456. *The Catechins of Green Tea. Part II.*

By A. E. Bradfield and (Miss) M. Penney.

In continuation of previous work (Bradfield, Penney, and Wright, *J.*, 1947, 32), (−)-*epi*catechin, (−)-*epi*catechin gallate, (−)-*gallocatechin gallate*, and a *substance*, which on tannase hydrolysis yields gallic acid and a new *gallocatechin*, have been isolated from green tea.

In Part I (Bradfield, Penney, and Wright, *loc. cit.*) a method was described of separating the ether-soluble polyphenols of green tea into three fractions—(*a*), (*b*), and (*c*)—by partition chromatography. Fraction (*c*) was identified as (−)-gallocatechin, while fraction (*b*) is probably (±)-gallocatechin [or (±)-*epi*gallocatechin]. Fraction (*a*) is a mixture of substances. By rechromatographing fraction (*a*) on a series of columns, using ether and a mixture of ethyl acetate and carbon tetrachloride as solvents, four main fractions—(2), (2*a*), (3), and (4)—are obtained. These appear homogeneous when again chromatographed with ether or ethyl

acetate–carbon tetrachloride, and from them crystalline substances, referred to in the following as " substance (2) " etc., are obtained. An additional substance, (2*X*), which has not yet been obtained crystalline, and traces of several other constituents have also been isolated.

Substance (2) is (−)-*epi*catechin gallate, first isolated from Japanese green tea by Tsujimura (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1930, **14**, 63; 1931, **15**, 155; 1935, **26**, 186). It has now been shown that on hydrolysis by tannase it yields gallic acid and (−)-*epi*catechin, the identity of the latter being established by direct comparison of the Debye–Scherrer diagrams given by its acetyl derivative with that of the acetate of authentic (−)-*epi*catechin from the heartwood of *Acacia catechu*. This confirms the constitution assigned to the substance by Tsujimura.

Substance (2*X*), present in relatively small amounts, gives with aqueous ferric sulphate solution a bright green colour which changes to dirty green and finally to yellow. With aqueous sodium cyanide it gives a very faint pink colour, which slowly deepens to orange, without showing any signs of fading. These colour tests indicate that the substance is a catechol derivative.*

Substance (2a) crystallises from water as minute needles or laths having $[\alpha]_D^{22°}$ −46° in acetone. It yields an amorphous acetyl derivative. The presence of a pyrogallol grouping is indicated by the deep blue colour given by aqueous ferric sulphate, the colour rapidly fading to pale blue-grey, and also by the immediate pinkish-orange colour produced by sodium cyanide, which fades on standing and is restored by shaking the solution. A phloroglucinol nucleus is indicated by the vanillin test. Hydrolysis with tannase yields gallic acid and a substance (2*b*), which crystallises from water as minute needles, decomp. 200—205°, $[\alpha]_D$ ±0·0°. The colour tests given by the substance with ferric salt, sodium cyanide, and vanillin are similar to those given by the original material (2*a*). Acetylation of (2*b*) yields an *acetyl* derivative $C_{27}H_{26}O_{13}$, m. p. 140—142°. This hydrolysis product thus appears to be one of the stereoisomeric forms of gallocatechin, which is either optically inactive or of very low rotation, differing not only from (−)-gallocatechin and (±)-gallocatechin (Part I), but also from the gallocatechin isolated by Osima (*Bull. Agric. Chem. Soc. Japan*, 1939, **15**, 636) from the bark of *Casuarina equisetifolia*. It follows that substance (2*a*) is a galloyl derivative of a new gallocatechin.

The properties of substance (3) correspond with those of a substance first isolated by Tsujimura (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1929, **10**, 253) from Japanese green tea, which, from a study of its degradation reactions, she concluded to be (−)-*epi*catechin. Comparison of the Debye–Scherrer photographs of the acetate of substance (3) from tea with the acetate of (−)-*epi*catechin from *Acacia catechu* establishes the identity of the two substances.

