Flavaspidic acid-*PB* (III). $C_{23}H_{28}O_8$, m.p. 154–6° (yellow powder from *n*-hexane). IR ν_{max}^{KBr} cm^{-1} 3520, 3230 (OH), 2960 (methylene), 1640–1610 (enolic 1,3-diketo system or 2-hydroxyarylketone), 1195, 1153. UV λ_{max}^{EtOH} nm (log ϵ) 223 (4·94), 299 (4·79), 349 (4·93). UV $\lambda_{max}^{EtOH+NaOH}$ nm (log ϵ) 239 (4·79), 317 (5·00). R_f 0·14 on TLC in $CHCl_3$–MeOH–H_2O (7:3:1, lower) spot color gave orange-red with diazotized benzidine and dark brown with $FeCl_3$. The NMR spectrum (NMR analysis in pyridine-d_5 using TMS as internal reference showed ppm) shows signal attributable to: 0·90 (3H, *t* $-COCH_2CH_2C\underline{H}_3$), 1·25 (3H, *t* $-COCH_2C\underline{H}_3$), 1·56 (6H, *s gem*-dimethyl), about 1·85 (2H, *m* $-COCH_2C\underline{H}_2Me$), 2·38 (3H, *s* aromatic $C\underline{H}_3$), 3·26 (4H, *m* $-COC\underline{H}_2CH_2C\underline{H}_3$, $-COC\underline{H}_2CH_3$), 3·99 (2H, *s* methylene bridge between propionylfilicinic acid and methylphlorobutyrophenone), 9·33 (5H, *br* OH) quenched by addition of D_2O. The MS, *m/e* 432 (M^+), significant peaks at *m/e* 222, 210, 193, 167.

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BIFLAVONES IN THE LEAVES OF TWO *JUNIPERUS* PLANTS

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Key Word Index—*Juniperus horizontalis*; *Juniperus recurva*; Cupressaceae: biflavones; sciadopitysin; 7,7″-di-*O*-methylcupressuflavone

A number of *Juniperus* plants has already been examined[1–3] for biflavones. We now report the isolation of sciadopitysin[4] (I, 7,4′,4‴-tri-*O*-methylamentoflavone) from *Juniperus horizontalis* Moench[5] and 7,7″-di-*O*-methylcupressuflavone[6,7] (II) from *J. recurva* Buch.-Ham.[5] Some other biflavones including cupressuflavone and its monomethyl ether are detected in the leaf extracts of the two plants by TLC examinations. This constitutes the

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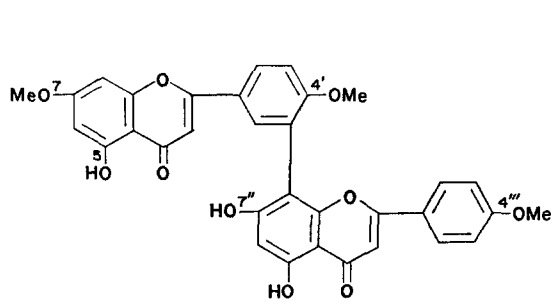
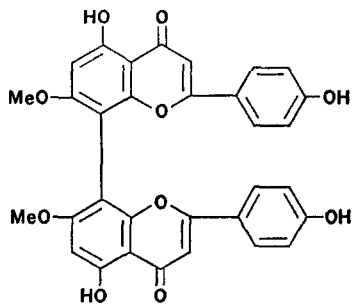
first example of the occurrence and isolation of cupressuflavone and its methyl ethers in *Juniperus* plants.



(I)



(II)

The separation and detection of biflavones from the leaf extracts were carried out by a reported method.[7,8] The purified leaf extract obtained from *J. horizontalis* gave four bands termed as JH1, JH2, JH3 and JH4 on a preparative TLC corresponding to amentoflavone and its mono-, di- and tri-methyl ethers respectively. JH1 was found to be amentoflavone because on methylation it showed only one spot on TLC[9] corresponding to amentoflavone hexamethyl ether ($AmMe_6$). JH2 and JH3 were considered to be hinokiflavone and its monomethyl ether respectively because on methylation each of them showed one spot of kinokiflavone pentamethyl ether ($HiMe_5$) on TLC.[9] However, on methylation followed by preparative TLC JH4 gave two compounds identified as $AmMe_6$ and $HiMe_5$ (m.m.p. and NMR spectra). Therefore, JH4 was considered to be a mixture of amentoflavone trimethyl ether and hinokiflavone dimethyl ether. On fractional recrystallizations JH4 gave a major compound, whose acetate, m.p. 261–262° was identified as sciadopitysin triacetate (m.m.p. and NMR spectra).

On similar treatments the purified extract obtained from the dried leaves of *J. recurva* gave three bands termed as JR1, JR2 and JR3 on TLC corresponding to amentoflavone and its mono- and di-methyl ethers respectively. On the basis of observations of methylation followed by TLC examinations it was considered that JR1 is a mixture of amentoflavone and cupressuflavone and that JR2 is a mixture of amentoflavone monomethyl ether, cupressuflavone monomethyl ether and hinokiflavone. On similar basis JR3 was found to be a mixture of amentoflavone dimethyl ether and cupressuflavone dimethyl ether. Therefore, JR3 (65 mg) was subjected to a countercurrent distribution between methyl ethyl ketone and a borate buffer of pH 9·5. A major component (40 mg) was obtained from the Nos. 101–150 tubes of 350 transfers and characterized as 7,7''-di-*O*-methylcupressuflavone (II) by comparison of the NMR spectrum of its acetate, m.p. 273–275° with that of an authentic sample[7] and no m.p. depression on admixture of the acetates, whereas a minor component (Nos. 61–95) could not be characterized because of insufficient material.

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