

10-EPI-CUBEBOLXYLOSIDE FROM *IPHIONA SCABRA*

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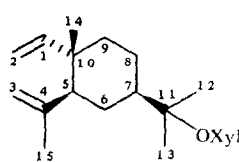
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Key Word Index—*Iphiona scabra*; Compositae; sesquiterpene xylosides; 10-*epi*-cubebol, α -elemol.

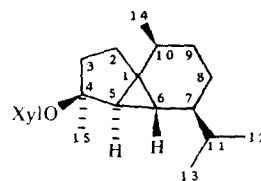
Abstract—The aerial parts of *Iphiona scabra* afforded in addition to some previously isolated xylosides two new ones derived from 10-*epi*-cubebol and α -elemol. The structures were elucidated by NMR spectroscopy.

INTRODUCTION

Iphiona scabra is the only species from the small genus which has been investigated chemically. In addition to a highly complex mixture of sesquiterpene xylosides [1] some flavanoids [2] were isolated. We now report the isolation of further compounds from this species.



1



2

Table 1. ^1H NMR spectral data of **1** and **2** (400 MHz, CDCl_3 , δ -values) and ^{13}C NMR spectral data of **2**, cubebol and *epi*-cubebol

H	1	2	C	2†	Cubebol‡	<i>epi</i> -Cubebol‡	Multiplicity
1	5.76 <i>dd</i> (10.5), (17.5)	—	1	33.5	33.4	34.8	<i>s</i>
2	{ 4.88 <i>d</i> (17.5) 4.87 <i>d</i> (10.5)	{ 1.70 <i>m</i> 1.50 <i>m</i>	2	30.2	29.6	39.7	<i>t</i>
3	{ 4.80 <i>br s</i> 4.56 <i>br s</i>	{ 1.50 <i>m</i> 1.30 <i>m</i>	3	34.9	36.3	36.6	<i>t</i>
5	1.92 <i>m</i>	0.84 <i>d</i> (3.5)	4	87.6	80.3	80.9	<i>s</i>
6	1.4 <i>m</i>	0.73 <i>dd</i> (3.5, 2)	5	36.4	39.1	39.8	<i>d</i>
7	*	1.28 <i>m</i>	6	21.6	22.6	25.3	<i>d</i>
8	*	{ 1.15 <i>m</i> 1.07 <i>m</i>	7	42.1	44.1	44.6	<i>d</i>
9	*	{ 1.30 <i>m</i> 1.21 <i>m</i>	8	19.3	26.5	27.0	<i>t</i>
10	—	1.92 <i>ddq</i> (2, 4.5, 7)	9	28.8	31.7	31.8	<i>t</i>
11	—	1.64 <i>ddq</i> (5, 7, 7)	10	29.4	30.8	30.2	<i>d</i>
12	1.20 <i>s</i>	0.97 <i>d</i> (7)	11	33.6	33.6	33.7	<i>d</i>
13	1.15 <i>s</i>	0.94 <i>d</i> (7)	12	19.9	20.0	20.0	<i>q</i>
14	0.96 <i>s</i>	0.97 <i>d</i> (7)	13	19.2	19.2	19.2	<i>q</i>
15	1.69 <i>br s</i>	1.27 <i>s</i>	14	17.2	18.7	19.8	<i>q</i>
1'	4.67 <i>d</i> (7)	4.68 <i>d</i> (7)	15	27.7	28.0	24.3	<i>q</i>
2'	4.89 <i>dd</i> (7, 9)	4.89 <i>dd</i> (7, 9)	1'	98.0 <i>d</i>			
3'	5.17 <i>dd</i> (9, 9)	5.12 <i>dd</i> (3, 9)	2'	71.3 <i>d</i>			
4'	4.94 <i>ddd</i> (5, 9, 9)	4.93 <i>ddd</i> (5.5, 9, 9)	3'	71.8 <i>d</i>			
5' ₁	4.09 <i>dd</i> (5, 12)	4.11 <i>dd</i> (5.5, 12)	4'	69.3 <i>d</i>			
5' ₂	3.31 <i>dd</i> (9, 12)	3.32 <i>dd</i> (9, 12)	5'	61.8 <i>t</i>			
OAc	2.01, 2.02, 2.04 <i>s</i>	2.01, 2.02, 2.04 <i>s</i>	OAc	170.1 <i>s</i> , 169.9 <i>s</i> , 169.3 <i>s</i> , 20.7 (3 \times) <i>q</i>			

* Obscured.

† Assigned by 2D-hetero correlated spectrum.

‡ Taken from refs [3, 4].

