Table 1. Chromatographic behaviour of compounds **1–5** on polyamide (A,B,C) and Si gel (D). Color observed on polyamide layer before and after spraying with Naturstoffreagenz A (β-amino-ethylester of boric acid): y = yellow, dk = dark, v = violet.

Compound	R_f in Solvents A	 B	 C	 D	Colour in UV_{366}
(**1**) 3,7,3′,4′,5′-penta*O*Me-Myricetin	0·92	0·96	0·72	0·68	black dull y
(**2**) 3,7,4′-tri*O*Me Kaempferol	0·90	0·96	0·59	0·80	dk.v.
(**3**) 3,7,3′,4′-tetra *O*Me-Quercetin	0·86	0·95	0·68	0·66	dk.v. dull y
(**4**) 7,4′-di*O*Me-A pigenin	0·72	0·88	0·50	0·75	dk.v. dull green-y.
(**5**) 3,7,3′-tri*O*Me-Quercetin	0·32	0·72	0·68	0·46	dk br y.

ether (pachypodol). MS (M^+ 344) is in accordance with literature [5] and shows same fragments as the isomeric 3,7,4′-trimethyl ether (ayanin). Differentiation from the latter is possible with the aid of the UV-spectra [5] and even of chromatographic behaviour (In A, B and D, R_f of pachypodol is a little higher than that of ayanin; colors on polyamide in UV before and after spraying are somewhat different).

Six rather common flavonoid aglycones had been tabulated *B. nigra* as a result of TLC investigations [1]. It was noted there that some other substances were present. Now, by use of material from a large number of buds, *the above* five rare flavonoids have been identified. Data of their occurrence are given in detail in order to complete tables 6.2 and 7.6 of [6]. Combretol, **1**: *Combretum quadrangulare* [6]. Kaempferol 3,7,4′-tri-Me, **2**: *Cheilanthes farinosa*, *Aframomum giganteum* [6], *Cheilanthes longissima* [7] and *Ostrya virginiana* (comp. [1]). Retusin, **3**: *Ariocarpus retusus*, *Aframomum giganteum*, *Larrea cuneifolia* [6] and *Geranium macrorhizum* [8]. Apigenin 7,4′-diMe, **4**: "birch buds" (1933, comp. [1]), *Beyeria* sp. [9], propolis [10], *Andrographis paniculata* [11], *Piper peepuloides* [12] and *Baccharis rhomboidalis* [6]. Pachypodol, **5**: *Larrea cuneifolia*, *Euodia glabra* [6], *Pachypodatium confine* [5] and *Larrea tridentata* [13].

This is only the second report of natural occurrence of **1**. For the family Betulaceae **1**, **2** and **5** had not been known before, while **4** had been found in buds of 9 species of *Betula* and in *Alnus japonica* and **3** in *Ostrya virginiana* buds.

The lipophilic excretion of *B. nigra* buds still contains some unknown aglycones, possibly new flavones, which could not be analysed because of lack of material.—It should be noted that trees from other places showed slight (quantitative) variation of the flavonoid pattern which, as a whole, is very characteristic for this species. Some of the terpenoids which were obtained as "by-products" of this work are under investigation.

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D-FRUCTOSE IN FLAVONOL AND FLAVANONE GLYCOSIDES FROM *CAMELLIA SINENSIS*

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Key Word Index—*Camellia sinensis*; Theaceae; commercial tea; D-fructose in flavonol and flavanone glycosides.

The first occurrence of D-fructose in phenolic glycosides was reported in the rind of *Pajanelia rheedii* [1]. In recent years, D-fructose has been identified as the carbohydrate component in anthocyanins and leucoanthocyanins from inflorescence of *Mentha piperita* [2] and has been reported as a constituent of an anthocyanin pigment of *Salix purpurea* bark [3]. This paper deals with the presence of D-fructose in two flavonoid glycosides from commercial tea. A naringenin glycoside was identified in fresh tea leaves and a quercetin glycoside was shown to be present only in the processed leaf.

Flavonoid glycosides (FG1 and FG2) were isolated from aqueous extracts of commercial tea (TE'ATI, black tea) by preparative PC. The aglycones were obtained by acid hydrolysis (2N HCl; 2 hr at 100°) and identified as quercetin and naringenin by PC (three solvents) and UV spectroscopy.

