6-Methoxy-5-vinylbenzofuran (1) Oil, $C_{11}H_{10}O_3$ UV λ_{max}^{MeOH} nm (log ε) 246 (4 10), 311 (3 61), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1625, 1610, 1580, 1430, 1300, 1210, 1150, 1090, ^1H NMR ($CDCl_3$) δ 7 50 (1H, *d*, $J = 2$ Hz, H-2), 6 60 (1H, br *d*, $J = 2$ Hz, H-3), 7 69 (1H, *s*, H-4), 7.00 (1H, *br* s, H-7), 7 40–6 90 (1H, *m*, A part of AX_2, H_α), 5 83–5 13 (2H, *m*, X_2 part of AX_2, H_β), 3 86 (3H, *s*, OMe), ^{13}C NMR ($CDCl_3$) δ 155 7, 155 6 (C-6, C-7a), 144 2 (C-2), 132 3 (C-8), 123 8, 120 5 (C-3a, C-5), 118 3 (C-4), 113 5 (C-9), 106 4 (C-3), 94 5 (C-7), 55 9 (OMe), MS m/z (rel int.) 174 $[M]^+$ (100), 159 (31), 131 (37)

2,4-Dimethoxystyrene (**2**) Oil, $C_{10}H_{12}O_2$ UV λ_{max}^{MeOH} nm (log ε) 261 (4 00), 303 (3 64), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1620, 1600, 1500, 1410, 1260, 1150, 1120, ^1H NMR ($CDCl_3$) δ 7 36 (1H, *d*, $J = 8$ Hz, H-6), 7 26-6 70 (1H, *m*, A part of AX_2, H_α), 6 46(1H, *dd*, $J = 8$ Hz + 2 Hz, H-5), 6 40(1H, *d*, $J = 2$ Hz, H-3), 5 73-5 00 (2H, *m*, X_2 part of AX_2, H_β), 3 76 (6H, *s*, 2xOMe), ^{13}C NMR ($CDCl_3$) δ 160 6(C-4), 157 9(C-2), 131 3 (C-7), 127 3 (C-6), 112 2 (C-8), 104 8 (C-5), 98 4 (C-3), 55 5 (OMe), 55 4 (OMe), MS m/z (rel int) 164 $[M]^+$ (100), 149 (53)

Oxidation of **2** Compound **2** (110mg) in Me_2CO (3 ml) was added dropwise to a stirred soln of $NaIO_4$ (1 2 g) and $KMnO_4$ (47 mg) in H_2O (4 ml)–Me_2CO (8 ml). The mixture was stirred for 20 hr at room temp Evapn of the Me_2CO and extraction with $CHCl_3$ gave a residue which on silica gel yielded 2,4-dimethoxybenzaldehyde (24 mg) and 2, 4-dimethoxybenzoic acid (20 mg), identified by comparison with authentic samples

4,6-Dimethoxy-5-vinylbenzofuran (**3**) Oil, $C_{12}H_{12}O_3$ UV λ_{max}^{MeOH} nm (log ε) 244 (4 54), 306 (3 47), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1620, 1600, 1580, 1530, 1400, 1350, 1300, 1140, 1100, ^1H NMR ($CDCl_3$) δ 7 43 (1H, *d*, $J = 2$ Hz, H-2), 6 80 (1H, *br d*, $J = 2$ Hz, H-3), 6 76 (1H, *br* s, H-7), 7 23-6 70 (1H, *m*, A part of AX_2, H_α), 6 03–5 10 (2H, *m*, X_2 part of AX_2, H_β), 4 00 3 86 (3H each, 2 × s, 2 × OMe), ^{13}C NMR ($CDCl_3$) δ 157 1, 156 (C-7a, C-5), 151 9 (C-4), 142 7 (C-2), 127 7 (C-8), 117 5 (C-9), 113 8, 112 4 (C-5, C-3a), 104 6 (C-3), 90 0 (C-7), 60 0 (4-OMe), 55 9 (6-OMe), MS *m/z* (rel int.) 204 $[M]^+$ (100), 189 (68), 161 (44).

