Treatment of this solid with petrol and then with Et_2O left a colourless residue which on purification by preparative TLC on Si gel G (EtOAc–MeOH–H_2O, 100:16.5:13.5; R_f 0.62) gave compound A (0.3 g). The petrol-soluble portion was similar to the petrol extract of the bark. A TLC examination of the ether solubles showed the presence of 5 compounds; only compounds B, C and D, however, could be obtained in sufficient amounts by preparative TLC on Si gel G (C_6H_6–EtOAc; 4:1, R_f 0.76, 0.51 and 0.58 respectively).

Compound A. Crystallized from MeOH as colourless needles, mp 193–94°: $[\alpha]_D^{25} - 112°$ (*c*, 0.375, MeOH); ν_{max}^{KBr} 3440, 2920, 1625, 1585, 1500 and 1450 cm^{-1} (Found: C, 48.51; H, 6.69; $C_{15}H_{20}O_9.1\frac{1}{2}\ H_2O$ requires C, 48.51; H, 6.2%). The acetate crystallized from $CHCl_3$–petrol as colourless needles (0.025 g), mp 120–21° (Found: C, 54.5; H, 5.8; $C_{25}H_{30}O_{14}$ requires C, 54.15; H, 5.4%).

Acid hydrolysis of A. 0.060 g A was refluxed for 4 hr with MeOH (20 ml), H_2O (5 ml) and H_2SO_4 (sp. gr. 1.83; 1.8 ml). 20 ml of H_2O were then added and MeOH removed when a light yellow solid, identical with an authentic sample of 4-*O*-methylphloracetophenone, separated; mp 140–41° (light yellow plates from C_6H_6–EtOAc; Found: C, 59.2; H, 5.8; $C_9H_{10}O_4$ requires C, 59.3; H, 5.5%); ν_{max}^{KBr} 3080, 1640, 1580, 1510 and 1470 cm^{-1}. NMR (C_5H_5N, δ): 2.8 (3H, *s*, —COMe), 3.63 (3H, *s*, —OMe) and 6.25 (2H, *s*, aromatic); NMR (Me_2CO, δ) 11.5 (chelated phenolic —OH). The aq. filtrate was neutralized and concentrated to a syrup, which on PC examination was found to contain glucose.

Ethylation of A. 0.050 g A was refluxed with 0.020 ml Et_2SO_4, 0.700 g K_2CO_3 and 10 ml Me_2CO for 6 hr. The reaction mixture was then filtered and solvent removed when a colourless solid was obtained which on hydrolysis with 7% methanolic H_2SO_4 (25 ml) and working up yielded 2-*O*-ethyl-4-*O*-methylphloracetophenone as colourless needles, mp 134–35°. Its identity was confirmed by comparison with an authentic sample.

Permethylation of A. To a pre-heated (70°, 1 hr) mixture of NaH (0.060 g) and DMSO (0.8 ml) was added A (0.020 g) in DMSO (0.8 ml) and the mixture heated for 1.5 hr at 70°. This was cooled in ice, MeI (2 ml) added with stirring and the mixture left at room temp. for 16 hr. It was then diluted with H_2O, extracted with $CHCl_3$; the $CHCl_3$ layer washed, dried and evaporated. The syrupy mass (single spot on TLC in $CHCl_3$) was refluxed with Kiliani mixture for 4 hr. The hydrolysate was found to contain 2,3,4,6-tetra-*O*-methyl-D-glucose (by PC comparison with an authentic sample, *n*-BuOH:EtOH:H_2O::5:1:4) and 2,4-di-*O*-methylphloracetophenone (TLC comparison with an authentic sample, toluene–ethyl formate–formic acid, 5:4:1).

Compound B. This was obtained as light yellow plates (0.08 g) from EtOAc–C_6H_6, mp 141–42°; λ_{max}^{MeOH} nm (log ε): 285 (4.364); + NaOMe:295, 360 nm; + $AlCl_3$ + HCl:305 nm. The IR and NMR spectra of B were identical with those of the aglucone of A.

Compound C. This separated as light yellow plates (0.03 g) from Me_2CO, mp 216–18°; λ_{max}^{MeOH} nm (log ε): 286 (4.238); + NaOH: 315 nm; + $AlCl_3$ + HCl: 303 nm; ν_{max}^{KBr} 3540, 3470, 3100, 1625, 1560, 1520 and 1460 cm^{-1}; NMR (C_5H_5N, δ): 2.84 (3H, *s*, —COMe) and 6.37 (2H, *s*, aromatic).

