

6 β - TIGLOYLOXYGLECHOMAFURAN A NEW FURANOSSESQUITERPENE FROM SALVIA GLUTINOSA

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Abstract

The aerial parts of *Salvia glutinosa* afforded in addition to lupeol, α - and β -amyryn a furanosesquiterpene, its structure being established by high field NMR techniques. The relative configuration at C-1, C-10, C-4, C-5 and C-6 of 6 β -tigloyloxyglechomafuran **1** was determined by the observed NOE'S.

Introduction

Many species of the large genus *Salvia* have been studied chemically [1-4]. However, *Salvia glutinosa* so far has not been investigated and as a part of our continuing chemical investigations of Iranian *Salvia* species we have now examined *S. glutinosa* L. (*Labiatae*)

Results and Discussion

Careful separation of the extract of the aerial parts of *S. glutinosa* afforded lupeol, α - and β -amyryn and an oily compound, its IR spectrum contained a carbonyl stretching frequency at 1735 cm⁻¹, as well as furan bands at 1660, 1550 and 880 cm⁻¹.

The new furanogermacrane, 6 β -tigloyloxyglechomafuran **1**, was assigned the composition C₂₀H₂₆O₅ on the basis of mass spectrometry (M⁺, m/z 346, 18%).

Its ¹H-NMR spectrum (Table 1) indicated that a tiglate of a furanosesquiterpene was present. The presence of trisubstituted furan followed from the typical signals at δ 7.07 (1H) and 1.93 (3H). A doublet at δ 3.10 and a double doublet at 2.87 indicated the presence

of a diepoxide. This was supported by spin decoupling leading to sequence requiring a 1(10) and 4,5-bisepoxide. The H-5 signal was a doublet showing a vicinal coupling with a broadened singlet at δ 6.63.

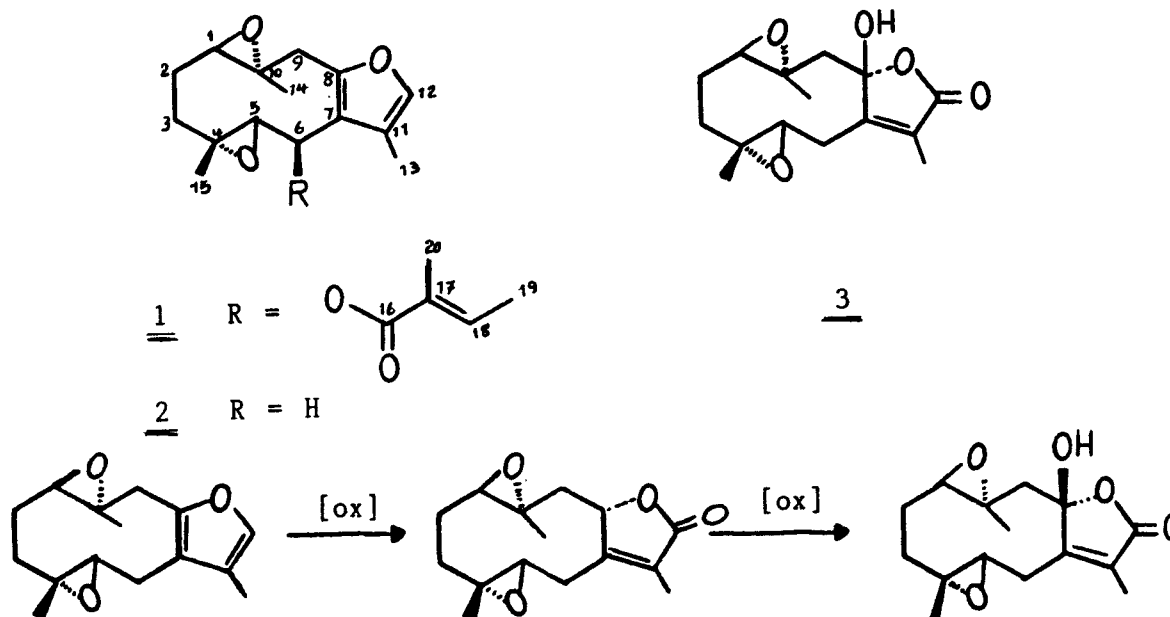
Accordingly, the tigloyloxy group most likely was at C-6. The small coupling already indicated that both H-5 and H-6 were α - oriented. This was established by the observed NOE'S. Thus clear effects were obtained H-3, H-5 (5%) and H-1 (2%), H-14 and H-9 (3%), H-13 with H-12 (7%) and H-6 (8%), H-1 and H-5 (6%) as well as between H-6, H-5 (6%) and H-13 (3%).

