methanolic extraction was partitioned between EtOAc and $H_2O$. The aq. layer was made alkaline with $NH_3$ (pH 9) and extracted repeatedly with $CHCl_3$. The alkaloid containing $CHCl_3$ layers were combined and evapd at red. pres. to afford a gummy residue, this was treated with $C_6H_6$ and the $C_6H_6$-soluble and $C_6H_6$-insoluble portions were obtained. The $C_6H_6$-soluble portion was selected for investigation and chromatographed on a neutral alumina column. The polar fractions were rechromatographed and yielded a colourless amorphous powder (12.2 mg).

*Prosopidione.* Mp 202° (decomp.); $[\alpha]_D = -19.2°$ (MeOH); UV $\lambda_{max}^{MeOH}$ nm (log ε): 202 (2.46), 228 (2.52), IR $\nu_{max}^{KBr}$ $cm^{-1}$: 1675 (α,β-unsaturated ketone), 1260 (C–O), 960 (C–H) stretching for C=C. $^1H$ NMR ($CD_3OD$): δ 0.81 (*d*, *J* = 6.8 Hz, H-13), 0.87 (*s*, H-11), 1.10 (*s*, H-12), 2.26 (*s*, COMe), 2.15 (*m*, H-2), 1.7 (*dd*, $J_{gem}$ = 12.56 Hz, $J_{5\alpha,6}$ = 6.6 Hz, H-5α), 1.8 (*dd*, $J_{gem}$ = 12.52 Hz, $J_{5\beta,6}$ = 4.84 Hz, H-5β), 1.5 (*m*, 2H-3), 4.5 (*m*, H-6), 6.33 (*d*, *J* = 16.04 H-7) and 6.88 (*d*, *J* = 16.04 Hz, H-8).

HRMS. *m/z* 208.14688 (calc. for $C_{13}H_{20}O_2$ 208.146321), 165.127075 ($C_{11}H_{17}O$ 165.127935), 140.10736 ($C_9H_{16}O$. 140.120109), 125.13072 ($C_9H_{17}$ 125.133019). $^{13}C$ NMR ($CD_3OD$, 75.43 MHz): δ 182.64 (C-1), 35.34 (C-2), 36.97 (C-3), 48.8 (C-4), 42.98 (C-5), 75.76 (C-6), 131.74 (C-7), 153.96 (C-8), 200.84 (C-9), 25.81 (C-10), 23.79 (C-11), 24.9 (C-12), 16.34 (C-13).

## REFERENCES


1. Nasir, E. and Ali, S. I. (1972) *Flora of West Pakistan*, p. 383. Fakhri, Karachi.
2. Kirtikar, K. R. and Basu, B. D. (1935) *Indian Medicinal Plants* Vol. 11, pp. 910. Leader Press, Allahabad.
3. Siddiqui, S. and Murthi, S. (1948) *J. Sci. Ind. Res.*, **7b**, 188.
4. Merzabani, M. M. El., Aaser, A. A., Attia, M. A., Duwemi, A. K. Al. and Ghazal, A. M. (1979) *Planta Med.* **36**, 150.
5. Ikram, M. (1983) *Fitotropia* 123.
6. Ahmed, A., Khan, K. A., Ahmad, V. U. and Qazi, S. (1986), *Planta Med.* 285.
7. Ahmad, V. U., Basha, A. and Haque, W. (1978) *Z. Naturforsch*, **33b**, 347.
8. Ahmad, V. U. and Qazi, S. (1985) *J. Chem. Soc. Pak.* 7, 347.


*Phytochemistry*, Vol. 28, No. 1, pp. 279–281, 1989.
Printed in Great Britain.

0031–9422/89 $3.00 + 0.00


# ISOLATION OF THE 1α-HYDROXYCYCLOARTENOID MOLLIC ACID α-L-ARABINOSIDE FROM *COMBRETUM EDWARDSII* LEAVES

C. B. ROGERS

Department of Chemistry, University of Durban-Westville, Private Bag X54001, Durban 4000, Republic of South Africa

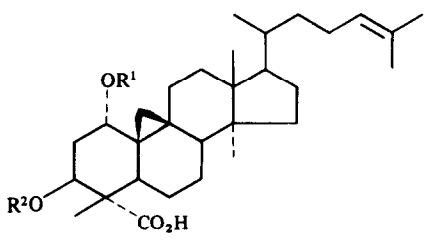
(*Received* 22 *March* 1988)

**Key Word Index**—*Combretum edwardsii*; Combretaceae; 1α-hydroxycycloartenoid arabinoside; $^{13}C$ NMR.

**Abstract**—The 1α-hydroxycycloartenoid glycoside, mollic acid 3-*O*-α-L-arabinopyranoside has been isolated from the leaves of *Combretum edwardsii*, revised $^{13}C$ NMR assignments for the aglycone mollic acid are given.

