Phytochemistry, Vol. 26, No. 5, pp. 1539–1540, 1987.
Printed in Great Britain.

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

GLUT-5(10)-EN-3-ONE FROM *ANDRACHNE CORDIFOLIA*

K. S. MUKHERJEE and P. BHATTACHARJEE

Department of Chemistry, Visva-Bharati, Santiniketan 731 235, West Bengal, India

(*Received* 5 *June* 1986)

Key Word Index—*Andrachne cordifolia*; Euphorbiaceae; glut-5(10)-en-3-one.

Abstract—Glut-5(10)-en-3-one, a new pentacyclic triterpene ketone, was isolated from *Andrachne cordifolia* (aerial parts and roots).

INTRODUCTION

In a previous communication [1], we reported the isolation of a new triterpene alcohol from *Andrachne cordifolia*. The present paper reports the isolation and structure elucidation of a new triterpene ketone, glut-5(10)-en-3-one (**1**) from the same plant [2].

RESULTS AND DISCUSSION

Glut-5(10)-en-3-one, $C_{30}H_{48}O$ ($[M]^+$ m/z 424), mp 250–254°, gives a positive Leibermann–Burchardt test for pentacyclic triterpenes and shows IR absorption bands at 1700 (carbonyl) and 1648 cm^{-1} (unsaturation). On treatment with 2,4-dinitrophenyl hydrazine it forms a crystalline derivative, mp 218–20°, and gives a positive Zimmermann test.

The ^1H NMR spectrum (90 MHz, $CDCl_3$) of the parent triterpene contains signals for eight C-methyls at δ0.82 (3H, *s*), 9.85 (3H, *s*), 0.93 (3H, *s*), 0.95 (6H, *s*), 1.05 (3H, *s*), 1.15 (3H, *s*), and 1.18 (3H, *s*). The absence of a signal for olefinic protons, shows the tetrasubstituted nature of the unsaturation present in the compound.

The mass spectrum of compound **1** is similar to that of other pentacyclic triterpenes [3]. The presence of peaks at m/z 424 $[M]^+$, 409, 396, 274, 259 and 205 are fully consistent with a glut-5(10)-en skeleton [4]. Further, from the mass values of the above peaks it is evident that the keto group in the triterpene is present in the A/B ring portion. Conclusive evidence regarding the glut-5(10)-en skeleton for the triterpene is provided by its conversion to glut-5(10)-ene (**2**) [5] by catalytic reduction. Finally, from biogenetic considerations as well as from the positive Zimmermann test, the keto group is placed at C-3. Consequently this new triterpene is glut-5(10)-en-3-one (**1**).

EXPERIMENTAL

All mps are uncorr. The plant was supplied by M/S, United Chemical & Allied Products, Calcutta, India (their specimen No. 906).

Extraction of A. cordifolia. Air-dried powdered plant (aerial parts and roots) (1 kg) was extracted for 56 hr. The extract was concd and chromatographed over 200 g of silica gel (mesh 60–120). Fractions 110–130 [petrol (bp 60–80°)–C_6H_6 (3:1)] were collected.

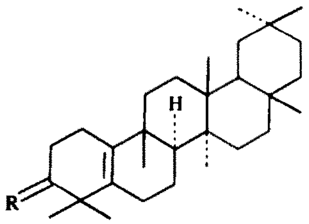
Isolation of glut-5(10)-*en*-3-*one* (**1**). Fractions 110–130 yielded a white solid (**1**) which was crystallized from $CHCl_3$ (yield 0.35 g), mp 250–254°. The IR, ^1H NMR (90 MHz $CDCl_3$), MS are described in Results.

Catalytic hydrogenation of glut-5(10)-*en*-3-*one*. Compound **1** (110 mg) in HOAc (50 ml) and cyclohexane (20 ml) was hydrogenated [PtO_2 (80 mg)/H_2] at room temp. and pressure. The catalyst was filtered off and the filtrate diluted with H_2O and extracted with Et_2O. The Et_2O layer was dried over Na_2SO_4, filtered and the filtrate evapd. The solid residue crystallized from EtOAc as colourless plates (**2**), $C_{30}H_{50}$ ($[M]^+$, m/z 410), mp 228°, $[\alpha]_D - 40$. The physical properties of **2** are the same as those reported in lit. [5].