Thus we were dealing with 6 β -tigloyloxy-1 β , 10 α , 4 α , 5 β , 8, 12-epoxygermacra -7, 12-diene (**1**), a derivative of glechomafuran **2**, typical for several Umbelliferae species [5].

The ¹³C NMR data (Table 1) also agree with the structure. The most polar fractions afforded a further sesquiterpene its ¹H-NMR data clearly showed that we were dealing with an oxidation product of **2**, the 1 β , 10 α , 4 α , 5 β - diepoxy- 8 β - hydroxy- 8- α - 12- olide **3** [6], most likely an artifact.

The isolation of **1** from a *Salvia* species is of interest as such sesquiterpenes with this type of skeleton so far have been reported only from one species (*S*).

Keywords: *Salvia glutinosa*, Labiatae, Furanosesquiterpene



palaeifolia) [7].

Table 1. NMR spectral data of compound 1

^1H	1	^{13}C	1
1	2.86 dd	1	64.9 d
2	2.13 dddd	2	23.1 t
2	1.52 dddd	3	37.6 t
3	1.33 ddd	4	59.8 s
3	2.22 dt	5	64.3 d
5	3.10 d	6	65.9 d
6	6.63 brs	7	118.4 s
9	2.77 d	8	148.5 s
9	3.43 d	9	37.5 t
12	7.07 q	10	61.8 s
13	1.93 d	11	121.7 s
14	1.44 s	12	138.5 d
15	1.50 s	13	9.0 q
18	6.83 qq	14	18.0 q
19	1.80 dq	15	18.5 q
20	1.84 dq	16	166.5 s
		17	128.2 s
		18	137.6 d
		19	14.6 q
		20	12.3 q

*Some signals may be interchangeable.

J_{H} : $1,2\alpha = 1.5$; $1,2\beta = 11$; $2\alpha, 2\beta = 14$; $2\alpha, 3\alpha = 3$; $2\alpha, 3\beta = 5$;
 $2\beta, 3\alpha = 2\beta, 3\beta = 13$; $3\alpha, 3\beta = 13$; $5,6 = 1.5$; $9\alpha, 9\beta = 16$
 $18,19 = 7$; $18,20 = 19,20 = 1.5$

Experimental Section



^1H -NMR spectra were recorded with a Bruker WM 400 ^{13}C -NMR in CDCl_3 , Bruker WH 270. TMS was used as an internal standard, and chemical shifts are reported on the (ppm) scale. IR spectra with a Perkin-Elmer 257. MS spectra with Varian-MAT 711 direct inlet at 70 ev. Analytical TLC was performed on aluminium sheets silica gel 60 F₂₅₄, layer thickness 0.2 mm, with Et_2O -petrol, Et_2O -MeOH solvent system and the spots were visualized under UV light and/or a ceric sulfate spray reagent. HPLC analyses were carried out with Knauer High pressure Liquid chromatograph with a UV detector. Optical rotations were measured on a Perkin-Elmer 241 polarimeter.

Extraction and Isolation

The air-dried aerial parts (350g, collected July 1990 in Nour Province, Mazandaran, Iran Voucher 90-205 deposited in the Herbarium of the Department of Botany, Shahid Beheshty University, Evin, Tehran, were extracted with Et_2O -MeOH-Petrol (1:1:1).

The extract obtained was defatted with MeOH (-20°C) and first separated by column chromatography (Silica gel). The fractions obtained with Et_2O -Petrol (3:2) were separated by prep. TLC (Silica gel, HF₂₅₄) affording 18 mg **1** (Et_2O -petrol 1:1, R_f 0.35) and 25 mg **2** (R_f 0.65). The Polar fractions (Et_2O to Et_2O -MeOH, 9:1) were further separated first by prep.

TLC and then by HPLC (MeOH-H₂O, 3:2, RP8, ca 100 bar flow rate ca 3 ml/min) affording 10 mg **3** (Rf 5.8 min).

6 β -tigloyloxy-1 β , 10 α , 4 α , 5 β , 8, 12-epoxygermacra 7,12-diene **1**. IR_{max}^{CHCl₃}, cm⁻¹: 1735 (ester), 1270 (epoxide), 1660, 1550 and 880 (furan); MS m/z (rel. int.): 346.427 [M⁺] (18) (calc. for C₂₀H₂₆O₅: 346.427), 246 [M-]⁺ (15), 231 [246-Me]⁺ (63) 216 [231-Me]⁺ (40), 108-()₂-(100) - [α]_D^{24°} + 84 (CHCl₃; c 0.54) .

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