2. Glasby, J. S. (1982) *Encyclopaedia of the Terpenoids* Vol. 2. Wiley, New York.
3. Horeau, A. and Nouaille, A. (1971) *Tetrahedron Letters* 1939.
4. Colonge, J. and Descotes, G. (1967) *α,β-Unsaturated Carbonyl Compounds as Dienes*, in *Organic Chemistry, a series of Monographs* (Blomquist, A. T. ed.) Vol. 8, p. 217. Academic Press, New York.
5. Takemoto, T. and Nakajima, T. (1957) *J. Pharm. Soc. Jpn* 77, 1157.
6. Nakajima, T. (1962) *J. Pharm. Soc. Jpn* 82, 1278.
7. Coxon, J. M., Hydes, G. J. and Steel, P. J. (1984) *J. Chem. Soc. Perkin Trans.* II 1351.
8. Russell, G. F. and Olson, K. V. (1972) *J. Food Sci.* 37, 405.
9. Abraham, R. J., Cooper, M. A., Indyk, H., Sieverns, T. M. and Whittaker, D. (1973) *Org. Magn Reson.* 5, 373.
10. Jefford, C. W., Boschung, A. F., Moriarty, R. M., Rimbault, C. G. and Laffer, M. H. (1973) *Helv. Chim. Acta* 56, 2649.

Phytochemistry, Vol. 26, No. 12, pp. 3353–3354, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00
Pergamon Journals Ltd.

ERANTHEMOSIDE, A NEW IRIDOID GLUCOSIDE FROM *ERANTHEMUM PULCHELLUM* (ACANTHACEAE)

HENRIK FISCHER W. JENSEN, SØREN ROSENDAL JENSEN and BENT JUHL NIELSEN

Department of Organic Chemistry, The Technical University of Denmark, Bygn. 201, DK-2800 Lyngby, Denmark

(*Received* 10 *March* 1987)

Key Word Index—*Eranthemum pulchellum*; Acanthaceae; iridoid glucoside; eranthemoside; betaine.

Abstract—A new iridoid glucoside, eranthemoside, has been isolated from *Eranthemum pulchellum* (Acanthaceae). The structure was established solely by spectroscopic means. The quaternary amino acid betaine was also isolated.

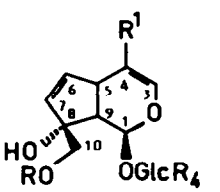
INTRODUCTION

Iridoid glucosides are commonly encountered in the Scrophulariaceae and related families, their presence being considered as a valuable systematic character [1]. In the Acanthaceae, however, iridoids do not appear to be commonly occurring except in seeds [1]. Only a few reports of these compounds in whole plants have been published [1–4]. During a search for iridoid glucosides in a number of species within Acanthaceae we encountered a new iridoid glucoside in *Eranthemum pulchellum* Andrews (= *E. nervosum*, (Vahl) R. Br.), the structure elucidation of which is reported here.

RESULTS AND DISCUSSION

An ^{1}H NMR spectrum of the crude aqueous extract of twigs of *E. pulchellum* showed several signals in the interval between 5 and 6 ppm indicating the presence of an iridoid glucoside. In addition a very intense signal could be seen at *ca* 3.2 ppm. Reversed phase chromatography of the extract gave two fractions. The most polar fraction contained the compound with the NMR signal at δ3.2. Silica gel chromatography (see Experimental) provided betaine.

The second fraction contained a new iridoid glucoside **1** which we have named eranthemoside. The ^{1}H NMR spectrum showed five signals in the interval δ5–6.5 ppm with a pattern suggesting a monotropein-like structure, though without the carboxyl group at C-4. In a decoupling experiment irradiation at δ3.3 (H-5, partially overlapping with the sugar protons) changed four of the low field signals, of which one pair then could be ascribed to H-3 and H-4 (6.20 and 5.13 ppm, respectively). The remaining signals, including a singlet at δ3.68 (10-CH_2OH) suggested the structure **1**. The ^{13}C NMR spectrum (see Table 1) contained 15 signals of which six could be ascribed to a β-glucopyranosyl moiety while the remaining signals were in accord with the structure **1**. Assuming the usual stereochemistry for iridoid glucosides at C-1, C-5 and C-9, the configuration at the remaining centre, C-8, could be determined by comparison with the spectra of galioside (**3**) and its 8-epimer, gardenoside. Thus the shift values arising from the cyclopentane carbon atoms (C-5–C-9) were almost coincident in the spectra of **1** and **3**, while



1 R = R^1 = H

2 R = Ac; R^1 = H

3 R = H; R^1 = COOMe

Table 1. ^{13}CNMR data*

C	1	2	galioside(3)	gardenoside
1	94.3	92.8	95.1	94.1
3	138.8[a]	137.4[a]	152.0	151.6
4	106.5	105.6	111.1	110.9
5	38.0	37.3	37.8	37.9
6	131.6	131.2	132.8	134.2
7	138.3[a]	136.9[a]	138.0	138.8
8	85.9	83.2	85.6	86.0
9	44.7	44.7	44.8	51.4
10	67.3	69.1	67.2	66.0
11			170.3	169.8
OMe			52.7	52.7
1′	98.8	95.5	99.1	99.0
2′	73.6	70.4	73.4	73.4
3′	76.5	71.9	76.4	76.3
4′	70.4	68.0	70.4	70.3
5′	77.0	72.2	77.0	77.0
6′	61.5	61.5	61.5	61.5

*Spectra were recorded in D_2O or $CDCl_3$ at 22.6 MHz and have been aligned to $\delta_{C\text{-}6'} = 61.5$ ppm.
[a]Interchangeable.

larger differences could be seen when comparing the spectra of **1** and gardenoside. The difference was particularly large for the C-9 signal, a well-known effect [5, 6]. Eranthemoside appeared to be rather unstable and turned purple in a few days. Acetylation provided a stable, crystalline pentaacetate (**2**).

