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Self-Cross-Linked Tannin-Aminated Tannin Surface Coatings for Particleboard

Bengang Zhang^{1,*}, Antonio Pizzi^{2,*}, Mathieu Petrissans¹, Anelie Petrissans¹ and Colin Baptiste¹

¹LERMAB, I.U.T. Hubert Curien, University of Lorraine, Épinal, 88000, France

²LERMAB-ENSTIB, University of Lorraine, Epinal, 88000, France

*Corresponding Authors: Bengang Zhang. Email: bengang.zhang@univ-lorraine.fr; Antonio Pizzi. Email: antonio.pizzi@univ-lorraine.fr

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ABSTRACT

Aminated tannins were prepared by reacting mimosa condensed tannin extract with ammonia yielding the substitution of many, if not all of the tannin hydroxyl groups with $-NH_2$ groups. A tannin-aminated tannin (ATT) particleboard coating was then prepared by reacting raw tannin extract with aminated tannin extract and thus cross-linking the two by substituting tannin's hydroxyl groups with the $-NH_2$ groups on the aminated tannin to form $-NH$ -bridges between the two. The resulting particleboard coating gave encouraging results when pressed at $180^\circ C$ for 3 min. Conversely, the system in which tannin was reacted/cross-linked with urea (ATU) by a similar amination reaction did not perform as well as the ATT system, and this even when a higher curing temperature and longer hot press time were used. In particular its water repellence was worse probably due to the presence of urea and such a system with lower reactivity. Nonetheless, substituting the tannin $-OH$ s with the urea $-NH_2$ groups appeared to also take place. ATT gave better results than ATU as regards water repellence and mechanical resistance as shown by the cross cut test. The ATT system was shown to be between 95% and 98% biosourced. The difference appeared to be due, by TMA analysis, to the much faster formation of the ATT hardened network leading to a better cross-linked polymer coating. The chemical species formed for both the ATT and ATU system were studied by MALDI ToF and CP MAS ^{13}C NMR.

KEYWORDS

Biocoatings; particleboard; aminated tannin; cross-linked tannin-aminated tannin; tannin-urea cross links; water repellence; cross cut test; MALDI ToF; ^{13}C NMR

1 Introduction

Surface coatings for particleboard and wood in general are a very important business area for the wood and wood panels industry. This field is dominated by the melamine based resins [1–5]. Melamine-formaldehyde or melamine-urea-formaldehyde resins [6–10] are the main exponents of this class of resins. Their advantages for coatings are in their good rate of pressing, transparent or white color and their excellent mechanical performance [11]. Melamine is obtained by the trimerization of urea, thus, it can even be considered biosourced like a number of other biosourced materials [12] thus a material to still consider in future. However, melamine, for all its great advantages, is also relatively expensive and its greatest drawback today is that it still uses formaldehyde in the formation of the coating resin. Interesting approaches to substitute formaldehyde such as melamine-glyoxal [13] and

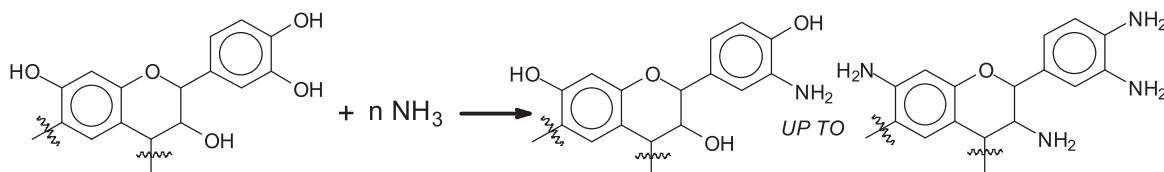


melamine-dialdehyde starch [14] to remedy this problem have been published but at this stage or they are still too new or they have not as yet retained the attention of the industry concerned.

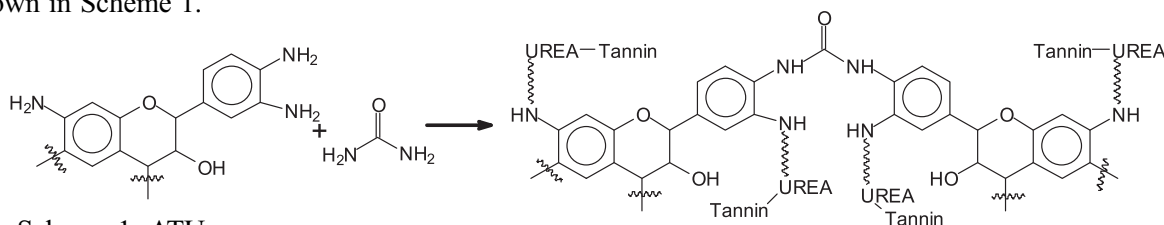
Tannin-based resins, as all biobased resins, have gained a marked increase in interest with researchers in recent years. Tannin-based resins, on top of the considerable body of research literature on such a subject, have already been used industrially for many years as wood panel adhesives [15,16]. Their use as coatings, although of interest, has been limited to the commercialization of metal primers for metal surfaces [17]. Notwithstanding the plethora of articles on wood adhesives using tannins as raw material, as regards coatings for wood and wood panels while a number of articles can be found in the literature, these are still relatively scarce [18–23]. These have taken a number of different approaches, varying from the early essays on direct application of mimosa or quebracho tannin hardened by paraformaldehyde applied directly or through impregnated paper on particleboard [18], to the more modern tannin-furanic systems without formaldehyde also applied directly or through impregnated paper on particleboard [19–21], to the even more recent use of both hydrolysable and condensed tannins used as non-isocyanate polyurethane (NIPU) surface coatings on solid wood [22,24]. However with what being said, what is really needed is a biosourced coating that is entirely based on a single biosourced material. This is the reason why this article adopts the approach of considering a single material of biological origin, through a simple transformation of part of this biosourced material. In this case, tannin was the chosen material.

A reasonably recent finding thus, has promise for a further approach in using these biomaterials as surface finishes for wood or wood panels, an approach even higher in percentage of biosourced materials used. Tannin react very readily with ammonia and amines [23,25–27], and such reaction products can be sought for coatings applications. This reaction that can be either by substitution of just one –OH of the tannin with an –NH₂ group [23] or up to being comprehensive of the total substitution of all the tannin –OH groups [26,27] could be used for surface coatings according to two different types of approach. Such approaches do not even use any aldehyde, not even the non-volatile non-toxic aldehydes generated from biosourced materials as proposed in adhesives [28,29] and used successfully at laboratory level for tannin-carbohydrate adhesives and other products [29–31].

The first reaction is the amination of the tannin, this reaction being already known [26,27].

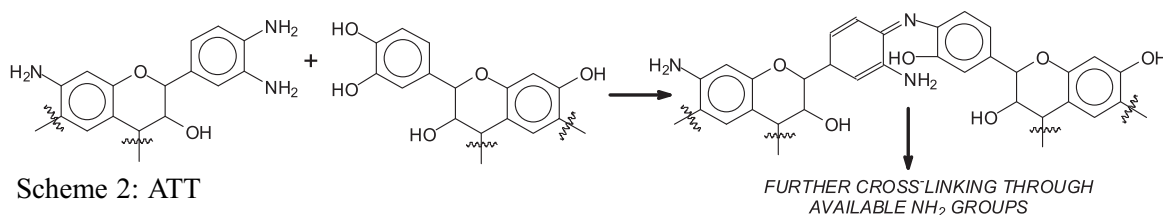


Once the aminated tannin is obtained, there are two options to make it undergo the polycondensation reaction. Of the two approaches for coating one is based on the reaction on urea cross-linking aminated tannin by tannin deamination, a reaction already used very recently for other biomaterials [32,33] as shown in Scheme 1.



Scheme 1: ATU

The second option is to continue the amine substitution of other flavonoids –OH groups by the amine groups already fixed on the aminated tannin (Scheme 2). The first step of such reaction has already been observed and studied for other applications [26,27].



It is these two approaches that have been tested in the research presented here to try to see if a surface coating for particleboard could be developed in this manner.

2 Materials and Methods

2.1 Materials

Commercial mimosa tannin extract from the bark of *Acacia mearnsii* (De Wild), supplied by Silva Chimica (St. Michele Mondovi, Italy) was used. It contained 80%–82% of actual phenolic flavonoid materials, 4%–6% of water, 1% of amino and imino acids, the remainder being monomeric and oligomeric carbohydrates, in general residual oligomes of cleaved hemicelluloses.

The ammonium hydroxide solution (25%) and urea (99.5%, ACS reagent) were both from Sigma-Aldrich (St. Louis, Missouri, USA). Distilled water was obtained in our laboratories.

2.2 Preparation of Aminated Tannins

10 g of mimosa tannin was dissolved in 10 mL of a 25 wt.% aqueous solution of ammonia. The solution was stirred during 1 h, and then it became very viscous and was left 1 day in a fume hood at room temperature. The resultant dry solid was washed with water (Dissolve solid tannins in water) and dried at 90°C. The dried solids are aminated tannins, which are ground for later use.

2.3 Reaction of Ammoniated Tannins with Raw Tannins (Named as ATT)

2 g aminated tannin + 2 g raw tannin + 4 g H₂O. TMA (Thermomechanical analysis) was tested after stirring for 30 min. MALDI ToF was tested after drying in an oven at 120°C for 2 h. The coating is hot pressed at 180°C for 3 min on a particleboard substrate.

2.4 Reaction of Ammoniated Tannins with Urea (Named as ATU)

2 g aminated tannin + 2 g urea + 4 g H₂O. TMA was tested after stirring for 30 min. MALDI ToF was tested after drying in an oven at 120°C for 2 h. The coating is hot pressed at 210°C for 3 min on a particleboard substrate.

2.5 Surface Properties

The samples were subjected to an adhesion test by the cross-cut test according to French (European) standard NF EN ISO 2409 [27]. For this, the hardened surface finishes were cut through to the particleboard substrate with a razor blade in order to produce edges from which the coating may then be lifted. The cutting pattern consisted of a 10 × 10 grid of vertical and horizontal cuts spaced at 1 mm × 1 mm. A strong adhesive tape was then applied over the cut area and tightly pressed. The tape was then rapidly pulled off. This operation was repeated three times. Finally the surface finishes were examined to determine the number of blocks removed, this constituting an evaluation of the coating adhesion.

