paper section in a separate small vial, moistening the paper with a soln of β-glucosidase, placing a strip of picrate paper in the top of the vial and closing with parafilm and a cork. After several hr at 37°, the presence of glycoside was indicated by the characteristic maroon discoloration of the picrate paper.[6] Two active bands were obtained at R_fs 0·51 and 0·26 respectively. These bands were cut out and the cyanogenic compounds desorbed with methanol, to yield cardiospermin (R_f 0·51) as a solid which we were not able to crystallize and a polar cyanogenic compound (R_f 0·26). We are currently investigating the structure of the second compound.

Identification of the sugar of cardiospermin. Cardiospermin (5 mg) was dissolved in H_2O (1 ml) and β-glucosidase (1 mg) added. The mixture was allowed to stand overnight at 40°. Comparison of the hydrolysate with glucose by both PC (Whatman 3MM, EtOAc–pyridine–H_2O (12:5:4)[7] and TLC on silica gel (Silica Gel G Merck, PrOH) indicated that the sugar produced on hydrolysis was glucose. Integral data from the NMR spectrum indicate cardiospermin is a monoglycoside.

Acetylation of cardiospermin with Ac_2O/NaOAc yielded a brown syrup. The NMR spectrum of this compound was measured in $CDCl_3$.

Preparation of TMS ether of cardiospermin. Samples of this glucoside were derivativized in a similar manner to that which Mabry *et al.*[7] used for flavonoids.

Measurements of total cyanide in Cardiospermum hirsutum. Because of the method of analysis and separation it was not possible to obtain an accurate yield of the glycoside. However, vegetative plant material of *C. hirsutum* liberates 18·5 μmol hydrocyanic acid per g fr. wt when analyzed for cyanogenic glycoside content[8] by colorimetric determination of the cyanide released following enzymatic hydrolysis for 48 hr.[9] This represents the cyanide contained in both the glycosides present.

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DAPHNEOLONE IN ROOTS OF *DAPHNE ODORA*

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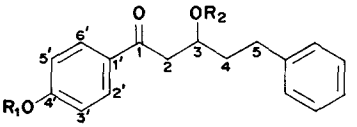
Key Word Index—*Daphne odora*; Thymeleaceae; δ-phenylvalerophenone; daphneolone.

In the course of the isolation of the nematocidal substances from the roots of *Daphne odora*,* we obtained a new phenolic compound, for which we proposed the name, daphneolone. In this communication we report the isolation and the structure of this compound.

* The isolation of nematocidal components will be reported in detail elsewhere.

Daphneolone (1) was obtained from the roots of *D. odora* by solvent extractions and subsequent column chromatography on silica gel and comprised about 0·002% of the fresh weight.



(1) $R_1 = R_2 = H$
(2) $R_1 = Me$, $R_2 = H$
(3) $R_1 = Me$, $R_2 = Ac$

The UV spectrum of daphneolone ($C_{17}H_{18}O_3$), λ_{max}(EtOH) 282 and 216 nm (ε, 16200, 14600), showed a bathochromic shift to 335 and 239 nm in an alkaline solution and was reversed by acids. These findings indicated the presence of a *p*-hydroxy-benzoyl chromophore.[1] Methylation of (1) with diazomethane yielded methyl-daphneolone (2), $C_{18}H_{20}O_3$, $\nu_{max}(CHCl_3)$ 3540 and 1664 cm^{-1}. (2) was further acetylated to give a mono-acetate (3), $C_{20}H_{22}O_4$ (M^+ 326),† $\nu_{max}(CCl_4)$ 1735 and 1675 cm^{-1}.

The NMR spectrum of daphneolone exhibited proton signals ascribed to the methine proton of a secondary hydroxy group (δ 4·19, 1H, quintet) three methylene groups (δ 3·08, 2H, doublet; 2·78, 2H, multiplet; 1·82, 2H, multiplet), and mono- and di-substituted benzene rings (δ 7·21, 5H, broad singlet; 6·91, 2H, doublet; 7·90, 2H, doublet). By decoupling experiments, the relationship of the hydroxy group and methylene groups was shown to have the partial structure (–CH_2–CH(OH)–CH_2–CH_2–).

Oxidation of (1) with Jones' reagent afforded oxodaphneolone (4), $C_{17}H_{18}O_3$ (M^+ 268).† The IR and UV spectrum of (4) had absorption bands indicative of a β-diketone group conjugated to a benzene ring [λ_{max}(EtOH) 329 and 230 nm (ε, 18900, 7900); $\nu_{max}(CHCl_3)$ 3580, 3250, 1715, 1662 cm^{-1}]. The NMR spectrum of (4) exhibited proton signals ascribed to an enolic hydroxy group (δ 16·10, broad), an olefinic proton (δ 6·05, 0·8H, singlet) and methylene groups (δ 3·10–2·55, 4·4H), indicating that the compound consists of a tautomeric mixture containing about 80% of the enol form.

The MS of daphneolone showed a M^+ ion at *m/e* 270 and prominent peaks at *m/e* 258 (M^+–H_2O), 136, 134, 121 (base peak), 105, 91, 77, 65 in agreement with the expected fragment ions of structure (1).

Some compounds with a C_6–C_5–C_6 carbon skeleton, such as δ-phenylvalerophenone derivatives have been synthesized by many workers,[2–4] but, daphneolone is the first C_6–C_5–C_6 compound found in higher plants.

