

groups. These results are consistent with the structure of chrysotalunin, a bianthraquinone isolated from certain Irish soils^{4,5}. Chrysotalunin has 4 hydroxyl groups and the mass spectrum of the tetra-acetate shows a very weak molecular ion at m/e 674, undetected in our mass spectrum.

The NMR-spectrum ($CDCl_3$) of the acetylated product is identical to the reported NMR-spectrum for chrysotalunin tetra-acetate⁵. The concentration of chrysotalunin in the humus B horizon of the Te Kopuru sand (200 mg/kg) is considerably higher than for most of the soils examined by McGrath⁶, although in 2 cases he reported 120 mg/kg occurring near the humus B horizons of 2 Irish podzols.

A positive test for chrysotalunin⁶ was also obtained from the Te Kopuru sand topsoil (0–12.5 cm), where its concentration was about 25% of the concentration in the humus B horizon. It was however absent from the Waipoua clay topsoil (0–10 cm), another New Zealand soil developed under kauri (*Agathis australis*).

The origin of the pigment is uncertain, although it appears most likely to be a fungal metabolite. A number of other bianthraquinones have been isolated from plants^{7,8} although the existence of chrysotalunin in plant materials has yet to be demonstrated. This is the first report of the occurrence of chrysotalunin in a Southern hemisphere soil.

Principal fragmentation peaks (greater than 10% intensity) of the pigment (probe temperature 260°C)

m/e	506	489	488	459	431	253	244
Percent intensity	100	47	60	16	14	20	15

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A new proanthocyanidin from the stem bark of *Acacia suma*¹

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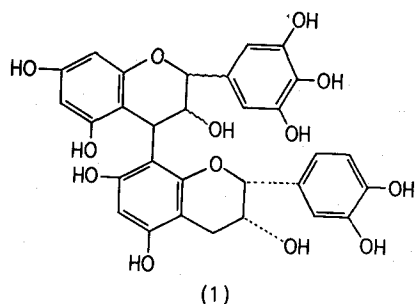
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Summary. From the stem bark of *Acacia suma*, a new proanthocyanidin (**1**) with a C–C linkage between the 4-position of 3,3', 4', 5,5', 7-hexahydroxyflavan and the 8-position of the (–)epicatechin part was isolated.

An alcoholic extract concentrate of the stem bark of *Acacia suma* was extracted successively with chloroform and ethyl acetate. From the ethyl acetate extract, an almost colourless amorphous powder was obtained. It had no definite m.p. decomposing from 240°C onwards. It gave a bluish-green colour with alcoholic ferric chloride and on treatment with hot acids a deep red colour developed, indicating a proanthocyanidin. The presence of the phloroglucinol system was indicated by the vanillin-hydrochloric acid test³. The molecular formula, $C_{30}H_{26}O_{13}$, was deduced from an analytical study of its derivatives. Acetylation of the proanthocyanidin yielded a colourless product (m.p. 141–145°C, ν 1740 cm^{-1}) which was found to contain 11 acetoxy groups. The methyl ether (m.p. 163–166°C) obtained by the methylation of the proanthocyanidin further underwent acetylation to yield a diacetate, $C_{43}H_{48}O_{15}$, showing the presence of 2 alcoholic hydroxyls and 9 phenolic hydroxyl groups. The absence of an 1,2-glycolic system was indicated by the failure of the methyl ether of proanthocyanidin to react with sodium metaperiodate. Mild acid hydrolysis of the proanthocyanidin gave besides delphinidin chloride, (–)

epicatechin and unidentified products having lower R_f values. Vigorous acid hydrolysis using higher acid concentrations gave delphinidin chloride in good yields, identical with an authentic sample in its colour reactions, chromatography and spectral properties^{4,5}. Based on the above degradative and analytical studies, structure **1** has been assigned for the new proanthocyanidin.

The NMR-spectrum of the proanthocyanidin acetate showed the following signals: δ $CDCl_3$ 6.6 (s, 1H) assigned to the proton at the 6 position of the epicatechin part, 6.5 to 6.1 (q, 2H) to the metacoupled 6,8 protons of the leucodelphinidin part, 7.2 to 6.9 (m, 5H) to the protons of ring B, 5.6 to 4.5 (m, 4H) to 2 methine protons and 2 protons α to the aliphatic acetoxy groups, 4.25 (s, 1H) to proton at position 4 of leucodelphinidin moiety, 3.1 to 2.8 (m, 2H) to the benzylic protons of the epicatechin moiety, 2.4 to 1.6 (m, 33H) to the aromatic and aliphatic acetoxy groups. As the phloroglucinol proton quartet (6.5 to 6.1) and the benzylic protons (3.1 to 2.8) have both only 2 protons, the 2 flavanic units must be linked between the benzylic carbon of the 3,3', 4', 5,5', 7-hexahydroxyflavan moiety and the carbon 8 of the (–)epicatechin moiety.



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