+ 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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ABIESIN, A BIFLAVONOID OF *ABIES WEBBIANA*

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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.

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

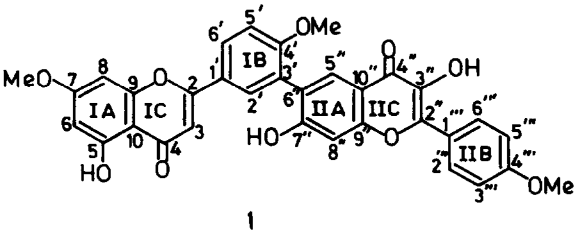

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Table 1. ^{13}C NMR data of abiesin (1) in DMSO-d_6

Sl. No.	Carbon members	Ring	Chemical shifts in ppm (δ)	Multiplicity	Ring	Chemical shifts in ppm (δ)	Multiplicity
1	C-2	IC	163.57	*s*	IIC	165.12	*s*
2	C-3	IC	103.20§	*d*	IIC	145.76	*s*
3	C-4	IC	182.01	*s*	IIC	181.86	*s*
4	C-5	IA	162.16†	*s*	IIA	119.06	*d*
5	C-6	IA	98.06	*d*	IIA	103.20§	*s*
6	C-7	IA	161.13‡	*s*	IIA	163.01†	*s*
7	C-8	IA	92.64	*d*	IIA	93.01	*d*
8	C-9	IA/IC	157.28	*s*	IIA/IIC	154.32	*s*
9	C-10	IA/IC	104.73§	*s*	IIA/IIC	103.82§	*s*
10	C-1′	IB	122.79	*s*	IIB	122.41	*s*
11	C-2′	IB	128.23	*d*	IIB	127.70	*d*
12	C-3′	IB	121.67	*s*	IIB	114.46	*d*
13	C-4′	IB	160.65‡	*s*	IIB	160.54‡	*s*
14	C-5′	IB	111.73	*d*	IIB	114.46	*d*
15	C-6′	IB	130.84	*d*	IIB	127.70	*d*
	MeO						
16	C-4′	IB	55.91*	*q*	IIB	55.91*	*q*
17	C-7	IA	55.41*	*q*			

*, †, ‡, §Values may be interchanged.

bathochromic shift on addition of boric acid to the NaOAc solution. The nature of the shifts observed [$\lambda_{\max}^{\mathrm{EtOH}+\mathrm{NaOMe}}$ (log ε): 226 (4.59), 286 (4.62) and 391 nm (4.20)] with NaOMe solution indicated the presence of both 7- and 3-hydroxyl groups and also suggested that the 4′-hydroxyl groups of both B-rings were substituted [3–5].

The 400 MHz ^{1}H NMR spectrum (DMSO-d_6) showed the presence of an AA′BB′ system (2H, *d* each, *J* = 9.00 Hz) at δ6.92 (H-3‴ and H-5‴) and 7.59 (H-2‴ and H-6‴), and an ABX system with the signals at δ7.35 (H-5′, 1H, *d*, *J* = 9.00 Hz), 8.07 (H-2′, 1H, *d*, *J* = 2.5 Hz) and 8.22 (H-6′, *dd*, *J* = 2.5 and 9.00 Hz) in the aromatic region. Two *meta*-coupled protons at C-6 and C-8 were discernible at δ6.35 and 6.78 (2H, *d* each, *J* = 2.5 Hz) respectively and an uncoupled proton at 6.41 (H-3). The one proton singlets (exchangeable with D_2O) each at δ10.84 and 10.09 were attributed to the hydroxyls at C-7″ and C-3″ and that at δ13.04 to the chelated hydroxyl at C-5. The three proton singlets each at δ3.80, 3.77 and 3.72 confirmed the presence of three methoxyls at C-7, C-4′ and C-4‴. The *para*-coupled protons (H-5″ and H-8″ of ring IIA, 1H, *d* each, *J* = 0.9 Hz) appeared at δ7.30 and 6.90. The very fact that the H-5″ appeared further upfield (δ7.30) than expected (~ δ8.00) [6] confirmed the hydroxyl at C-3″. Chelation of the latter with the 4″-carbonyl eliminated the effect of the *peri*-carbonyl on H-5″ [6].

The mass fragmentation pattern was in conformity with the proposed structure, the significant peaks appearing at *m/z* 580 (M^+, 100%), 565, 551, 417, 267 and 135. The structure 1 received unambiguous proof from the ^{13}C NMR data of the compound (Table 1). This is the first report of a biflavonoid from a member of the Pinaceae.

EXPERIMENTAL

Plant material. The leaves of *A. webbiana* were collected from the Botanic Garden, Sibpur, Howrah. A voucher specimen (No. Aw-1) has been preserved in our laboratory.

Isolation and properties of 5,3″,7″-trihydroxy-7,4′,4‴-trimethoxy-(3′,6″)-biflavone (1). The dried and powdered leaves (2 kg) of *A. webbiana* were extracted with EtOAc in a Soxhlet under refluxing conditions (40 hr). The EtOAc extract was concd and chromatographed over silica gel (BDH, 60–120 mesh). The C_6H_6–$CHCl_3$ (1:3) eluates afforded 1 as yellow crystals (yield 0.001%), mp 281–282° (EtOH), $[\alpha]_D^{24}$ −3.6° (pyridine); IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3200 (*br*, OH), 1660 (chelated > CO) and 1610, 1580, 1500 (aromatic); MS: *m/z* 580 (M^+, base peak), 565, 551, 417, 267, 167 and 135.

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