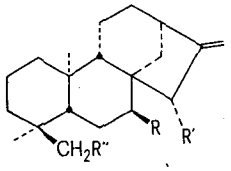
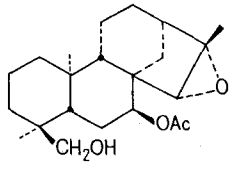
Sideritis sicula. Direct comparison (m.p., IR, NMR) proved the identity of the products: hence natural eubotriol does have structure (**I**).

Eubol (**II**) $C_{22}H_{34}O_4$, m.p. 190–191 °C (bright prisms from AcOEt), gave a negative TNM test; IR (nujol) 3450–3300 (OH), 1721 and 1266 (OAc), 1642 and 900 cm^{-1} ($C{=}CH_2$); MS 302 (M–AcOH), 287 (M–AcOH–CH_3), 271 (M–AcOH–CH_2OH), 254 (M–AcOH–CH_2OH–OH), 109 m/e (ring A, $C_6H_7Me_2$); NMR (60 MHz, CD_3–CO–CD_3) 0.75 (s, 4α–CH_3), 1.14 (s, 10α–CH_3), 3.05 and 3.42 (q_{AB}, J 11 Hz, 4β–CH_2OH), 1.94 (s, OAc), 2.75 (m, 13α–H), 4.00 (br, 15β–H), 4.87 (br, $W^1/_2$ 8 Hz, 7α–H), 4.96 and 5.13 δ (br s, $C{=}CH_2$). The spectra and the occurrence of an acetyl group suggested that eubol is a monoacetyl-derivative of eubotriol; the downfields shift of 7α–H indicated that 7β–OH is acetylated. On alkaline hydrolysis, eubol afforded eubotriol; by treatment with Ac_2O-pyridine, both eubol and eubotriol gave the same triacetal-eubotriol (**III**), m.p. 167–169 °C (from AcOEt), NMR (60 MHz, CD_3–CO–CD_3) 0.85 (s, 4α–CH_3), 1.10 (s, 10α–CH_3), 1.98–2.03–2.04 (s, 3 OAc), 3.71 (s, 4β–CH_2OAc), 2.82 (m, 13α–H), 4.95 (br, $W^1/_2$ 8 Hz, 7α–H), 5.40 (br, 15β–H), 5.03 and 5,21 δ (br s, $C{=}CH_2$). Therefore eubol has structure (**II**) of ent-kaur-16-ene-7α-acetoxy-15β,18-diol. This was confirmed by partial synthesis starting from natural epoxysiderol[4] (**IV**); the latter (50 mg) dissolved in dry Me_2SO (10 ml) was treated[9] with freshly distilled BF_3–Et_2O complex (2 drops) and heated at 100 °C for 20 h; usual work-up yielded (**II**) (40 mg), m.p. 190–191 °C, identical (m.p., IR, NMR) with natural eubol, thus confirming the stereochemistry at C–15.

It is noteworthy that eubol and eubotriol are the first kaurene derivatives found in Sideritis species growing in the Central and Eastern Mediterranean area, all the other diterpenes having isokaurene skeleton. Otherwise kaurene derivatives are widespread in Sideritis species occurring in Western Mediterranean area.



(**I**) R,R′,R″ = OH
(**II**) R′,R″ = OH; R = OAc
(**III**) R,R′,R″ = OAc



(**IV**)

8 F. Piozzi, P. Venturella, A. Bellino and A. Selva, Gazz. chim. ital. *99*, 582 (1969).
9 F. Piozzi, P. Venturella, A. Bellino and M. L. Marino, J. chem. Soc. Perkin *1*, 1164 (1973).

Isolation of chrysotalunin, a red pigment from a New Zealand soil

L. Y. Foo and K. R. Tate[1]

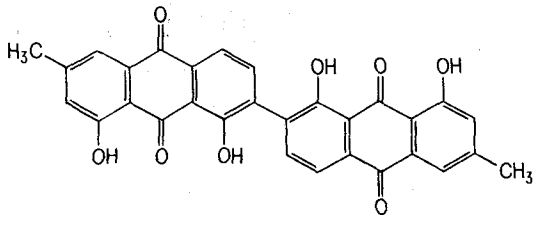
Chemistry Division, D.S.I.R., Private Bag, Petone (New Zealand), and Soil Bureau, D.S.I.R., Private Bag, Lower Hutt (New Zealand), 14 March 1977

Summary. Benzene extraction of Te Kopuru sand, a podzol located in the subtropical region of New Zealand, yielded a high melting pigment. Spectroscopic data showed it to be the bianthraquinone chrysotalunin. This is the first report of its occurrence in the Southern hemisphere soil.

