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A FURANOEUDESMANE FROM THE FRUITS OF *SMYRNIUM OLUSATRUM*

AYHAN ULUBELEN, SEVIL OKSÜZ, NEZHUN GÖREN, TOM J MABRY* and FERDINAND BOHLMANN†

Faculty of Pharmacy, University of Istanbul, Istanbul, Turkey, *Department of Botany, University of Texas, Austin, TX 78712, U S.A, †Institute for Organic Chemistry, Technical University of Berlin, D1000 Berlin-12, W Germany

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Key Word Index—*Smyrnium olusatrum*, Umbelliferae, furanogermacranes, furanoeudesmane, eudesmanolides

Abstract—In addition to two known acetoxy-eudesmanolides and two furanogermacranes from the fruits of *Smyrnium olusatrum* a new highly unstable acetoxy-furanoeudesmane was obtained, which obviously is the precursor of the two acetoxy-eudesmanolides

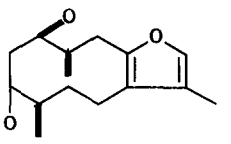
In a previous study we have obtained glechomafuran from the fruits of *Smyrnium olusatrum* in high yield [1] A reinvestigation of the petrol–diethyl ether extract of the fruits of *S olusatrum* yielded, in addition to glechomafurane, four sesquiterpenes, one of them being a new acetoxy-furanoeudesmane The known compounds glechomafurane (**1**) [1–3], furodien (**2**) [4, 5], 1β-acetoxy-eudesmane-4(15),7(11)-dien-8α,12-olide (**3**) [2] and 1β-acetoxy-8β-hydroxy-eudesmane-4(15),7(11)-dien-8α,12-olide (**4**) [2] were identified by comparing their spectra and R_f values with those of authentic samples The new acetoxy-furanoeudesmane (**5**) had the molecular formula $C_{17}H_{22}O_3$ as shown by high resolution MS Its IR (KBr) spectrum contained an acetoxy band at 1730, 1235 cm^{-1} and furan bands at 1640, 1560, 880 cm^{-1} The structure of the new compound was established by ^1H NMR spectroscopy spin decoupling experiments, as well as by studying Dreiding models The acetyl signal was a singlet at δ2 06, an olefinic methyl signal was at 1 92 (*d*, *J* = 1 Hz, H-13), a second methyl singlet at 0 81 (H-14) The signals of H-15 and H-15′ were at 4 92 and 4 79 as doublets (*J* = 1 Hz) indicating the presence of an exocyclic methylene group, while the double doublet at 4 83 (*J* = 4 5 Hz and 12 Hz) was due to H-1 and its coupling indicating the equatorial orientation of the acetoxy group The furan ring proton showed a broadened singlet at 7 04 (H-12) The signals of geminal coupled protons at 2 57 (1H, *d*, *J* = 17 Hz, H-9) and 2 41 (1H, *d*, *J* = 16 Hz, H-9′) indicated an isolated methylene group The double quartet at 1 90 (H-2) and four-fold doublets at 1 58 (H-2′) and a multiplet centred at 2 25 (H-3 and H-3′) were assigned by spin decoupling The signals at 2 47 (1H, *dd*, *J* = 5 Hz and 12 Hz, H-6) and 2 40 (1H, *dd*, *J* = 5 Hz and 12 Hz, H-6′) and at 2 33 (1H, *dd*, *J* = 3 Hz and 12 Hz, H-5) indicated that H-5 was coupled with H-6 and H-6′ while the latter protons showed a geminal coupling with each other Irradiation of H-15 caused sharpening of the signals of H-3 and H-3′ as well as of those of H-6 and H-6′ while irradiation of the signal H-9 collapsed the signal of H-9′ to a singlet The new compound was thus assigned structure **5**

Either in solution or in solid state **5** oxidizes to **3** and **4** within 1 hr In order to minimize this oxidation, **5** was kept in a deep freeze until its spectra were recorded

EXPERIMENTAL

The plant material was collected from the European section of Turkey, near Istanbul Voucher No ISTE 14970, deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul.