The contact angles of a drop of water on the two types of surface finishes cured at different temperatures were tested and compared to the same for an untreated surface of uncoated samples from the same particleboard. The contact angle of the treated and untreated board surfaces was obtained from the water drop being placed on the surface with a syringe and measured with an EasyDrop contact angle apparatus, using a drop shape analysis software (Krüs GmbH, Hamburg, Germany).

2.6 Thermomechanical Analysis (TMA)

30 mg of the coatings prepared were applied to beech wood strips, with dimensions of $21 \text{ mm}^3 \times 5 \text{ mm}^3 \times 1.1 \text{ mm}^3$, and stacked together to form two-ply samples. The relationship of modulus of elasticity (MOE) against temperature was recorded by TMA (Mettler Toledo 40, Zurich, Switzerland) following the method of three-points bending on a span of 18 mm exercising a force cycle of 0.1/0.5 N on the specimens with each force cycle of 12 s (6 s/6 s) at a heating rate $10^\circ\text{C}/\text{min}$ in the range 30°C – 250°C [34], and the relevant curves of modulus of elasticity (MOE) against temperature were registered.

2.7 Matrix Assisted Laser Desorption Ionization Time of Flight (MALDI ToF) Mass Spectrometry

The samples (4 mg/mL) were dissolved in water/acetone (50/50 by volume) and the solutions were added to the matrix solution of 10 mg/mL in acetone. 2,5-dihydroxy benzoic acid was used as the matrix to ease placing the sample on the sample-holder plate. Red phosphorus was used for instrument calibration (LaserBio Labs, Valbonne, France). A concentrated solution of 10 mg/ml of sodium chloride (NaCl) in distilled water was mixed to the matrix to enhance ion formation. The sample was added into the matrix solutions and was divided into three parts of the matrix solution. Three parts of the sample solution and a part of NaCl solution; 0.5 to 1 μL were put on the MALDI target. The MALDI target was placed into the spectrometer after solvent evaporation. The peaks in the spectrum can present themselves at the actual molecular weight of the chemical species or increased by 23 Da, this being the molecular weight of the Na^+ linked to the molecule from the NaCl added to the matrix to facilitate the flight of heavier oligomers. Sometime both forms of the same species, with and without Na^+ can be present in the same spectrum. The MALDI-TOF spectra were recorded on an AXIMA Performance instrument (Shimadzu Scientific Instruments; Manchester, UK). The irradiation source was a pulsed nitrogen laser with 3-ns intervals at a wavelength of 337 nm. The measurements were carried out using the following conditions: polarity: positive; flight path: linear; mass: high (20-kV accelerating voltage) and 100 to 150 pulses per spectrum. The delayed extraction technique was used to apply delay times of 200 to 800 ns. The ion gate was set at 0, 500 and 1000 Da, respectively. The spectra are exact at +1 Da.

2.8 Cross Polarization Magic Angle Spinning Carbon 13 Nuclear Magnetizing Resonance (CP-MAS ^{13}C NMR) Spectrometry

Solid state CP-MAS (cross-polarisation/magic angle spinning) ^{13}C NMR spectra of the oven-dried solids of the reaction of tannin with ammonia were recorded on a Bruker MSL 300 spectrometer at a frequency of 75.47 MHz. Chemical shifts were calculated relative to tetramethyl silane (TMS). The rotor was spun at 4 kHz on a double-bearing 7 mm Bruker probe. The spectra were acquired with 5 s recycle delays, a 90° pulse of 5 μs and a contact time of 1 ms. The number of transients was 3000.

3 Results and Discussion

An example of the application of ATT and ATU as a directly applied coating on particleboard is given in Fig. 1. This was subjected first of all to the sessile drop test and its evolution as a function of time. The results of this are shown in Fig. 2 that clearly indicates that the ATT system gives a better water repellence than the ATU system. This is most likely due to the presence of urea that may tend to absorb water more easily than the ATT structures. A further indication of the better performance of the ATT coatings than the ATU one is clearly given by the TMA results (Fig. 3), where the rate of curing of the ATT resin is definitely faster than that of the ATU system. This is clear as the ATT coatings does increase in strength much more rapidly and at much lower temperature than the ATU one, and it reaches a definitely higher value of the MOE, and this is faster than for the ATU. All this indicates that the ATT reactions of cross-linking are faster, require less energy, and yield a better cross-linked coating, hence of better performance. This conclusion is also supported by the results of the cross-cutting test (Fig. 4), where the ATT coatings detaches much less traces of material from the surface on which it has been applied, an indication of better curing of the

coatings itself and of a tighter surface structure of the ATT coating. The color variation of the coated board surfaces in relation to the original color of the particleboard substrate are shown in Fig. 5.



Figure 1: Particleboard panels coated with ATT (left), and with ATU (right)

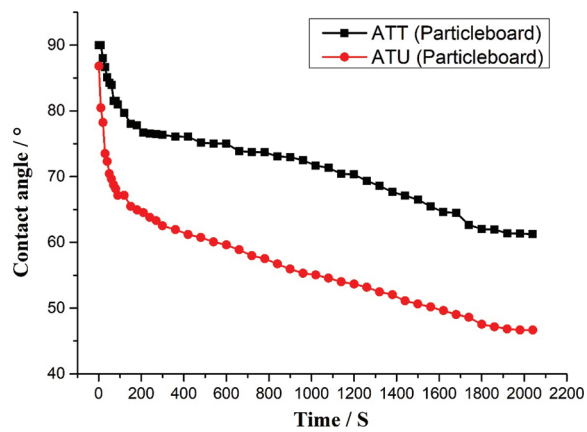


Figure 2: Sessile drop contact angle as a function of time for ATT and ATU coatings on particleboard

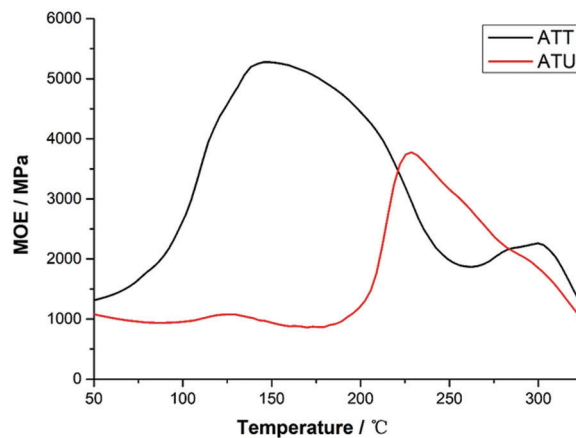


Figure 3: TMA of ATT and ATU coatings showing the rate of curing of each of the two finishes

