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CONFIGURATION OF THE DOUBLE BOND AND PARTIAL SYNTHESIS OF ALLYLCEMBROL

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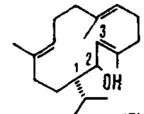
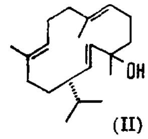
From the epigeal part of Commiphora mukul, Ruker [1] isolated a new cembrane alcohol, which he called allylcembrol. This compound has been isolated by Patil [2] from the resin of the same plant under the name of "mukulol." The structure of allylcembrol (I) was shown by the production of cembrene from it on mild dehydration and on the basis of spectral characteristics. The configurations of the C_3 double bond and of the C_2 asymmetric center remained unknown. We have synthesized allylcembrol and its C_2 epimer from isocembrol (II).

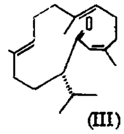
The treatment of isocembrol with the Jones reagent in aqueous acetone (0°C, 30 min) gave a complex mixture the chromatography of which on SiO_2 (petroleum ether containing increasing concentrations of diethyl ether as eluent) gave successively fractions of hydrocarbons (yield 24%), ketones (20%), epoxyketones (21% – mixture of three stereoisomeric 3,4-epoxycembra-7,11-dien-2-ones), and 2,3-epoxycembra-7,11-dien-4-ol (30%) with mp 94-95°C (from ethanol), $[\alpha]_D^{20}$ +44.4° (c 5.43; chloroform). The ketone fraction was rechromatographed on SiO_2. The first ketone isolated from the column was (III) with n_D^{22} 1.5166, $[\alpha]_D^{22}$ +110.1° (c 5.43; chloroform); IR spectrum (in CCl_4) 1690, 1625, 1385 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ 242 nm (log ε 3.97); NMR spectrum (here and below, in CCl_4, 100 MHz, TMS, ppm): 1.53 (6H, C_8-CH_3 and $C_{12}-CH_3$), 1.81 (3H, C_4-CH_3), 4.6-5.1 (2H, multiplet, H_7 and H_{11}), and 5.95 (1H, narrow multiplet, H_3).



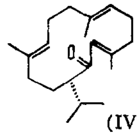
(I)



(II)



(III)



(IV)

The second ketone (IV) with n_D^{22} 1.5040, $[\alpha]_D^{23}$ +106.9° (c 8.84; chloroform) was identical, according to its NMR spectrum, with a ketone isolated by Patil from mukulol. The absence of an intramolecular nuclear Overhauser effect between H_3 and C_4-CH_3 in the ketone (IV) shows [3, 4] the trans configuration of the C_3 double bond and, consequently, the trans configuration of the same bond in allylcembrol (mukulol). Thus, the second ketone has a cis configuration of the C_3 double bond. This could not be shown by means of the Overhauser effect, since when the oxygen was eliminated by Kaiser's method [5] from a solution of the ketone (III) in CCl_4 it isomerized completely into the trans ketone (IV). A mixture of equal amounts of these ketones was obtained after a 5% solution of the ketone in CCl_4 had been kept at 20°C for a week. A similar instability of a macrocyclic cis-2-enone system has also been observed by Nozaki [6] for cis-dodecen-2-one.

The reduction of the ketone (IV) with $LiAlH_4$ in diethyl ether (20°C, 5 min) gave a mixture of secondary alcohols which was chromatographed on SiO_2 + 5% $AgNO_3$. Petroleum ether containing 10% of diethyl ether

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eluted a mixture of stereoisomeric cembra-7,11-dien-2-ols (yield 25%). Petroleum ether containing 12% of diethyl ether eluted 2-epiallylcembrol (8.5%) with n_D^{23} 1.5050, $[\alpha]_D^{23}$ −64.6° (c 8.1; chloroform); IR spectrum (in CCl_4) 3630, 1385, 1375, 1025 cm^{-1}; NMR spectrum (ppm): 1.52 and 1.55 (3H each, C_8-CH_3 and $C_{12}-CH_3$), 1.63 (3H, C_4-CH_3), 4.08 (1H, triplet, $J_{1,2} = J_{2,3} = 9.0$ Hz, H_2), 4.8-5.1 (2H, multiplet, H_7 and H_{11}), 5.15 (1H, doublet, $J_{2,3} = 9.0$ Hz, H_3). Petroleum ether containing 15% of diethyl ether eluted allylcembrol (I) (46%) with mp 37-38°C $[\alpha]_D^{21}$ +58.5° (c 6.14: chloroform); literature data: mp 37-38°C $[\alpha]_D$ +53° [2]; $[\alpha]_D$ +55.4° (c 2.06; chloroform) [1].

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HARPAGIDE AND HARPAGIDE ACETATE FROM SOME SPECIES OF THE FAMILY LABIATAE

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UDC 615.32

It is known that some species of the family Labiatae contain iridoid compounds [1]. We have investigated a number of species of this family for their contents of harpagide and harpagide acetate: Stachys iberica Bieb., St. balansae Boiss et Ky., St. spectabilis Choisy, St. fruticulosae, Bieb., St. grossheimii Kapeller., St. sylvatica L., St. lavandulifolia Vahl., St. germanica L., St. inflata Benth., St. atherocalyx C. Koch., Betonica macrantha C. Koch., B. nivea Stev., B. orientalis L., B. officinalis L., Ajuga reptaus L.

By paper chromatography in the butan-1-ol−acetic acid−water (4 : 1 : 2) system, harpagide and harpagide acetate were detected in St. iberica Bieb., St. atherocalyx C. Koch., Ajuga reptaus L., Betonica macrantha C. Koch., B. nivea Stev., B. orientalis L., B. officinalis and harpagide in St. spectabilis Choisy., St. fruticulosa Bieb., St. grossheimii Kapeller., St. lavandulifolia Vahl., St. sylvatica L. When the chromatograms were treated with a 3% ethanolic solution of p-dimethylaminobenzaldehyde containing 1.5% of hydrochloric acid (Stahl's reagent) [2], they appeared in the form of deep blue spots with R_f 0.41 and 0.51, respectively.

The iridoids were isolated from the epigeal parts of the separate species in the following way: The comminuted raw material was treated with 80% ethanol, the extract was evaporated to an aqueous residue, and this was freed from chlorophyll and lipophilic substances with chloroform. To separate the flavonoids, the purified aqueous fraction of the extract was deposited on a column of polyamide sorbent and washed with water.

The combined iridoids free from flavonoids was separated on a column of polyamide sorbent with elution by chloroform and then mixtures of chloroform and ethanol with increasing concentrations of the latter. Two substances were isolated − harpagide acetate (R_f 0.51) and harpagide (R_f 0.41). The harpagide acetate was crystallized from a mixture of chloroform and ethanol (4 : 1) in the form of white acicular crystals with mp 153-155°C, $[\alpha]_D^{20}$ −111° (c 0.1; ethanol), $C_{17}H_{26}O_{10}$. On hydrolysis by the enzymes of the grape snail, it decomposes into D-glucose, acetic acid, and an aglycone which, as it separated out, colored the solution deep blue with a subsequent separation of a dark-colored precipitate.

To obtain the deacetyl derivative, the substance was saponified with 5% alcoholic caustic soda. A product $C_{15}H_{24}O_9$, $[\alpha]_D^{20}$ −133° (c 0.1; ethanol) was obtained which could not be crystallized.

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