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METHYLATED FLAVONOLS FROM BUDS OF SEVERAL SPECIES OF *POPULUS*

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Key Word Index—*Populus*; Salicaceae; flavonoids; quercetin and kaempferol methyl ethers.

Plants. Various species of *Populus*. *Source*. Forschungsinstitut für Pappelwirtschaft, Hann. Münden. *Previous work*. Flavones, flavonols and flavanones from bud oil of *P. nigra*;¹ chalkones from bud oil of some species of *Populus*;² pinobanksin 3-acetate from many species.³

Present work. Buds were extracted with acetone and the solution concentrated. Flavonoids were isolated by preparative TLC on polyamide (solvent A, C₆H₆–petrol./MeCOEt–MeOH, 60:26:7:7, B, C₆H₆–dioxane–MeOH, 8:1:1) and silica gel (C₆H₆–Me₂CO, 9:1) and identified by co-chromatography with authentic substances and UV-spectra.

Flavonols. Besides many of the flavonoids described earlier from *P. nigra*, we have now found the following: quercetin-3,3'-dimethyl ether. Dark spot on polyamide, *R_f* 0.1 (A), 0.31 (B), yellow with "Naturstoffreagenz A" (colours in UV). UV λ_{\max} 366, 268 (shoulder) and 255 nm; with added AlCl₃ 396, 368, (300) and 270 nm; with NaOEt 408, 326 and 268 nm; with NaOAc 368, 321 and 272 nm; no shift with NaOAc–H₃BO₃. Quercetin 3,7-dimethyl ether. Dark reddish-brown spot on polyamide, *R_f* 0.18 (A), 0.45 (B), orange-yellow with Naturstoffreagenz. UV λ_{\max} 363, 257 nm; with AlCl₃ 403, 365 and 270 nm; with NaOEt 400 and 270 nm; with NaOAc 364 and 257 nm; with NaOAc–H₃BO₃ 382 and 258 nm. Kaempferol 7,4'-dimethyl ether. *R_f* 0.78 (A), 0.98 (B). Kaempferol 4'-methyl ether. *R_f* 0.18 (A), 0.45 (B). Apigenin 4'-methyl ether. *R_f* 0.24 (A), 0.54 (B).

The two rare dimethyl derivatives of quercetin have been also found recently together in *Larrea cuneifolia*.⁴ *Distribution*. Qu 3,3'-dimethyl ether in *P. deltoides*, *P. sargentii* and one clone of *P. euramericana*. Qu 3,7-dimethyl ether in *P. wislicenii*, *P. euramericana*, *P. acuminata*, *P. cathayana*, *P. simonii*, *P. szechuanica*, *P. candicans*, *P. generosa*, *P. deltoides* × *P. simonii*. Km 7,4'-dimethyl ether in *P. androscoquin* (*P. maximowiczii* × *P. tricho-*

* β -Aminoethyl ester of diphenyl boric acid.

¹ WOLLENWEBER, E. and EGGER, K. (1971) *Phytochemistry* **10**, 225.

² WOLLENWEBER, E. and WEBER, W. (1973) *Z. Pflanzenphys.* **66**, 125.

³ WOLLENWEBER, E., CHADENSON, M. and HAUTEVILLE, M. (1974) *Z. Naturf.*, in press.

⁴ VALJESI, A. G., RODRIGUEZ, E., VANDER VELDE, G. and MABRY, T. J. (1972) *Phytochemistry* **11**, 2821.

carpa) only. Km 4'-methyl ether in *P. androscoggin*, *P. maine* (*P. candicans* × *P. berlinensis*) and *P. tremula*. Ap 4'-methyl ether in *P. generosa*, *P. androscoggin* and *P. maine*.

A survey of the distribution of all the flavonoids now identified in all species and hybrides at our disposal will appear elsewhere.

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