

SESQUITERPENE XYLOSIDES FROM *IPHIONA MUCRONATA*

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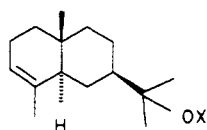
ABSTRACT.—Six sesquiterpene xylosides have been isolated from the polar extract of the aerial parts of *Iphiona mucronata*, including a previously unreported one. The structures were elucidated by spectroscopic methods and correlated with known compounds.

Earlier investigations of the flavonoids of two species of the small genus *Iphiona* Cass. (Family Compositae, Tribe Inuleae) have been studied. *Iphiona scabra* and *Iphiona mucronata* (Forssk.) Asch. et Schweinf. (1,2) revealed that polysulfated flavonoids were the major constituents and seem to be characteristic for the genus. Aerial parts of *I. scabra* afforded a complex mixture of sesquiterpene xylosides (3,4). Nothing is known in the literature concerning the terpenoids of *I. mucronata*

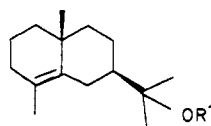
with the exception of the report of thymol derivatives (5,6). We therefore studied *I. mucronata* for its terpenoids.

The polar extract of the aerial parts of *I. mucronata* afforded six sesquiterpene xylosides, 1–6, which could be separated in pure state without prior acetylation. The ¹H nmr of the acetylated products of 1–6 were identical to those which have been reported from *I. scabra* (3).

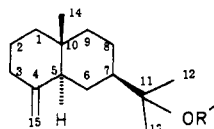
The ¹H-nmr data of 1 differed from those of 2 by the absence of the acetate methyl signal at δ 1.99 and the upfield



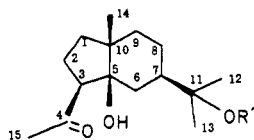
1 X=R
 2 X=R'



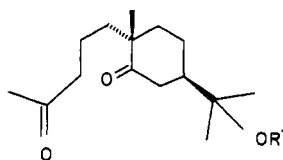
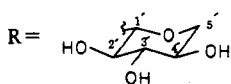
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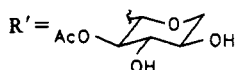
4



5



6



shift of the double doublet at δ 4.62 in **2** to δ 3.30 in **1**. This suggested that **1** contained no acetyl group. Furthermore, the chemical shifts as well as the coupling constants of the sugar protons indicated clearly that a xylopyranoside was present (H-1' at δ 4.53 d, H-2' at δ 3.30 dd, H-3' at δ 3.47 dd, H-4' at δ 3.57 ddd, H-5' at δ 3.95 dd and 3.25 dd). The signals for the sesquiterpene skeleton, including a sharp three-proton singlet, showed that we were dealing with β -eudesmol. The Δ^3 bond was indicated by the broadened signal at δ 5.26, while the olefinic methyl appeared as a broad singlet at δ 1.55. The chemical shift of the isopropyl methyl signals at δ 1.19 and 1.18 showed that the sugar moiety could be at C-11. Similarly, the coupling constant and the chemical shift of H-5 as well as the chemical shift of H-14 confirmed the 5,10 trans skeleton. The ^1H nmr, ms, and ir of the acetylated products of **1** and **2** were completely identical with the previous report (3). Compounds **2** and **3** have been reported in mixture (3). We isolated both compounds in the pure state, and **1** has not been previously reported.

In conclusion, it seems that sesquiterpene xylosides as well as polysulfated flavonoids are typical for the genus *Iphiona* and may be of chemotaxonomic value.

EXPERIMENTAL

PLANT MATERIAL.—The aerial part of *I. mucronata* were collected from Wadi Houf, near Cairo, Egypt in April 1987. A voucher specimen (A. Ahmed 109) is deposited in the Department of Botany, El-Minia University.

EXTRACTION AND ISOLATION OF TERPENOID.—The air-dried aerial parts (500 g) of *I. mucronata* were extracted with Et_2O -MeOH-petroleum ether (40–60°) (1:1:1) at room temperature as reported elsewhere (7). The polar fraction, which was eluted with Et_2O -MeOH (9:1), was further separated by cc (using CH_2Cl_2 with increasing the amounts of MeOH) to give several fractions. The obtained fractions were purified by hplc [RP-8, MeOH- H_2O (1:1)] and afforded **1** (15 mg), **2** (300 mg), **3** (10 mg), **4** (18 mg), **5** (7 mg), and **6** (6 mg).

γ -EUDES MOL (α -XYLOPYRANOSIDE) [1].—Ms m/z (rel. int.) 354 (1.2), 336 (0.6), 205 (93), 204 (90), 149 (72), 133 (88), 73 (100); ^1H nmr (400 MHz, $\text{CDCl}_3 + \text{CD}_3\text{OD}$, TMS as internal standard) δ 5.26 (1H, br s, H-3), 4.53 (1H, d, $J = 7.5$ Hz, H-1'), 3.95 (1H, dd, $J = 5$ and 12 Hz, H-5'a), 3.57 (1H, ddd, $J = 5, 9$, and 9 Hz, H-4'), 3.47 (1H, dd, $J = 9$ and 9 Hz, H-3'), 3.30 (1H, dd, $J = 7.5$ and 9 Hz, H-2'), 3.25 (1H, dd, $J = 9$ and 12 Hz, H-5'b), 1.55 (3H, br s, H-15), 1.19 (3H, s, H-12), 1.18 (3H, s, H-13), 0.72 (3H, s, H-14).

γ -EUDES MOL (α -XYLOPYRANOSIDE 2-ACETATE) [2].—Ir ν (CHCl_3) max cm^{-1} 1780, 1290; ms m/z (rel. int.) 396 (2), 353 (4), 205 (70), 176 (60), 157 (100); ^1H nmr (400 MHz, CDCl_3 , TMS as internal standard) δ 5.20 (1H, br s, H-3), 4.62 (1H, dd, $J = 7.5$ and 9 Hz, H-2'), 4.40 (1H, d, $J = 7.5$ Hz, H-1'), 3.81 (1H, dd, $J = 5$ and 12 Hz, H-5'a), 3.53 (1H, ddd, $J = 5, 9$ and 9 Hz, H-4'), 3.38 (1H, dd, $J = 9$ and 9 Hz, H-3'), 3.11 (1H, dd, $J = 9$ and 12 Hz, H-5'b), 1.99 (3H, s, OAc), 1.49 (3H, br s, H-15), 1.09 (3H, s, H-12), 1.05 (3H, s, H-13), 0.66 (3H, s, H-14).

γ -EUDES MOL (α -XYLOPYRANOSIDE TRIACETATE).—Ir (CHCl_3) max cm^{-1} ν 1750, 1250; ms m/z (rel. int.) 480 (0.1), 259 (45), 205 (55), 204 (100); ^1H nmr (400 MHz, CDCl_3 , TMS as internal standard) δ 5.23 (1H, br s, H-3), 5.13 (1H, dd, $J = 10$ and 10 Hz, H-3'), 4.90 (1H, ddd, $J = 5, 9$, and 9 Hz, H-4'), 4.86 (1H, dd, $J = 7.5$ and 9 Hz, H-2'), 5.11 (1H, d, $J = 7.5$ Hz, H-1'), 4.04 (1H, dd, $J = 5$ and 12 Hz, H-5'a), 3.27 (1H, dd, $J = 9$ and 12 Hz, H-5'b), 2.07 (3H, s, OAc), 2.02 (6H, s, OAc), 1.54 (3H, br s, H-15), 1.15 (3H, s, H-12), 1.04 (3H, s, H-13), 0.70 (3H, s, H-14).

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