Isolation and determination of the compounds **1–5** Air-dried and powdered fruits of *Smyrnium olusatrum* L (250 g) were extracted with petrol (bp 40–70°)–Et_2O (1 1) overnight After filtration the extract was coned *in vacuo* at room temp The residue was subjected to CC over silica gel (3 × 50 cm) by rapid elution using petrol, Et_2O was added up to 100% Fractions were collected within 2 hr Compounds **1** and **2** were obtained from the



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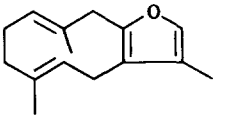

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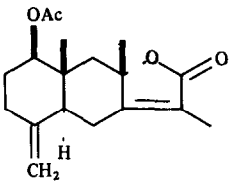

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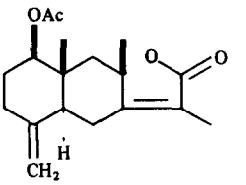

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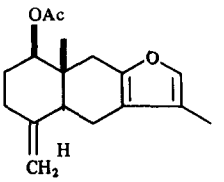

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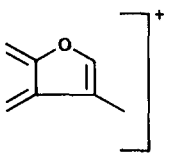

a

column as single compounds, crystallized from Et_2O Compounds **3**, **4** and **5** were obtained as a mixture which was separated by prep TLC A part of **5** was used to record UV and IR spectra, the rest was kept in a deep freeze to prevent oxidation before recording its ^1H NMR and mass spectra.

Compound **1** yield 3 g, spectral data including X-ray given in [1] Compound **2** yield 600 mg, spectral data including ^{13}C NMR given in refs [4, 5] Compounds **3** and **4** yield 20 mg and 25 mg, respectively, spectral data including ^{13}C NMR given in [2] Compound **5** yield 50 mg, amorphous UV λ_{max}^{MeOH} nm 220 (log ε4 6), IR ν_{max}^{KBr} cm^{-1} 2940, 2840, 1730, 1640, 1560, 1440, 1360, 1235, 1110, 1080, 1070, 1040, 1020, 1005, 880 ^1H NMR (Bruker WM, 400 MHz) given in text MS (Varian MAT 711) (direct inlet, 70 eV), *m/z* (rel int) 274 157 ($C_{17}H_{22}O_3$) $[M]^+$ (42), 215 $[M-OAc]^+$ (24), 214 $[M-AcOH]^+$ (100), 199 $[214-Me]^+$ (68), 185 $[214-CHO]^+$ (46), 172 $[214-C_3H_6]^+$ (98), 108 [a] (54)

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A REARRANGED EUDESMANE AND FURTHER VERBESINDIOL DERIVATIVES FROM *VERBESINA EGGERSII*

SHANTA BANERJEE, JASMIN JAKUPOVIC, FERDINAND BOHLMANN, ROBERT M KING* and HAROLD ROBINSON*

Institute for Organic Chemistry, Technical University of Berlin, D-1000 Berlin 12, West Germany, *Smithsonian Institution, Department of Botany, Washington, DC 20560, U S A

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Key Word Index—*Verbesina eggersii*, Compositae, sesquiterpenes, eudesmane derivatives, rearranged eudesmane, benzofuran

Abstract—A reinvestigation of *Verbesina eggersii* gave in addition to compounds isolated previously two further verbesindiol derivatives, a rearranged eudesmane and a benzofuran related to tremetone

From most species of the large genus *Verbesina* (Compositae, tribe Heliantheae, subtribe Ecliptinae) verbesindiol derivatives like **1** and **2** [1–3] have been isolated The configuration at C-4 has been assigned differently but in one case was determined by X-ray analysis [4] We have reinvestigated *V eggersii* Hieron which is rich in these eudesmane derivatives Clear NOEs between H-14 and H-15 with **1** and **2** agreed with the configuration assigned for C-4 [1, 3] and therefore the proposed change [2] was an error Also the corresponding *p*-coumarate and ferulate [2] obviously have a 4α-hydroxy group In addition to known compounds the 15-hydroxy derivatives **3** and **4** as well as the rearranged eudesmane **6** and the triol **9** were isolated

The structures of **3** and **4**, which was isolated as its diacetate **5** followed from the spectral data which were close to those of **1** and **2** In the ^1H NMR spectrum of **3** (Table 1) the H-15 singlet in the spectrum of **1** was replaced by a pair of signals at δ3 72 and 3 33 The latter was a narrowly split doublet, which was due to a W-coupling, usually indicating an axial orientation of the very likely hydroxy methyl group A clear NOE between H-14 and H-15 established this assumption Similarly the configuration of **5** at C-4 followed from the NOE of H-14 with H-15 The signals of H-1 and H-15 were shifted downfield Furthermore, in the mass spectra a strong fragment ion appeared for $M-CH_2OAc$

The acid **6** showed some ^1H NMR signals similar to those of **1** (Table 1) However, as followed from the IR spectrum and the mass spectrum an acid was present The H-5 signal was assigned by spin decoupling. As it only showed a coupling with H-6 the carbonyl group had to be placed at C-4 In agreement with this assignment a proton at the neighbouring carbon was seen as a downfield shifted double doublet at δ2 36 (H-2α) Spin decoupling allowed the assignment of the signals of H-2β, H-1α and H-1β Inspection of a model showed that the couplings observed agreed well with the observed angles Most likely