Phytochemistry, Vol. 23, No. 3, pp. 703–704, 1984.
Printed in Great Britain.

0031-9422/84 \$3.00 + 0.00

TWO ISOMERIC FLAVANONES FROM *VITEX NEGUNDO**

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(*Revised received* 10 *September* 1983)

Key Word Index—*Vitex negundo*; Verbenaceae; flavanones; 5,3′-dihydroxy-6,7,4′-trimethoxyflavanone; 5,3′-dihydroxy-7,8,4′-trimethoxyflavanone.

Abstract—Two new flavanoids, characterized as 5,3′-dihydroxy-7,8,4′-trimethoxyflavanone and 5,3′-dihydroxy-6,7,4′-trimethoxyflavanone, have been isolated from the leaves of *Vitex negundo*.

INTRODUCTION

As a part of a screening programme, we undertook a thorough chemical investigation of the leaves of *Vitex negundo* L. from which 5,3′-dihydroxy-3,6,7,4′-tetramethoxyflavone [1] and 5-hydroxy-3,6,7,3′,4′-pentamethoxyflavone [2] have earlier been obtained. We now report the isolation and structure elucidation of two hitherto unknown flavanones, **1a** and **2a**.

RESULTS AND DISCUSSION

Compound **1a**, a light yellow amorphous material forming a crystalline diacetate (**1b**), exhibited a UV maximum at 288 nm which underwent a bathochromic shift of 22 nm with aluminium chloride. No significant change on further addition of hydrochloric acid indicated the presence of a 5-hydroxyl group in the flavanone nucleus.

In the ^{1}H NMR spectrum, the one-proton signal at δ11.96 (exchangeable with D_2O) confirmed a chelated hydroxyl group at C-5. Presence of a set of signals comprising one-proton double doublets at δ5.36 (J = 12, 4 Hz), 3.08 (J = 16, 12 Hz) and 2.82 (J = 16, 4 Hz) was in conformity with the normal flavanone skeleton. Three methoxy signals were also observed at δ3.76, 3.86 and 3.88, while an exchangeable signal at δ5.70 signified a phenolic group. In the aromatic region, a singlet at δ6.09 indicated the A ring to be trisubstituted, while a three-proton multiplet at δ6.88–7.04 could be ascribed to ring B which must be disubstituted.

The mass spectrum of the diacetate **1b** (M^+, m/z 430) showed, apart from successive loss of two molecules of ketene, prominent retro-Diels–Alder fragmentation peaks at m/z 196 and m/z 150. The spectrum thus not only supported the above substitution pattern but also indicated the nature of the substituents of rings A (monohydroxy dimethoxy) and B (monohydroxy monomethoxy) in **1a**. The location of hydroxyl and methoxy groups in ring B was then deduced from the ^{1}H NMR comparison of **1a** and **1b** with vanillyl and isovanillyl alcohols and their acetates.

The 5-hydroxy-7,8-dimethoxy substitution pattern in ring A was suggested by the chemical shift (δ6.30) of the aromatic proton singlet of **1b** which was almost identical with that (δ6.33) of 5-acetoxy-7,8-dimethoxyflavanone [3]. The structure of the compound could thus be established as 5,3′-dihydroxy-7,8,4′-trimethoxyflavanone (**1a**).

Compound **2a**, a yellowish crystalline material, could be inferred to be a 5-hydroxyflavanone like **1a** on the basis of the virtually identical UV and ^{1}H NMR spectra. The mass and ^{1}H NMR spectra of the corresponding diacetate (**2b**) indicated the isomeric nature of the two compounds with identically substituted ring B. The difference between the two isomers obviously lies in the substitution pattern of ring A. Now, the significant deshielding (0.35 ppm) of the aromatic proton singlet on acetylation indicated the location of this proton *ortho* or *para* to the 5-hydroxyl group. The structure of compound **2a** must then be 5,3′-dihydroxy-6,7,4′-trimethoxyflavanone since the possible alternative structure has already been established for **1a**.

EXPERIMENTAL

All mps are uncorr. UV: 95% EtOH. IR: KBr. ^{1}H NMR: 100 MHz, $CDCl_3$, δ values in ppm downfield from TMS; MS: 70 eV.