Substance (4) crystallises from water as colourless needles, decomp. 215—216°, $[\alpha]_D^{18°}$ −179°. With aqueous ferric sulphate it gives a violet-blue colour, which fades to nearly colourless in one or two minutes. With aqueous sodium cyanide an immediate pinkish-orange is obtained, which fades and is restored by shaking, and with vanillin an orange colour, soon changing to ruby red and then to magenta. The presence of pyrogallol and phloroglucinol groups is indicated. The substance has been acetylated under a variety of conditions, but the product was always a white amorphous powder which could not be induced to crystallise. With diazomethane an amorphous product was obtained, from which no crystalline fraction could be isolated. On hydrolysis of substance (4) by tannase, gallic acid and (−)-gallocatechin are obtained, both these substances and their acetates being positively identified by comparison of their Debye–Scherrer photographs with authentic specimens. Neither substance (4), nor the galloyl ester, substance (2*a*), gave entirely satisfactory carbon or hydrogen analyses, but molecular weight determinations by Barger's isopiestic method (*J.*, 1904, **85**, 286) showed both substances to be monogalloyl esters. In neither case is there, at present, any evidence to show with which hydroxyl group of the gallocatechin moiety the gallic acid is combined.

From an aqueous infusion of a Ceylon green tea, yields of the various catechins, as percentages of the total extractable polyphenols, were: (−)-gallocatechin, 11·7; (±)-gallocatechin, 5·8; (−)-*epi*catechin, 3·2; substance (2*X*), 1·2; (−)-gallocatechin gallate, 36·0; substance (2*a*), 4·7, (−)-*epi*catechin gallate, 7·5. Results closely similar have been obtained by examination of another specimen of Ceylon green tea, a China (Young Hyson) green tea, and specimens of dried leaf from Ceylon and Assam.

* *Note added April 23rd*, 1948.—Substance (2*X*) has now been obtained from water as minute needles, which on heating appear to lose water of crystallisation at ~100—110°. Slight decomposition begins at 200° and becomes vigorous at 210—215°. The optical rotation is very low or zero. The acetyl derivative crystallises from aqueous acetic acid as white needles, m. p. 164—165° (Found: C, 59·9; H, 5·10. Calc. for $C_{25}H_{24}O_{11}$: C, 60·0; H, 4·83%). These properties and those recorded above agree with the properties of (±)-catechin, a usual concomitant of (−)-*epi*catechin in plant material (Freudenberg, " Tannin, Cellulose, Lignin ", Berlin, 1933).

It has already been pointed out (Bradfield, *Chem. and Ind.*, 1946, 242) that the rather scanty evidence available suggests some resemblance in regard to their polyphenol content between tea leaf and such widely differing leaves as those of oak and chestnut. This resemblance has been heightened by the discovery, according to a recent abstract, of ellagic acid in tea (Tsujimura, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1941, **38**, 487; *Chem. Abs.*, 1947, **41**, 5924).

Light Absorption.—The tea catechins all absorb in the ultra-violet, showing a band at 270—280 mμ; the band for (−)-gallocatechin gallate is bifurcated, however, with twin peaks at $\lambda_{max.}$ 275 mμ and 279·5 mμ. In addition, in all cases very strong absorption takes place below about 240 mμ. Data for tea catechins and some related simpler substances in alcohol solution are given in Table I.

TABLE I.

		$\varepsilon_{max.}$	$\lambda_{max.}$			$\varepsilon_{max.}$	$\lambda_{max.}$
(*a*)	* Catechol	2600	278	(*f*)	(−)-Gallocatechin	1,340	271
(*b*)	† Pyrogallol	800	266	(*g*)	(±)-Gallocatechin	1,290	271
(*c*)	‡ Gallic acid	7900	272	(*h*)	(−)-*epi*Catechin gallate	13,600	280
(*d*)	* 5 : 7-Dihydroxy-2 : 2-dimethylchroman	624	272	(*i*)	(−)-Gallocatechin gallate	9,500 9,250	275 279·5
(*e*)	(−)-*epi*Catechin	3300	280	(*j*)	Substance (2*a*)	13,600	276

* Morton and Sawires, *J.*, 1940, 1052.

† Goslawski and Marchlewski, *Bull. Acad. Polonaise*, 1931, *A*, 383.

‡ Hertzowna and Marchlewski, *ibid.*, 1934, *A*, 55, give $\varepsilon_{max.}$ 7600, $\lambda_{max.}$ 265 mμ for the aqueous solution.

