m.p. 246–248° and 256–258°, UV λ_{max}^{EtOH} nm (log ε): 274 (4.28), 310_i (4.08)[4], 326 (4.13), 360 (4.09)) (lit.[1] m.p. 242–244° and 254–256°) (the triacetate (X): m.p. 170–171°; lit.[1] m.p. 167–168°), whose identity with the natural product was confirmed by mixed m.p. determination and UV- and IR-spectral comparison.

II was also obtained from 3, ω-dimethoxy-2, 4, 6-trihydroxyacetophenone (XI) in a manner similar to that described earlier[2,6]. Condensation of XI with IV gave a mixture of flavones. After partial acetylation[7], the reaction mixture was purified by recrystallization from ethyl acetate to give 7-acetoxy-4′-benzyloxy-3, 6-dimethoxy-5-hydroxyflavone (XII, m.p. 209–210°, Found: C, 67.47; H, 4.86. $C_{26}H_{22}O_8$ requires: C, 67.52; H, 4.80%). The residue of the mother liquor was hydrolyzed with alkali to give 4′-benzyloxy-5, 7-dihydroxy-3, 8-dimethoxyflavone (XIII, m.p. 193–194°, UV λ_{max}^{EtOH} nm (log ε): 275.5 (4.39), 320 (4.25). Found: C, 68.54; H, 4.68. $C_{24}H_{20}O_7$ requires: C, 68.56; H, 4.80%). Debenzylation of XIII afforded II, which was identical with the sample described above.

Treatment of XII with alkali, followed by debenzylation, gave 3, 6-dimethoxy-5, 7, 4′-trihydroxyflavone, an isomer of II, (XIV, m.p. 227–228°, UV λ_{max}^{EtOH} nm (log ε): 271 (4.16), 340 (4.22). Found: C, 61.93; H, 4.21. $C_{17}H_{14}O_7$ requires: C, 61.82; H, 4.27%) (the triacetate (XV): m.p. 170–172°). It has been observed[6,8] that in the NMR-spectra of the aromatic proton of the ring A in flavonoid, a signal of C_6-H appeared at upper field than that of C_8-H. Due to this fact, an aromatic proton signal of XV appearing at 7.31 (singlet) corresponds to C_8-H and a signal of X at 6.78 corresponds to C_6-H[9].

Zusammenfassung. 3, 8-Dimethoxy-5, 7, 4′-trihydroxyflavon und 3, 6-Dimethoxy-5, 7, 4′-trihydroxyflavon wurden synthetisiert.

K. Fukui, T. Matsumoto,
M. Nakayama and T. Horie

*Department of Chemistry, Faculty of Science,
Hiroshima University, and Department of
Applied Chemistry, Faculty of Engineering,
University of Tokushima (Japan),
16 December 1968.*

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[6] K. Fukui, T. Matsumoto, S. Nakamura, M. Nakayama and T. Horie, Experientia *24*, 108 (1968); Bull. chem. Soc. Japan *41*, 1413 (1968). – K. Fukui, M. Nakayama and T. Horie, Experientia *24*, 769 (1968). – T. Horie, Experientia *24*, 880 (1968).

[7] M. Simokoriyama, Bull. chem. Soc. Japan *16*, 284 (1941).

[8] C. A. Henrick and P. R. Jefferies, Aust. J. Chem. *17*, 934 (1964).

[9] The NMR-spectra were measured with Hitachi R-20 NMR-spectrometer, using tetramethylsilane as internal standard (δ-value in $CDCl_3$).

The Structure of WI3, the First Optically Active Biflavone of the Amentoflavone Series

We have previously reported the isolation from *Araucaria cookii* of the first optically active naturally occurring biflavones, these being members of the cupressuflavone series[1]. From the same source we have isolated a new substance WI3, m.p. 273°, $C_{34}H_{26}O_{10}$ (mol. wt. 594.151227), $[\alpha]_D^{34°}$ (pyridine-ethanol) +41° λ_{max} (ethanl) 274,334 nm, diacetate (mol. wt. 678.176231), m.p. 220–225°, $C_{38}H_{30}O_{12}$ and a dimethyl ether m.p. 217–218°, $C_{36}H_{30}O_{10}$ (mol. wt. 622.182339).

The UV-spectra of these compounds and the usual colour tests indicated that the molecules were flavonoid in nature. The mass spectrum of the dimethyl ether showed a large peak at *m/e* 311, indicating that each flavonoid unit had 3 methoxy groups.

The NMR-spectrum of the substances made it clear that WI3 and its derivatives are not members of the cupressuflavone series[1]. The dimethyl ether was investigated in detail, using double irradiation techniques, and it was possible to assign a τ value to every proton, with the exception of H-3 and H-3″ which could not be distinguished (see Table). In particular, associated with rings B and E, there is evidenced an A_2B_2 system and also an ABX system. Thus a ring B of a flavone unit is associated with a linkage to ring A of another such unit. In particular the τ values show that C-3′ is linked to C-6″ or C-8″.

