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CHALCONES FROM *ONYCHIUM AURATUM*

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Key Word Index—*Onychium auratum*; Cryptogrammataceae; Chalcones; Pashanone; Pinostrobin chalcone.

Plant. Onychium auratum. Source. United Chemicals, Calcutta (India). *Previous work.* None. *Present work.* The occurrence of 2′,6′-dihydroxychalcones in nature is somewhat rare, possibly because of their ready conversion to the corresponding flavanones which are stabilized due to hydrogen bonding between 5-hydroxyl and 4-carbonyl groups.[1] In this communication the isolation of two such chalcones from the fern, *Onychium auratum* (Cryptogrammataceae) is discussed.

The plant was powdered and extracted with light pertoleum (Soxhlet, 8 hr) which, on concentration, deposited a dark red solid. Column chromatography (silica gel) of this solid gave two crystalline compounds **1** and **2.**

Compound **1.** Compound **1** was isolated from light petroleum–benzene (1:2) eluate as a red crystalline solid (m.p. 148°, $C_{17}H_{16}O_5$, M^+ 300, yield 0·53%). Colour reactions and UV [λ_{max}^{MeOH} 336 nm, log ϵ (4·3)] data suggested that **1** was a polyhydroxychalcone.[2,3] IR (KBr) ν cm^{-1}, 3400, OH; 1645 conjugated CO and 693 monosubstituted phenyl groups. Presence of chelated OH was indicated by $FeCl_3$ and a shift of +32 nm in the UV on addition of $AlCl_3$/HCl. It gave a diacetate (m.p. 105°). NMR spectrum δ ($CDCl_3$) of **1** showed the presence of two OMe (3·85 *s*, and 3·87, *s*) α, β protons (7·98, *d*, *J* 7 Hz); one isolated aromatic proton (6·10, *s*) and 5 protons of monosubstituted phenyl (7·25–7·70, m). Two singlets at δ 7·00 and 13·83 (exchangeable with D_2O) were due to phenolic hydroxyl groups. On refluxing (1 hr) with alcoholic HCl (4%), **1** gave a mixture which could be separated by preparative TLC into two colourless crystalline solids **3** (m.p. 150°) and **4** (m.p. 98°). From NMR, IR and UV data **3** and **4** were identified as 5-hydroxy-6,7-dimethoxyflavanone and 5-hydroxy-7,8-dimethoxyflavanone respectively. Their identity was further confirmed by comparison with the synthetic samples of **3** and **4.**[4] Formation of isomeric 5-hydroxyflavanones **3** and **4** suggested that **1** was 2′,6′-dihydroxy-4′,5′-dimethoxychalcone. The MS showed *m/e* (M^+, 300 base peak) and fragments 285, 233, 196, 181, 168, 104 and 77, which agreed with the structure **1.** Recently, a compound having structure **1,** called pashanone has been reported by Seshadri *et al.* from *Didymocarpus pedicellata.*[5] Our data agree well with those of pashanone.

Compound **2.** Compound **2** was obtained as a yellowish red crystalline solid (m.p. 152°, $C_{16}H_{14}O_4$, M^+ 270, yield 0·2%) from benzene eluate. The properties and spectral data were similar to those of **1** and suggested that **2** was also a chalcone with chelated hydroxyl

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[2] VENKATARAMAN, K. (1962) *The Chemistry of Flavonoid Compounds* (GEISSMAN, T. A. ed.) pp. 70–106, Pergamon Press, Oxford.
[3] JURD, L. See Reference (2), pp. 107–155.
[4] AIYAR, S. N., ISHWAR DAD and SESHADRI, T. R. (1957) *Proc. Ind. Acad. Sci.* **46A,** 238.
[5] AGARWAL, S. C., ANIL BHASKAR and SESHADRI, T. R. (1973) *Indian J. Chem.* **11,** 9.

group(s). It gave a diacetate (m.p. 143°). On treatment with acid (1 hr, 4% alcoholic HCl), **2** gave a colourless crystalline compound **5** (m.p. 101°), which was identified as 5-hydroxy-7-methoxyflavanone (pinostrobin). Hence **2** has been assigned the structure 2',6'-dihydroxy-4'-methoxychalcone. MS is in complete agreement with the assigned structure.

A small amount of (±) pinostrobin was also isolated from the light petroleum extract. Presumably this has been formed from **2** during isolation.

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FLAVONOIDS FROM *ALNUS CRISPA*, *A. JAPONICA*, *A. KOEHNEI* AND *A. SINUATA*

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Key Word Index—*Alnus* species; Betulaceae; bud excretion; flavonoid aglycones.

Plants. Alnus crispa Pursh.; *A. japonica* Sieb. et Zucc.; *Alnus x koehnei* Call.; *A. sinuata* Rydbg. *Source.* Botanic gardens of Darmstadt (*A. crispa*, *A. koehnei*) and Heidelberg (*A. japonica*, *A. sinuata*). *Previous work.* Two flavones from *Alnus japonica*;[1] comp.[2]

Present work. Lipophilic material, excreted by winter buds of all the *Alnus* species examined contains, besides triterpenoids, a number of flavonoid aglycones.

RESULTS

Alnus crispa. The bud excretion of this tree contains: kaempferol 3,7-dimethyl ether (kumatakenin), quercetin 3,7-dimethyl ether and quercetin-3,7,4'-trimethyl ether (ayanin).

Alnus japonica. Buds of this species produce many more flavonoids. The occurrence of the rare compounds luteolin 7,4'-dimethyl ether (pilloin) and scutellarein-6,7,4'-trimethyl ether (salvigenin) has already been reported.[1] Further aglycones are: kaempferide, isohamnetin, rhamnazin, quercetin-7,3',4'-trimethyl ether, the 3,6,4'-trimethyl ether of 6-hydroxykaempferol (3-methylbetuletol), acacetin, apigenin-7,4'-dimethyl ether and scutellarein-6,4'-dimethyl ether (pectolinarigenin).

Alnus koehnei. The following compounds were found: kaempferol, kaempferide, rhamnetin, isorhamnetin, quercetin-3,7-dimethyl ether, quercetin-3,3'-dimethyl ether, quercetin-7,3',4'-trimethyl ether; the 3,6-dimethyl ether, 6,4'-dimethyl ether (betuletol) and 3,6,4'-trimethyl ether of 6-hydroxykaempferol; quercetagetin-3,6,4'-trimethyl ether (centaureidin); acacetin and salvigenin.

Alnus sinuata. Buds contain only: kumatakenin, quercetin-3,7-dimethyl ether and genkwanin.

[1] WOLLENWEBER, E. and WASSUM, M. (1972) *Tetrahedron Letters*, 797.
[2] WOLLENWEBER, E., FAVRE-BONVIN, J. and JAY, M. (1974) *Phytochemistry*, **13**, (in press).