Schmp. 202–204° und $[\alpha]_D^{22}$ + 490° (*c* 1,0, $CHCl_3$). Das in Äther schwerlösliche Produkt A wird in 100 ml Me_2CO unter Erwärmen auf 50° aufgenommen, der ungelöste Anteil (B) abgesaugt, das Filtrat mit Aktivkohle behandelt und bis zur Kristallisation eingeengt. Das resultierende Material wird abgesaugt, mit $CHCl_3$ gewaschen um wenig Usninsäure wegzulösen und erneut 2 × aus Me_2CO bzw. MeOH–H_2O umkristallisiert: 1,5 g (4,9%) *α-Acetylsalazinsäure* (**1**) in Nädelchen vom Schmp. 195–197° (Zers.); eine durch langsames Eindunsten einer acetonischen Lösung erhaltene Probe schmilzt bei 205–207° (Zers.). R_f 0,55 (Kodak Chromagram 6061, AcOH–Toluol–Et_2O = 0,5:3:6, *p*-Phenylendiamin → gelb). $C_{20}H_{14}O_{11}$ (430,3); gef. C, 55,82; H 3,28; ber. C, 55,71; H, 3,20. IR: ν_{max}^{KBr} 790, 806, 840, 860, 900, 960, 1020, 1090, 1140, 1160, 1200, 1250, 1290, 1372, 1390, 1450, 1570, 1648, 1732 und 3490 cm^{-1}.

Acetylierung von 0,25 g **1** mit 1,5 ml eines Gemisches aus 5 ml Ac_2O und 1 Tropfen konz. H_2SO_4 in 3 Stdn. bei 20° gibt nach zweimaliger Kristallisation aus Aceton 0,15 g Prismen vom Schmp. 176–178°, im Mischschmp., IR- und NMR-Spektrum identisch mit Hexaacetylsalazinsäure (**2**).

Der in Me_2CO schwer lösliche Anteil B liefert nach Kristallisation aus Me_2CO–H_2O 0,6 g (1,9%) *Salazinsäure* in Nädelchen, die sich ab 240° zersetzen. In der Mutterlauge läßt sich mittels TLC *Norstictinsäure* nachweisen.

α-Acetylsalazinsäure (**1**) *aus Salazinsäure.* 0,5 g Salazinsäure werden mit 100 ml HOAc 1 Std. unter Rückfluß erhitzt; anschließend wird der Ansatz auf etwa 15 ml eingeengt, das ausgeschiedene Material abfiltriert und das Filtrat mit H_2O verdünnt. Der Niederschlag wird abgesaugt, mit H_2O gewaschen, bei 20° getrocknet und dreimal aus Me_2CO, MeOH bzw. MeOH–H_2O umkristallisiert: 0,12 g **1** in Nädelchen vom Schmp. 205–206° (Zers.).

α-Acetylsalazinsäureanil. 0,2 g **1** werden in 15 ml siedendem EtOH gelöst und mit 0,5 ml frisch destilliertem Anilin versetzt, wobei sofort gelbe Plättchen ausfallen, die noch heiß abgesaugt und mit EtOH gewaschen werden; Schmp. 260–262° (Zers.).

4,3′,7′-*Triacetylsalazinsäure.* Aus 2,0 g Salazinsäure und 60 ml Ac_2O in 30 min unter Rückfluß nach [5]. Nach zweimaliger Kristallisation aus Me_2CO–MeOH Nadeln vom Schmp. 206–208° und dem R_f-Wert 0,76 (Kodak Chromagram 6061, AcOH–Toluol–Et_2O = 0,5:3:6, *p*-Phenylendiamin → gelb). Asahina und Asano [5] geben den Schmp. 205–206° an. IR: ν_{max}^{KBr} 715, 750, 790, 810, 864, 885, 900, 916, 990, 1010, 1050, 1090, 1136, 1156, 1175, 1200, 1220, 1240, 1278, 1316, 1330, 1362, 1442, 1480, 1565, 1640, 1740, 1770, 3000 und 3500 cm^{-1}.

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RARE METHOXY FLAVONOIDS FROM BUDS OF *BETULA NIGRA*

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Key Word Index—*Betula nigra*; Betulaceae; bud excretion; methylated flavonoids; combretol; kaempferol 3,7,4′-trimethyl ether; retusin; apigenin 7,4′-dimethyl ether; pachypodol.

Plant. Betula nigra L. *Source.* Botanic Garden of TH Darmstadt. *Previous work.* Flavonoids from other species, common flavonoids from *B. nigra* [1]. *Present work.* Lipophilic material excreted by winter buds of *Betula nigra* was recovered by treatment with acetone at room temperature. After column chromatography on silica gel and on polyamide (both eluted with C_6H_6 and increasing quantities of MeCOEt and MeOH), followed by preparative TLC on polyamide, five flavonoid aglycones could be identified. Although buds of a whole tree have been worked up, only traces of compounds **1**–**5** could be isolated, the buds being very small and the excretion consisting mainly of terpenoids. TLC comparison was on polyamide (solvent A, petrol 60–80°–C_6H_6–MeCOEt–MeOH 70:20:8:2; solvent B, C_6H_6–petrol 100–140°–MeCOEt–MeOH 60:26:7:7; solvent C, HAc–dioxan–DMF–H_2O 2:6:3:3) and on silica gel (solvent D, C_6H_6–Me_2CO 9:1). Numbering of compounds follows decreasing R_f on polyamide in the non-polar solvent A. If no other details are given, they have been identified by chromatographic comparison with authentic samples in the four solvent systems (see Table 1), UV spectra (comp.[2]), and by complete demethylation (treatment with pyr-HBr at 250° for 5 min, [3]).

Compound **1**. Myricetin 3,7,3′,4′,5′-pentamethyl ether (combretol). Light yellow needles from MeOH, mp 144–146° (lit. 145–147°, [4]). MS 70 eV *m/e* (rel. int.): 388 M^+ (base peak), 373 (M–Me, 85), 357 (M–OMe, 16), 345 (M–MeCO, 37). Compound **2**. Kaempferol 3,7,4′-trimethyl ether; Compound **3**. Quercetin 3,7,3′,4′-tetramethyl ether (retusin); Compound **4**. Apigenin 7,4′-dimethyl ether; Compound **5**. Quercetin 3,7,3′-dimethyl

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′-pentaOMe-Myricetin	0·92	0·96	0·72	0·68	black dull y
(2) 3,7,4′-triOMe Kaempferol	0·90	0·96	0·59	0·80	dk.v.
(3) 3,7,3′,4′-tetra OMe-Quercetin	0·86	0·95	0·68	0·66	dk.v. dull y
(4) 7,4′-diOMe-A pigenin	0·72	0·88	0·50	0·75	dk.v. dull green-y.
(5) 3,7,3′-triOMe-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