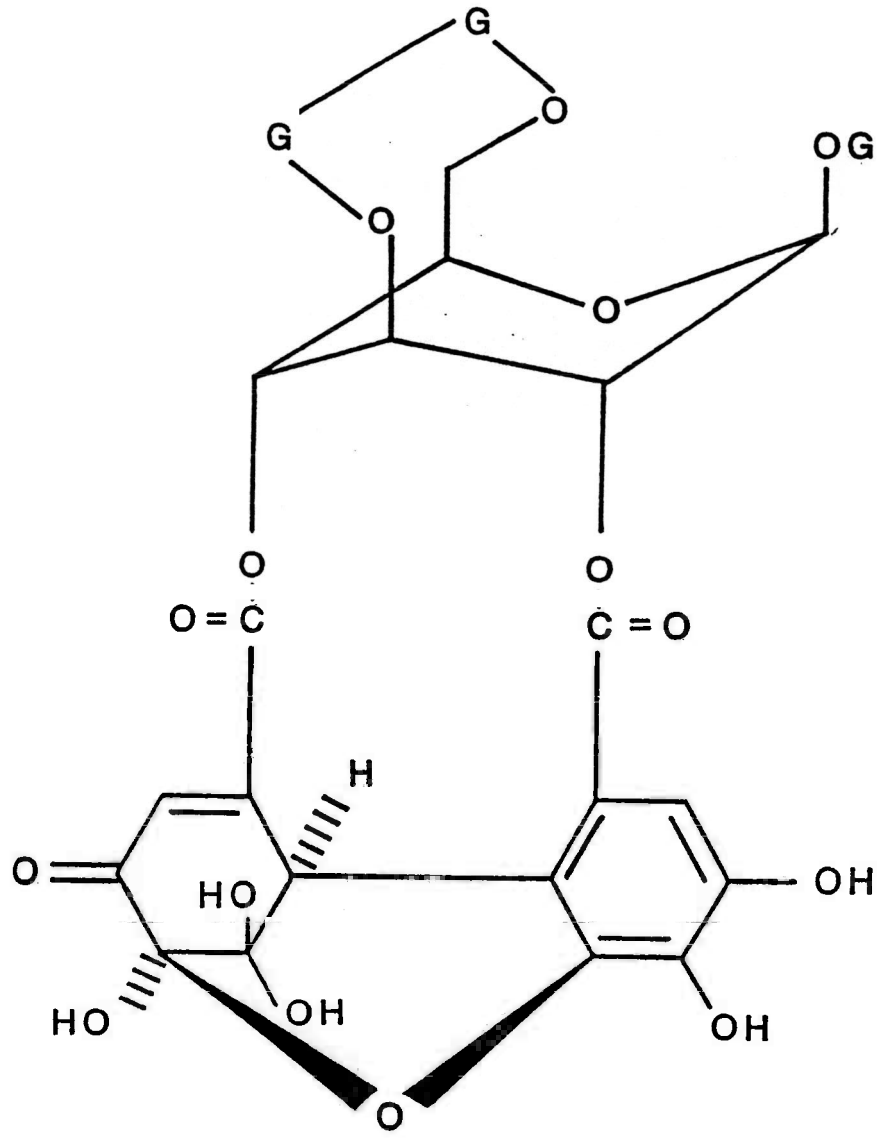
Compo d 27







Compound 33



Compound (28): Geranin

Compound 52