EXPERIMENTAL

Isolation of daphneolone. Fresh roots (20 Kg) of *Daphne odora* Thunb. collected at Inazawa, Aichi, in July 1972, were cut into pieces and extracted with MeOH (3 × 20 l.). The combined extracts were evaporated under red. pres. and the residue dissolved in EtOAc (2 × 3 l.) and extracted with aq HCl (pH 2) and then with $NaHCO_3$ soln (pH 9). The EtOAc layer was evaporated under red. pres. to give a brownish gum (800 g). This material was subjected to column chromatography over silica gel (7 Kg) and elution with hexane–EtOAc gave 6 fractions. The second fraction (15 g) eluted with hexane containing 20–50% EtOAc was rechromatographed on silica gel with C_6H_6–MeOH and gave colorless needles which recrystallized from Et_2O–petrol., m.p. 119–120° (uncorr.).

† The homogeneity of the derivatives of I were characterized by TLC as well as MS and NMR spectroscopy.

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$[\alpha]_D^{23}$ +10° (c, 1·1 MeOH). λ_{max}(EtOH) 282 and 216 nm (ε, 16200, 14600), λ_{max}(EtOH–aq NaOH) 335, 239, and 213 nm, λ_{max}(EtOH–aq HCl) 282 and 216 nm. ν_{max}(KBr) 3450, 3250, 1650, 1600, 1578, 1513 cm^{-1}. NMR 100 MHz TMS δ (CD_3COCD_3) 7·90 (2H, *d*, *J*9 Hz), 7·21 (5H, broad *s*), 6·91 (2H, *d*, *J*9 Hz), 4·19 (1H, quintet, *J*6 Hz), 3·08 (2H, *d*, *J*6 Hz), 2·78 (2H, *m*), and 1·82 (2H, *m*). MS *m/e* (%) 270 (5), 252 (11), 136 (37), 134 (37), 121 (100), 91 (76), 77 (15), 65 (23). (Found: C, 75·98; H, 6·85. $C_{17}H_{18}O_3$ requires C, 75·53; H, 6·71%).

Methylation of daphneolone. To daphneolone (10 mg) in MeOH (2 ml) was added ethereal CH_2N_2 (4 ml). After 3 hr, the solvent was removed and the residue was crystallized from Et_2O–petrol to give methyl daphneolone (8·5 mg), m.p. 69·5–70·5°. λ_{max}(EtOH) 275 and 215 nm (ε, 18400, 17400). ν_{max}($CHCl_3$) 3450, 1664, 1600, 1574, 1512 cm^{-1}. NMR 100 MHz TMS δ ($CDCl_3$) 8·05 (2H, *d*, *J*9 Hz), 7·30 (5H, broad *s*), 7·07 (2H, *d*, *J*9 Hz), 4·22 (1H, quintet, *J*6 Hz), 3·86 (3H, *s*), 3·13 (2H, *d*, *J*6 Hz), 2·78 (2H, *m*), 1·83 (2H, *m*). MS *m/e* (%) 284 (8), 266 (12), 150 (26), 135 (100), 134 (15).

Acetylation of methyl daphneolone. Methyl daphneolone (25 mg) was treated with C_5H_5N (0·2 ml) and $(MeCO)_2O$ (1·0 ml) at 20° overnight. The solvent was removed and the residue was chromatographed on silica gel. Elution with C_6H_6–MeOH (9:1) gave methyl daphneolone acetate (25 mg). $C_{20}H_{22}O_4$ (M^+ 326). ν_{max}(CCl_4) 1735, 1675, 1600, 1575, 1510 cm^{-1}. NMR 100 MHz TMS δ ($CDCl_3$) 7·98 (2H, *d*, *J*9 Hz), 7·26 (5H, broad *s*), 6·97 (2H, *d*, *J*9 Hz), 5·46 (1H, *m*), 3·86 (3H, *s*), 3·35 (1H, *m*), 3·04 (1H, *m*), 2·85–2·60 (2H, *m*), 2·12–1·90 (2H, *m*), 1·97 (3H, *s*). MS *m/e* (%) 326 (9), 266 (26), 175 (8), 150 (13), 135 (100).

Oxidation of daphneolone. Daphneolone (36 mg) in $(Me)_2CO$ (2 ml) was treated with Jones' reagent (0·3 ml) for 10 min. The reaction mixture was neutralized, extracted with EtOAc and purified by preparative TLC on silica gel to give oxodaphneolone (7 mg), oil. $C_{17}H_{16}O_3$ (M^+ 268). λ_{max}(EtOH) 329 and 230 nm (ε, 18900, 7900), λ_{max}(EtOH–aq NaOH) 352 and 296 (sh) nm. ν_{max}($CHCl_3$) 3580, 3250, 1715, 1662, 1600, 1512 cm^{-1}. NMR 100 MHz TMS δ ($CDCl_3$) 7·85 (2H, *m*), 7·30 (5H, broad *s*), 6·92 (2H, *m*), 6·10 (0·8H, *s*), 4·02 (*s*, exchangeable with D_2O), 3·1–2·6 (4·4H, *m*), 16·10 (0·8H, broad, exchangeable with D_2O). MS *m/e* (%) 268 (64), 163 (84), 136 (43), 121 (100), 105 (4), 91 (36), 69 (32).

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EIN NEUES FURANOCUMARINGLYKOSID AUS HERACLEUM MANTEGAZZIANUM

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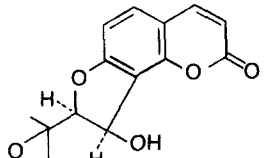
Pflanze. Heracleum mantegazzianum Somm. et Lev. aus dem 'Heempark' der Stadt Leyden, gesammelt im September 1972. *Untersuchte Pflanzenteile.* Wurzeln der einjährigen Pflanzen. *Bisher gefunden.* Freie Furanocumarine **(1)**.[1]



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