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NEW FLAVONOIDS FROM *BETULA NIGRA*

ECKHARD WOLLENWEBER

Botanisches Institut der TH, D-6100 Darmstadt, W. Germany

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In previous work on bud flavonoids of Betulaceae [1] and of *Betula nigra* L. [2] eleven aglycones were reported to occur in the lipophilic excretion of this species, namely kaempferol, kaempferol 7-methyl ether (rhamnocitrin), kaempferol 3,4'-dimethyl ether (ermanin), kaempferol 7,4'-dimethyl ether, kaempferol 3,7,4'-trimethyl ether, quercetin 3'-methyl ether (isorhamnetin), quercetin 3,7,3'-trimethyl ether (pachypodol), quercetin 3,7,3',4'-tetramethyl ether (retusin), myricetin 3,7,3',4',5'-pentamethyl ether (combretol), apigenin 7,4'-dimethyl ether and scutellarein 6,7,4'-trimethyl ether (salvigenin). Now it has been possible to identify in addition eight minor components: the flavonols kaempferol 3-methyl ether (isokaempferide), quercetin 3-methyl ether, quercetin 3,7-dimethyl ether, quercetin 3,3'-dimethyl ether, quercetin 3,3',4'-trimethyl ether and the flavones apigenin, scutellarein 6,7-dimethyl ether (cirsimaritin) and luteolin.

The natural occurrence of quercetin 3,3',4'-trimethyl ether has recently been reported for the first time in *Ericameria diffusa* [3], so this is only the second report of this flavonol as a natural product. The same is true for the myricetin pentamethyl ether combretol [2]. The other flavonoids are not so rare (comp. [4]) and they have been found as aglycones in various combinations in buds of Betulaceae [1], of *Aesculus* [5] and of *Populus* [6]. All the methylated derivatives of quercetin shown here (except quercetin 3-methyl ether) occur jointly, too, in the external leaf resin of two *Larrea* species [7]. It is surprising that quercetin 3-methyl ether is not encountered more often in such lipophilic materials, where a number of other methyl ethers of quercetin as well as the corresponding derivatives of kaempferol are abundant. Luteolin, though a common flavone, has not been found before among bud flavonoids; only its 7,4'-dimethyl ether (pilloin) had been detected in *Alnus japonica* [8]. Scutellarein 6,4'-dimethyl ether (pectolinarigenin) and scutellarein 6,7,4'-trimethyl ether (salvigenin) are known from several species of *Alnus* and *Betula* [1], whereas scutellarein 6,7-dimethyl ether (cirsimaritin) is new for Betulaceae and for bud excretions in general.

It should be noted here that the 6,7,4'-trimethyl ether of 6-hydroxykaempferol (mikanin), given in table 1 of [1] for *Betula nigra* could not be detected in the bulk material worked up here, and kaempferol 3,7-dimethyl ether (kumatakenin), cited there with question mark, is absent from all samples. On the other hand there are still some ten flavonoids excreted by these buds, which because of their extremely small quantities could not be identified.

In all, nineteen flavonoid aglycones have been found in buds of *Betula nigra*. Some are found only in this species and give prominent spots on thin-layer chromatograms even when present as minor components; the species is thus readily distinguished by comparative chromatography (using solvent B) from other *Betula* taxa. When bud extracts of *Betula nigra* from different Botanic Gardens were compared only minimal (mainly quantitative) differences were observed. Thus the flavonoid pattern of the bud excretion appears to be a species-specific characteristic.

EXPERIMENTAL

Plant material. Winter buds of *Betula nigra*, collected from a tree cut in March 1975 at the Botanic Garden of TH Darmstadt, were extracted with acetone at room temperature.

Isolation. After column chromatography on silica gel and polyamide (eluted with C_6H_6 and increasing quantities of MeCOEt and MeOH), partly after preparative TLC, the eleven flavonoids reported earlier [1; 2] were isolated. Now from various remaining mother liquors and intermediate fractions after repeated preparative TLC the right compounds described here could be isolated in minimal amounts.

Identification. The flavonoid aglycones were identified by comparison with authentic substances on polyamide thin layers (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 Si gel (solvent **D**, C_6H_6–Me_2CO (9:1)). Identity was confirmed by comparison of UV spectra (comp. [9]).

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