By analogy with cupressuflavone hexamethyl ether, the single methoxy group showing below τ 6.0 is assigned to the 5″-OMe, attached to an 8-linked flavone unit, whilst the protons on ring A are assigned by analogy with 5, 7-dimethoxyflavone[2]. All methoxy groups were moved upfield on change of solvent from chloroform to benzene, as with cupressuflavone hexamethyl ether[1], showing that every methoxy group has a least one *ortho*-proton, and therefore a C-8 rather than a C-6 linkage is indicated. An authentic sample of (±)-amentoflavone hexamethyl ether was obtained[3] and shown to give an NMR-spectrum identical with WI3 dimethyl ether in all respects including solvent dependent methoxy shifts. The IR-, UV- and mass spectrum were also identical.

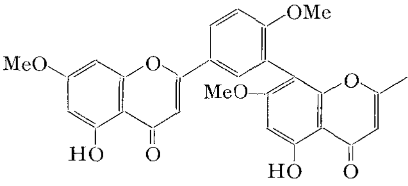
WI3 diacetate has 3 singlets, 2 like those in the dimethyl ether at τ 3.50 and τ 3.44, but the other had moved downfield to τ 3.27, a shift of the order to be expected of H-6 on acetylation of a 5-hydroxy group of

Proton	Methyl WI3	Acetyl WI3	WI3
H-2′	2.10q $J_1 = 8$ c/s $J_2 = 3$ c/s	2.08q $J_1 = 9$ c/s $J_2 = 3$ c/s	2.08q
H-3′	2.88d $J = 8$ c/s	2.86d $J = 9$ c/s	2.89d $J = 9$ c/s
H-6′	2.16d $J = \sim 3$ c/s	2.13d $J = \sim 3$ c/s	2.16d
H-2‴ (6‴)	2.62d $J = \sim 9$ c/s	2.64d $J = 9$ c/s	2.56d $J = 9$ c/s
H-3‴ (5‴)	3.24d $J = \sim 9$ c/s	3.23d $J = 9$ c/s	3.21d $J = 9$ c/s
H-3	3.48s	3.50	3.50
H-3″	3.42s	3.44	3.44
H-6″	3.38s	3.27	3.42
H-6	3.66d $J = 3$ c/s	3.42d $J = 3$ c/s	3.68d $J = 3$ c/s
H-8	3.52d $J = 3$ c/s	3.19d $J = \sim 3$ c/s	3.60d $J = 3$ c/s
OMe	5.94, 6.08 6.12, 6.18, 6.25 6.27	6.16 (6H) 6.23, 6.25	6.17, 6.19 6.22, 6.24
OAc	–	7.52, 7.59	–
OH	–	–	−2.56, −3.07

Figures given in τ values. Methyl WI3 and Acetyl WI3 run in $CDCl_3$, WI3 in $(CD_3)_2CO$ with Me_4Si as internal standard.

the ring A of a flavone, but too small for that expected of H-8[2]. This confirms that such shifts, observed in the monomers, may also be used in the dimers. The structure of WI3 itself was made absolutely clear as this compound had 2 peaks at τ-2.56 and τ-3.07, exchangeable with deuterium oxide. There are thus present 2 strongly hydrogen-bonded hydroxy groups, which must be assigned to a 5-OH and a 5″-OH.

WI3 therefore is (+)-4′, 4,‴ 7, 7″-tetra-*O*-methyl-amentoflavone (I). The racemate corresponding to WI3 has been produced from (±)-amentoflavone[4,5] and has also been isolated by Hodges[3]. Further, WI3 is the first optically active member of the amentoflavone series to be characterized.



(I)

The isolation of optically active kawaflavone[5] from the same source as well as amentoflavone itself will be reported in detail in a full paper.

Résumé. Araucaria cookii donne les premières bisflavones optiquement actives de la série des amentoflavones. Une analyse complète des spectra de RNM des substances de cette série a été faite. Les déplacements méthoxyliques induits par le solvant s'ajoutent aux résultats de l'analyse de RNM et les confirment.

A. PELTER, R. WARREN, M. ILYAS,
J. N. USMANI, S. P. BHATNAGAR,
R. H. RIZVI, M. ILYAS and W. RAHMAN

University of Manchester, Department of Chemistry, Manchester 13 (England) and
Aligarh Muslim University, Aligarh (India),
16 December 1968.

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[1] M. ILYAS, J. N. USMANI, S. P. BHATNAGAR, M. ILYAS, W. RAHMAN and A. PELTER, Tetrahedron Lett. 5515 (1968).