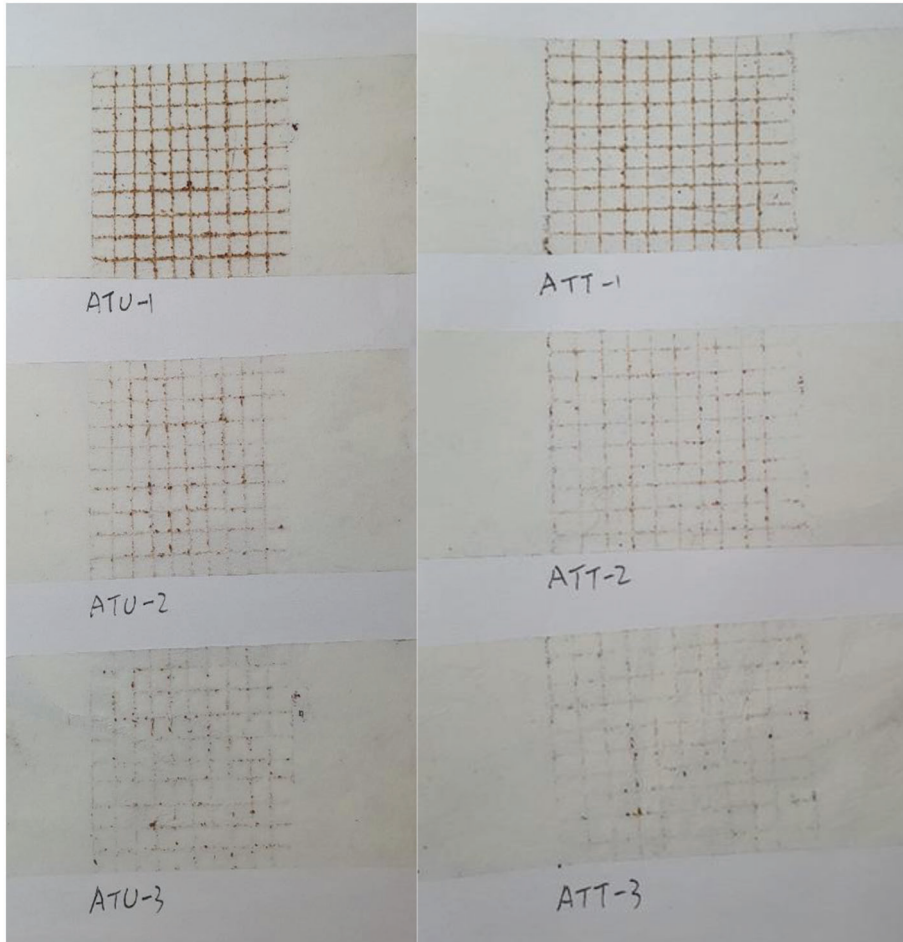


Figure 4: Cross-cut test for ATU and ATT coatings on particleboard

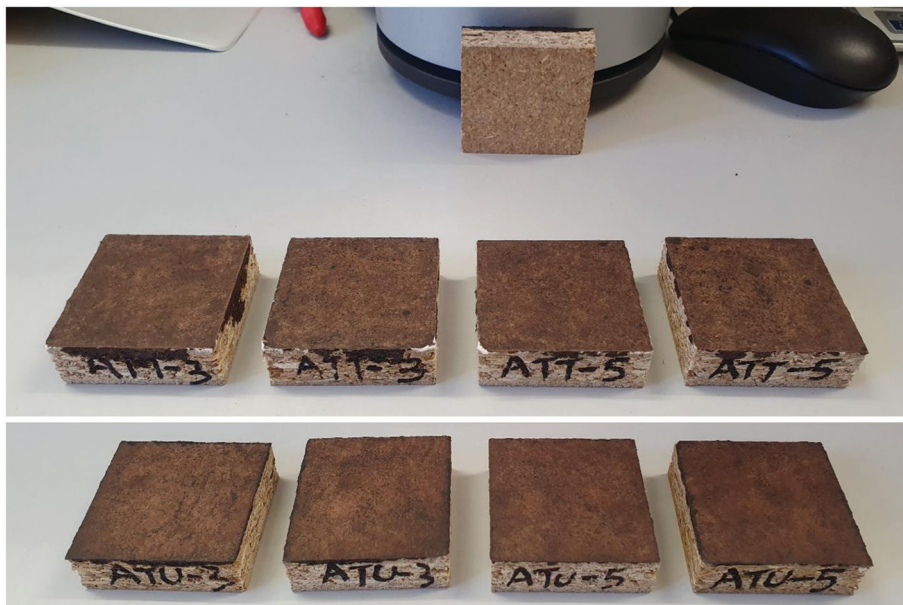
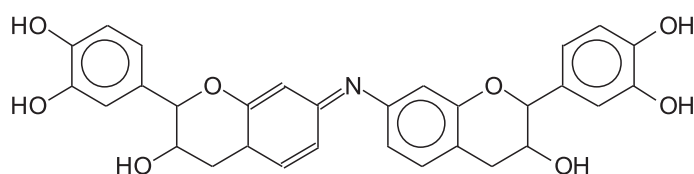


Figure 5: Surface color comparison before and after coating

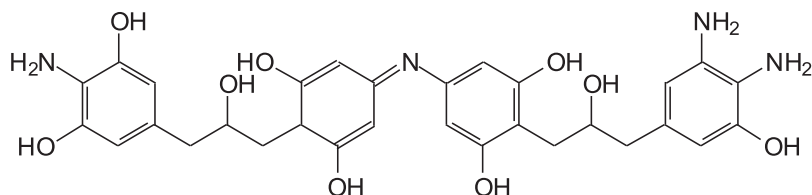
High temperatures can definitely cause degradation of the material. However, in this work, TMA is mainly used to understand the curing temperature and curing rate of the material, while TGA is mainly used to explain the pyrolysis of the material at high temperature (the maximum temperature of the material can reach 650°C–700°C). This study did not address thermal degradation content, so TG was not tested.

In the Appendix are shown in [Table A1](#) all the species formed in the ATT system. As the applied results for the ATU system were worse than for the ATT system, MALDI ToF spectra for the ATU system and the oligomer species assignments are only presented in the Appendix ([Fig. A1](#) and [Table A2](#)). In the Appendix are also shown in [Table A1](#) all the species formed in the ATT system.

Given the results reported it is worth to consider what does occur at the molecular level in the reaction of a condensed tannin with either ammonia or urea. As the better result is with the ATT coating this will be discussed first ([Fig. 6](#)). Mimosa tannin is mainly composed of robinetidin, fisetinidin and catechin. There are, according to its origin also cases of flavonoid gallates, but these are unusual in this tannin and when they are present they are only in very small proportions/traces. In the MALDI ToF, dimers, trimers and tetramers of just flavonoid units are present (See [Table A1](#)). Dimers of the type already formed in the reaction of a flavonoid model compound with NH₃ are clearly present as the 551 peak (with 23 Da of Na⁺), and also the open flavonoid form as the species at 617 Da that can be exclusively assigned to an open form of gallocatechin dimer partially aminated.



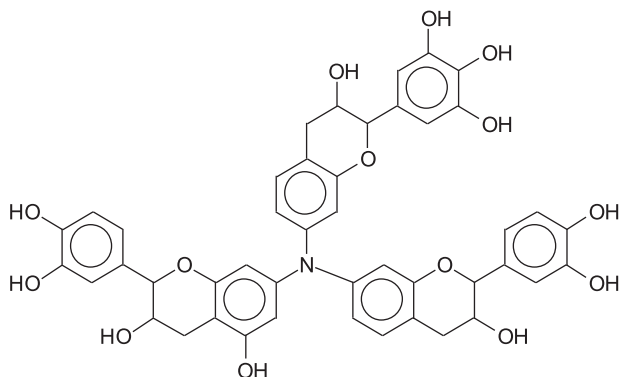
551Da



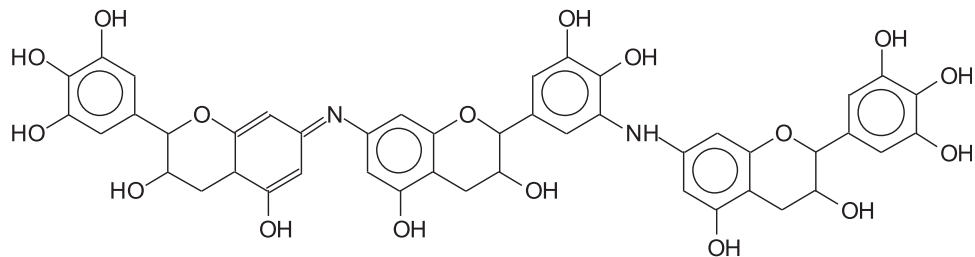
617 Da

Other open structure of the same type could be present such as those at 563 and 601 Da, but these can be also assigned to other types of flavonoid dimers.

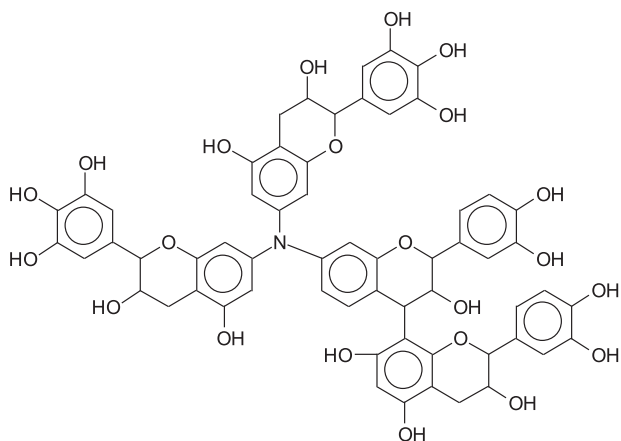
Or structures in which the central nitrogen atom functions as a knot of tridimensional cross-linking such as in the structure at 840 Da (with Na⁺).



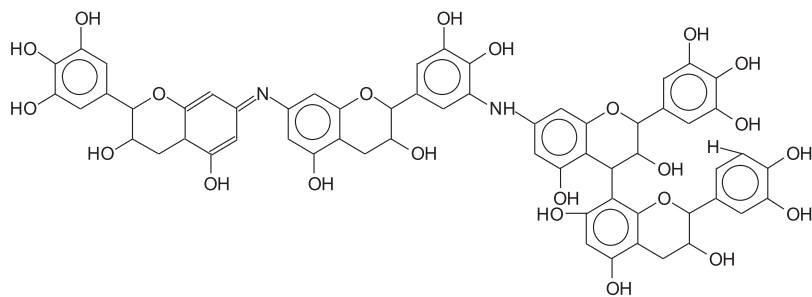
And linear structures such as the one at 905 Da (with Na⁺).



Equally structures where flavonoid dimers are linked to three dimensional or linear structures are found, such as those assigned for example to the peaks at 1177 Da.

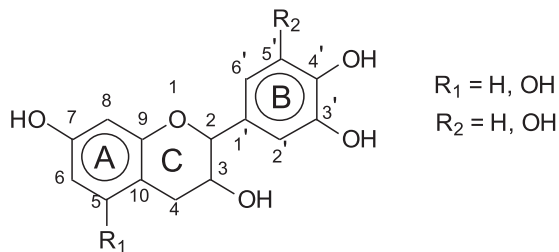


And the linear one at 1192 Da.

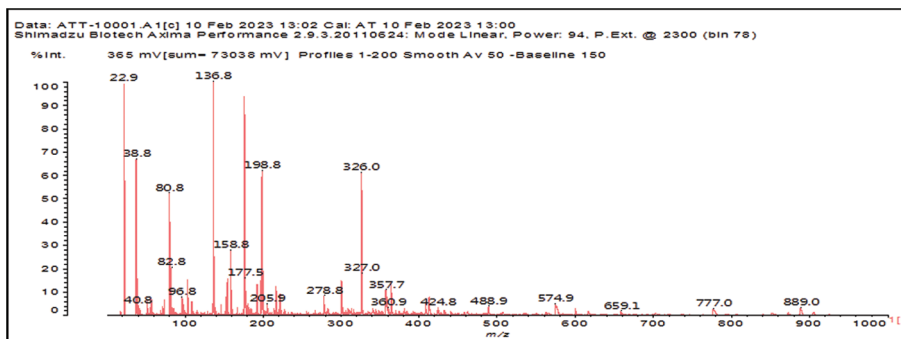


The complete set of molecular structures identified are shown in [Table A1](#).

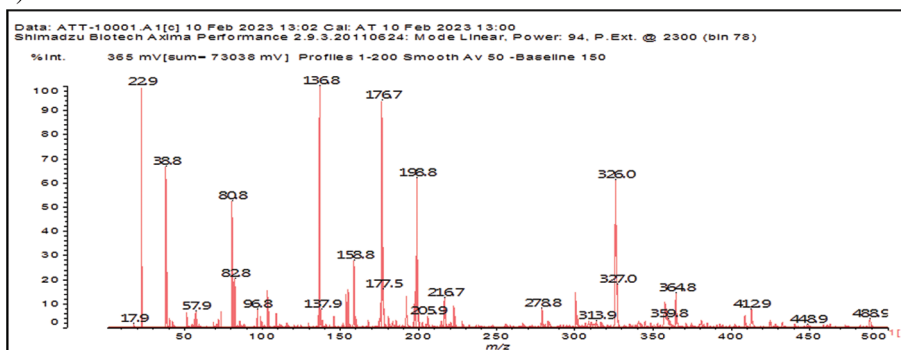
The aminated tannin product obtained showed by CP-MAS ¹³C NMR ([Fig. 6](#)) shows some characteristics related to what already found previously with models [[26,27](#)]. Thus, on a flavonoid unit.