Plant material. Vitex negundo. A voucher specimen identified by the National Botanical Garden (Calcutta) is available in the herbarium of the suppliers Messrs United Chemicals and Allied Products, Calcutta.

Isolation of the constituents. Dried powdered leaves of *V. negundo* (5 kg) were extracted successively with petrol and $CHCl_3$ in a Soxhlet. The $CHCl_3$ extract was concd and the residue chromatographed over silica gel. Petrol–$CHCl_3$ (60:40) eluate afforded the two flavones; the mixture (100 mg) of **1a** and **2a** obtained with petrol–$CHCl_3$ (1:1) was resolved by prep. TLC on silica gel plates using the solvent C_6H_6–Me_2CO (9:1).

5,3′-Dihydroxy-7,8,4′-trimethoxyflavanone (**1a**). Amorphous powder. UV λ_{max} nm (log ε): 210 (4.07), 230 sh (3.92), 288 (3.86), 340 (3.26); +$AlCl_3$ 215 (4.37), 310 (4.13), 365 (3.86); +$AlCl_3$

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*Part 74 in the series "Studies on Indian Medicinal Plants". For Part 73 see Chakravarty, A. K., Das, B. and Pakrashi, S. C. (1983) *Phytochemistry* **22**, 2843.

+ HCl 215 (4.35), 308 (4.12), 360 (3.90); + NaOH 210 (4.19), 285 (3.84), 360 (3.58); + NaOAc 210 (4.98), 285 (4.22), 340 (3.68). ^{1}H NMR 2.82 (1H, *dd*, $J = 4$, 16 Hz), 3.08 (1H, *dd*, $J = 12$, 16 Hz), 3.76 (3H, *s*), 3.86 (3H, *s*), 3.88 (3H, *s*), 5.36 (1H, *dd*, $J = 4$, 12 Hz), 5.70 (1H, *s*), 6.09 (1H, *s*), 6.88–7.04 (3H, *m*), 11.96 (1H, *s*).

Acetate of **1a**. Acetylation of **1a** with C_5H_5N–Ac_2O at room temp overnight yielded a crude viscous mass which on crystallization from $CHCl_3$–petrol afforded yellowish crystals of **1b**, mp 78–80°. IR ν_{max} cm^{-1}: 1770 (ester), 1680 (C=O), 1620 (C=C); MS *m/z* (rel. int.): 430 $[M]^+$ (9), 388 (12.5), 346 (2.5), 196 (100), 181 (30), 167 (20), 150 (17.5); ^{1}H NMR: 2.30 (3H, *s*, COMe), 2.36 (3H, *s*, COMe), 2.76 (1H, *dd*, $J = 4$, 16 Hz, H-3_{eq}), 3.02 (1H, *dd*, $J = 12$, 16 Hz, H-3_{ax}), 3.80 (3H, *s*, OMe), 3.82 (3H, *s*, OMe) 3.88 (3H, *s*, OMe), 5.44 (1H, *dd*, $J = 4$, 12 Hz, H-2), 6.30 (1H, *s*, H-6), 6.98 (1H, *d*, $J = 8$ Hz, H-5′), 7.16 (1H, *d*, $J = 4$ Hz, H-2′), 7.30 (1H, *dd*, $J = 4$, 8 Hz, H-6′).

5,3′-Dihydroxy-6,7,4′-trimethoxyflavanone (**2a**). Crystallized from $CHCl_3$–petrol as yellowish needles, mp 136–138°. UV λ_{max} nm (log ε): 210 (4.52), 228 (4.47), 285 (4.45), 340 (3.74); + $AlCl_3$ 218 (4.75), 306 (4.57), 358 (4.06); + $AlCl_3$ + HCl 222 (4.76), 310 (4.59), 358 (4.18); + NaOH 210 (4.75), 238 sh (4.51), 290 (4.41), 370 (4.11); + NaOAc 210 (4.75), 230 (4.54), 285 (4.45), 335 (3.88); ^{1}H NMR: 2.76 (1H, *dd*, $J = 4$, 16 Hz, H-3_{eq}), 3.08 (1H, *dd*, $J = 12$, 16 Hz, H-3_{ax}), 3.82 (3H, *s*, OMe), 3.86 (3H, *s*, OMe), 3.90 (3H, *s*, OMe), 5.32 (1H, *dd*, $J = 4$, 12 Hz, H-2), 5.70 (1H, *s*, 3′-OH), 6.09 (1H, *s*, H-8), 6.88–7.04 (3H, *m*, H-2′, H-5′ and H-6′).