[2] J. MASSICOT, J. P. MARTHE and S. HEITZ, Bull. Soc. chim. Fr. 1962 (1963); 2712 (1964).

[3] We thank Dr. N. KAWANO, University of Nagasaki, for this and other samples.

[4] R. HODGES, Aust. J. Chem. *18*, 1491 (1965).

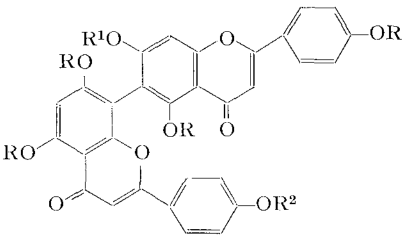
[5] W. BAKER, A. C. M. FINCH, W. D. OLLIS and K. W. ROBINSON, J. chem. Soc. (London) 1487 (1963).

The Isolation and Characterization of Two Members of a New Series of Naturally Occurring Biflavones

Further to our studies[1,2] of biflavones produced by *Araucariaceae*, we here report the isolation from *Agathis palmerstonii* of 2 optically active biflavones of the hitherto unknown 6,8-linked series.

The first compound, WA^{I}, $C_{31}H_{20}O_{10}$ (mol. wt. 552.106312) had m.p. > 320°, $[\alpha]_D^{34°}$ (pyridine-ethanol) −50°, λ_{max} (EtOH) 278, 339 nm; (*M*/500 NaOEt) 285, 372, 398 nm. It gave a penta-acetate, WA^{II}, $C_{41}H_{30}O_{15}$ (mol. wt. 762.158625), m.p. 165–168° and a pentamethyl ether, WA^{III}, $C_{36}H_{30}O_{10}$ (622.185718), m.p. 162–164°. The second compound WA^{VII}, $C_{32}H_{22}O_{10}$ (mol. wt. 566.121348) had m.p. 212–213°, $[\alpha]_D^{34°}$ (pyridine-ethanol) −55°, λ_{max} (EtOH), 277, 337 nm; (*M*/500 NaOEt) 287, 382 (inflex.), 403 nm, yielding a tetra-acetate WA^{VIII}, $C_{40}H_{30}O_{14}$ (mol. wt. 734.162447) and the same methyl ether WA^{III}, as given by WA^{I}.

The UV-spectra and colour tests indicate a flavone structure and therefore WA^{III} represents a biflavone hexamethyl ether. The only peak other than the molecular ion of any significance in the mass spectrum of WA^{III} is at *m/e* 311, indicating that there are 3 methoxy groups in each flavone portion of the molecule. The NMR-spectrum, however, shows the molecule is not symmetrical (see Table), nor are the B or E rings concerned in linking the 2 flavonoid units as there are present 2 sets of A_2B_2 protons centred at τ 2.99, 2.12 (J = 9 c/s) and τ 3.22 and 2.63 (J = 9 c/s), the pairings being proven by double irradiation experiments. The coupling constant is characteristic of *ortho*-coupled protons. The linkage cannot be through C-3 or C-3″ as in both WA^{II} and WA^{III} there are 2 almost invariant protons at ~ τ 3.4–3.5. Moreover this linkage would lead to at least one *meta*-coupled pair associated with rings A or D, and none in fact is observed. This leaves only rings A and D implicated in the linkage, and as the compound is unsymmetrical (i.e. not 8,8″ nor 6,6″) the linkage must be 6,8″. WA^{III} is then unambiguously represented by (Id).



(Ia) R = R¹ = R² = H
(b) R = R² = H; R¹ = Me
(c) R = R² = Ac; R¹ = Me
(d) R = R¹ = R² = Me
(e) R¹ = R² = Me; R = H
(f) R¹ = R² = Me; R = Ac

Of the greatest interest was the behaviour of the 6 methoxy groups of (Id) on change of solvent from deuteriochloroform to benzene (see Figure). Five methoxy groups (with an *ortho*-hydrogen atom) behave as expected and show large upfield shifts. The methoxy group below τ 6.0 is identified as being the 5″-OMe by comparison with 8-linked biflavones of the cupressuflavone[1] series and the amentoflavone series[2]. One methoxy group is unique in that up to ~50% dilution with benzene no shift is seen and then a strong *downfield* shift is evidenced, a phenomenon seen in neither the amentoflavone nor cupressuflavone hexamethyl ethers. It is reasonable to assume that the methoxy group in question is the one

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[1] M. ILYAS, J. N. USMANI, S. P. BHATNAGAR, M. ILYAS, W. RAHMAN and A. PELTER, Tetrahedron Lett. 5515 (1968).

[2] A. PELTER, R. WARREN, M. ILYAS, J. N. USMANI, S. P. BHATNAGAR, R. H. RIZVI, M. ILYAS and W. RAHMAN, Experientia *25*, 350 (1969).