A chemical investigation of Te Kopuru sand, a Northern sand podzol developed in a subtropical climate in New Zealand under kauri (Agathis australis) forest, revealed several pigmented fractions when alkali extracts of the humus B (B_{2h}) horizon (depth 40–50 cm) of the soil were separated on sephadex G-25 (K. R. Tate, unpublished results). This observation led to the present investigation. The humus B horizon was air-dried at 20 °C, sieved (< 2 mm) to remove plant fragments and exhaustively extracted by Soxhlet extraction with methanol, which yielded mainly waxy materials, followed with benzene which gave a high melting (m.p. > 350 °C) reddish crystalline compound. The pigment was insoluble in most organic solvents and sparingly soluble in CH_2Cl_2 or $CHCl_3$. The electron fragmentation data of the compound are summarized in the table.

The accurate mass measurement of the highest peak (MW 506.09732) which is also the base peak gave the molecular formula as $C_{30}H_{18}O_8$. The loss of multiple units of m/e 28 (CO) is suggestive of a quinone type structure. The presence of a strong peak at m/e 253, corresponding to exactly one half mass of the molecular ion suggests a symmetrical dimeric structure composing of 2 $C_{15}H_9O_4$ units.

The quinone structure is confirmed by IR and UV absorption data as characteristic of hydroxy anthraquinones[2,3]. Acetylation with acetic anhydride and pyridine gave a yellow compound, m.p. 296–300 °C (sublimes), as the major product. The mass spectrum of this product showed highest peak at m/e 632. The peak at m/e 632 and the stepwise loss of acetyl (m/e 42) units suggested that the parent compound contained at least 3 hydroxyl



1 Acknowledgment. The authors wish to thank Dr B. K. G. Theng, Soil Bureau, D.S.I.R., Lower Hutt, for the sample of the Te Kopuru sand podzol humus B horizon and Dr D. J. Wright of the Chemistry Department, University of Canterbury, for the high resolution mass spectral data.
2 J. B. Harborne, Phytochemical Methods, p. 84. Chapman and Hall Ltd, London 1973.
3 T. H. Beynon and A. E. Williams, Appl. Spectrosc. *14*, 156 (1960).

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-acetate[5]. 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 McGrath[6], although in 2 cases he reported 120 mg/kg occurring near the humus B horizons of 2 Irish podzols.

A positive test for chrysotalunin[6] 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 chrysoltalunin 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

4 D. McGrath, Nature *215*, 1414 (1967).
5 D. McGrath, Chemy Ind. *1970*, 1353.
6 D. McGrath, Geoderma *1972*, 167.
7 V. B. Patil, A. V. Rao and K. Nenkataraman, Indian J. Chem. *8*, 109 (1970).
8 N. L. Dutta, A. C. Ghosh, P. M. Nair and K. Venkataraman, Tetrahedron Lett. *1964*, 3023.

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

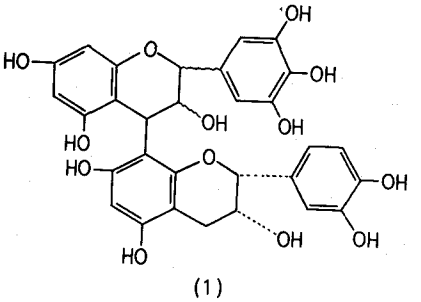
P. Gandhi[2]

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012 (India), 22 November 1976

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 test[3]. 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 acetoxyls. 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 acetoxyls, 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.



(1)

1 Part of this work was done at Allahabad University, Chemical Laboratories, and the author is grateful to Prof. R. D. Tiwari for encouragement and valuable discussion.
2 Present address: Central Food Technological Research Institute, Mysore 570 013, India.
3 K. Freudenberg and K. Weinges, Z. Fortschr. Chem. Org. Naturf. *16*, 1 (1958).
4 E. C. Bate-Smith, J. exp. Bot. *4*, 1 (1953).
5 H. W. H. Schmidt and H. Neukom, J. agric. Fd Chem. *17*, 344 (1969).