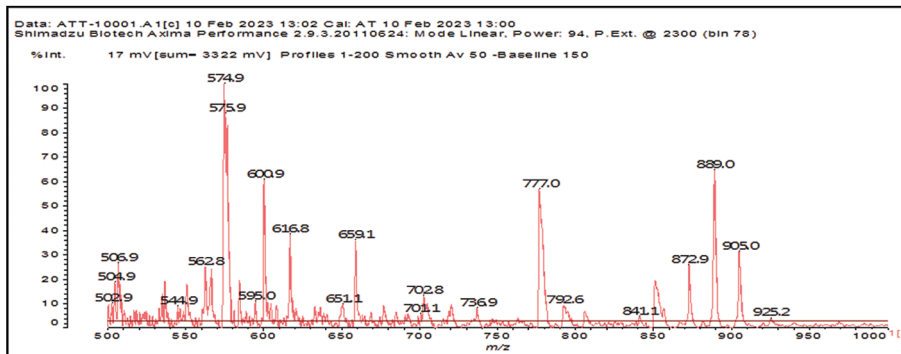
(A)



(B)



(C)



(D)

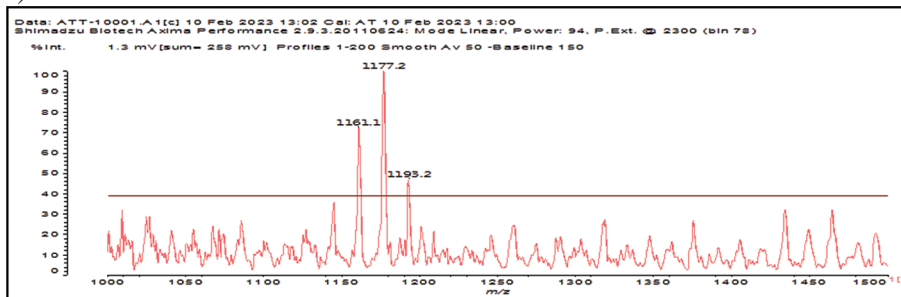


Figure 6: MALDI ToF mass spectra of the ATT coating

Notes: In [Figs. 6A–6D](#) respectively represent the MALDI spectra in the ranges of 0–1000, 0–500, 500–1000, and 1000–1500 Da, thus without the ion gate being applied for A and B, and with the ion gate set respectively at 500 Da (C), and 1000 Da (D).

The peaks of C2', C5' and C6' at 117 ppm are relatively lower than what observed in the spectrum of mimosa tannin alone (cf. Figs. 6–8). Equally relatively lower are the C3' and C4' peaks at 144–145 ppm, even if the small proportion of C=N-C bridges linking flavonoid units A-rings is superimposed in this peak. This shows that these carbons after reaction exist in a changed environment than that of mimosa tannin alone. While the peak at 144–145 ppm presents the shift characteristic of the C3' and C4' of a normal catechin flavonoid, this is much lower in the aminated tannin (Fig. 6) than on the unreacted tannin spectrum (Fig. 8) indicating that some of the B-ring –OH groups have also been substituted by –NH₂ groups on the B-rings of flavonoid units. Consequently, it appears that several, although not all phenolic –OHs have undergone substitution mostly B-ring ones. The MALDI results are thus confirmed by these NMR shifts. It is then the extensive substitution by nitrogen causing cross-linking explaining tannin cross-linking. The unreacted tannin does not present a 166 ppm shift for the –C=N- bridge, shift that instead exists, although small, in the aminated tannin NMR (Fig. 7). As this peak is not present in the unreacted tannin spectrum (Fig. 8) this means that as for the catechin model the –C=N- bridge does also occur in the tannin, but proportionally less [26,27]. However, the presence of this small peak is assigned to the double bond of the –C=N- bond which forms on the C9 of the A-ring in some of the open forms of the flavonoid units. The peak at 130–131 ppm is the one assigned to the C1' of flavonoid units, while the 109 and 106 ppm are respectively assigned to their interflavonoid C4–C6 and C4–C8 bond, and to the free C6 and C8 of the flavonoid unit A-rings.

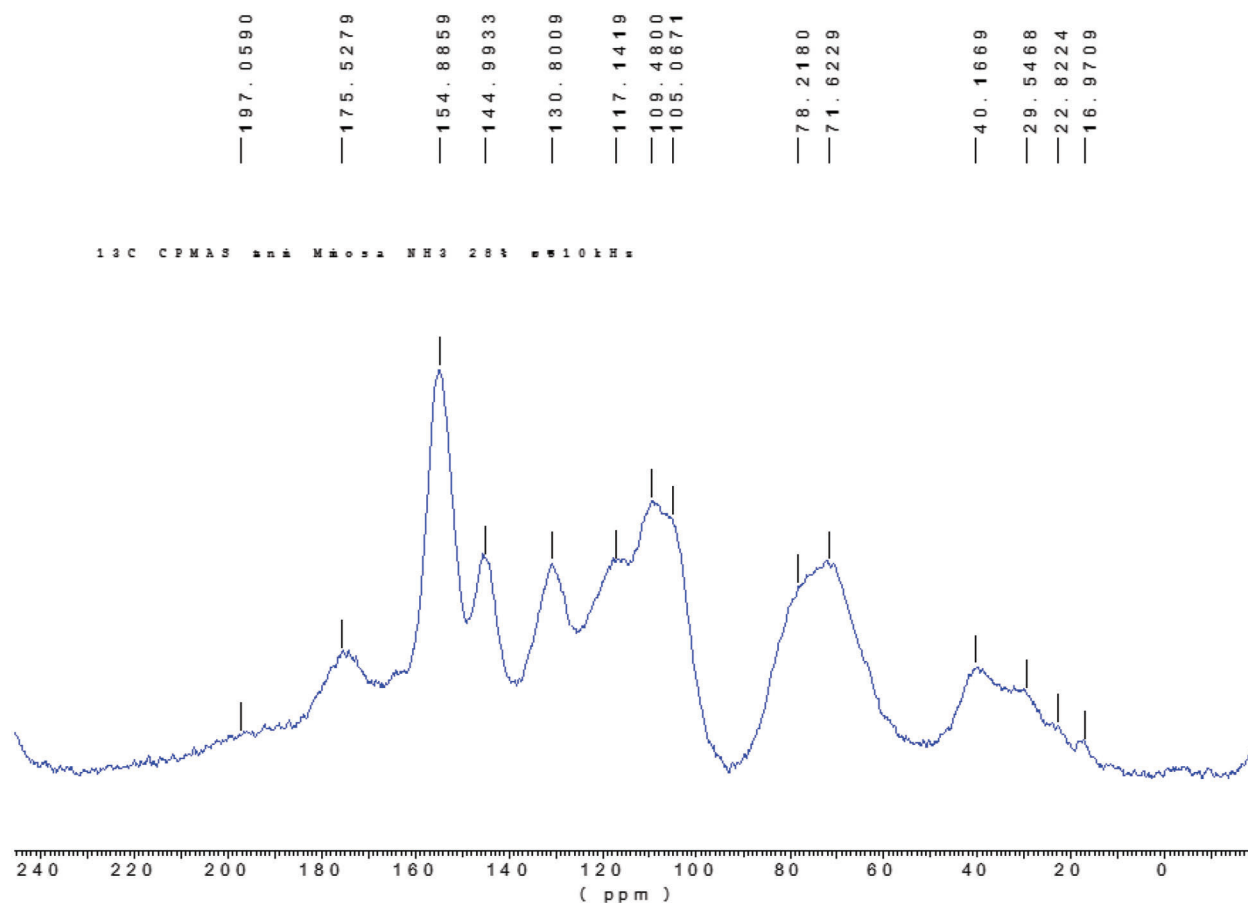


Figure 7: CP MAS ¹³C NMR spectrum of the ATT coating formed by condensation of tannin-aminated tannin

