remove waxy matter; thus producing, a red, free-flowing solid (*ca* 10 mg/l. broth).

Isolation of bostrycin (**1**). Bostrycin was isolated by dissolving the above extract (250 mg) in warm HOAc, filtering to remove insoluble material, then allowing the soln to cool. Dark red crystals deposited (203 mg), mp 236–237°, $[\alpha]_D^{25}$ −81° (*c*, 1.19 in DMSO), which were identical to bostrycin (*vide supra*).

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COUMARINS FROM *APIUM GRAVEOLENS* SEEDS

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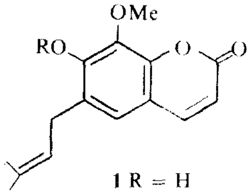
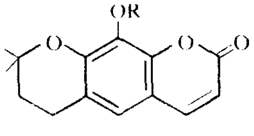
Key Word Index—*Apium graveolens*; Umbelliferae; seeds; seselin; bergapten; isoimperatorin; isopimpinellin; 7-hydroxy-8-methoxy-6-(3-methyl-2-butenyl)2H-1-benzopyran-2-one; apigravin; osthenol; structural determination.

Continuing our investigation [1–3] of *Apium graveolens* seeds, we now wish to report the isolation of 6 coumarins from the petrol extract of the seeds. Three of the coumarins not previously reported from *A. graveolens* seeds are seselin, isoimperatorin and osthenol, the other two, bergapten and isopimpinellin, are known [4, 5]. The sixth, a novel coumarin named apigravin, has been assigned the structure 7-hydroxy-8-methoxy-6-(3-methyl-2-butenyl)2H-1-benzopyran-2-one, **1**, based on the following experimental evidence.

Spectral data of **1** and its Me ether revealed the presence of a coumarin skeleton with a OH, a OMe and a C-prenyl group in it. Its ^{1}H NMR spectrum indicated that the 3-, 4- and 5-positions in the coumarin are unsubstituted. The similarity in the UV spectrum of **1** (λ_{max}^{MeOH} nm: 260, 325) and umbelliferone indicated oxygenation at the 7-position. **1** readily formed a cyclized product (HCO_2H), **2**, suggesting that the OH and prenyl groups are *ortho* to each other, and that the prenyl group occupies the 6- or 8-position. The IR and UV absorptions of **1** were different from those reported for 7-hydroxy-6-methoxy-8-*C*-prenyl coumarin [6] indicating the placement of the prenyl group at the 6-position. The negative Gibb's reaction [7] of **1** and a positive Gibb's test of its demethylated derivative (**4**), obtained by treating **1** with pyridinium hydrobromide [8], suggested the presence of the OMe group at the 5- or 8-position. The possibility of **1** having a 5,6,7-substitution pattern was ruled out by direct comparison of its Me ether (**3**) with an authentic sample of 5,7-dimethoxy-6-*C*-prenyl coumarin (toddaculin) [9].



1 R = H
3 R = Me



2 R = Me
4 R = H

EXPERIMENTAL

Isolation. Dried *A. graveolens* seeds (4 kg) were extracted with petrol. The petrol extract was concd and chromatographed on Si gel (1 kg) using petrol with increasing amounts of C_6H_6 as eluent. The 6 main fractions obtained were crystallized to yield compounds A, B, C, D, E and F, respectively.

