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SPECIALIA

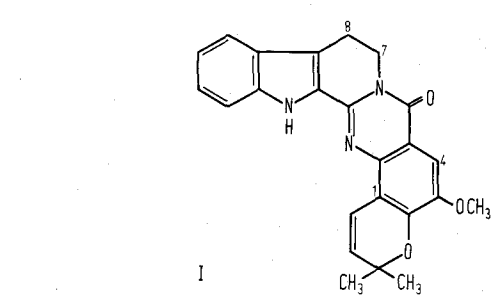
Paraensine, a New Indolopyridoquinazoline Alkaloid from *Euxylophora paraënsis* Hub.

The bark of *Euxylophora paraënsis* Hub. has proved to be a rich source of indolopyridoquinazoline alkaloids and up to date 5 alkaloids of this rare class have already been isolated and their structure elucidated[1,2]. The present communication describes the structure of one more base, named by us paraensine, which appears to be the first alkaloid of the above-mentioned class containing a isopreniod moiety.

Paraensine (I), $C_{24}H_{21}N_3O_3$ (M^+, 399), mp 281–2° (from benzene); ν_{max}(nujol) 3310 (NH), 1650 (amidic CO), 1640, 1600, 1550 (unsaturation and aromatic system) had an UV-spectrum, λ_{max} (CH_3OH), 342, 358 and 376 nm (log ε 4.32, 4.42 and 4.29 respectively). The NMR spectrum ($CDCl_3$) showed the following signals: δ 1.48, s, 6, $-C(CH_3)_2$; 3.12, t (J=7 Hz), 2, $>-CH_2-CH_2-N<$; 3.89, s, 3, $-OCH_3$; 4.51, t (J=7 Hz), 2, $>C-CH_2-CH_2-N<$; 5.63, d (J=10 Hz), 1, olefinic H; further on there were the signals of 7 protons between 7.2–7.7 δ (aromatic, benzylic methine and NH protons) including a singlet at 7.53 for the proton at C_4–H. In C_5D_5N solution, the signals appeared respectively at δ 1.48; 3.10; 3.76; 4.62; 5.56; 7.05–7.85 and 7.88. The mass spectrum of paraensine showed, apart from the molecular ion peak, intense peaks at 384 (base peak), 369, 358, 128 and 115.

The combined data and particularly the similarity of the UV- and NMR-spectra (except the signals of the chromene ring protons) with that of Euxylophoricine A[1], led to the structure (I) for paraensine. This was confirmed by synthesis of the dihydroderivative (IV) obtained through hydrogenation of paraensine on 10% Pd in ethanolic solution.

2, 2-dimethyl-6-formyl-8-methoxychromane[3] was nitrated, oxidized with Ag_2O in dioxane-water to an acid, which was methylated with diazomethane and then catalytically reduced with 10% Pd/C in acetic acid to give the 5-amino-6-carbomethoxy-2, 2-dimethyl-8-methoxychromane (II), mp 122° (from benzene-hexane); ν_{max}(nujol) 3460, 3360 (NH_2), 1680 (ester), 1620, 1600 and 1570 cm^{-1}



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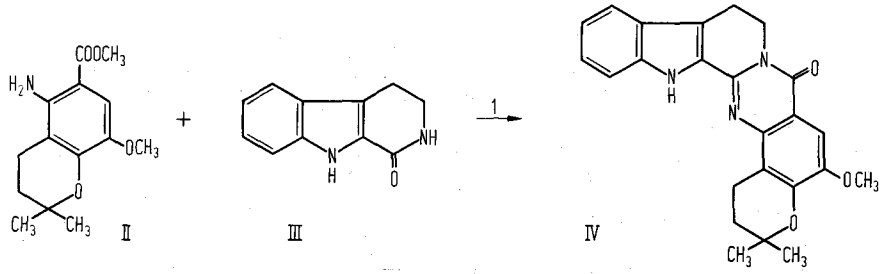

II III IV

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(aromatic system). The NMR spectrum of (II) showed the following signals: δ 1.40, s, 6, $-C(CH_3)_2$; 1.89, t (J=7 Hz), 2; $\geqslant C-CH_2-CH_2-C-O$; 2.48, t (J=7 Hz), 2, $\geqslant C-CH_2-CH_2-C-O$; 3.80, s, 3, $-COOCH_3$; 3.83, s, 3, $-OCH_3$; 5.63, m, 2, NH_2; 7.27, s, 1, aromatic proton.

Condensation of (II) with 1,2,3,4-tetrahydronorharman-1-one (III) performed with $POCl_3$ in refluxing toluene[1], gave the dihydroparaensine (IV), $C_{24}H_{23}N_3O_3$ (M+ 401), mp 305° (from isopropyl ether) which was found to be identical (mixed mp, TLC and IR spectrum) with the dihydroderivative of the natural product.

Riassunto. Dalla corteccia della *Euxylophora paraënsis* Hub. viene isolata la paraensina (I) che si rivela essere il primo alcaloide di tipo indolopiridochinazolinico a contenere una unità isoprenica.

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CMR Spectral Analysis of Tetrahydrocannabinol and its Isomers[1]

The biologically active constituents of *Cannabis sativa* L. (marijuana) have aroused much public and scientific interest in recent years. In view of the advent of a powerful, new tool of structure analysis, ^{13}C nuclear magnetic resonance (cmr) spectroscopy, its application to investigations of the chemical make-up of the major psychotomimetic marijuana (hashish) principle, **1**-Δ^9-tetrahydrocannabinol (Δ^9-THC) (**1a**), and related substances was undertaken.

The δ values of all carbons of six tetrahydrocannabinol substances and model **5**, olivetol dimethyl ether, derived from their noise resonance decoupled and single frequency decoupled spectra[1] are listed in the Table. Assignment of the chemical shifts of the aromatic carbons is based on chemical shift theory[2] and former electron density calculations[3]. Shift data of **5** and consideration of substituent effects among alkanes[4] leads to the identification of three centers of the *n*-pentyl chain. The remaining β and γ carbons can be distinguished by inspection of the single frequency decoupled spectrum of a β, β-dideutero derivative of **5**, prepared by sodium deuteroxide-induced deuteration of *n*-butyl 3,5-dimethoxyphenyl ketone and treatment of the product with lithium aluminum hydride and aluminum chloride[5].

[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopy of Naturally Occurring Substances. IX. For the preceding article see E. WENKERT, C.-J. CHANG, D. W. COCHRAN and R. PELLICCIARI, Experientia *28*, paper No. 1099 (1972).

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