The catechin molecule may be considered to consist of two chromophores, the phloroglucinol and the catechol (or pyrogallol) nuclei, acting practically independently, and since these nuclei all absorb in the same region of the spectrum, the values of $\varepsilon_{max.}$ 3300 for *epi*catechin and $\varepsilon_{max.}$ 1340 for gallocatechin correspond approximately with the sum of the values of $\varepsilon_{max.}$ for 5 : 7-dihydroxy-2 : 2-dimethylchroman and catechol or pyrogallol respectively ($a + d = 3224$; $b + d = 1424$). The spectra of the acetyl derivatives are very similar to those of the parent catechins. The galloyl catechins show much higher values of $\varepsilon_{max.}$, a result to be expected from the introduction of a powerful chromophore. The values of $\varepsilon_{max.}$ 9500 and 9250 for the twin peaks of gallocatechin gallate are very close to the sum of the values for the three chromophores in the molecule ($b + c + d = 9324$). Acetylation of gallic acid results in the virtual disappearance of the band at $\lambda_{max.}$ 272 mμ, only a point of inflexion remaining, with ε at this point decreased to 730. Correspondingly, the amorphous acetyl derivative of (−)-gallocatechin gallate shows only a point of inflexion at λ 270 mμ, with ε decreased to 3000, the decrease being approximately equal to that resulting from acetylation of gallic acid.

For (−)-*epi*catechin gallate, on the other hand, a single peak only is observed, at $\lambda_{max.}$ 280 mμ. The value of the extinction coefficient depends on dilution, $\varepsilon_{max.}$ 11,600 at a concentration of $1{\cdot}47 \times 10^{-4}$ g./l. rising to $\varepsilon_{max.}$ 13,600 at half this concentration. In the presence of approximately 10^{-3} M-hydrochloric acid, the latter value is reduced to $\varepsilon_{max.}$ 12,200, suggesting that the anomaly is due to dissociation of the phenolic hydroxyl groups. The value of $\varepsilon_{max.}$ obtained by summing the tabulated values for *a*, *c*, and *d* is 11,124. It is rather surprising to find that the absorption spectrum for substance (2*a*) consists of a single peak with $\varepsilon_{max.}$ 13,600, $\lambda_{max.}$ 276 mμ, and thus resembles the spectrum of (−)-*epi*catechin gallate rather than that of (−)-gallocatechin gallate. Explanation of this anomaly must await more complete knowledge of substance (2*a*).

EXPERIMENTAL.

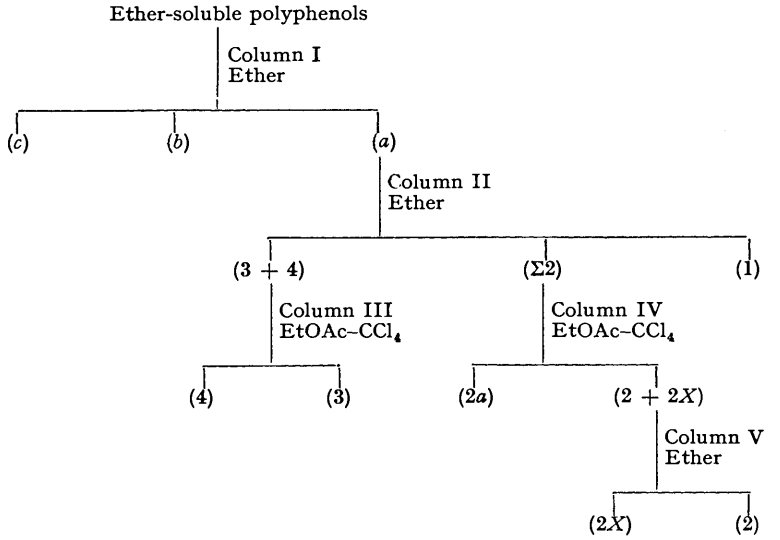
(Microanalyses are by Drs. Weiler and Strauss, Oxford.)

Preparation of Silica Gel.—For the preparation of silica gel as described in Part I, water-glass sold by Messrs. Jos. Crosfield as "special adhesive No. 2" is employed. With other commercial types of water-glass the method is not always applicable.

