

(+)-3-Carene as a Versatile Precursor for Indoloterpenoids

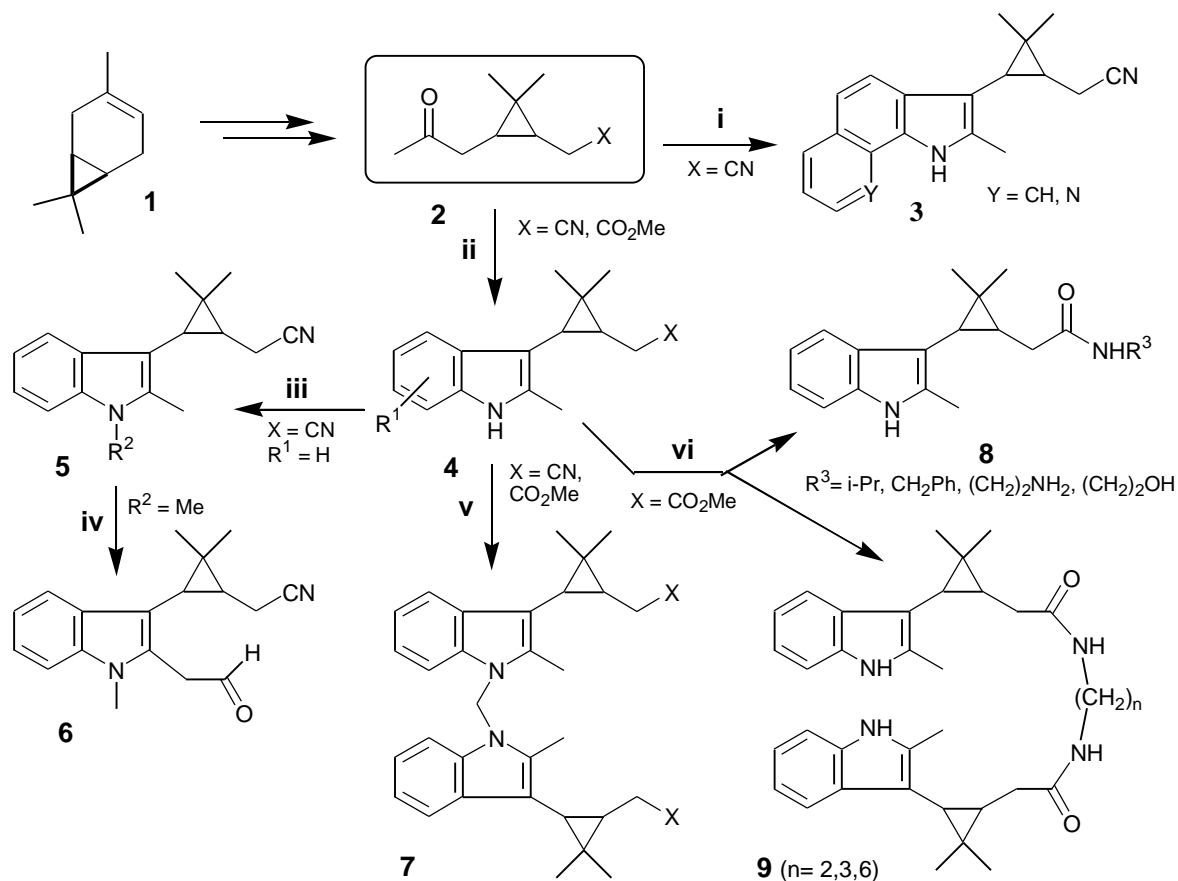
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Keto nitrile **2** (X = CN) and keto ester **2** (X = CO₂Me) derived from natural monoterpene hydrocarbon (+)-3-carene (**1**) have been found to be precursors for a number of biologically active organic substances - fumigants, repellents and insecticides. Now we report on synthesis of new indole type derivatives starting from these *seco*-derivatives.

Indoles **3** and **4** were obtained by Fisher's method, which included the reaction of ketones **2** (X = CN, CO₂Me) with different arylhydrazines (R¹ = *ortho*-Br, *ortho*- and *para*-OMe). Alkylation of compound **4** (X = CN) under phase-transfer catalysis resulted in *N*-substituted indoloterpenes **5** (R² = Me, All, CH₂Ph), alkylation with dibromomethane giving dimers **7** (X = CN, CO₂Me). Acylation of indole **4** (X = CN, R¹ = H) were succeed by Vilsmeier-Haack formylation only (treating with POCl₃ in DMF) to give product **5** (R² = CHO) in 80% yield. Under the same reaction conditions, compound **5** (R² = Me) were converted to aldehyde **6**.



i - ArN₂H₃/AcOH, 32-48%; ii - ArN₂H₃/AcOH, 23-79%; iii - R²Hal/50% aq. NaOH/CH₂Cl₂/TEBA, 72-84%; iv - POCl₃/DMF, 60%; v - CH₂Br₂/50% aq. NaOH/CH₂Cl₂/TEBA, 35%; vi - R³NH₂ or H₂N(CH₂)_nNH₂, 31-44%

Amides **8** and **9** were prepared from ester **4** (X = CO₂Me) by nucleophilic substitution of methoxy-group by different primary amines. Substances **8**, **9** and **3** (Y = N) are prospective chiral nitrogen-containing ligands in complexes of the type «host-guest», in particular as a potential receptor for the oriented binding of the uric acid type molecules.