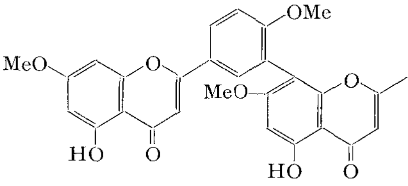
the ring A of a flavone, but too small for that expected of H-8[2]. This confirms that such shifts, observed in the monomers, may also be used in the dimers. The structure of WI3 itself was made absolutely clear as this compound had 2 peaks at τ-2.56 and τ-3.07, exchangeable with deuterium oxide. There 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.

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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).

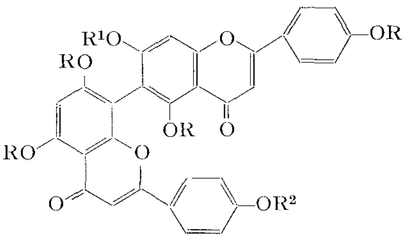
[5] W. Baker, A. C. M. Finch, W. D. Ollis and K. W. Robinson, J. chem. Soc. (London) 1487 (1963).

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 $\sim\tau$ 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) $R = R^1 = R^2 = H$
(b) $R = R^2 = H;\ R^1 = Me$
(c) $R = R^2 = Ac;\ R^1 = Me$
(d) $R = R^1 = R^2 = Me$
(e) $R^1 = R^2 = Me;\ R = H$
(f) $R^1 = R^2 = Me;\ R = Ac$

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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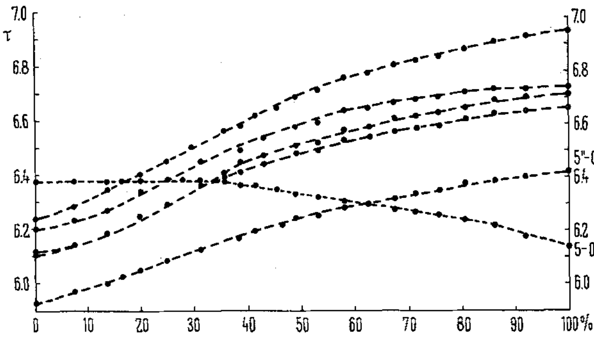
[1] M. Ilyas, J. N. Usmani, S. P. Bhatnagar, M. Ilyas, W. Rahman and A. Pelter, Tetrahedron Lett. 5515 (1968).

[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).

at C-5, flanked by ring D on one side and a carbonyl group on the other. This is confirmed by the upfield methoxy shift of 72 c/s for WA^{II} (7-OMe) and of 68 c/s and 75 c/s for WA^{VIII} (7,4'''-OMe). As the 5''-methoxy group at τ 5.95 also moves upfield, the only methoxy group unaccounted for is at C-5. This result supports structure (Id) and makes the method of methoxy shifts seem most suitable for sorting out the often vexed question of whether biflavonoids are 6- or 8-linked.

The allocation of τ values of protons to WA^{III} is not so certain. The singlet at τ 3.36 is assigned to H-6'' as this position of an 8-linked flavone is very similar to that of H-6 of cupressuflavone hexamethyl ether (τ 3.44) and 4',4''',7,7''-tetramethyl ether (τ 3.42 shifting on acetylation to τ 3.19). Similarly this proton shows at τ 3.41 in amentoflavone hexamethyl ether. Perforce the singlet at τ 3.09 is assigned to H-8, in line with the observation that H-6 in 5,7-dimethoxyflavone appears $\sim\tau$ 0.2 above H-8[3]. Similarly the protons assigned to ring E fit well for amentoflavone hexamethyl ether (τ 3.28, 2.68), 4',4''',7,7''-tetramethyl ether (τ 3.20, 2.56), cupressuflavone hexamethyl ether (τ 3.20, 2.62) and 4',4''',7,7''-tetramethyl ether (τ 3.16, 2.57). All these are on a ring B of a flavone unit linked to another via C-8. The A_2B_2 doublets at τ 2.19, 2.99 are assigned to the flavonoid unit linked at C-6, for which no models are available. It is not possible to distinguish H-3 and H-3''.



Change of solvent from deuteriochloroform to benzene.

