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STRUCTURE AND SYNTHESIS OF FURANOSESQUITER PENES FROM EUMORPHIA PROSTATA

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Summary: A reinvestigation of Eumorphia prostata afforded two new furanosesquiterpenes. The structure of eumorphistonol has been determined by synthesis. Two further furans were prepared and the absolute configuration of the main compound was deduced by a chiral synthesis.

From Eumorphia prostata several furanosesquiterpenes were isolated [1]. As the structure of one carbinol was not really established [1] we have reinvestigated this species. In addition to the compounds isolated previously we got the furanoketones 2 and 3. The structure of 2, named cyclodehydromyopyrone A, clearly followed from the 1 H NMR data $[(CDCl_{2}): \delta$ 7.26 br s (H-1), 6.24 t (H-2, J = 1 Hz), 1.57 and 1.98 m (H-5), 2.16 and 1.98 m (H-6), 2.51 dtq (H-7, J = 6, 9, 7), 2.76 d (H-8, J = 9), 6.01 qq (H-10, J = 1, 1), 1.79 d (H-12, J = 1), 1.93 d (H-13, J = 1), 1.08 d (H-14, J = 7), 7.27 t (H-15, J = 1)]. The stereochemistry was deduced by the observed n Oe's between H-14 and H-8 (10 %) as well as between OH and H-8 (5 %). The 1 H NMR data of 3, named cyclodehydromyopyrone B, showed that this isomer was a furan derivative with a β -keto group [(CDCl₂): δ 7.41 t (H-1, J = 1 Hz), 6.76 d (H-2, H = 1), 3.58 t (H-5, J = 8), 2.16 and 1.65 m (H-6), 2.33 m (H-7), 2.06 dd (H-8, J = 10, 13), 1.76 dd (H-8', J = 7, 13), 5.29 gg (H-10, J = 1, 1), 1.73 d (H-12, J = 1), 1.54 d (H-13, J = 1), 1.08 d (H-14, J = 7), 8.05 t (H-15, J = 1)]. NOe's between OH and H-5 (6 %) as well as between H-5 and H-7 (5 %) indicated the stereochemistry. The structure of 4 (erro neously drawn as a cyclohexane derivative, compound 16 in lit.[1]) was established by synthesis.

Condensation of the anion of 3-methyl-2-cyclopentenone with 3-furancarb aldehyde gave

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the ketone $\frac{7}{2}$ which after protection of the hydroxy group and hydrogenation afforded the ketone $\frac{9}{2}$. Reaction with isobutenyl lithium gave the carbinol $\frac{9}{2}$. Treatment with fluoride ions and oxidation with PDC, which also induced allylic rearrangement, afforded in addition to isomers the ketone $\frac{4}{2}$, identical with the natural product. The configuration of the 9,10-double bond was established by the nOe between H-8 and H-13 as well as by the chemical shift of H-10 ($\frac{4}{2}$: 5.86 br s). Oxidation of $\frac{9}{2}$ with manganese dioxide gave after elimination of water the ketone $\frac{6}{2}$. Reaction of $\frac{8}{2}$ with methallyl magnesium chloride followed by oxidation with PDC and elimination of water with Burgess reagent afforded the isomeric diene $\frac{5}{2}$.

Finally the absolute configuration of $\underline{1}$ was established by synthesis starting with the chiral ester $\underline{10}$ which easily can be obtained from pulegone [2]. Ozonolysis, reaction with β -lithium furan and protection of the hydroxy group gave the furan derivative $\underline{11}$. Reduction of the ester group with dibah, addition of isobutenyl lithium, fluoride hydro-lysis and oxidation gave R-dehydromyopyrone ($\underline{1}$) ($[\alpha]_D^{24^0}$ + 14.1, CHCl₃) identical with the natural ketone. Similar also R-myopyrone ($\underline{12}$) was obtained ($[\alpha]_D^{24^0}$ + 4.5, CHCl₃). Intra-molecular aldol condensation afforded S-myomontanone ($\underline{13}$) [3] ($[\alpha]_D^{24^0}$ + 26, CHCl₃) and the isomer $\underline{16}$ [3] ($[\alpha]_D$ + 87, CHCl₃). Under mild conditions $\underline{12}$ gave the isomeric ketol $\underline{14}$ which after elimination of water afforded isomyomontanone ($\underline{15}$) [3]. Similar reactions of $\underline{1}$ led to complex mixtures, although in the plant surely the ketone $\underline{1}$ is the precursor for $\underline{2} - \underline{6}$.







a) ClSiMe₂(CMe₃)/imidazole; b) H_2/PtO_2 ; c) Me₂C=CHLi (from Me₃CLi and Me₂C=CHBr); d) Bu₄N⁺F⁻; e) PDC/DMF/-20⁰; f) MnO₂/CH₂Cl₂; g) H₂C=C(Me)CH₂MgCl; h) PDC/CH₂Cl₂; i) Burgess-reagent [4]; j) PCC/Al₂O₃/pentane; k) MeOH, O₃, -30⁰, Me₂S; l) β -lithium furan ; m) dibah; n) Me₂CHCH₂Li; o) KOCMe₃; p) LiN(SiMe₃)₃, -78⁰, 2 h.

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