## INTRODUCTION

The leaf extract of *C. edwardsii* has been found to be remarkably similar to that of *C. molle* in that they both contain mollic acid [**1**], and its arabinoside, glucoside and xyloside. However, whereas mollic acid β-D-glucoside is the major constituent and mollic acid α-L-arabinoside the minor constituent in *C. molle* [1, 2], the situation is reversed in *C. edwardsii*, which contains barely discernible quantities of the glucoside, but large quantities of the arabinoside and xyloside. No other *Combretum* species screened thus far have these four compounds [3], which suggests that these two species have a common ancestry despite now having marked differences in habitat and taxonomy; *C. edwardsii* is a climber restricted to a few forested areas of central and coastal Natal in South Africa, whereas *C. molle* is a medium sized tree distributed in a great variety of habitats throughout south, central and north-east Africa. The isolation of 9,19-cycloartenoids from yet another *Combretum* species also suggests that at some stage in the development of this genus a chemotaxonomically significant bifurcation in triterpenoid synthesis occurred, resulting in certain species, *C. molle* [1], *C. edwardsii*, and *C. eleaegnoides* [4], producing these compounds and other species, *C. imberbe* [5], *C.*




**1** $R^1 = R^2 = H$
**2** $R^1 = H$, $R^2$ = L-Ara
**2a** $R^1$ = Ac, $R^2$ = L-Ara(Ac)$_3$
**3** $R^1 = H$, $R^2$ = D-xyl

*kraussii* [6], *C. apiculatum* [C. B. Rogers unpublished results], *C. padoides* [C. B. Rogers unpublished results], producing oleane type pentacyclic triterpenoids containing 29-carboxy-1α-hydroxy groups. The extent of this bifurcation will only become apparent as more *Combretum* species are investigated. This paper describes the isolation and characterisation of mollic acid 3-*O*-α-L-arabinopyranoside (**2**), previously identified in but never isolated from *C. molle* [2].

## RESULTS AND DISCUSSION

The white precipitate from the ether extract of *C. edwardsii* leaves was found by TLC and $^{13}$C NMR to comprise almost equal quantities of the xyloside and arabinoside of mollic acid (**1**) plus trace amounts of the glucoside. Mollic acid (**1**) was also identified in the mother liquor of the extract by co-chromatography. Repeated prep TLC separation of the ether precipitate yielded mollic acid 3-*O*-β-D-xyloside (**3**), and an almost pure fraction of mollic acid 3-*O*-α-L-arabinoside (**2**), which was purified to TLC purity by recrystallization from ethanol. The $^1$H and $^{13}$C NMR of **2** and **3** and their peracetates differed only in the sugar region and, as expected, the two peracetates gave identical EI mass spectra [2]. Excellent agreement in chemical shifts in the sugar region of the $^{13}$C NMR spectra of **2** and its tetraacetate **2a** with equivalent shifts for cholesteryl 3-*O*-α-L- arabinoside and its triacetate [2] and with known compounds [4], furnished unequivocal proof that the sugar in **2** was arabinose (assumed to be the L-form on biogenetic grounds). On this evidence **2** must be mollic acid 3-*O*-α-L-arabinopyranoside (4α-carboxy-4β, 14α-dimethyl-1α-hydroxy-9β,19-cyclo-5α-cholest-24-en-3β-yl-α-L-arabinopyranoside).

Revised $^{13}$C NMR assignments for mollic acid (**1**) and the assignments for **2** and **2a** are given in Table 1. The original assignments for **1** were based on those for cycloartenol and related compounds [7] and were deduced by the usual methods [8]. Recent studies of the $^{13}$C NMR spectra of $^{13}$C-enriched cycloartenol have resulted in changes to the assignments of C-7, C-11, C-16, C-18, C-21 and C-32 [9]. Assignments for these carbons in **1** have been changed accordingly.

## EXPERIMENTAL

Mp: uncorr. $^1$H and $^{13}$C NMR were recorded at 80 and 20 MHz respectively, IR were recorded in KBr while MS were measured at 70 eV with direct inlet. Prep TLC was carried out on Merck Kieselgel 60 (Art. 4745) plates using EtOAc–$CHCl_3$–$HCO_2H$ (5:4:1) as eluant.

*Plant material.* Leaves were collected from the Umtamvuna Nature Reserve, Natal, Republic of South Africa in February 1986. The dried, milled leaves were extracted as described previously [1]. The white pp. collected from the ether extract was applied to each of 5 prep plates (30 mg extract per plate) which were then developed twice. The upper band yielded mollic acid β-D-xyloside (**3**), which was identified as such by $^1$H and $^{13}$C NMR spectroscopy and the MS of its tetraacetate [1]. The lower band yielded crude **2** which was purified by recrystallization from EtOH.

*Mollic acid 3-O-α-L-arabinopyranoside* (**2**). Colourless needles from EtOH (44 mg), mp 234–235°, $[\alpha]_D$ + 44.5° ($C_5D_5N$; *c* 1.0); IR $\nu_{max}$ cm$^{-1}$: 3485–3370 (OH), 3045 (cyclopropyl CH), 2630 ($CO_2H$ dimer), 1676 (carboxy C=O), 1445, 1374, 1280, 1245, 1091, 1068, 1011, 990, 920; $^1$H NMR ($C_5D_5N$): δ 0.13 (1H, *d*, *J* = 4 Hz, H-19), 0.38 (1H, *d*, *J* = 4 Hz, H-19), 0.63–1.35 (6 × Me), 3.08–4.10 (arabinose protons; H-1β), 4.63 (1H, *d*, *J* = 6.5 Hz, H-1′), 4.88–5.18 (2H, *m*, H-3α, H-24); $^{13}$C NMR ($C_5D_5N$): see Table 1.