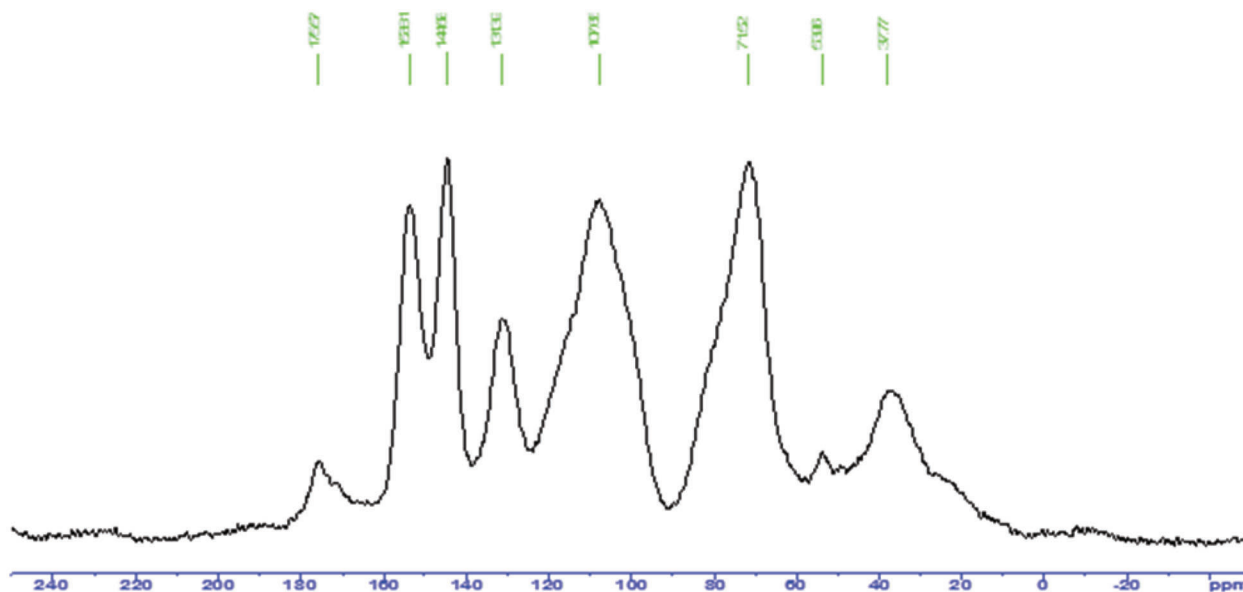


Figure 8: CP MAS ^{13}C NMR spectrum of the unreacted mimosa tannin extract

Clear 40, 30, 22 and 18 ppm shifts also occur. The 40 and 30 ppm peaks are assigned to the free, unreacted C4 site of the flavonoid, the two belonging respectively to close and open flavonoid units. While it is not easy to explain the 18 and 22 ppm ($-\text{CH}_3$ and $-\text{CH}_2-$) peaks, the 40 ppm peak could also belong to a $-\text{C}-\text{N}-$ (Fig. 7), present in the tannin spectrum, thus confirming multiamination and the previous structures. That multiamination has occurred is also confirmed by the shoulder at 65 ppm (Fig. 7) indication of the same type of $-\text{C}-\text{N}-$ group observed for model compound reactions with ammonia [26,27]. The existence of two different chemical environments for $-\text{C}-\text{N}-$ groups is inferred by the two $-\text{C}-\text{N}-$ shifts. This confirms multiamination. The two peaks at 71 and 78 ppm are assigned respectively to the flavonoid units C3 to which is linked an alcoholic $-\text{OH}$ group, and to the to the carbohydrate oligomers from cleaved hemicelluloses that are always present in commercial tannin extracts. The peak at 175 ppm is assigned to the glucuronic acids also generated by the cleavage and hydrolysis of hemicellulose. The presence of traces of quinones is inferred by the rather small 196–197 ppm shift and are the consequence of some residual phenolic $-\text{OH}$ s being oxidized during reaction. One must notice however, that different spectra shifts are obtained by treating tannins with an alkali different than ammonia, for example sodium hydroxide, with the aminated tannin shifts not being present, as ascertain from previous work [35–38].

4 Conclusions

The results of a tannin-aminated tannin (ATT) particleboard coating obtained by the reaction of the two materials gave encouraging results. The aminated tannin was obtained by reaction of the raw tannin with ammonia. The system instead in which tannin was reacted/cross-linked with urea (ATU) did not perform to the same level of the ATT system, although tannin $-\text{OH}$ s substitution with the urea $-\text{NH}_2$ groups appeared to also take place. ATT gave better results than ATU as regards water repellence and mechanical resistance as shown by the cross cut test. The difference appeared to be due, by TMA analysis, to the much faster formation of the ATT hardened network leading to a better cross-linked polymer coating.

Examination by MALDI ToF of both systems and of ATT by CP MAS ^{13}C NMR showed a variety of cross-linked species being formed in both systems.

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Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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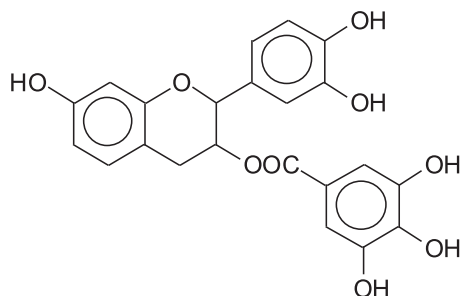
Appendix

Table A1: Assignment of MALDI ToF analysis peaks to relevant structures of ATT surface coating

278 Da = Fisetinidin no Na⁺, protonated fisetinidin

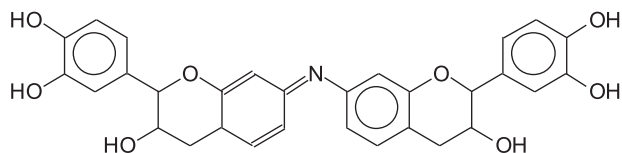
326 Da = with Na⁺, triaminated gallo catechin

449 Da = fisetinidin-gallate, non aminated, with Na⁺, calc = 449 Da

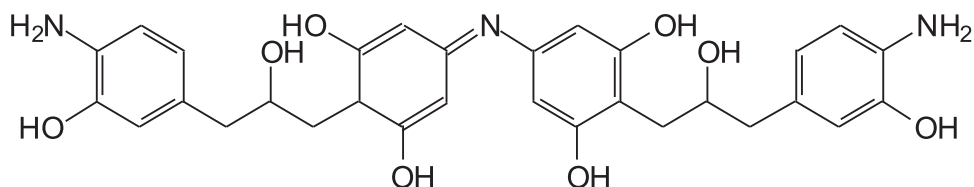


545 Da = fisetinidin dimer monoaminated, no Na⁺,

551 Da = with Na⁺, two fisetinidins linked by a -N = bridge+ one monoaminated, some -NH₂ could also be present

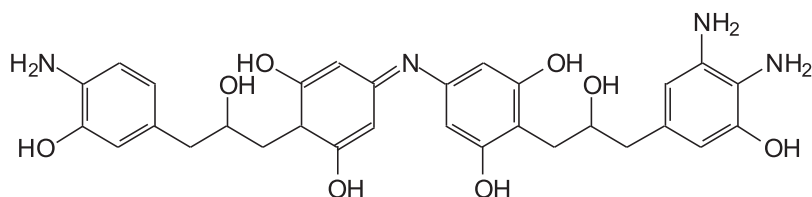


563 Da = robinetinidin-fisetinidin dimer, no Na⁺, some -NH₂ could also be present AND/OR, deprotonated, no Na⁺



575-576 Da = no Na⁺, deprotonated robinetinidin-robinetinidin dimer (or catrchin-robinetinidin dimer (most likely) some -NH₂ could also be present

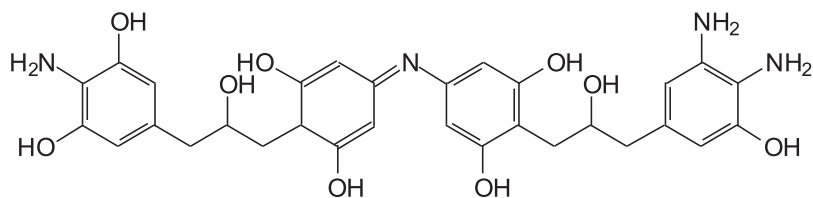
601 Da = with Na⁺, protonated, catechin-catechin dimer or robinetinidin-catechin dimer, some -NH₂ could also be present AND/OR, with Na⁺, deprotonated



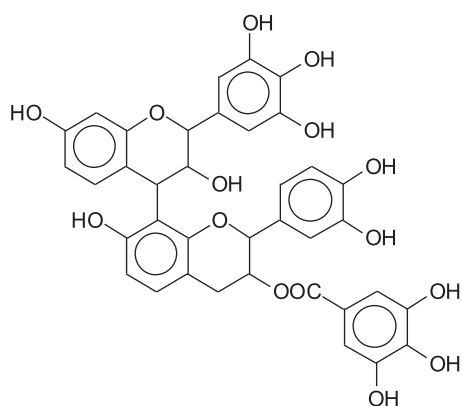
617 Da = with Na⁺, open partially aminated gallo catechin-gallo catechin dimer

(Continued)

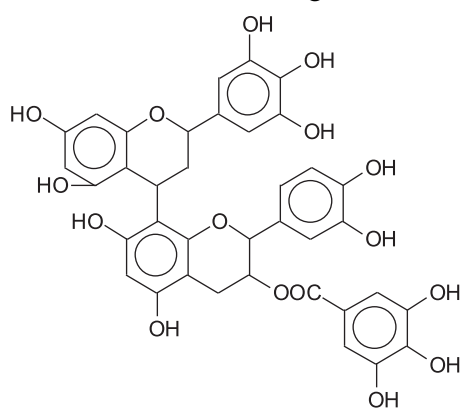
Table A1 (continued)



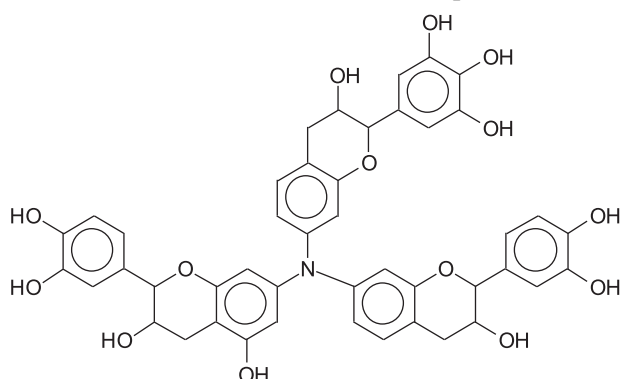
737 Da = with Na^+ , robinetinidin-fisetinidin gallate



777 Da = with $2 \times \text{Na}^+$, gallocatechin-catechin gallate dimer



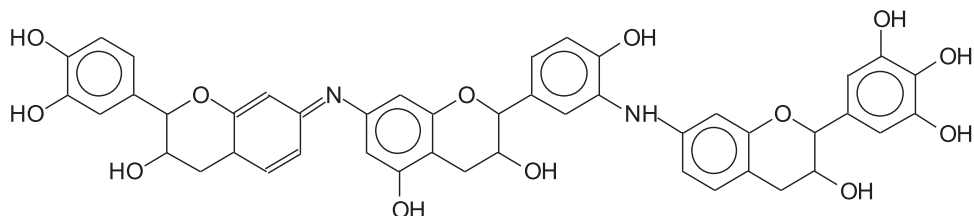
840 Da = with Na^+ , an $-\text{N}=\text{C}$ bridge linking three flavonoids, namely a catechin, a robinetinidin and a fisetinidin, some $-\text{NH}_2$ could also be present



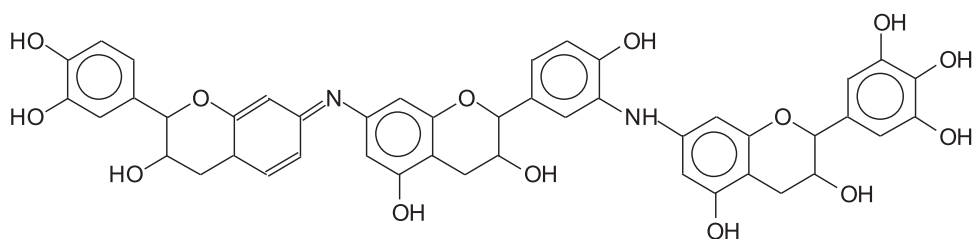
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Table A1 (continued)

