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CONFIRMATION OF THE STRUCTURES OF THE PHYTOALEXINS LATHODORATIN AND METHYL-LATHODORATIN BY SYNTHESIS

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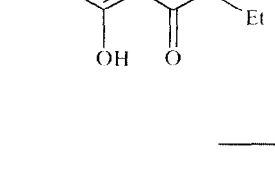
Key Word Index—*Lathyrus odoratus*; Vicieae; Leguminosae; sweet pea; phytoalexins; chromones; fungitoxicity.

Abstract—The two chromone phytoalexins were synthesized by condensing 2,4,6-trihydroxybutyrophenone with dimethylformamide.

The phytoalexins lathodoratin (**1**) and methyl-lathodoratin (**2**) were recently isolated from the sweet pea, *Lathyrus odoratus*, inoculated with *Helminthosporium carbonum*, and the unusual 3-ethylchromone structures were assigned by spectroscopy [1]. We have now synthesized lathodoratin by a method analogous to that reported by Bass [2] involving condensation of 2,4,6-trihydroxybutyrophenone with dimethylformamide. Methyl-lathodoratin was prepared from lathodoratin by selective methylation of the 7-hydroxy group. The spectroscopic data (UV, ^{1}H NMR, MS) from the synthetic chromones agreed closely with those from the natural products. Furthermore, the synthetic and natural lathodoratin co-chromatographed on TLC (silica gel and *n*-pentane–diethyl ether–acetic acid, 75:25:3); the synthetic 2-ethyl isomer, 5,7-dihydroxy-2-ethylchromone [1], was clearly distinguished from the natural material in this system.

EXPERIMENTAL

Lathodoratin. A soln of 2,4,6-trihydroxybutyrophenone (10.70 g, 54.6 mmol) in DMF (300 ml) was treated with $BF_3 \cdot Et_2O$ (30.96 g, 218 mmol) and $MeSO_2Cl$ (18.86 g, 165 mmol) [2] to give 5,7-dihydroxy-3-ethylchromone (lathodoratin, **1**) (10.81 g, 96%), which crystallized from EtOAc–*n*-hexane as pale pink prisms, mp 201.5–202.5° (uncorr.) R_f (Et_2O:Si gel) 0.60. UV λ_{max}^{EtOH} nm: 211, 228, 251, 259, 295, 322 sh. (Maxima showed similar shifts to those observed for the natural product on treatment with NaOAc and $AlCl_3$ [1].) IR ν_{max}^{nujol} cm^{-1}: 3330, 3125, 1660, 1640, 1595, 1570, 1500, 1400, 1330, 1300, 1175, 1075, 1060, 820, 800 and 700. ^{1}H NMR (100 MHz, CD_3OD, TMS reference): δ 1.18 (3 H, *t*, J = 7 Hz, $-CH_2\underline{CH}_3$), 2.42 (2 H, *q*, J = 7 Hz, $-\underline{CH}_2Me$), 6.22 and 6.30 (each 1 H, *d*, J = 2 Hz, H-6 and H-8), 7.86 (1 H, *s*, H-2). MS *m/z* (rel. int.): 207 (14), 206 (M$^+$, 100), 205 (75), 191 (23), 178 (17), 177 (8), 163 (16), 153 (9), 152 (6), 137 (6), 136 (5), 124 (8). (Found: C, 64.0; H, 4.9. Calc. for $C_{11}H_{10}O_4$: C, 64.1; H, 4.9%).



1 R = H
2 R = Me

Methyl-lathodoratin. Lathodoratin was selectively methylated at the 7-position (the non-chelated hydroxyl group) by the following procedure. Lathodoratin (2.51 g, 12.2 mmol) was dissolved in a soln of NaOH (490 mg, 12.2 mmol) in H_2O (10 ml), Me_2SO_4 (1.54 g, 12.2 mmol) was added, and the resulting mixture was stirred at room temp. for 3 hr. $CHCl_3$ extracts of the reaction mixture were treated with charcoal, then dried and concd to give 5-hydroxy-7-methoxy-3-ethylchromone (methyl-lathodoratin, **2**) (2.42 g, 90%), which crystallized from MeOH as pale yellow prisms, mp 68–69.5° (uncorr.). R_f (Et_2O/Si gel) 0.65. UV λ_{max}^{EtOH} nm: 211, 229, 251, 258, 291, 318 sh. IR ν_{max}^{nujol} cm^{-1}: 1665, 1635, 1595, 1500, 1315, 1295, 1220, 1200, 1170, 1070, 1055, 990, 900, 830, 800 and 695. ^{1}H NMR (100 MHz, CD_3OD, TMS reference): δ 1.18 (3 H, *t*, J = 7 Hz, $-CH_2\underline{CH}_3$), 2.42 (2 H, *q*, J = 7 Hz, $-\underline{CH}_2Me$), 3.85 (3 H, *s*, —OMe), 6.27 and 6.40 (each 1 H, *d*, J = 2 Hz, H-6 and H-8), 7.85 (1 H, *s*, H-2). MS *m/z* (rel. int.): 221 (15), 220 (M$^+$, 100), 219 (73), 205 (21), 192 (9), 191 (10), 177 (17), 167 (6), 166 (4), 151 (5), 138 (5). (Found: C, 65.6; H, 5.5. Calc. for $C_{12}H_{12}O_4$: C, 65.5; H, 5.5%).

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