Table 1. $^{13}$C NMR spectral data for compounds **1**, **2** and **2a**

| C | 1* | 2* | 2a† | C | 1 | 2( )‡ | 2a( )§ |
|---|---|---|---|---|---|---|---|
| 1 | 72.8 | 72.5 | 75.3 | 18 | 18.3 | 18.5 | 18.1 |
| 2 | 38.5 | 37.7 | 32.9 | 19 | 29.9 | 29.8 | 27.8 |
| 3 | 70.4 | 81.5 | 80.3 | 20 | 36.3 | 36.4 | 35.7 |
| 4 | 55.7 | 55.0 | 53.6 | 21 | 19.6 | 19.7 | 18.9 |
| 5 | 37.7 | 38.0 | 38.7 | 22 | 36.3 | 36.1 | 36.2 |
| 6 | 23.4 | 23.3 | 22.0 | 23 | 25.5 | 25.5 | 24.8 |
| 7 | 25.9 | 26.0 | 24.5 | 24 | 125.9 | 126.0 | 125.1 |
| 8 | 48.2 | 48.4 | 46.4 | 25 | 130.8 | 131.0 | 130.8 |
| 9 | 21.1 | 21.1 | 21.2 | 26 | 25.9 | 26.0 | 25.6 |
| 10 | 30.5 | 30.3 | 27.2 | 27 | 17.8 | 18.0 | 17.5 |
| 11 | 26.5 | 26.3 | 25.9 | 30 | 179.9 | 180.2 | 180.4 |
| 12 | 36.9 | 36.9 | 35.3 | 31 | 9.6 | 10.5 | 8.8 |
| 13 | 45.8 | 48.5 | 45.0 | 32 | 18.7 | 18.7 | 17.6 |
| 14 | 49.3 | 49.3 | 48.7 | 1′ | | 106.3 (103.3) | 101.8 (99.3) |
| 15 | 33.5 | 33.5 | 32.5 | 2′ | | 73.0 ( 72.7) | 69.1 (69.1) |
| 16 | 28.4 | 28.6 | 28.1 | 3′ | | 74.4 ( 74.8) | 69.9 (69.9) |
| 17 | 52.8 | 52.8 | 52.1 | 4′ | | 69.3 ( 69.7) | 67.5 (67.5) |
| | | | | 5′ | | 66.5 ( 67.0) | 62.8 (62.8) |

* Measured in $C_5D_5N$ relative to TMS.

† Measured in $CDCl_3$ relative to TMS.

( ) Equivalent assignments for ‡ cholesteryl α-L-arabinoside.

§ Cholesteryl α-L-arabinoside tetraacetate [2].

*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 $\nu_{max}$ $cm^{-1}$: 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 ($CDCl_3$): δ 0.51 (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.

*Acknowledgements*—I wish to thank Mr A. Abbott (Umtamvuna Nature Reserve) for leaf material and Dr D. H. Pienaar for running NMR spectra.

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.

*Phytochemistry*, Vol. 28, No. 1, pp. 281–282, 1989.
Printed in Great Britain.

0031-9422/89 $3.00 + 0.00


# ANTHRAQUINONE DERIVATIVES FROM *GLADIOLUS SEGETUM*

A. A. ALI, O. M. ABDALLAH and W. STEGLICH*

Pharmacognosy Department, Faculty of Pharmacy, Assiut University, Assiut, Egypt; *Institut für Organische Chemie und Biochemie der Universität Bonn, Gerhard-Domagk-Straße 1, D-5300 Bonn 1, F.R.G.

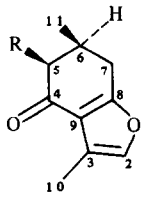
(*Received* 10 *May* 1988)

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

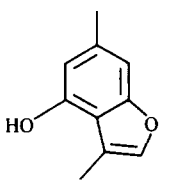
**Abstract**—Rhizomes of *Gladiolus segetum* contain, in addition to desoxyerythrolaccin, the new anthraquinone pigment 3,8-dihydroxy-6-methoxy-1-methylanthraquinone-2-carboxylic acid.

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 [$\lambda_{max}$ (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*, δ 7.61) and two *meta*-coupled aromatic protons (*d*, *J* = 2.5 Hz, δ 6.84 and 7.13). The α-position of the C-methyl group follows from its signal at δ 2.67 (*s*, 3H) which indicates the deshielding by the neighbouring carbonyl group. The position of the *O*-methyl group at C-6 (*s*, δ 3.89, 3H) follows from the presence of a free chelated hydroxy group (*s*, δ 13.18) and




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




**A**, *m/z* = 162