Mollic acid 3-O-α-L-arabinopyranoside tetraacetate (**2a**). Acetylation of **2** (40 mg) with Ac_2O following the usual method gave **2a** as colourless needles (35 mg) from $CHCl_3$–EtOH, mp 108–110°, $[\alpha]_D + 29.9°$ ($CHCl_3$; *c* 1.0); IR ν_{max} cm^{-1}: 2630 (CO_2H dimer), 1740 (acetoxy C=O), 1700 (carboxy C=O), 1443, 1370, 1250–1210 (acetate C–O–C), 1173, 1103, 1057, 1022, 990, 963, 940; MS *m/z* 772 $[M]^+$ (identical to mollic acid β-D-xyloside [2]); ^1H NMR ($CDCl_3$): δ0.51 (1H, *d*, $J = 4$ Hz, H-19), 0.78 (1H, *d*, $J = 4$ Hz, H-19), 0.90 (9H, 18-, 21-, and 32-Me), 1.11 (3H, *s*, 31-Me) 1.60 (3H, *s*, Me), 1.67 (3H, *s*, Me), 1.99, 2.02, 2.09 and 2.11 (each 3H, *s*, acetoxy Me), 3.48–4.01 (2H, *br m*, H-5′), 4.47 (1H, *d*, $J = 6.3$ Hz, H-1′), 4.66 (1H, *t*, H-1), 4.70–5.08 (4H, *br m*, H-2′, H-3′, H-4′, H-3α), 5.19 (1H, *t*, H-24); ^{13}C NMR ($CDCl_3$): see Table 1.

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REFERENCES

1. Pegel, K. and Rogers, C. B. (1985) *J. Chem. Soc. Perkin Trans. I* 1711.
2. *Rogers, C. B. and Thevan, I.* (1986) *Phytochemistry* **25**, 1759.
3. Carr, J. D. and Rogers, C. B. (1987) *S. Afr. J. Botany* **53**, 173.
4. Osborne, R. and Pegel, K. H. (1984) *Phytochemistry* **23**, 635.
5. Rogers, C. B. and Subramony, G. (1988) *Phytochemistry* **27**, 531.
6. Osborne, R. (1982) M.Sc. Thesis, University of Natal, Durban.
7. Khuong-Huu, F., Sangare, M., Chari, V. M., Bekaert, A., Devys, M., Barbier, M. and Lukacs, G. (1975) *Tetrahedron Letters* **22**, 1787.
8. Stothers, J. B. (1972) *Carbon-13 NMR Spectroscopy*. Academic Press, New York.
9. Kamisako, W., Honda, C., Suwa, K. and Isoi, K. (1987) *Magn. Reson. Chem.* **25**, 683.

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ANTHRAQUINONE DERIVATIVES FROM *GLADIOLUS SEGETUM*

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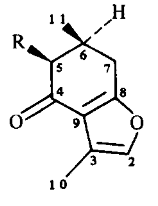
Key Word Index—*Gladiolus segetum*; Iridaceae; rhizomes; pigments; anthraquinones; desoxyerythrolaccin; 3,8-dihydroxy-6-methoxy-l-methylanthraquinone-2-carboxylic acid.

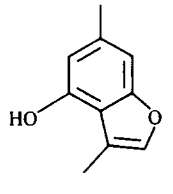
Abstract—Rhizomes of *Gladiolus segetum* contain, in addition to desoxyerythrolaccin, the new anthraquinone pigment 3,8-dihydroxy-6-methoxy-1-methylanthraquinone-2-carboxylic acid.

Young subterranean parts and rhizomes of *Gladiolus segetum* Ker-Gawler afforded on extraction with methanol and chromatography on silica gel two anthraquinone pigments **1** and **2** which were separated by chromatography on Sephadex LH 20. The spectral data (UV, ^1H NMR, MS) and the mp of **1** were coincident with those of desoxyerythrolaccin, an isomer of emodin reported before from *Aloe saponaria* [1] and the insect *Laccifer lacca* (Coccidae) [2]. The ^1H-coupled ^{13}C NMR spectrum of **1** is given in Table 1.

The second compound, mp 238–240°, $C_{17}H_{12}O_7$, exhibits UV/vis absorption maxima characteristic of a 1-hydroxyanthraquinone [λ_{max} (log ε) nm: 227 (4.09), 283 (4.15), 344 (3.29), 429 (3.59)]. In the mass spectrum loss of water from the molecular ion (*m/z* 328) to form the base peak (*m/z* 310) as well as strong fragments at $[M - CO_2]^+$ (284) and $[M - CO_2H_2]^+$ (282) indicate the presence of a carboxyl group *ortho* to a hydroxyl function. The ^1H NMR spectrum (DMSO-d_6) shows signals for an isolated aromatic proton (*s*, δ7.61) and two *meta*-coupled aromatic protons (*d*, $J = 2.5$ Hz, δ6.84 and 7.13). The α-position of the C-methyl group follows from its signal at δ2.67 (*s*, 3H) which indicates the deshielding by the neighbouring carbonyl group. The position of the O-methyl group at C-6 (*s*, δ3.89, 3H) follows from the presence of a free chelated hydroxy group (*s*, δ13.18) and



1 R = H
2 R = OH
3 R = OAc
4 *p*-Br-Ph-COO
5 R = H, 4-desoxy



A, *m/z* = 162

Table 1. ^{13}C NMR data for compounds **1** and **2** (100.4 MHz, DMSO-d_6, TMS as int. standard)