The presence of very fine particles in the purified gel retards the flow of solvent through a column prepared from the gel to an undesirable extent. Removal of a fine fraction by sifting (*e.g.*, with a 325-mesh sieve) is possible, but in practice clogging of the sieve is rather a handicap. We find sedimentation from water to be more convenient and more effective. For example, 100 g. of the purified silica, passing a 120-mesh sieve, is well stirred in a large beaker with 1300 c.c. of water. After the suspension has remained undisturbed for 5 minutes, the fluid portion is decanted into another beaker, and the residue filtered and dried (50 g.). After a further 30 minutes, decantation of the suspension yields a second sediment (35 g.). The first, coarser, sediment when used for a column permits very rapid passage of the solvent without noticeable loss of efficiency. With the second sediment rather lower rates are obtained, and the two materials can be mixed in suitable proportions to secure a desired rate. Using this sedimented silica, it is possible, because of the greater rate of flow, to effect two, three or four similar separations on one column within a working period of 8—10 hours, fresh portions of solution being placed on the column at such times that the first fraction from the new portion reaches the end of the column at a

convenient distance behind the last fraction of the previous portion of the solution. This practice of multiple addition results in a considerable saving of time and labour.

Chromatographic Procedure.—The complete scheme for the separation of the tea catechins is shown below, the solvent used in each case being indicated.



In general the apparatus and procedure were similar to those described in Part I, where details of Column I are given. The main data relating to Columns II—V are shown in Table II. In each case, (1) the tube used had an internal diameter of 3·1—3·3 cm., (2) the silica was mixed with 65% of its weight of water, (3) the developing solvent was the same as that used for making the solution. The ethyl acetate–carbon tetrachloride solvent used for columns III and IV was a mixture of these liquids in the proportions of 2 : 1 by volume (d 1·121), saturated with water immediately before use. In using this solvent, the rubber bung at the top of the column was replaced by a waxed cork. The products were isolated by removal of the solvent mixture under reduced pressure in a carbon dioxide atmosphere, and washed out of the flask with ether, which was then evaporated at a low temperature. The recovered solvent was washed, dried, distilled, adjusted to the correct density, and saturated with water for further use.

The position of the bands is indicated in Table II by the approximate values of R_1 and R_2 corresponding to the leading and rear edges respectively. These values vary somewhat for different specimens of silica, and depend to some extent on the relative amounts of the fractions. Although this is not shown by the approximate values of R given, the conditions are such that a small gap occurs between the fractions. In the case of column II, several narrow bands immediately precede fraction (2), the last one overlapping it slightly. These bands arise from traces of green and yellow pigments, gallic acid and of two phenolic substances.

TABLE II.

Column no.	Wt. of silica (g.).	Solution.	Fractions obtained.	R_1.	R_2.
II	70	0·5 G. fract. (*a*) in 10 c.c. ether	2	0·75	0·45
			(3 + 4)	0·45	0·26
III	50	0·25 G. fract. (3 + 4) in 5 c.c. EtOAc–CCl_4	3	0·58	0·47
			4	0·42	0·27
IV	70	0·2 G. fract. (Σ2) in 5 c.c. EtOAc–CCl_4	(2 + 2*X*)	0·85	0·55
			2*a*	0·55	0·35
V	70	0·25 G. fract. (2 + 2*X*) in 5 c.c. ether	2	0·77	0·55
			2*X*	0·55	0·47

(−)-epi*Catechin Gallate.*—Substance (2) (0·5 g.) crystallised from water (10 c.c.) as colourless needles, decomp. 252—254°, $[\alpha]_D^{21°}$ −190° (*c*, 0·25, in alcohol) (Found : C, 59·8; H, 4·40. Calc. for $C_{22}H_{18}O_{10}$: C, 59·7; H, 4·10%). With ferric salt the aqueous solution gave a blue colour. No immediate colour was given on addition of aqueous sodium cyanide, but a yellow-orange colour which slowly developed did not fade. With vanillin–hydrochloric acid a red to magenta colour developed. The acetyl derivative crystallised from dilute acetic acid as silky white needles, m. p. 119·5—120·5°, $[\alpha]_D^{25°}$ −96° (*c*, 0·56 in benzene). The properties correspond to those given by Tsujimura (*locc. cit.*) for (−)-*epi*-catechin gallate.