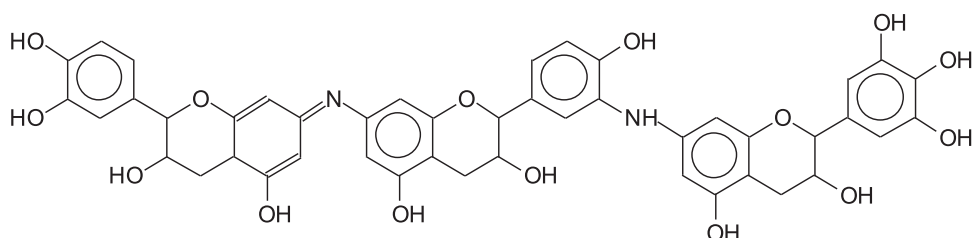
AND/OR some $-NH_2$ could also be present



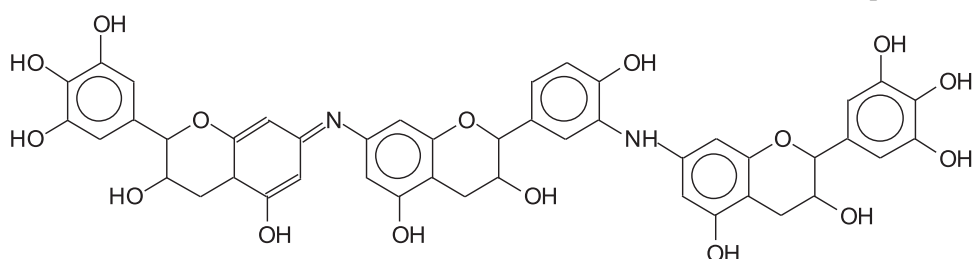
856 Da = with Na^+ , some $-NH_2$ could also be present



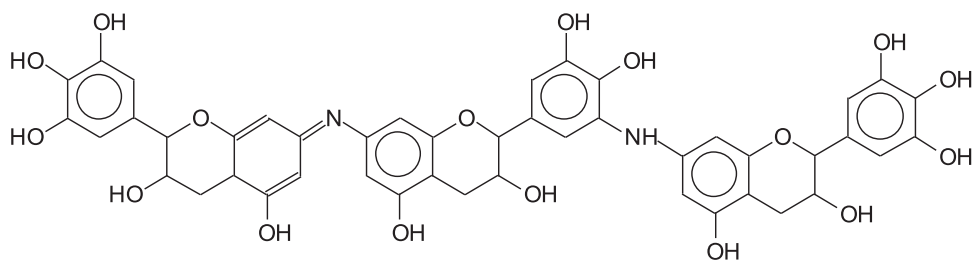
872 Da = with Na^+ , or some $-NH_2$ could also be present AND OR fisetinidingallate-fisetinidingallate dimer. But Gallated flavonoids do not exist in mimosa tannin, thus the second option is the correct one



889 Da = with Na^+ , some $-NH_2$ could also be present AND OR catechingallate-fisetinidingallate dimer. But Gallated flavonoids do not exist in mimosa tannin, thus the second option is the correct one.

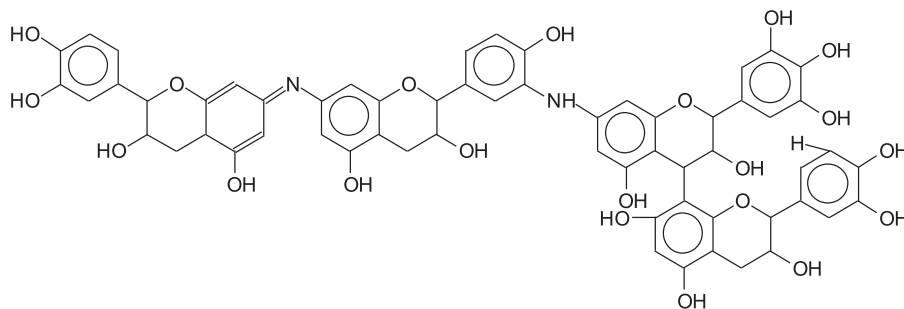


905 Da = with Na^+ , catechingallate-catechingallate dimer, AND OR

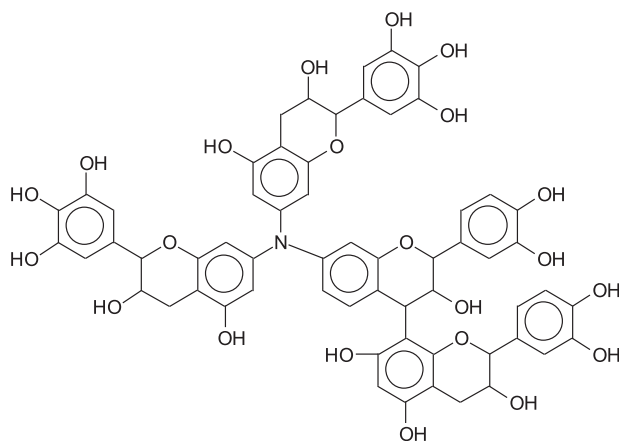
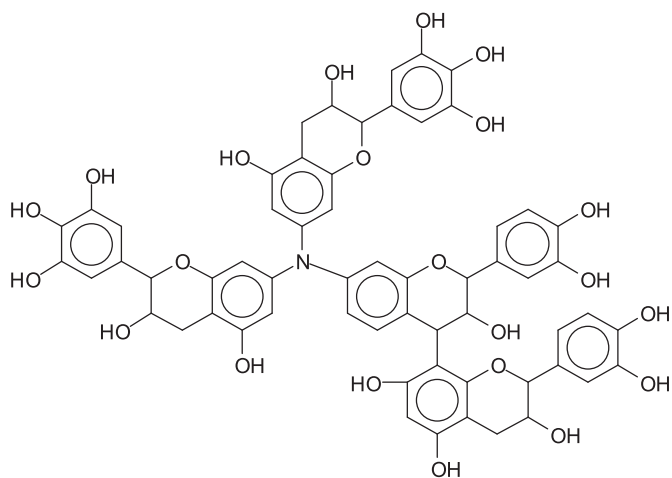


But as Gallated flavonoids do not exist in mimosa tannin, thus the second option is the correct one.

(Continued)

Table A1 (continued)1161 Da = with Na⁺, one biflavonoid attached

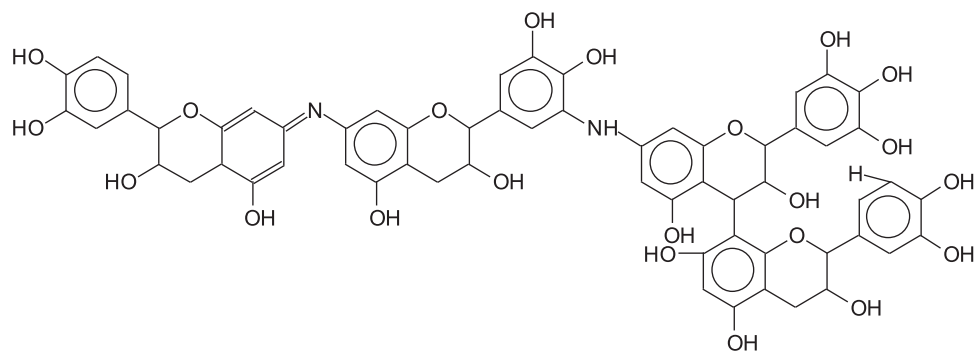
AND/OR

1177 Da = with Na⁺,

OR/AND

(Continued)

Table A1 (continued)



1192 Da = with Na⁺, This is obliged to be linear and not tridimensional on N as there is no more sites on the tridimensional to add another -OH group