Acknowledgement—We wish to thank RSIC (Madras) for spectral analysis. Financial assistance from UGC is also gratefully acknowledged.

REFERENCES

1. Mukherjee, K. S., Bhattacharjee, P., Mukherjee, R. K. and Ghosh, P. K. (1986) *Phytochemistry* **25**, 2669.
2. Chopra, R. N., Nayer, S. L. and Chopra, I. C. (1956) in *Glossary of Indian Medicinal Plants*, p. 18. Council of Scientific & Industrial Research, India.



1 R = O

2 R = $<^{H}_{H}$

3. Budziewicz, H., Wilson, J. M. and Djerassi, C. (1963) *J. Am. Chem. Soc.* **85**, 3688.
4. Anjeneyulu, A. S. R., Rao, Ramachandra, Subrahmanyam, C. and Murty, K. Suryanarayana (1973) *Tetrahedron* **29**, 3909.
5. Beaton, J. M., Spring, F. S., Stevenson, R. and Stewart, J. L. (1958) *Tetrahedron* **2**, 246.
6. Courtney, J. L., Gascoingne, R. M. and Szumer, A. Z. (1958) *J. Chem. Soc.* 881.

Phytochemistry, Vol. 26, No. 5, pp. 1540–1541, 1987.
Printed in Great Britain.

0031-9422/87 $3.00 + 0.00

ENT-ISOLARICIRESINOL IN *RESEDA SUFFRUTICOSA*

J. G. Urones, J. de Pascual Teresa, I. Sánchez Marcos and D. Díez Martín

Departamento de Química Orgánica, Facultad de Química, Universidad de Salamanca, Salamanca, Spain

(*Received* 20 *June* 1986)

Key Word Index—*Reseda suffruticosa*; Resedaceae; *ent*-isolariciresinol; lignan.

Abstract—A new lignan, *ent*-isolariciresinol, has been isolated from the ethanolic extract of the aerial parts of *Reseda suffruticosa* together with sitosterol glucoside.

INTRODUCTION

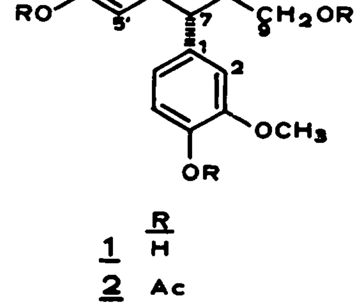
This communication is the first to describe the compounds of the *Reseda suffruticosa*, an endemic plant of Spain and present throughout the Iberian Peninsula on calcareous soil.

RESULTS AND DISCUSSION

Reseda suffruticosa specimens were collected in July at Chinchón (Madrid, Spain). They were submerged in EtOH for several days at room temperature. From the ethanolic extract of *Reseda suffruticosa*, 5.5 % of the aerial parts of the plant (dry weight), the benzene-soluble part (45.7 %) was separated and the residue was separated into a water-soluble (48.0 %) and a *n*-BuOH-soluble fractions (52.0 %). The *n*-BuOH-soluble fraction was separated by CC and **1** crystallized from the $CHCl_3$–MeOH (9:1) eluate. After acetylation of the residual liquids and further CC, the acetyl derivatives **2** and **3** were isolated.

Compound **1** is an aromatic hydroxy derivative (3400, 1615, 1525 cm^{-1} in IR spectrum). The ^1H NMR spectrum (Table 1) shows signals of two OMe and the following groups: two $CH–CH_2OH$ and $Ar–CH_2–CH$. One of the aromatic systems was found to be 1,3,4-trisubstituted, while the other was 1,2,4,5-tetrasubstituted. The ^{13}C NMR spectrum reveals signals for 21 carbons: three Me, three CH_2, eight CH (five sp^2) and seven completely substituted carbons of which six are sp^2 hybridized. Compound **2** was obtained by acetylation with $Ac_2O–C_5H_5N$ and in its ^1H NMR spectrum (see Table 1) four signals corresponding to acetoxyl groups could be observed.

The physical and spectroscopic properties of **2** ($[\alpha]_D$ + 3.6) and those of isolariciresinol tetraacetate [1] ($[\alpha]_D$ − 3.5) are the same except the sign of rotation, since **1** has a *ent*-isolariciresinol structure. Compound **3** is identified as sitosterol glucoside.



	R
1	H
2	Ac