C	**1**	**2**
1	144.9 *q*, $J = 6$ Hz	140.0 *q*, $J = 6$ Hz
1a	122.3 *m*	122.4 *dq*, $J = 7, 3$ Hz
2	124.6 *ddq*, $J = 160, 5, 5$ Hz	131.5 *dq*, $J = 5, 5$ Hz
3	161.8 *s*	158.1 *s*
4	107.1 *dm*, $J = 162$ Hz	112.1 *d*, $J = 165$ Hz
4a	134.2 *s*	133.8 *s*
5	112.1 *dd*, $J = 164, 5$ Hz	106.0 *dd*, $J = 167, 5$ Hz
5a	136.6 *s*	136.0 *s*
6	164.5 *br s*	164.9 *m*
7	108.1 *dd*, $J = 165, 5$ Hz	106.8 *ddd*, $J = 162, 8, 5$ Hz
8	164.1 *s*	164.4 *t*, $J = 4.5$ Hz
8a	109.9 *t*, $J = 5.5$ Hz	110.9 "*q*", $J = 5.5$ Hz
9	187.9 *s*	188.0 *s*
10	182.3 *t*, $J = 4.5$ Hz	181.7 *t*, $J = 4.5$ Hz
Me	23.5 *qd*, $J = 129, 6$ Hz	19.7 *q*, $J = 130$ Hz
CO_2H	—	168.1 *s*
MeO	—	56.1 *q*, $J = 146$ Hz

the signal enhancement of both the doublets at $\delta 6.84$ and 7.13 on irradiation at the methoxyl frequency. The structure of the pigment is thus assigned as 3,8-dihydroxy-6-methoxy-1-methylanthraquinone-2-carboxylic acid (**2**), which is in full accord with the ^1H-coupled ^{13}C NMR spectrum (Table 1).

Anthraquinone pigments with the same substitution pattern have been obtained before from *Aloe saponaria* (Liliaceae) [1] and *Eleutherine americana* (Iridaceae) [3]. The *O*-demethyl derivative of pigment **2**, laccaic acid D, occurs as its methyl ester in *Aloe saponaria* [1]. The isolation of **1** and **2** from *Gladiolus* underlines the chemotaxonomic relationship between both plant families [4].

EXPERIMENTAL

General. ^1H NMR spectra were measured at 90 or 400 MHz and chemical shifts are given in δ values with TMS as int. standard. MS were determined at 70 eV. TLC was performed on silica gel 60 (Merck) using $CHCl_3$–MeOH (4:1).

Plant material. The material for this investigation was obtained from cultivated plants collected at Assiut University Campus during flowering. The identity of the species was confirmed by Prof. Dr N. El-Hadidi (Faculty of Science, Cairo University). A voucher sample is kept in the Faculty of Pharmacy, Assiut University.

Extraction and isolation. Air-dried subterranean parts and rhizomes (2 kg) were subjected to continuous Soxhlet extraction using petrol (60–80°) for defatting followed by exhaustive extraction with MeOH. The crude MeOH extract was passed through a silica gel column (5 × 80 cm). The orange coloured fractions eluted with $CHCl_3$–MeOH (4:1) were collected and applied to a Sephadex LH 20 column (5 × 60 cm). 50 ml fractions were eluted with MeOH–Me_2CO (4:1) and monitored by TLC. Fractions 15–30 contained pigment **1** (R_f 0.71), fractions 90–100 **2** (R_f 0.14).

Desoxyerythrolaccin (**1**). Fractions 15–30 afforded orange needles (30 mg) on crystallization from MeOH, mp 300° (lit. mp 300° [1]). UV, IR and ^1H NMR data were in agreement with lit. [1]. The ^{13}C NMR data are recorded in Table 1.

3,8-*Dihydroxy*-6-*methoxy*-1-*methylanthraquinone*-2-*carboxylic acid* (**2**). Fractions 90–100 afforded orange crystals (80 mg) on crystallization from MeOH, mp 238–240°. UV λ_{max} nm (log ε): 227 (4.09), 283 (4.15), 344 (3.29), 429 (3.59); IR ν_{max} cm^{-1}: 3385, 3320, 3300, 2930, 2600, 1718, 1707, 1623, 1570, 1440, 1105. ^1H NMR (90 MHz, DMSO-d_6): $\delta 2.67$ (*s*, C-1-Me), 3.89 (*s*, OMe), 6.84 (*d*, $J = 2.5$ Hz, 7-H), 7.13 (*d*, $J = 2.5$ Hz, 5-H), 7.61 (*s*, 4-H), 7.70 (*br s*, OH), 13.18 (*s*, OH); ^{13}C NMR see Table 1; MS *m/z* (rel. int.): 328.0575 $[M]^+$ (55.5%, calculated for $C_{17}H_{12}O_7$ 328.0583), 310 $[M-H_2O]^+$ (100), 284 $[M-CO_2]^+$ (43), 282 $[M-CO_2H_2]^+$ (26), 266 $[C_{16}H_{10}O_4]^+$ (11), 254 $[C_{15}H_{10}O_4]^+$ (32), 226 $[C_{14}H_{10}O_3]^+$ (14), 211 $[C_{13}H_7O_3]^+$ (9).

REFERENCES

1. Yagi, A., Makino, K. and Nishioka, I. (1974) *Chem. Pharm. Bull.* **22**, 1159.
2. Mehendale, A. R., Rama Rao, A. V., Shaikh, I. N. and Venkataraman, K. (1968) 2231.
3. Komura, H., Mizukawa, K., Minakata, H., Huang, H., Quin, G., Xu, R. (1983) *Chem. Pharm. Bull.* **31**, 4206.
4. Williams, C. A. and Harborne, J. B. (1985) *Z. Naturforsch.* **40c**, 325.