EXPERIMENTAL

Microanalyses were done by NOVO Microanalytical Laboratory, Bagsvaerd, Denmark. Mps are corrected. The plant material was grown in a greenhouse in The Botanical Garden, Copenhagen. The voucher is kept in the herbarium of the Garden (No. 4087-1). Flowering stems of *E. nervosum* (140 g) were homogenized in EtOH (0.5 l). The filtrate was taken to dryness and partitioned in H_2O–Et_2O, after which the aq. fraction was passed through a column of Al_2O_3 (140 g) and the column washed with H_2O (400 ml). Evaporation gave a residue (2.64 g) which by trituration with MeOH and treatment with act C gave 1.47 g of a colourless syrup. An ^{1}H NMR spectrum of this mixture showed several absorptions above δ5 and in addition a very intense signal at δ3.2. Reversed phase chromatography [Merck Lobar RP-8 (B)] eluting with H_2O–MeOH (25:1 followed by 10:1) gave first a polar fraction (1.16 g), then pure eranthemoside (**1**, 97 mg; 0.07 %) as an amorphous powder after lyophilization; $[\alpha]_D^{20}$ −98° (EtOH; *c* 0.9); ^{1}H NMR (90 MHz, D_2O): δ6.20 (*dd*, *J* = 6 and 2 Hz, H-3), 6.11 (*dd*, *J* = 5.5 and 3 Hz, H-6), 5.69 (*dd*, *J* = 5.5 and 2 Hz, H-7), 5.52 (*d*, *J* = 1.7 Hz, H-1), 5.13 (*dd*, *J* = 6 and 3 Hz, H-4), 4.84 (*d*, *J* = *ca* 7 Hz, H-1′), 3.68 (*s*, 10-CH_2O), *ca* 3.3 (*m*, H-5), 2.59 (*dd*, *J* = 8.5 and 1.7 Hz, H-9). (Found: C, 49.6; H, 6.6. $C_{15}H_{22}O_9$, H_2O requires: (C, 49.5; H, 6.6 %). Acetylation of **1** (Ac_2O/Py, 2 hr) provided the pentaacetate **2**, mp (EtOH) 104–105°; $[\alpha]_D^{20} = -109°$ ($CHCl_3$; *c* 0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ6.15 (*dd*, *J* = 6.0 and 1.9 Hz, H-3), 5.96 (*dd*, *J* = 5.6 and 2.6 Hz, H-6), 5.66 (*dd*, *J* = 5.6 and 1.8 Hz, H-7), 5.48 (*d*, *J* = 2.5 Hz, H-1), 5.00 (*dd*, *J* = 6.1 and 3.0, H-4); 4.22 and 4.12 (AB-system, *J* = 11.4 Hz, 10-CH_2OAc), 3.22 (*m*, H-5), 2.59 (*dd*, *J* = 8.5 and 2.5 Hz, H-9), 2.10, 2.09, 2.03, 2.03 and 2.01 (*s*'s, 5 × AcO). (Found: C, 54.0; H, 5.9, $C_{25}H_{32}O_{14}$ requires: C, 54.0; H, 5.8 %).

The polar fraction above was evapd onto Si gel (30 g) which was placed on top of a further amount (50 g) of Si gel in a column. Elution with EtOH (200 ml), MeOH (200 ml) followed by H_2O–MeOH (1:9, 200 ml) gave in the last fraction betain (410 mg, 0.3 %), identified by the ^{1}H NMR spectrum (90 MHz, D_2O): δ3.91 (*s*, 2H); 2.38 (*s*, 9H).

Acknowledgements—We thank Dr Bertel Hansen, The Botanical Museum, Copenhagen for supplying and authenticating the plant material. Access to NMR facilities from the Danish Natural Science Council and the Carlsberg Foundation are acknowledged.

REFERENCES

1. Hegnauer, R. and Kooiman, P. (1978) *Planta Med.* **33**, 1.
2. Damtoft, S., Jensen, S. R. and Nielsen, B. J. (1982) *Tetrahedron Letters* 4155.
3. Jensen, S. R. and Nielsen, B. J. (1985) *Phytochemistry* **24**, 602.
4. Suksamrarn, A. (1986) *J. Nat. Prod.* **49**, 179.
5. Chaudhuri, R. K., Affifi-Yazar, F. Ü., and Sticher, O *Helv. Chim. Acta* **62**, 1603.
6. Damtoft, S., Jensen, S. R. and Nielsen, B. J. (1981) *Phytochemistry* **20**, 2717.