Compound D. This was obtained as crystalline solid (0.015 g), mp 169–171°; λ_{max}^{MeOH} nm (log ε): 264 (3.297) and 321 (4.191): + NaOAc:267 and 320 nm; + NaOH:330 and 385 nm; ν_{max}^{KBr}: 3320, 1700, 1615, 1555, 1500 and 1465 cm^{-1}.

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4-METHOXY-2-(*TRANS*-1-PROPENYL)PHENYL (±)-2-METHYLBUTANOATE FROM ANISE PLANTS

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Key Word Index—*Pimpinella anisum*; Umbelliferae; anise; phenylpropenoid derivatives.

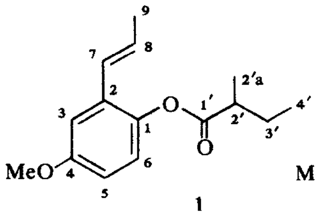
The constituents of anise plants, *Pimpinella anisum* L., have been extensively investigated since the early work of Dumas [1]. Recent work includes the quantitation of myristicin in the seeds [2], comparison of essential oil components of roots and seeds [3], and the identification of some sterols and coumarins in root tissue [4].

Steam distillation of the aerial portions of mature anise plants (grown from seeds on the University of Wisconsin Experimental Farm at Arlington), followed by ether extraction of the distillate, yielded an oil from which the title compound was isolated by column chromatography on silicic acid and preparative silica gel TLC. Column fractions 280–350 (200 g Mallinckrodt SilicAR CC-4, in a 3 × 55 cm column, eluted with Skellysolve B, 10.5 ml fractions) upon further purification on TLC (silica gel H and silica gel PF-254, developed with Skellysolve B) gave the title compound (R_f 0.4) in 1.5% yield (based on oil). This substance has not been reported previously as a natural product.

Structure 1 was deduced from spectral data and chemical transformations. The high resolution mass spectrum established the composition $C_{15}H_{20}O_3$ for the molecular ion ($M^+ = 248$) and exhibited peaks at *m/e* 164 (31%, M-C_5H_8O), 149 (27%, M-C_5H_8O-Me) and

85 (1.6%, C_5H_9O) typical for phenolic esters [5]. IR absorption (in CCl_4) at 1754 cm^{-1}, and UV maxima (in MeOH) at 246 and 292 nm (shoulder) are compatible with a phenolic ester function and a phenylpropenoid skeleton. A *trans*-propenyl substituent was indicated by the typical ABX_3 pattern in the NMR spectrum ($CDCl_3$, 90 MHz) at δ 5.94–6.46 (2H, AB, $J_{7,8} = 15.0$ Hz, C-7, 8-H) and δ 1.87 (3H, X_3, C-9-H). Other proton resonances and their assignments are as follows: δ 6.67–7.00 (3H, *m*, C-3,5,6-H), 3.79 (3 H, *s*, OMe), 2.64 (1 H, sextet, $J_{2',2'a} = J_{2',3'} \approx 7$ Hz, C-2′-H), 1.6 (2 H, *m*, C-3′-H), 1.31 (3 H, *d*, $J_{2',2'a} = 6.84$ Hz, C-2′a-H), 1.03 (3 H, *t*, $J_{3'4'} = 7.25$ Hz, C-4′-H).

Ozonolysis of **1** gave ester-aldehyde **2**: IR (CCl_4) 1762 cm^{-1} (ester), and 1692 cm^{-1} (aldehyde); NMR (90 MHz, $CDCl_3$), δ 10.09 (1 H, *s*, CHO), 6.8–7.4 (3 H, *m*, C-3,5,6-H), 3.85 (3 H, *s*, OMe), 2.70 (2 H, sextet, J = 6.84 Hz, C-2′-H), 1.5–2.0 (2 H, *m*, C-3′-H), 1.34 (3 H, *d*, J = 7.08 Hz, C-2′a-H), 1.04 (3 H, *t*, J = 7.20 Hz, C-4′-H); mass spectrum, *m/e* 236 (M^+, 2), 153(10), 152(100), 151(10), 137(22), 85(17). Hydrolysis of **2** gave a phenolic aldehyde, shown to be identical with authentic 2-hydroxy-5-methoxybenzaldehyde by spectroscopic (IR, NMR, MS) and chromatographic (GLC, TLC) comparisons, and an acid, whose methyl ester was identified as methyl 2-methylbutanoate by GC–MS comparison with authentic material. Neither compound **1** nor the derived butanoic acid exhibit optical activity, indicating the natural product to be a racemic mixture.



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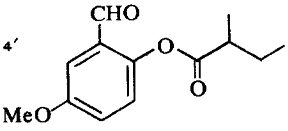

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