Action of Tannase on (−)-epi*Catechin Gallate.*—To a tannase solution prepared by rubbing up the dried mycelium (0·2 g.) of *Aspergillus niger* with water (9 c.c.) was added a solution of substance (2) (0·1 g.). The solution, covered with toluene, was kept at 30° for 10 days. The products were isolated by continuous extraction with ether for 72 hours, and the ether solution concentrated and chromatographed

(silica gel, 70 g.; water, 45·5 c.c.) with ether as developing solvent. Two bands corresponding to the passage of 255—322 c.c. and 515—663 c.c., respectively, of solvent through the column were obtained. From the first fraction, gallic acid, decomp. 245° (29 mg.), was obtained on evaporation. The product from the second band (40 mg.) yielded an acetyl compound, white needles, m. p. 151·5—152·5°, both alone and mixed with an authentic specimen of (−)-*epi*catechin acetate prepared from the heartwood of *Acacia catechu* by the method of Freudenberg and Purrman (*Annalen*, 1924, **437**, 274). The identity of the two acetyl compounds was confirmed by comparison of their *X*-ray diagrams.

Substance (2a).—The *substance* (0·15 g.) crystallised from water (0·2 c.c.) as minute needles, decomp. 217—219°, $[\alpha]_D^{22°}$ −46° (*c*, 0·43 in acetone) [Found: C, 56·6; H, 4·42; *M*, 436 (acetone), 431 (methyl ethyl ketone). $C_{22}H_{18}O_{11}$ requires C, 57·6; H, 3·96%; *M*, 458]. The acetyl derivative could not be obtained crystalline.

Action of Tannase on Substance (2a).—A solution of substance (2*a*) (0·15 g.) in water (2 c.c.) was treated with a solution prepared from dried mycelium of *A. niger* (0·3 g.) and kept at 30° for 14 days. The products, after extraction with ether, were chromatographed (silica, 40 g., water, 26 c.c.), and yielded two bands corresponding to the passage of 119—209 c.c. and 642—876 c.c. of solvent respectively. From the first of these fractions gallic acid was isolated (32·5 mg.) and from the second, substance (2*b*) (53 mg.), which crystallised from water as minute needles, decomp. 200—205°, $[\alpha]_D$ ±0·0° (*c*, 0·9 in alcohol). It yielded an *acetyl* derivative, m. p. 140—142° (Found: C, 58·2; H, 5·17. $C_{27}H_{26}O_{13}$ requires C, 58·1; H, 4·69%).

(−)-epi*Catechin*.—Substance (3) crystallised from water in rectangular tablets, decomp. 236—237°, and yielded an acetyl derivative, m. p. 151—152·5°, both alone and mixed with authentic (−)-*epi*catechin acetate. The identity of the two acetates was further confirmed by the *X*-ray method.

(−)-*Gallocatechin Gallate*.—*Substance* (4) (0·19 g.) crystallised from water (0·6 c.c.) as white needles which very readily became brown on exposure to air and light, decomp. 215—216°, $[\alpha]_D^{24°}$ −179° (*c*, 0·28 in alcohol) [Found: C, 56·9; H, 4·55; *M*, 443 (acetone), 437 (methyl ethyl ketone). $C_{22}H_{18}O_{11}$ requires C, 57·6; H, 3·96%; *M*, 458]. Acetylation and methylation products could not be obtained crystalline.

Action of Tannase on (−)-*Gallocatechin Gallate*.—To substance (4) (0·4 g.) in water (4 c.c.) was added a tannase solution from dried mycelium of *A. niger* (0·4 g.) and water (15 c.c.) and a few drops of toluene. After being kept at 30° for 7 days, the solution was extracted with ether, and the ether solution concentrated and chromatographed on a column prepared from silica (40 g.) and water (26 c.c.). Two bands only were observed, corresponding to the passage of 111—206 c.c., and 1232—1929 c.c., respectively, of ether through the column. From the first of these fractions gallic acid (0·115 g.), decomp. 245° (triacetate, m. p. 168—169°, both alone and mixed with an authentic specimen), was isolated. The substance (0·16 g.) isolated from the second fraction crystallised from water, decomp. 212—215°, and yielded an acetyl derivative, m. p. 191—193°, both alone and mixed with authentic (−)-gallocatechin hexa-acetate. The identity of both hydrolysis products was conclusively established by the *X*-ray method.