The sugars attached to flavonoid glycosides were obtained by controlled acid hydrolysis (10% HOAc; 3,5 hr under reflux) and identified by PC (six solvents) and colour reactions with diphenylamine-*p*-anisidine [4]. Both glycosides gave glucose and fructose and FG1 in addition gave a dissacharide. This latter sugar (R_G 0·64) was unaffected by β-glucosidase; on acid hydrolysis it gave glucose and fructose and no intermediate could be detected during degradation. This compound is thus a fructosylglucose. In order to ascertain whether these two flavonoid glycosides are artifacts, fresh tea leaves were extracted with water; from the aqueous extracts the product FG2 was isolated by band chromatography and identified by UV spectroscopy and PC (three solvents); the identification was confirmed by acid hydrolysis. Since compound FG1 was absent from aqueous extracts of fresh tea leaves, it is presumably a product of tea processing.

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FLAVONOL METHYL ETHERS FROM *ERICAMERIA DIFFUSA*

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Two new flavonol aglycones, kaempferol 3,5,7-trimethyl ether (**1**) and quercetin 3,3′,4′-trimethyl ether (**2**), were characterized from *Ericameria diffusa* (Compositae) in connection with our chemosystematic study of the genus *Ericameria*. In addition, ten known aglycones were detected in this same species: galangin 3-methyl ether (**3**), kaempferol 3,4′-dimethyl ether (**4**), kaempferol 3,7-dimethyl ether (**5**), kaempferol 3-methyl ether (**6**), quercetin

Table 1. NMR Spectra of *Ericameria diffusa* flavonol aglycones

										OMe in CCl$_4$ C$_6$D$_6$		
Compound	H-2′	H-6′	H-3′	H-5′	H-4′	H-8	H-6	3-OMe	5-OMe	7-OMe	3′-OMe	4′-OMe
1*	7·88*dd* (*J* 2·0)† (*J* 8·5)	7·88*dd* (*J* 2·0) (*J* 8·5)	6·88*dd* (*J* 2·0) (*J* 8·5)	6·88*dd* (*J* 2·0) (*J* 8·5)	—	6·83*d* (*J* 2·5)	6·44*d* (*J* 2·5)	3·85 —	3·71 —	3·82 —	—	—
2	7·53*d* (*J* 2·0)	7·68*dd* (*J* 2·0) (*J* 8·5)	—	6·88*d* (*J* 6·0)	—	6·40*d* (*J* 2·0)	6·11*d* (*J* 2·0)	3·82 (Δ + 0·03)	—	—	3·80 (Δ + 0·26)	3·80 (Δ + 0·32)
3*	signals overlapping 7·55–7·95					6·44*d* (*J* 2·0)	6·23*d* (*J* 2·0)	3·81 —	—	—	—	—
4	7·99*dd* (*J* 2·0) (*J* 9·0)	7·99*dd* (*J* 2·0) (*J* 9·0)	6·90*dd* (*J* 2·0) (*J* 9·0)	6·90*dd* (*J* 2·0) (*J* 9·0)	—	6·49*d* (*J* 2·5)	6·28*d* (*J* 2·5)	3·82 (Δ + 0·02)	—	—	—	3·82 (Δ + 0·38)
5	7·95*dd* (*J* 2·0) (*J* 8·5)	7·95*dd* (*J* 2·0) (*J* 8·5)	6·85*dd* (*J* 2·0) (*J* 8·5)	6·85*dd* (*J* 2·0) (*J* 8·5)		6·43*d* (*J* 2·5)	6·15*d* (*J* 2·5)	3·83 (Δ + 0·02)	—	3·83 (Δ + 0·51)	—	—
7	7·55*d* (*J* 2·0)	7·55 *d* (*J* 2·0) (*J* 5·5)	—	6·79*d* (*J* 5·5)	—	6·41*d* (*J* 2·0)	6·11*d* (*J* 2·0)	3·82 (Δ + 0·01)	—	3·82 (Δ + 0·37)	—	3·82 (Δ + 0·31)
8	7·54*d* (*J* 2·0)	7·60*dd* (*J* 2·0) (*J* 5·0)	—	6·83*d* (*J* 5·0)	—	6·41*d* (*J* 2·0)	6·09 (*J* 2·0)	3·87 (Δ + 0·05)	—	—	—	3·85 (Δ + 0·41)
9	7·66*d* (*J* 2·0)	7·43*dd* (*J* 2·0) (*J* 8·5)	—	6·85*d* (*J* 8·5)	—	6·45 (*J* 2·5)	6·17 (*J* 2·5)	3·84 (Δ + 0·01)	—	3·78 (Δ + 0·45)	—	—

* Spectra were recorded for the underivatized flavonoid in DMSO$_6$. All other compounds were trimethylsilated and spectra were recorded in CCl$_4$ and C$_6$D$_6$ (only OMe signals are given for the latter solvent). Values are given in ppm (δ-scale) relative to TMS. † Numbers in parentheses denote coupling constants in Hz. Signals are singlets unless otherwise noted: *d* (doublet), *dd* (double doublet).