Identification. Compounds A, B, C, D and F were identified as seselin, bergapten, isoimperatorin, isopimpinellin and osthenol, respectively. Compound E (**1**) crystallized from MeOH as white needles (60 mg), mp 168–70°; R_f: 0.36 (Si gel, C_6H_6–Me_2CO, 19:1), 0.38 (Si gel, C_6H_6–EtOAc, 23:2); MS: M^+ 260. It gave a green fluorescence under UV light and a negative Gibb's test. λ_{max}^{MeOH} nm: 260, 325 (log ε: 3.05, 3.58); ν_{max}^{KBr} cm^{-1}: 3430, 1738, 1640, 1462, 1220, 952 and 830; ^1H NMR ($CDCl_3$): δ 1.29 (6H, *s*, *gem*diMe), 3.32 (2H, *d*, Ar—CH_2—), 4.1 (3H, *s*, −OMe), 5.3 (1H, *m*, =CH—), 6.17 (1H, *d*, $J = 10$ Hz, H-3), 6.91 (1H, *s*, H-5) and 7.54 (1H, *d*, $J = 10$ Hz, H-4). It formed a Me ether derivative, **3** (CH_2N_2), mp 93–5° (petrol). λ_{max}^{MeOH} nm: 260, 335; ν_{max}^{KBr} cm^{-1}: 1700, 1620, 1446, 1215 and 952; ^1H NMR ($CDCl_3$): δ 1.66 (6H, *s*, *gem*diMe), 3.25 (2H, *d*, Ar—CH_2—), 3.89 and 3.93 (3H each, *s*, 2 × —OMe), 5.13 (1H, *m*, =CH—), 6.2 (1H, *d*, $J = 10$ Hz, H-3), 6.89 (1H, *s*, H-5), 7.62 (1H, *d*, $J = 10$ Hz, H-4); MS *m/e* (% abundance): 274 (M^+, 10), 227 (13), 226 (100), 211 (55), 195 (42), 183 (13), 155 (45), 109 (14) and 66 (27). **3** was different from toddaculin on direct comparison (TLC, IR). **1** formed a cyclized derivative (HCO_2H), **2**, mp 135–6° (EtOAc–petrol); MS: M^+ 260; λ_{max}^{MeOH} nm: 260, 325 (log ε: 3.55, 3.99); ν_{max}^{KBr} cm^{-1}: 1725, 1620, 1457, 1216 and 949; ^1H NMR ($CDCl_3$): δ 1.41 (6H, *s*, *gem*diMe), 1.8 (2H, *t*, $J = 7$ Hz, Ar—CH_2—$C\underline{H}_2$—), 2.77 (2H, *t*, $J = 7$ Hz, Ar—$C\underline{H}_2$—), 3.92 (3H, *s*, —OMe), 6.16 (1H, *d*, $J = 10$ Hz, H_3), 6.86 (1H, *s*, H-5) and 7.49 (1H, *d*, $J = 10$ Hz, H-4). The demethylated and cyclized product, **4** (pyridinium hydrobromide), mp 207–8°, gave a positive Gibb's test. λ_{max}^{MeOH} nm: 265, 330 (log ε: 3.91, 4.15); ν_{max}^{KBr} cm^{-1}: 3400, 1700, 1620, 1450, 1202 and 937. The Me ether (CH_2N_2) of **4** was identical (TLC, IR) with **2**.

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OCCURRENCE OF (−)-ISOLONCHOCARPIN IN THE ROOTS OF *TEPHROSIA PURPUREA*

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Key Word Index—*Tephrosia purpurea*; Leguminosae; (−)-isolonchocarpin; pongamol; lanceolatins A and B; flavonoids.

Earlier investigations [1, 2] on *Tephrosia* have revealed the presence of rotenoids and flavonoids. Examination of the roots of *T. purpurea* Pers., which is medicinally useful [3], has now resulted in the isolation of laevorotatory isolonchocarpin and pongamol (lanceolatin C) [4] besides the earlier reported lanceolatin B [5] and lanceolatin A [6].

EXPERIMENTAL

The roots of *T. purpurea* collected around Waltair were powdered and the material was extracted with hot $CHCl_3$. The $CHCl_3$ extract was divided into petrol solubles and benzene solubles. Chromatography of the petrol solubles gave a compound, pale yellow needles from petrol–ether (1:1), mp 108–110°. It gave a single blue fluorescent spot on TLC and analysed for $C_{20}H_{18}O_3$ (M^+ 306). $[\alpha]_D^{28}$ −93° (chloroform). UV λ_{max}^{MeOH} nm: 266, 314; $\lambda_{max}^{MeOH+NaBH_4}$ nm: 232, 280. IR ν_{max}^{Nujol} cm^{-1}: 1680 s (C=O of flavanone); 730 and 700 s (unsubstituted phenyl nucleus) and the other bands are at 1630 m, 1590 s, 1270 m and 1200 m. ^1H NMR (δ values, solvent $CDCl_3$, 100 MHz): A one proton-quartet at 5.48 and two proton-multiplet at 2.84–3.04 were assigned to H-2 and H-3 (*cis*) and H-3 (*trans*) of flavanone. An unsubstituted phenyl nucleus was indicated by a broad multiplet centred at 7.30–7.54. Two doublets at 7.75 and 6.50, each for one proton with $J = 8$ Hz, were assigned to H-5 and H-6 of the A-ring. The remaining signals in the ^1H NMR spectrum indicated the presence of a 2,2-dimethylchromene system and they are at 1.5 (*s*, 6H, gem-dimethyl) 5.57 (*d*, 1H, $J = 10.5$ Hz, 3″-H) and 6.67 (*d*, 1H, $J = 10.5$ Hz, 4″-H). The chromene ring is in the angular position since the coupling constant of the two protons at C-5 and C-6 is high. The mass fragments are at 306 (30.8 %) (M^+), 305 (0.5) (M − 1), 291 (82.5) (M − Me), 202 (3.5) (ring A fragment after diene decomposition), 187 (100) (202 − Me), 104 (10) (ethylene fragment). These data led to structure **1**, a flavanone earlier prepared as a racemate by cyclization of the