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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*

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(*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

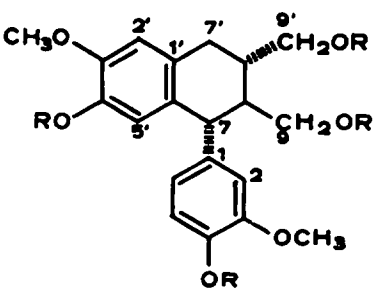
This communication is the first to describe the compounds of the *Reseda suffruticosa*, an endemic plant of Spain and present throughout the Iberian Peninsula on calcareous soil.

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

Table 1. ^{1}H NMR of lignans

	1 (CD_3OD)	2 ($CDCl_3$)	2 (C_6D_6)
H-2	6.60 *d* (1.98)	6.71 *d* (1.95)	6.69 *d* (1.95)
H-5	6.66 *d* (7.90)	6.97 *d* (8.06)	6.96 *d* (8.06)
H-6	6.52 *dd* (7.90, 1.98)	6.70 *dd* (8.06, 1.95)	6.60 *dd* (8.06, 1.95)
H-7		3.95 *d* (10.71)	3.83 *d* (10.74)
H-8	1.69 *m*		1.92 *m*
H-9^a_b	3.21 *m*	4.08 *dd* (11.7, 2.98) 3.98 *dd* (11.7, 3.49)	4.04 *m*
H-2′	6.11 *d* (0.79)	6.42 *d* (0.98)	6.45 *d* (0.98)
H-5′	6.54 *d* (0.79)	6.67 *d* (0.98)	6.74 *d* (0.98)
H-7′^a_b	2.68 *d* (7.30)	2.89 *d* (7.30)	2.68 *d* (7.32)
H-8′	1.91 *m*		2.11 *m*
H-9′^a_b	3.31 *m*	4.24 *dd* (11.30, 4.30) 4.1 *d* (11.30)	4.24 *dd* (11.47, 4.39) 4.04 *m*
OMe	3.65 *s*	3.76 *s*	3.36 *s*
OMe	3.67 s	3.81 s	3.31 s
CH_3–COO			1.87 *s* 1.76 *s* 1.75 *s* 1.73 *s*

Table 2. ^{13}C NMR data for *ent*-isolariciresinol and its acetate

C	1 (CD_3OD)	2 ($CHCl_3$)
1	134.1	138.77
2	114.0	113.42
3	147.1	151.32
4	145.1	142.86
5	116.0	122.93
6	123.1	121.63
7	48.0	47.36
8	48.0	43.62
9	62.5	63.28
1′	129.0	134.16
2′	112.4	112.03
3′	148.9	149.54
4′	145.8	138.28
5′	117.3	123.80
6′	138.5	131.28
7′	33.5	33.10
8′	40.1	35.36
9′	66.0	66.34
OMe	56.4	56.04
OMe	56.4	55.97

The acetyl C=O and Me shifts are 170.98, 170.82, 169.10, 168.92 and 20.86, 20.81, 20.69, 20.61, respectively.

EXPERIMENTAL

Mps uncorr; ^{1}H NMR: 200 MHz, $CDCl_3$, TMS as int. standard; ^{13}C NMR: 50.3 MHz.

Extraction and isolation. The aerial part (830 g) of *R. suffruticosa* collected at Chinchón (Madrid, Spain), was dried and extracted with EtOH for several days. The EtOH extract (46 g) was concentrated *in vacuo* and extracted with benzene (21 g). The insoluble residue (25 g) was fractionated with *n*-BuOH (13 g) and H_2O (12 g). CC of the *n*-BuOH extract, the fraction eluted with $CHCl_3$–MeOH (9:1), yielded by crystallization 1 and by treatment of the residue with Ac_2O–C_5H_5N and CC, later eluting with hexane–AcOEt, 2 and 3.

ent-*Isolariciresinol* (1). Mp 152–154° (from $CHCl_3$–MeOH); $[\alpha]_D^{25}$ −53.8 (*c*, 1.47, MeOH).

ent-*Isolariciresinol tetraacetate* (2). Mp 163°; $[\alpha]_D^{25}$ +3.6 (*c*, 1.15, $CHCl_3$).

Sitosterol β-D-glucoside (3). Mp 169°, $[\alpha]_D^{25}$ −35 (*c*, 0.4, $CHCl_3$); IR, ^{1}H and ^{13}C NMR and MS spectral data identical to lit. values.

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