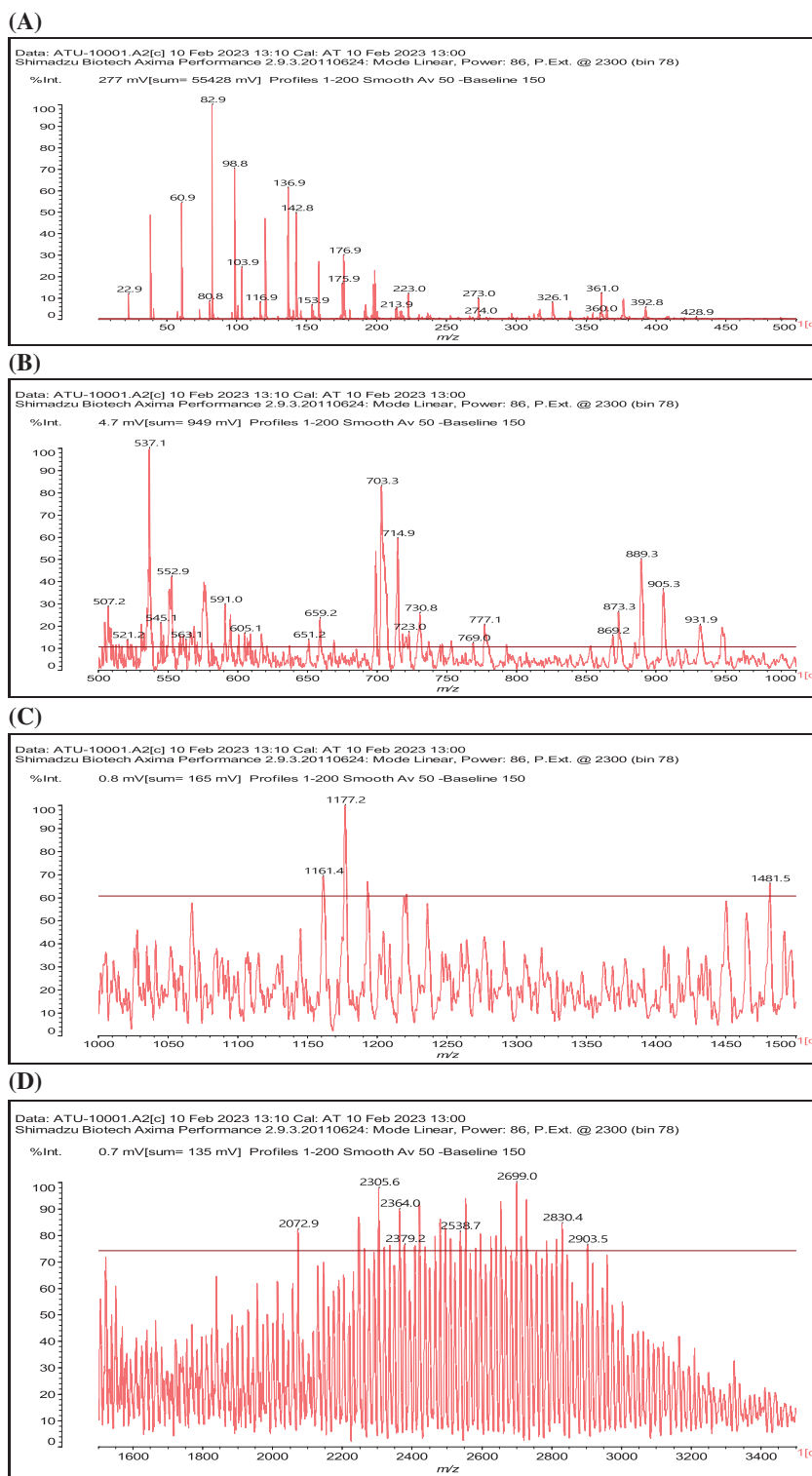


Figure A1: Assignment of MALDI ToF analysis peaks to relevant structures of ATU surface coating

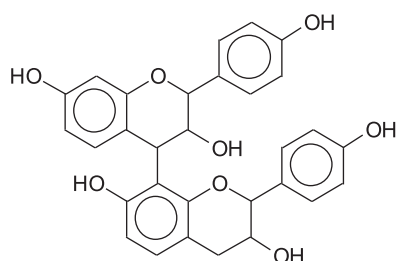
Table A2: Assignment of MALDI ToF analysis peaks to relevant structures of ATU surface coating

273 Da = Fisetinidin no Na⁺, aminated fisetinidin

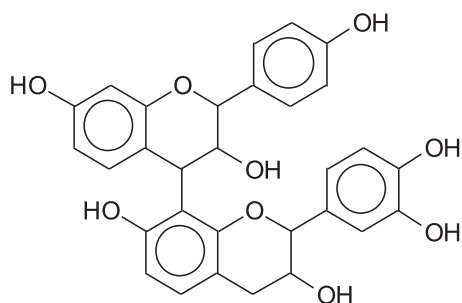
274 Da = Fisetinidin no Na⁺, normal, not aminated

326 Da = no Na⁺, triaminated delphinidin

537 Da = with Na⁺

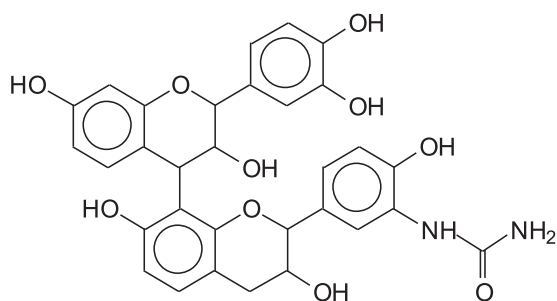


553 Da = with Na⁺

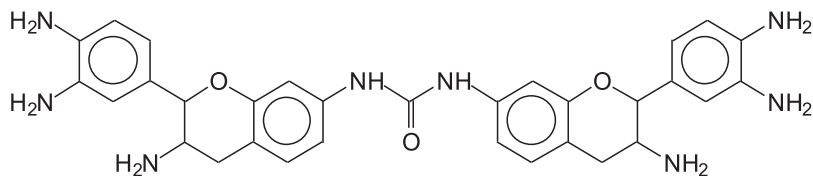


545 Da = no Na⁺, fisetinidin dimer monoaminated

590 Da = Na⁺, fisetinidin dimer monoaminated with a 44 Da CH₂N-C=O of urea linked to it

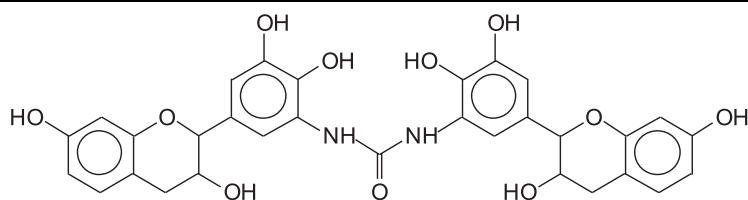
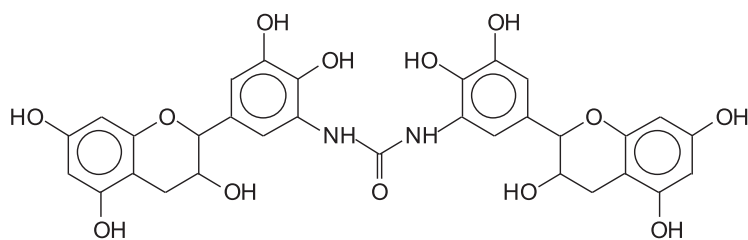
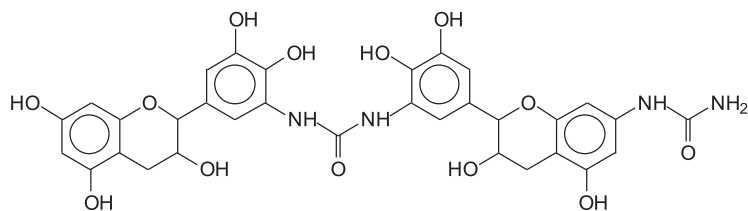
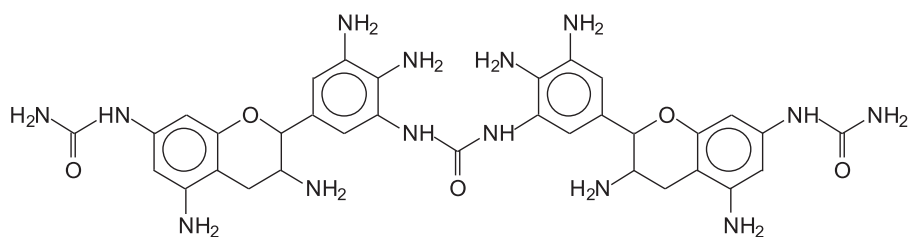
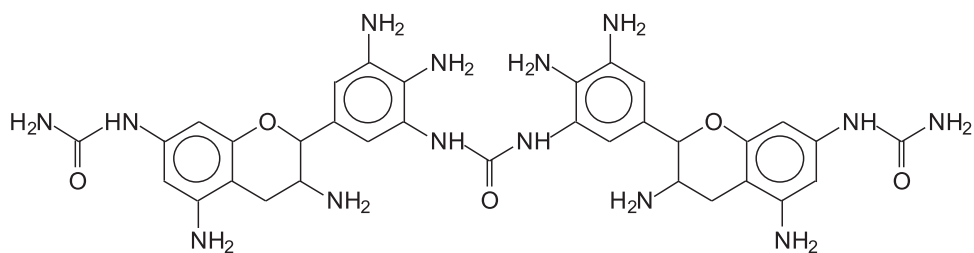


AND/OR, with Na⁺

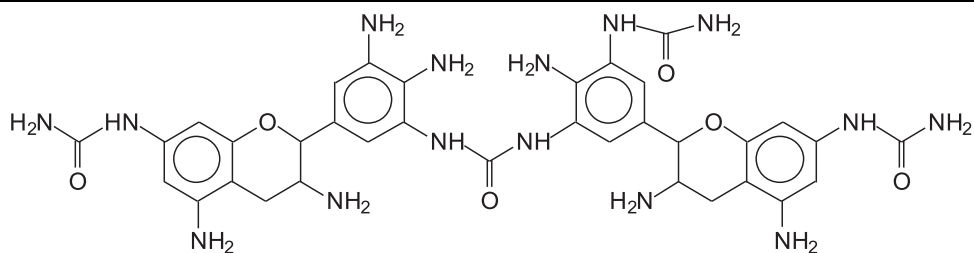
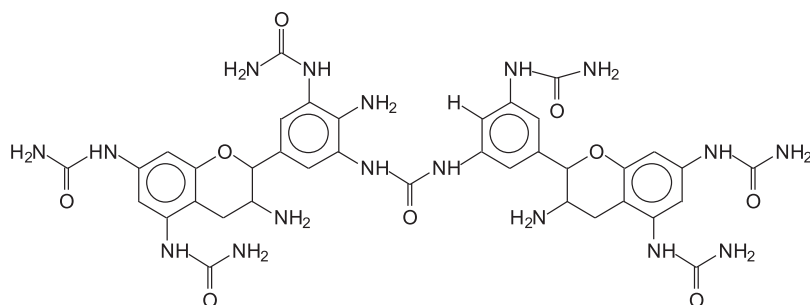
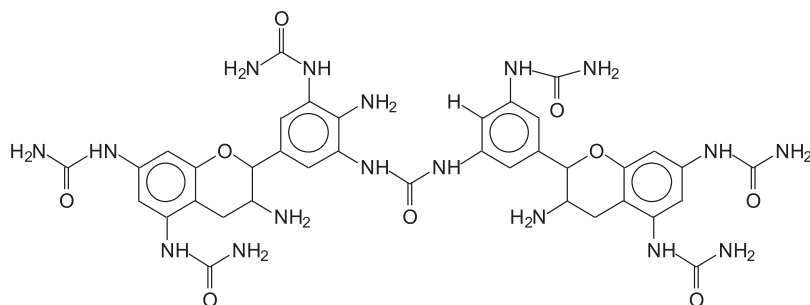
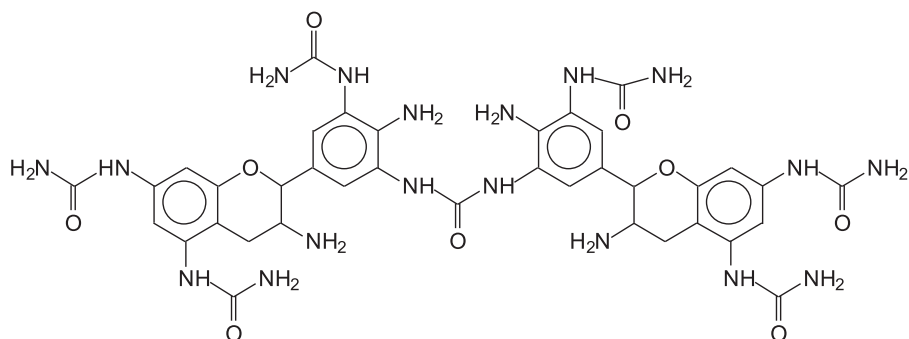