RESULTS AND DISCUSSION

The ^1H NMR spectrum of the polar fraction of the aerial parts of *Iphiona scabra* indicated a mixture of 2-*O*-acetates of sesquiterpene xylosides. After acetylation and separation, two new compounds (**1** and **2**) were obtained in addition to the known xylopyranoside triacetates of α -, β - and γ -eudesmol [1], 5,6-dehydro- α -eudesmol and 3 α -acetoxy-11-hydroxy-*iso*-iphiona-4-one.

The structure of **1** followed from the ^1H NMR spectrum which in addition to the xylopyranoside triacetates signals showed those typical for an elemene derivative. Two methyl singlets at δ 1.15 and 1.20 for a hydroxy-isopropyl group indicated the presence of an elemol. The NOE between H-1 and H-5 and absence of an effect with H-5 by irradiation of H-14 required the proposed stereochemistry. Thus **1** is α -xylopyranoside triacetate of α -elemol.

The structure elucidation of **2** turned out to be more difficult. From the ^1H NMR spectrum the presence of an α -xylopyranoside triacetate was deduced and the ^{13}C NMR spectrum revealed a tricyclic aglycone. By spin decoupling all signals were assigned leading to a sequence as in cubelol. As the chemical shifts of some signals in both the ^1H and ^{13}C NMR spectra showed differences to those of cubelol and 4-*epi*-cubebol, an isomer, probably at C-10, was likely. This was confirmed by NOE experiments. In particular the effects between H-5, H-10 and H-15 were conclusive and settled the stereochemistry at C-4 and C-10. Further effects were observed between H-6, H-11, H-12 and H-13 but no effect was seen with H-5. This indicated their *trans*-orientation which already followed from the small coupling constant ($J_{5,6} = 3.5$ Hz). In Table 1 the ^{13}C NMR data of cubebol and 4-*epi*-cubebol [3, 4] are added for comparison.

EXPERIMENTAL

The air-dried aerial parts (850 g, collected in April 1987 at Sinai on Dahab-Sharm-el-Sheikh road, voucher deposited in Herbarium of Botany Department, University of Cairo, Egypt) were extracted with petrol-Et₂O-MeOH (1:1:1) and the extract obtained separated by CC (silica gel). The most polar fraction was acetylated (Ac₂O, reflux, 3 hr) and separated again by MPC into three fractions. HPLC of one-fifth of the fraction 1 (RP 8, MeOH-H₂O, 17:3) gave 7 mg α -, 3 mg β - and 8 mg γ -eudesmol- $[\alpha$ -xylopyranoside-triacetate], 5 mg **1** (*R*, 9.6 min) and 16 mg **2**. One-tenth of the fraction 2 gave 20 mg α -, 3 mg β - and 7 mg γ -eudesmol- $[\alpha$ -xylopyranoside-triacetate] as well as 5 mg 5,6-dehydro- α -eudesmol- $[\alpha$ -xylopyranoside-triacetate]. Fraction 3 gave 40 mg 3 α -acetoxy-11-hydroxy-*iso*-iphiona-3-one- $[\alpha$ -xylopyranoside-triacetate].

α -Elemol- $[\alpha$ -xylopyranoside-triacetate] (**1**). Colourless oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1760, 1230 (OAc); MS m/z (rel. int.): 259 [$\text{M} - \text{C}_{15}\text{H}_{25}\text{O}$]⁺ (4), 163 (3), 147 (3), 121 (4.5), 81 (100), 69 (98), 55 (94).

10-*epi*-Cubebol- $[\alpha$ -xylopyranoside-triacetate] (**2**). Colourless oil; IR $\nu_{\text{max}}^{\text{CCl}_4}$ cm⁻¹: 1760, 1230 (OAc); MS m/z (rel. int.): 480.272 [M]⁺ (0.2) (calc. for C₂₆H₄₀O₈: 480.272), 259 [$\text{M} - \text{C}_{15}\text{H}_{25}\text{O}$]⁺ (16), 205 [$\text{C}_{15}\text{H}_{25}$]⁺ (75), 199 [$259 - \text{AcOH}$]⁺ (17), 161 (35), 157 [$199 - \text{ketene}$]⁺ (40), 59 (100); [α]_D²⁸ - 59° (CHCl₃; *c* 1.2).

REFERENCES

1. El-Ghazouly, M. G., El-Sebakhy, N. A., Seif El-Din, A. A., Zdero, C. and Bohlmann, F. (1987) *Phytochemistry* **26**, 439.
2. Ahmed, A. A. and Mabry, T. J. (1987) *Phytochemistry* **26**, 1517.
3. Suzuki, M., Kowata, N. and Kurosawa, E. (1981) *Bull. Chem. Soc. Jpn* **54**, 2366.
4. Bowden, B. F., Coll, J. C. and Tapiolas, D. M. (1983) *Aust. J. Chem.* **36**, 211.