Proton	WA^{I}	WA^{II}	WA^{III}	WA^{VII}	WA^{VIII}
H-2',6'	2.0d	2.08d	2.12d	2.19d	2.08d
H-3',5'	2.95d	2.62d	2.99d	2.91d	2.73d
H-2''',6'''	2.41d	2.50d	2.63d	2.34d	2.60d
H-3''',5'''	3.38d	2.94d	3.22d	3.07d	3.19d
H-3 H-3''	3.61, 3.40	3.42, 3.38	3.49, 3.47	3.59, 3.33	3.46, 3.38
H-6 H-8	3.28, 3.16	3.01, 3.00	3.36 3.09	3.24, 3.02	2.99, 3.02
OMe	6.13	6.20	5.95, 6.12 6.14, 6.22 6.26, 6.41	6.11, 6.20	6.21, 6.24
OAc	–	7.56, 7.66 7.76, 7.86 7.91	–	–	7.56, 7.67 7.86, 7.91
OH	0.8–1.2(3H) –3.07(1H) –3.3(1H)	–	–	0.7–1.0(2H) –3.04(1H) –3.3(1H)	–

WA^{II}, WA^{III}, WA^{VIII} run at 100 Mc in $CDCl_3$ as solvent; WA^{I}, WA^{VII} run in $(CD_3)_2CO$ as solvent, $SiMe_4$ internal standard. Values are on the τ scale. For all doublets, $J = 9$ c/s.

To WA^{II} is assigned structure (Ic). The singlet at τ 3.36 in WA^{III} has moved to τ 3.00 (or 3.01) showing 2 acetoxy groups are present on ring D[3]. This compares well with H-6'' of sciadiopitysin triacetate at τ 3.04 in an entirely similar environment[4]. H-6 of 5,7-diacetoxyflavone is at τ 3.15, H-8 being at τ 2.45[3]. Further confirmation that the single methoxy group is at C-7, comes in considering the situation if it were placed at C-7''. The proton at C-6'' in WA^{II} would then be expected at $\sim\tau$ 3.2 as in 4',4''',7,7''-tetra-*O*-methylcupressuflavone-5,5''-diacetate (τ 3.22), 7,7''-di-*O*-methylcupressuflavone-4',4''',5,5''-tetra-acetate (τ 3.19) and 4',4''',7,7''-tetra-*O*-methylamentoflavone-5,5''-diacetate (τ 3.27), and no protons are seen in this region. Both pairs of A_2B_2 sets are shifted downfield relative to WA^{III}, indicating 4'- and 4'''-acetoxy groups in WA^{II}. The methoxy shifts indicate no methoxy groups at C-5, and in WA^{I} itself there are certainly 2 hydrogen-bonded hydroxy groups at τ-3.07 and τ-3.3 as would be expected for 5- and 5''-hydroxy groups. Therefore WA^{I} itself must be represented by (Ib). To avoid a plethora of trivial names we propose that the parent compound (Ia) of the series be called 'agathisflavone' and hence WA^{I} is (–)-7-*O*-methylagathisflavone.

WA^{VII} must have the same skeleton and oxygenation patterns as WA^{I} as it yields WA^{III} on methylation. Turning to WA^{VIII}, similar arguments to those used above place one of the 2 methoxy groups at C-7 (see Table). In this compound the A_2B_2 system of ring E is at τ 3.22 and 2.63, very little moved from the same pair in WA^{III} (the other A_2B_2 pair having moved downfield). Hence the extra methoxy group of WA^{VIII}, as compared with WA^{II}, is at C-4''', assuming the original assignment of protons to ring E of WA^{III} to be correct. The most probable structure of WA^{VII} is therefore (–)-4''',7-di-*O*-methylagathisflavone. If the assignment of protons to rings E and B of WA^{III} were reversed then the extra methoxy group would be at C-4' rather than C-4'''. Although by analogy this is very unlikely, until synthetic products of this series are examined for their physical properties, it must remain a possibility. It is interesting to note that members of the *Araucariaceae* produce biflavones in which units of the same oxygenation pattern are linked 8,8''[1], 3',8''[2] and 6,8'' – all presumably by a similar radical coupling. That this is not a random series of reactions, however, is shown in that these same biflavones are the only optically active biflavones known and are therefore presumably produced enzymically.

Résumé. Quelques bisflavones qui contiennent un lien 6,8'' ont été isolées et charactérisées pour la première fois. Les déplacements méthoxyliques permettent de décider si l'on a affaire à des éléments flavanoïdes liées 6, ou 8''. Le contrôle enzymique de la production de bisflavones dans le genre *Auraucariaceae* est démontré.

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16 December 1968.

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[4] A. PELTER, unpublished observations.