605 Da = no Na⁺,

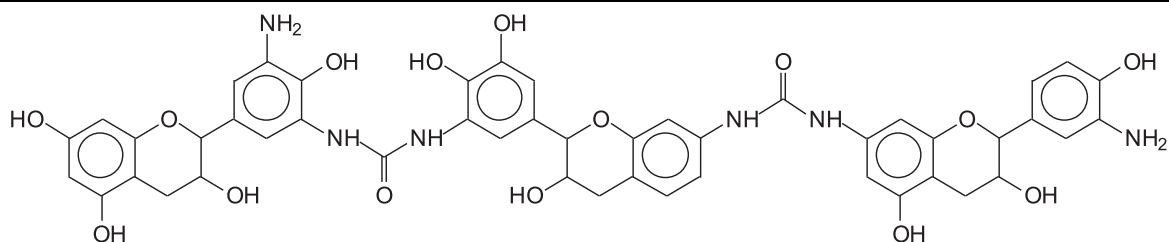
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Table A2 (continued)659 Da = with Na⁺703 Da = with Na⁺, deprotonated715 Da = no Na⁺731 Da = with Na⁺, deprotonated777 Da = with Na⁺, deprotonated

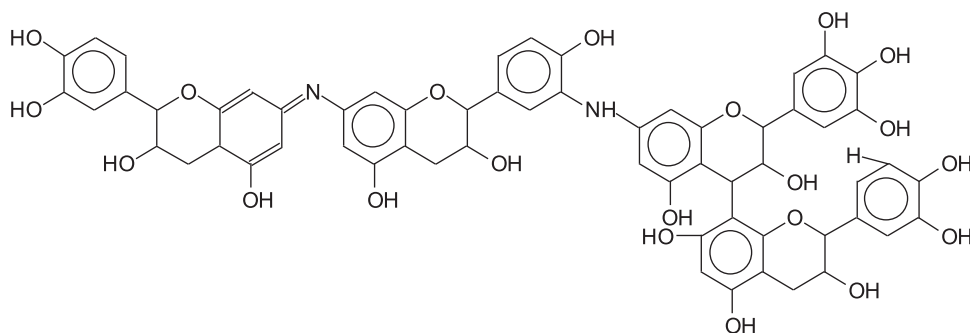
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Table A2 (continued)869 Da = no Na⁺889 Da = with Na⁺, deprotonated905 Da = with Na⁺, deprotonated932 Da = no Na⁺, biaminated, 3 flavonoids linked by 2 ureas

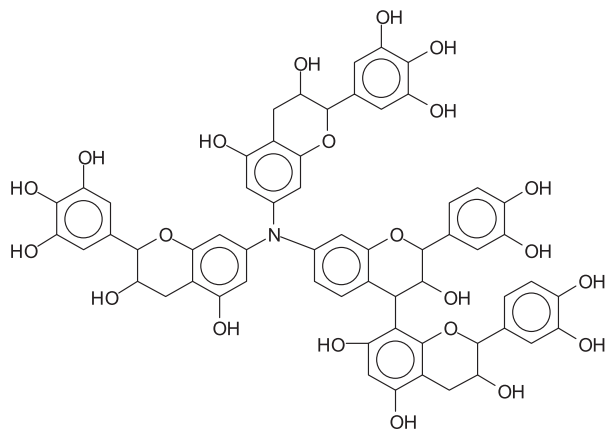
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Table A2 (continued)

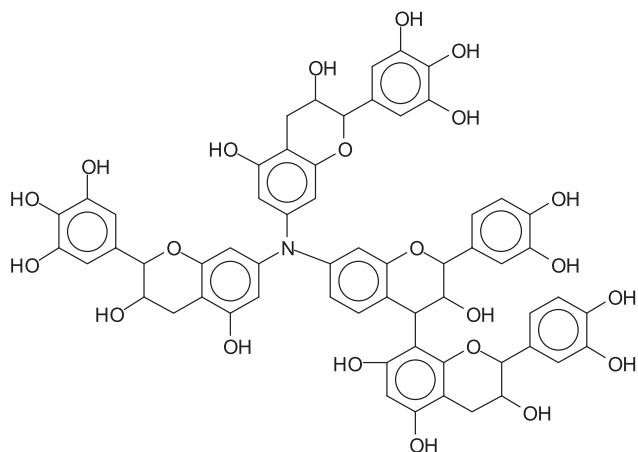
1161 Da = with Na⁺, one biflavonoid attached



AND/OR



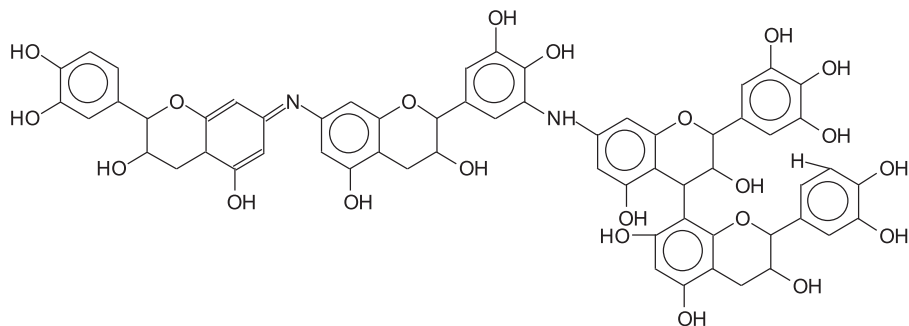
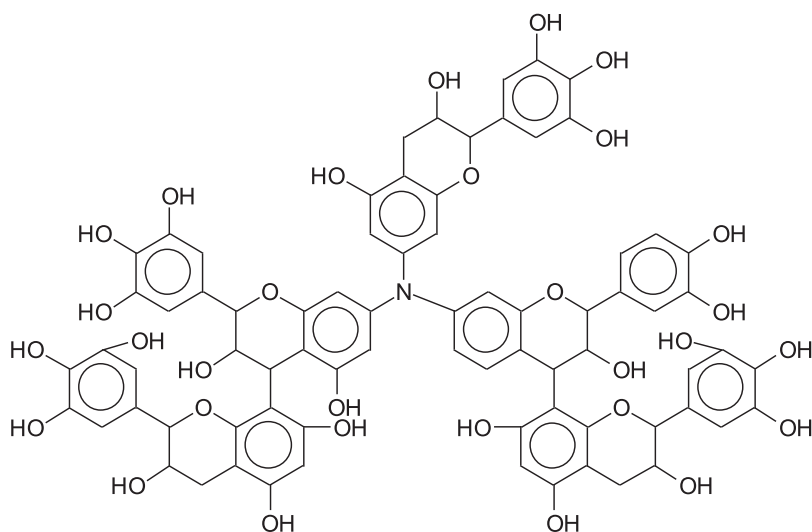
1177 Da =with Na⁺



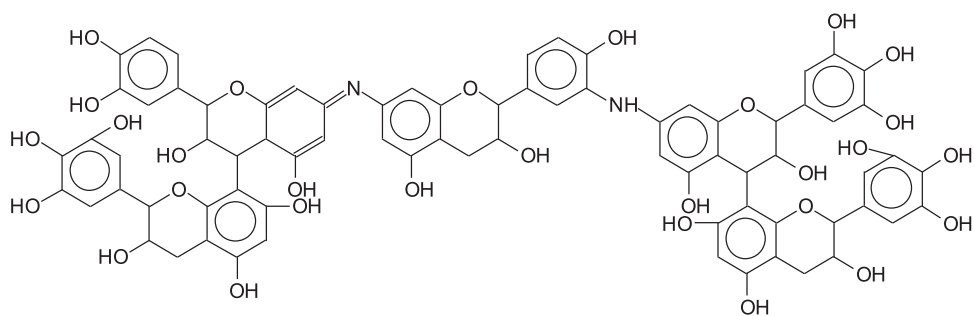
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Table A2 (continued)

OR/AND

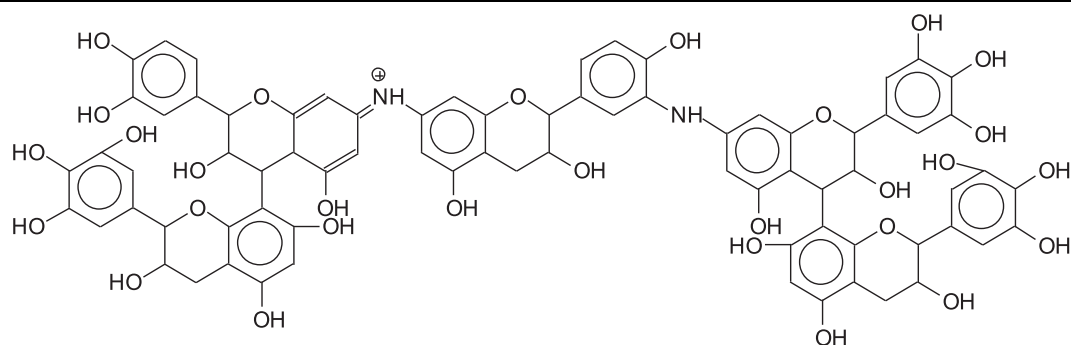
1481 Da = with Na⁺

AND/OR



AND/OR

(Continued)

Table A2 (continued)2305 Da, no Na⁺, protonated