Acetate of **2a**. On treatment with C_5H_5N–Ac_2O at room temp overnight **2a** afforded a crude viscous material, crystallized from $CHCl_3$–petrol to yield **2b** as needles, mp 118–120°. IR ν_{max} cm^{-1}: 1770 (ester), 1680 (C=O), 1620 (C=C); MS *m/z* (rel. int.): 430 $[M]^+$ (10), 388 (14), 346 (3), 196 (100), 181 (40), 167 (15), 150 (18); ^{1}H NMR: 2.30 (3H, *s*, COMe), 2.42 (3H, *s*, COMe), 2.68 (1H, *dd*, $J = 4$, 16 Hz, H-3_{eq}), 3.00 (1H, *dd*, $J = 12$, 16 Hz, H-3_{ax}), 3.74 (3H, *s*, OMe), 3.82 (3H, *s*, OMe), 3.86 (3H, *s*, OMe), 5.36 (1H, *dd*, $J = 4$, 12 Hz, H-2), 6.44 (1H, *s*, H-8), 6.98 (1H, *d*, $J = 8$ Hz, H-5′), 7.14–7.3 (2H, *m*, H-2′ and H-6′).

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Phytochemistry, Vol. 23, No. 3, pp. 704–705, 1984.
Printed in Great Britain.
0031-9422/84 \$3.00 + 0.00

ABIESIN, A BIFLAVONOID OF *ABIES WEBBIANA*

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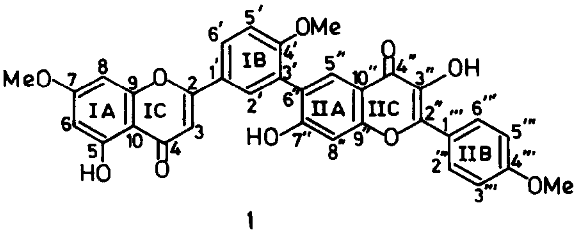
(*Received* 9 *August* 1983)

Key Word Index—*Abies webbiana*; Pinaceae; biflavonoids; 5,3″,7″-trihydroxy-7,4′,4‴-trimethoxy-(3′,6″)-biflavone.

Abstract—Abiesin, a new biflavonoid, has been isolated from the leaves of *Abies webbiana* and identified as 5,3″,7″-trihydroxy-7,4′,4‴-trimethoxy-(3′,6″)-biflavone.



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This paper reports the isolation of a new biflavone, abiesin, and its characterization as 5,3″,7″-trihydroxy-7,4′,4‴-trimethoxy-(3′,6″)-biflavone (**1**). The compound was isolated from the ether soluble ethyl acetate extract of the leaves of *A. webbiana* Lindl. The new compound, $C_{33}H_{24}O_{10}$, (M^+ 580), mp 281–282°, $[\alpha]_D^{24}$ −3.6° (pyridine) exhibited UV absorption maxima characteristic of flavone [λ_{max}^{EtOH} (log ε): 272 (4.52) and 332 nm (4.46)]. The bathochromic shift observed on addition of $AlCl_3$ was characteristic of the presence of a 3,5-dihydroxy system, [$\lambda_{max}^{EtOH + AlCl_3}$ (log ε): 283 (4.81), 339 (4.78) and 395 nm (4.56)] [1] while with NaOAc the compound showed shifts [$\lambda_{max}^{EtOH + NaOAc}$ (log ε) 272 (4.52), 283 (4.51), 315 sh (4.43) and 350 nm (4.42)] for a 7-hydroxyl group [2]. The absence of *ortho*-dihydroxyl groups in both flavonoid moieties was apparent from the absence of a

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