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ON THE BISFLAVONES IN THE LEAVES OF ARAUCARIA BIDWILLII HOOKER

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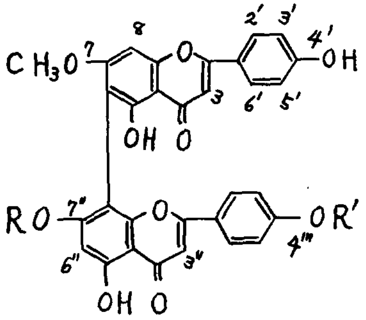
The species so far examined from the genus Araucaria were found to contain optically active bisflavones belonging to amentoflavone and cupressuflavone series.[1-3] However, the homogenous components isolated from Agathis palmerstonii were characterized as members (I and III) belonging to a new agathisflavone series.[4] We now report the isolation and identification of 7-O-methylagathisflavone (I) and a new compound (II) from the leaves of Araucaria bidwillii Hooker. The latter has been characterized as 7,7"-di-O-methylagathisflavone (II) by NMR studies.



I R=R'=H
II R=CH_3, R'=H
III R=H, R'=CH_3

Thin-layer chromatography (TLC) examinations of purified phenolic extractives of the dried and powdered leaves revealed four major bands. They were separated by preparative TLC. Two fractions, WN-1 and WN-3 proved to be homogenous and gave the same hexamethyl ether ($AgMe_6$), m.p. 160-162°, $[\alpha]_D^{34}$ -56.5° (optically active $AgMe_6$,[4] m.p. 162-164°; racemic form,[5] m.p. 242°). Rf values, fluorescence in UV light and NMR spectra of the two methyl ethers obtained from WN-1 and WN-3 were identical with those of an authentic sample (WA-III,[4] Table 1). The NMR spectrum (Table 1) of WN-1 acetate, m.p. 165-166° (lit.[4] m.p. 163-168°) was also similar to that of 7-O-methylagathisflavone pentaacetate (WA-II[4]). WN-1 is therefore characterized as the structure I.

However, the chemical shifts of WN-3 were not the same as those of formerly reported 7,4'''-di-O-methylagathisflavone (III).[4] The two sets of A_2B_2 type doublets of WN-3 acetate, m.p. 169-170°, $[\alpha]_D^{34}$ -12.50° ($CHCl_3$) are almost the same as those of WN-1 acetate, suggesting that no methoxy group is present at the positions 4' and 4'''. This is also supported by the downfield shifts of 2''',6''' (7.40 → 7.54 ppm) and 3''',5''' (6.81 → 7.09 ppm) protons from those of III-acetate (WA-VIII[4] in Table 1) because of 4'''-acetoxy group. On the other hand, the 6" proton shows a considerable upfield shift (6.98 → 6.77 ppm) from that of WA-VIII, suggesting 7"-methoxy group in WN-3 instead of 7"-acetoxy group of WA-VIII. The two methoxy and four acetoxy proton signals are in good accordance with the structure of 7,7"-di-O-methylagathisflavone (II) tetraacetate as shown in Table 1. WN-3 is therefore assigned as the structure II.

The other two fractions, WN-2 and WN-4 although homogenous chromatographycally were found by TLC examination of the methylated products to be mixtures of amentoflavone and cupressuflavone with hinokiflavone as traces in the former. It is in accordance with our recent findings[6] that mixtures of (a) hinokiflavone, monomethyl ethers of amentoflavone and cupressuflavone and (b) monomethyl ether of hinokiflavone, dimethyl ethers of amentoflavone and cupressuflavone, although undetectable as such are clearly distinguishable and effectively separable by TLC at the fully methylated stage.

WN-2 was, therefore, considered to be a mixture of monomethyl ethers of amentoflavone and cupressuflavone with traces of hinokiflavone. Separation of WN-2 by counter current distribution gave two homogenous components characterized as bilobetin[7] and 7-O-methylcupressuflavone by comparison of

Table 1. NMR signals (ppm) in $CDCl_3$ solution (100 Mc)

Position	$AgMc_6$	WA-III*	WN-1-acetate	WA-II*	WN-3-acetate	WA-VIII*
2', 6'	7.92 (2H, d, J=9 cps)	7.88 d	7.97 d	7.92 d	7.97 d	7.92 d
3', 5'	7.06 (2H, d, J=9 cps)	7.01 d	7.30 d	7.38 d	7.30 d	7.27 d
2''', 6'''	7.41 (2H, d, J=9 cps)	7.37 d	7.51 d	7.50 d	7.54 d	7.40 d
3''', 5'''	6.82 (2H, d, J=9 cps)	6.78 d	7.11 d	7.06 d	7.09 d	6.81 d
8	6.94 (1H, s)	6.91 s	7.05 s	7.00 s	7.04 s	7.01 s
6"	6.70 (1H, s)	6.64 s	7.05 s	6.99 s	6.77 s	6.98 s
3	[6.60 (1H, s)	[6.53 s	[6.69 s	[6.62 s	[6.69 s	[6.62 s
3"	6.55 (1H, s)]	6.51 s]	6.64 s]	6.58 s]	6.58 s]	6.54 s]
4'	3.61 (3H, s)	3.59 s	(2.14 s)	(2.14 s)	(2.12 s)	(2.14 s)
4'''	3.76 (3H, s)	3.74 s	(2.24 s)	(2.24 s)	(2.24 s)	3.76 s
7	3.80 (3H, s)	3.78 s	3.81 s	3.80 s	3.81 s	3.79 s
7"	3.88 (3H, s)	3.86 s	(2.09 s)	(2.09 s)	3.83 s	(2.09 s)
5	3.90 (3H, s)	3.88 s	(2.33 s)	(2.34 s)	(2.33 s)	(2.33 s)
5"	4.07 (3H, s)	4.05 s	(2.45 s)	(2.44 s)	(2.47 s)	(2.44 s)

* These data were introduced from reference No. 4. The others were taken on JNM-4H-100 NMR instrument with TMS as internal standard. Numbers in parentheses show the chemical shifts of acetyl protons.

the NMR spectra with those of authentic samples. The latter was recently isolated from Agathis alba[8] as a new compound.

WN-4, on similar grounds, was considered to be a mixture of dimethyl ethers of amentoflavone and cupressuflavone. The acetylated product of WN-4 on repeated crystallizations followed by chromatographic treatments gave a pure compound, m.p. 275-280° which was identified as 7,7"-di-O-methylcupressuflavone tetraacetate by comparison of NMR spectrum with that of an authentic sample.[8]

In conclusion, 7-O-methylagathisflavone (I), 7,7"-di-O-methylagathisflavone (II), bilobetin, 7-O-methylcupressuflavone and 7,7"-di-O-methylcupressuflavone were isolated and identified. Besides them, hinokiflavone and a dimethyl ether of amentoflavone were detected by TLC. This means that the leaves of this plant contain all kinds of bisflavone series, amentoflavone, hinokiflavone, cupressuflavone and agathisflavone.

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