Nous nous chargenos maintenant de la recherche sur la toxicologie en ce qui concerne les mammifères et l'activité sur les insectes et les plantes.

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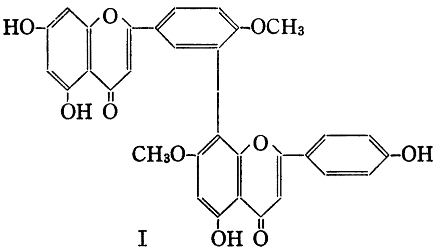
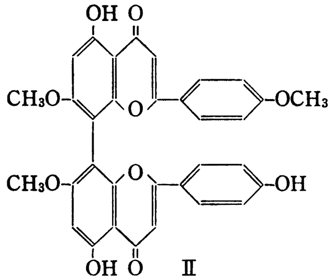
Two New Biflavonyls from *Araucaria cunninghamii*

The isolation and characterization of four biflavonyls, 4',4''',7,7''-tetra-O-methylcupressuflavone, 7,7''-di-O-methylcupressuflavone (8,8''-bisgenkwanin), 4',4''',7,7''-tetra-O-methylamentoflavone and 4',4''',7''-tri-O-methylamentoflavone (kayaflavone) as major constituents of the leaf extracts of *Araucaria cunninghamii* have already been reported.[1-3] The presence of monomethyl ethers of agathisflavone, cupressuflavone, amentoflavone and hinokiflavone along with traces of the parent hinokiflavone and a dimethyl ether of agathisflavone has also been detected (thin-layer chromatography (TLC)).[4] In the present communication, we report the isolation of two new biflavonyls from the same source. They have been characterized as 4',7''-di-O-methylamentoflavone (I) and 4',7,7''-tri-O-methylcupressuflavone (II) by nuclear magnetic resonance (NMR) studies.



I



II

Extraction of the fresh leaves followed by solvent fractionaction and preparative TLC gave seven fractions labelled as ACuI—ACuVII. TLC examination of the methylated products of chromatographically homogeneous ACuIV and V revealed them as mixtures, in un-

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[1] Mohd.Ilyas, J.N. Usmani, S.P. Bhatnagar, M. Ilyas, W. Rahman and A. Pelter, *Tetrahedron Letters*, **1968**, 5515.

[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).

[3] Ph. D. Thesis of Mohd. Ilyas, Aligarh Muslim University, 1970.

[4] Nizam U. Khan, W.H. Ansari, M. Ilyas and W. Rahman, *Phytochemistry*, in press.

equal proportion, of (a) 7,7″-di-O-methylcupressuflavone[1] and a dimethyl ether of amentoflavone and (b) kayaflavone and a trimethyl ether of cupressuflavone respectively. ACuIV on repeated acetylation and deacetylation gave a product, the homogeneity and identity of which was established by TLC examination of its methyl ether as amentoflavone hexamethyl ether. ACuV constituting kayaflavone as major component, was enriched by solvent fractionation in cupressuflavone trimethyl ether content. It separated into two fractions by counter current distribution (CCD) between ethyl methyl ketone and borate buffer.

The NMR signals (in pyridine solution) of the amentoflavone dimethyl ether (from ACu-IV) acetate showed two methoxyl (δ 3.72 and 3.80) and four acetoxyl (δ 2.17, 2.24, 2.49 and 2.59) groups suggesting 4′,7″-di-O-methylamentoflavone tetracetate in comparison with the reported data of known compounds.[5] The presence of 7-acetoxyl group was supported by the chemical shifts of H-6 and H-8 (δ 6.80 d and 7.27 d, 1H each, $J=2$ cps) taken in $CDCl_3$ solution because they were similar to those of kayaflavone triacetate (δ 6.78 d and 7.27 d) and different from those of sciadopitysin (7,4′,4‴-tri-O-methylamentoflavone) triacetate (δ 6.56 d and 6.78 d). On the other hand, the NMR signal for H-3‴,5‴ (δ 7.03 d, 2H, $J=9$ cps) in comparison with that of sciadopitysin triacetate (δ 6.77 d, 2H, $J=9$ cps) suggested the presence of 4‴-acetoxyl group. Similarly, the difference of the chemical shift of H-6″ between the dimethyl ether (from ACuIV) tetracetate (δ 6.75 s) and sciadopitysin triacetate (δ 6.96 s) suggested the presence of 7″-methoxy group. This is further supported by comparing H-6″ shift (δ 6.80 s) in kayaflavone triacetate having a similarly constituted ring D.

The cupressuflavone trimethyl ether (from ACuV) acetate showed the NMR signals ($CDCl_3$) of three methoxyl (δ 3.85 s, 6H and 3.79 s, 3H) and three acetoxyl (δ 2.53 s, 6H and 2.28 s, 3H) groups. The structure, 4′,7,7″-tri-O-methylcupressuflavone triacetate is easily deducible by comparison with the chemical shifts of 7-O-methylcupressuflavone pentacetate and 7,7″-di-O-methylcupressuflavone tetracetate.[6] The NMR spectrum of this compound is found in full agreement with that of synthetic 4′,7,7″-tri-O-methylcupressuflavone triacetate.[7]

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[5] H. Miura, T. Kihara and N. Kawano, *Tetrahedron Letters*, **1968**, 2340.

[6] T. Mashima, M. Okigawa, N. Kawano, Nizam U. Khan, M. Ilyas and W. Rahman, *Tetrahedron Letters*, **1970**, 2939.

[7] W. Rahman, unpublished work.