Molecular Weights.—Barger's method (*loc. cit.*) was followed, except that longer slugs (0·3—1·0 cm.) of the solutions were used, and measurements made with a travelling microscope. The liquid was introduced into the capillary by connecting it by means of narrow rubber tubing to the upper end of an apparatus constructed as follows. To the lower end of a thick-walled glass tube (30 cm. long, 0·2 cm. internal diameter), held vertically, a 3-inch length of rubber tubing, closed by a piece of glass rod, was attached. By pressure from a screw clip, water contained in the rubber tube was forced into the glass tube, and by subsequent manipulation of the screw clip, slugs of the required solutions could be easily drawn into, and moved up, the attached capillary. Solutions of pyrogallol were used as reference solutions. Final readings were taken with acetone as solvent after 15—18 hours, with methyl ethyl ketone after 18—40 hours.

Debye–Scherrer Photographs.—Powdered specimens of gallic acid, its acetyl derivative, and (−)-*epi*catechin acetate were made into solid cylinders (~0·3 mm. diameter) with gum tragacanth and water, and photographed by the procedure described in Part I, except that the specimens were not rotated. The remaining specimens were mounted in Lindemann glass and Perspex capillary tubes (~0·25 mm. internal diameter), and photographed using copper-$K\alpha$ nickel-filtered radiation (λ = 1·539 *kX*) from an *X*-ray tube operated at 40 ma. and 32 kv., the specimens being rotated throughout the exposures. Cylindrical cameras, 6 cm. and 9 cm. diameter, and a quarter-plate camera with a specimen-to-film distance of 5·25 cm., were used. Exposure times ranged from 2 to 16 hours. Interplanar spacings in *kX* units and relative intensities were derived as before (D = diffuse, S = strong, M = medium, W = weak, V = very, F = fairly).

Gallic acid.

7·45 (M.)	5·48 (S.)	4·67 (M.)	4·49 (M.)	3·61 (V.W.)	3·49 (F.S.)
3·34 (V.W.)	3·21 (V.S.)	3·12 (V.W.)	3·01 (W.)	2·84 (M.)	2·73 (V.W.)
2·59 (W.)	2·51 (W.)	2·45 (W.)	2·39 (W.)	2·32 (V.W.)	2·18 (V.W.)
2·09 (W.)					

This pattern was given both by an authentic specimen and by gallic acid obtained by hydrolysis of (−)-gallocatechin gallate.

Triacetylgallic acid.

9·64 (M.)	8·44 (V.S.)	7·70 (M.)	6·82 (F.S.)	6·61 (M.)	5·96 (F.S.)
5·38 (V.W.)	4·86 (F.S.)	4·25 (M.)	4·17 (M.)	3·93 (M.)	3·68 (V.S.)
3·60 (F.S.)	3·44 (W.)	3·37 (V.W.)	3·26 (W.)	3·12 (V.W.)	3·00 (W.)
2·91 (V.W.)	2·78 (V.W.)	2·68 (W.)	2·61 (W.)	2·52 (V.W.)	2·42 (V.W.)
2·31 (V.W.)	2·20 (V.W.)				

This pattern was given both by an authentic specimen and by triacetyl gallic acid obtained by hydrolysis of (−)-gallocatechin gallate.

