ferric perchlorate solution and the 0.2 M glucose plus 2×10^{-4} M ferric perchlorate solution were determined. From these the 'difference' action spectrum was obtained and is shown in the figure, b.

The 'difference' action spectrum and the absorption spectrum of the complex are similar, suggesting that excitation of a charge-transfer band of the ferric ion-glucose complex is responsible for the reduction of the ferric ion.

We observe that this reduction can be induced by light at wavelengths present in the solar spectrum on earth and although glucose is oxidized in the process it can be replaced cheaply. It is therefore possible to envisage a photochemical fuel cell based on the ferric ion-glucose complex making use of light at wavelengths < 400 nm.

Table 1 shows the chromatographic properties of the 2,4-dinitrophenylhydrazine derivatives of glucose photo-oxidation while table 2 gives some literature values[9,10].

Table 2. Literature values for $R_{glyoxal}$ of DNPH derivatives

Compound	Solvent systems* a[9]	b[9]	c[10]
Glyoxal	1	1	1
Pyruvaldehyde	1.05	1.17	–
Hydroxypyruvaldehyde	0.87	0.5	0.92
Glycolaldehyde	0.32, 0.45	0.14, 0.26	0.48
5(hydroxymethyl)furfural	0.45, 0.48	0.18, 0.27	0.60
Erythrose	0.81	0.39	–
Mesoxaldehyde	–	0.64, 0.43	–
Glyceraldehyde	0.09	–	–
Dihydroxyacetone	0.15	–	0.31
D-glucosone	0.05	–	0.13

* Solvent systems as in table 1.

All values are relative to glyoxal. For comparison, the chromatographic data from the thermal oxidation of glucose with ferric perchlorate[8] is given in the 4th column of table 1.

Apart from the compound, $R_g = 0.50$, all of the products observed in the thermal oxidation appear in the photochemical oxidation, within the experimental errors of the chromatography. There are also traces of 3 compounds not observed in the thermal oxidation.

Based on this chromatographic data, the presence of the following compounds can be reasonably inferred. (Experimental chromatographic R_g values from table 1 are given in parenthesis.)

Glyoxal	(a = 1, b = 1, c = 1)
Glycolaldehyde	(a = 0.31, 0.45, b = 0.12, 0.26, c = 0.5)
Glucosone	(a = 0.04, c = 0.14)
Erythrose	(a = 0.78, b = 0.38)
Pyruvaldehyde	(a = 1.05, b = 1.14, c = 1)
Hydroxypyruvaldehyde	(a = 0.89, b = 0.52, c = 0.90)

The principal products are glyoxal, pyruvaldehyde and hydroxypyruvaldehyde. The method of isolating products does not detect any nonketonic compounds, but as the total yield of products was in the order of a few mg, in the presence of vast excesses of glucose (necessary to ensure that the ferric ions are fully complexed) no other method appeared practical.

The DNPH derivatives of glucosone, glyoxal, erythrose, pyruvaldehyde and hydroxypyruvaldehyde were all clearly isolated from the thermal oxidation[8] and their assignment as photooxidation products of glucose in this work, although based only on chromatography, indicates that similar reaction-paths are followed by the thermal and photochemical oxidations.

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Eubotriol and eubol, new diterpenes from *Sideritis euboea*[1]

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Summary. 2 new diterpenes Eubotriol (ent-kaur-16-ene-7α, 15β, 18triol) (**I**), and eubol (ent-kaur-16-ene-7α-acetoxy-15β, 18 diol) (**II**) have been isolated from Sideritis euboea Helder.

Recently[2] we reported the isolation of 5 tetracyclic isokaurene diterpenes from the aerial part of Sideritis euboea Helder (Labiatae), a species growing in Euboea, (Greece). They were identified with siderol[3], epoxysiderol[4], isolinearol[5], sideridiol[3], sideroxol[6], which are already known. We describe now 2 minor components, eubotriol (**I**) and eubol (**II**), isolated from the same extract by chromatography on silica gel: (**II**) appeared in the cyclohexane-Et_2O 1:1 fraction, (**I**) in the Et_2O-AcOEt 1:3 fraction.

Eubotriol (**I**) $C_{20}H_{32}O_3$, m.p. 193–194 °C (bright prisms from AcOEt), gave a negative TNM test; IR (nujol) 3600–3350 (OH), 1655 and 897 cm^{-1} ($C{=}CH_2$); MS[7] 302 ($M-H_2O$), 287 ($M-H_2O-CH_3$), 272 ($M-OH-CH_2OH$), 254 ($M-H_2O-OH-CH_2OH$), 109 m/e (ring A, $C_6H_7Me_2$); NMR (100 MHz, pyridine-d_5) 0.92 (s, 4α–CH_3), 1.05 (s, 10α–CH_3), 2.80 (m, 13α–H), 3.47 and 3.63 (q_{AB}, J 11 Hz, 4β–CH_2OH), 4.23 (t, ~ 2 Hz, 7α-H), 4,45 (t, J 1 Hz, 15β–H), 5.19 and 5.44 δ (br s, $W^1/_2$ 3 Hz, $C{=}CH_2$).

The spectra of eubotriol (typical of an ent-kaur-16-ene skeleton with an oxygenated function on C-15) and the physical constants are in perfect agreement with those reported for ent-kaur-16-ene-7α,15β,18-triol (**I**), previously obtained[8,9] as a by-product during the partial synthesis of sideritriol[8], another natural diterpene from

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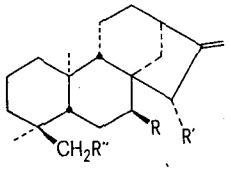
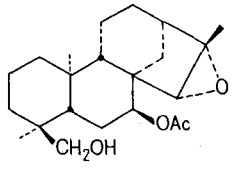
Sideritis sicula. Direct comparison (m.p., IR, NMR) proved the identity of the products: hence natural eubotriol does have structure (**I**).

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**)

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

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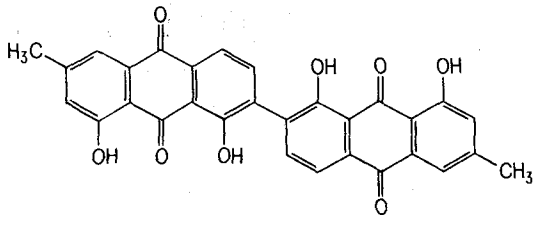
Summary. Benzene extraction of Te Kopuru sand, a podzol located in the subtropical region of New Zealand, yielded a high melting pigment. Spectroscopic data showed it to be the bianthraquinone chrysotalunin. This is the first report of its occurrence in the Southern hemisphere soil.

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



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