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PHYTOCHEMICAL REPORTS

ISOLATION AND CHARACTERIZATION OF ATRANORIN AND 4,6 DIHYDROXY-2-METHOXY-3-METHYLACETOPHENONE FROM *STEREOCAULON VESUVIANUM*

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Key Word Index—*Stereocaulon vesuvianum*; lichen; 4,6-dihydroxy-2-methoxy-3-methylacetophenone; atranorin.

Plant. Stereocaulon Vesuvianum is a foliose lichen, abundantly growing over volcanic rocks; a sample of the species is deposited in A. Jacta Herbarius no. 40 of Istituto di Botanica dell' Universitá, of Naples. *Previous work.* On sister species only.[1,2]

This paper describes the isolation, from *S. Vesuvianum*, of atranorin, a compound usually occurring in lichens belonging to *Stereocaulon* genus, and of a phloracetophenone derivative, which has never been previously isolated from natural sources.

The plants, collected in summer 1973 on the slopes of Mt. Vesuvius near Naples, were powdered and extracted successively with EtOH and C_6H_6. The extracts were combined and concentrated *in vacuo* to a small volume, thus affording a whitish powder (yield 0·5%). Crystallization of the precipitate from C_6H_6 yielded white crystals, m.p. 193–194°, identified as atranorin on the basis of UV and IR spectra and other data in agreement with literature values.[3] The mother liquor was evaporated to dryness, taken up in Et_2O, and after washing with $NaHCO_{3_{aq}}$, was fractionated on a column of silica-gel. From the C_6H_6-eluted fraction, colourless crystals were isolated, m.p. 143–144°, and identified as an *O*-methyl methylphloracetophenone by chemical and spectroscopical evidences.

The NMR spectrum ($CDCl_3$) showed signals for a Ar-methyl (δ 2·10, 3H, *s*), an acetyl (δ 2·44, 3H, *s*), a methoxyl (δ 3·90, 3H, *s*), two hydroxyl groups (δ 5·19 and 11·98, two 1H, *s*, both D_2O changed) and for an aromatic proton (δ 6·19, 1H, *s*). The IR spectrum in $CHCl_3$ showed a strong band at 1656 cm^{-1} due to a conjugated-hydrogen-bonded carbonyl group, and bands at 3700 and 3350 cm^{-1} due to chelated and free OH groups, respectively.

The MS showed M^+ 196 (66%, calc. for $C_{10}H_{12}O_4$ 196·0735) and significant ion peaks at 165 (M^+ –MeOH, 98%), and 136 (M^+ –OH, –COMe, 100%). The UV spectrum displayed absorption maxima at 231 (log ϵ 4·32), 247 (4·21) and 305 nm (3·64), which on addition of 2 N NaOH were shifted bathochromically to 245 and 310 nm.

[1] HUNECK, S. and FOLLMANN, G. (1967) *Z. Naturforsch.* **22,** 461.
[2] FOX, H. C. and HUNECK, S. (1970) *Phytochemistry* **9,** 2057.
[3] HUNECK, S. (1968) *Progress in Phytochemistry*, p. 223. Interscience, New York.

The product obtained on methylation with $(Me)_2SO_4$ showed resonance signals at δ 2·10 (3H, *s*, methyl group), δ 2·88 (3H, *s*, acetyl group), δ 3·72, δ 3·78, δ 3·84 (3H, *s*, three methoxyl groups) and δ 6·42 (1H, *s*, aromatic proton).

The chemical and spectral evidence suggests that this compound is 4,6-dihydroxy-2-methoxy-3-methylacetophenone and this was further confirmed by the agreement of its melting point and that of dimethyl ether, respectively, with literature data.[4] It is noteworthy that the product cannot be considered a chemical artefact, as its presence has been shown directly in the crude extract by TLC in comparison with a pure sample.

Acknowledgement—The authors wish to express their thanks to Mr. C. Piscitelli for his help in experimental work.

[4] WHALLEY, W. B. (1955) *J. Chem. Soc.* **105.**

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BIFLAVONES FROM *PODOCARPUS NERIIFOLIUS*

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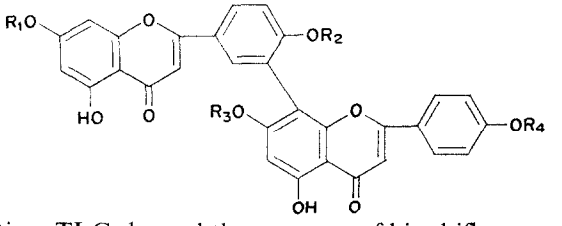
Key Word Index—*Podocarpus neriifolius*; Podocarpaceae; biflavones; amentoflavone, podocarpusflavone A; podocarpusflavone B; isoginkgetin.

Plant. Podocarpus neriifolius D. Don (Podocarpaceae). *Source.* Collected at Sipore, West Bengal, India. *Previous work.* On sister species[1-3] *Present work*: The phenolic extract obtained from the leaves and purified by usual methods gave four biflavones by preparative TLC and counter current distribution methods. They were characterized as amentoflavone (**1**), podocarpusflavone A (**2**), podocarpusflavone B (**3**) and isoginkgetin (**4**) by m.ps, m.m.ps and comparison of NMR spectra of their methyl ether and acetate derivatives with authentic samples respectively.



(1) $R_1 = R_2 = R_3 = R_4 = H$
(2) $R_1 = R_2 = R_3 = H$; $R_4 = Me$
(3) $R_2 = R_3 = H$; $R_1 = R_4 = Me$
(4) $R_1 = R_3 = H$; $R_2 = R_4 = Me$

In addition, TLC showed the presence of hinokiflavone and its monomethyl ether.

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[1] MIURA, H., KIHARA, T. and KAWANO, N. (1969) *Chem. Pharm. Bull. (Tokyo)* **17**, 150; (1968) *Tetrahedron Letters*, 2339.
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[3] HAMEED, N., ILYAS, M., RAHMAN, W., OKIGAWA, M. and KAWANO, N. (1973) *Phytochemistry* **12**, 1497.