(−)-epi*Catechin gallate.*

7·97 (V.W.)	7·03 (V.W.)	6·37 (M.)	5·87 (V.W.)	5·46 (V.W.)	5·20 (V.S.)
5·02 (V.W.)	4·82 (V.W.)	4·62 (W.)	4·38 (W.)	4·21 (W.)	4·03 (V.W.)
3·95 (V.W.)	3·80 (S.)	3·69 (V.W.)	3·47 (V.W.)	3·38 (S.)	3·25 (W.)
3·10 (M.)	2·95 (V.W.)	2·84 (M.)	2·75 (W.)	2·61 (W.)	2·49 (W.)
2·37 (M.)	2·26 (W.)	2·23 (V.W.)	2·11 (M.)	2·04 (W.)	1·99 (W.)
1·96 (V.W.)	1·92 (W.)	1·87 (W.)	1·81 (V.W.)	1·71 (D.W.)	1·62 (D.W.)
1·59 (V.W.)	1·56 (V.W.)	1·18 (V.W.)	1·14 (V.W.)		

Substance (2a).

10·8 (M.)	8·41 (D.W.)	7·32 (D.W.)	7·00 (W.)	6·62 (V.W.)	5·93 (M.)
5·41 (M.)	5·12 (V.W.)	4·69 (M.)	4·46 (V.W.)	4·21 (S.)	3·97 (V.W.)
3·80 (V.S.)	3·62 (W.)	3·37 (D.F.S.)	3·14 (W.)	2·98 (W.)	2·88 (W.)
2·74 (M.)	2·63 (D.W.)	2·57 (W.)	2·46 (V.W.)	2·38 (W.)	2·32 (V.W.)
2·27 (V.W.)	2·10 (W.)	2·05 (W.)	1·91 (W.)	1·86 (W.)	

Acetyl derivative of substance (2b).

14·8 (V.W.)	13·0 (V.S.)	11·0 (W.)	9·7 (V.W.)	8·95 (V.S.)	8·11 (V.W.)
7·52 (M.)	6·92 (W.)	6·40 (V.W.)	6·05 (V.W.)	5·49 (F.S.)	5·11 (F.S.)
4·95 (V.S.)	4·69 (M.)	4·41 (F.S.)	4·24 (F.S.)	4·11 (F.S.)	3·93 (F.S.)
3·81 (F.S.)	3·62 (V.W.)	3·52 (V.W.)	3·45 (S.)	3·37 (W.)	3·24 (V.W.)
3·11 (V.W.)	2·92 (M.)	2·76 (V.W.)	2·61 (V.W.)	2·52 (V.W.)	2·45 (V.W.)
2·28 (D.W.)	2·18 (W.)	2·08 (W.)	2·00 (D.W.)	1·86 (D.W.)	1·79 (V.W.)
1·73 (D.W.)					

(−)-epi*Catechin acetate.*

16·3 (F.S.)	13·16 (W.)	9·90 (M.)	8·66 (W.)	7·36 (W.)	6·55 (M.)
6·24 (M.)	5·70 (W.)	5·42 (M.)	5·20 (W.)	4·93 (M.)	4·76 (M.)
4·52 (W.)	4·30 (S.)	4·19 (S.)	4·00 (W.)	3·80 (W.)	3·61 (S.)
3·40 (M.)	3·27 (W.)	3·10 (V.W.)			

This pattern was given by the acetyl derivatives of (−)-*epi*catechin from *Acacia catechu*, substance (3), and an hydrolysis product of substance (2).

(−)-*Gallocatechin gallate.*

10·3 (M.)	8·58 (W.)	7·34 (M.)	6·77 (V.W.)	6·22 (V.W.)	5·96 (V.W.)
5·66 (M.)	5·43 (V.W.)	5·21 (M.)	5·01 (V.W.)	4·84 (V.W.)	4·56 (F.S.)
4·42 (V.W.)	4·29 (F.S.)	4·13 (F.S.)	3·95 (V.W.)	3·86 (V.W.)	3·76 (W.)
3·63 (V.S.)	3·44 (S.)	3·37 (V.W.)	3·19 (M.)	3·09 (F.S.)	3·01 (W.)
2·86 (W.)	2·75 (W.)	2·65 (W.)	2·53 (M.)	2·45 (V.W.)	2·43 (F.S.)
2·32 (D.W.)	2·23 (V.W.)	2·15 (M.)	2·04 (W.)	2·00 (V.W.)	1·94 (M.)
1·89 (W.)	1·85 (V.W.)	1·80 (V.W.)	1·77 (V.W.)	1·68 (D.W.)	1·61 (V.W.)
1·56 (V.W.)					

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