Acknowledgements–We thank Dr Luciano Polonelli and Dr Giulia Morace, Istituto di Microbiologia Universita Cattolica del S Cuore (Roma), for antimicrobic essays Thanks are also due to the Swedish Agency for Research Cooperation with Developing Countries (SAREC) for financial assistance and to Ato Hailelul Tebicke for his interest and encouragement

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Phytochemistry, Vol 27, No 4 pp 1228 1229, 1988
Printed in Great Britain

0031 9422 88 $3.00 + 0.00
Pergamon Journals Ltd

PELARGONIDIN 3-(6″-SUCCINYL GLUCOSIDE)-5-GLUCOSIDE FROM PINK *CENTAUREA CYANUS* FLOWERS

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(*Received* 7 *September* 1987)

Key Word Index—*Centaurea cyanus*, Compositae, pink flowers, acylated anthocyanin, succinic acid

Abstract—A new anthocyanin acylated with succinic acid has been isolated from pink flowers of *Centaurea cyanus* It has been identified as pelargonidin 3-(6″-succinylglucoside)-5-glucoside

While continuing our investigation of malonated and other acylated anthocyanins in plants of the Compositae [1], we found a new pigment in the pink flowers of a cultivated form of the corn poppy *Centaurea cyanus* L The mutation from the usual blue colour to pink is probably controlled by a single gene [2] The blue flowers were originally thought to contain cyanidin 3,5-diglucoside, but more recent work has shown that the pigment is cyanidin 3-(6″-succinylglucoside)-5-glucoside, this was the first anthocyanin to be found in association with succinic acid [3, 4] The same succinyl derivative was subsequently reported in six other *Centaurea* species [5] but a malonated cyanidin 3-glucoside was found to occur in leaves of *C cyanus* and in cell cultures of the same plant [6]

The new pigment of the pink flowers is a pelargonidin

derivative and it was readily characterized by standard procedures [1] as the analogous succinyl ester of pelargonin, i.e as pelargonidin 3-(6″-succinylglucoside)-5-glucoside. In particular, hydrogen peroxide oxidation gave 6-succinylglucose, identified by comparison with material produced from the cyanidin derivative. Additionally, fast atom bombardment mass spectroscopy (FAB-MS) gave a molecular ion at m/z 695, which sequentially lost succinate (m/z at 595), glucose (m/z at 533), and succinylglucose (m/z at 433). A metastable ion at 409 indicated that the ion at m/z 533 (M − 162) could be formed from the molecular ion in a single step process.

This is only the second anthocyanin succinate to be reported in nature and like the previous one, it appears to be restricted to the tribe Cynareae of the Compositae. All other tribes in the family appear to contain malonate esters instead [1]. Identification of this pigment brings the number of anthocyanins acylated with aliphatic dicarboxylic acids known in the Compositae to 14, but many related structures undoubtedly await discovery in these plants.

EXPERIMENTAL

Pink flowers of a garden form of *Centaurea cyanus* were collected from plants in the Botanic Garden of Tokyo Gakugei University. The pigment was isolated and purified as previously described [1], except that a further purification was carried out by means of HPLC on an ODS (10–20 μm) column (7 × 300 mm) eluted isocratically with HCO_2H–MeCN–MeOH–H_2O (2 2 1 20). Acid hydrolysis of the pure pigment gave pelargonidin and glucose, while alkaline hydrolysis yielded pelargonidin 3,5-diglucoside and succinic acid. H_2O_2 oxidation gave 6-succinylglucose, identified by direct chromatographic comparison [cf. 1] with an authentic sample similarly prepared from cyanidin 3-(6″-succinylglucoside)-5-glucoside. R_f (× 100) values of the new pigment, compared with pelargonidin 3,5-glucoside in parentheses, were: 70 (46) in HOAc–HCl–H_2O (15 3 82), 47 (25) in *n*-BuOH–HCl (1 1), 58 (49) in BAW (4 1 5) and 41 (21) in 1% HCl. HPLC was carried out on a C_8 column with gradient elution using 20% solvent B (MeOH–HOAc–H_2O, 18 1 1) in solvent A (HOAc–H_2O, 1 1) and increasing the proportion of B by 2% per min with a flow rate of 1 ml/min and a constant temp. of 25°. R_t s were 11.55 min for the succinate ester and 7.25 min for pelargonin. FAB-MS, in the positive ion mode, gave a molecular cation at m/z 695, an [M − 100] at 595, an [M − 162] at 533, an [M − 262] at 433 and an aglycone ion at m/z 271.

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