

JATAMANSONE

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THE results of our degradation studies on jatamansone,¹ the sesquiterpene ketone from Nardostachys jatamansi are reported here. Jatamansone was recovered unchanged after refluxing with 60 per cent sulphuric acid for 12 hr or after treatment with saturated ethereal hydrogen chloride for 48 hr. Wolff - Kishner reduction of jatamansone yielded the saturated hydrocarbon jatamansane, C₁₅H₂₈, b.p. 90°/0.5 mm. Analytical results on jatamansone, its derivatives and all the degradation products mentioned in the sequel were consistent with the formulation of jatamansone as C₁₅H₂₆O, which should therefore be a saturated bicyclic ketone.

Dehydration of jatamansol with PBr₃ - aniline yielded jatamansene, C₁₅H₂₆, b.p. 106-108°/4 mm, which on ozonolysis gave a dialdehyde, C₁₅H₂₆O₂, b.p. 138°/1 mm. The dialdehyde was converted by refluxing with alcoholic

¹ T. R. Govindachari, S. Rajadurai and B. R. Pai, Chem. Ber., 91, 908 (1958).

hydrochloric acid to an α : β -unsaturated aldehyde, $C_{15}H_{24}O$, b.p. $144^{\circ}/1.2$ mm, yielding a red 2:4-dinitrophenylhydrazone, m.p. 168° (from methanol), obtained also directly from the dialdehyde. The dialdehyde was oxidised by hydrogen peroxide to a diacid, jatamansic acid, $C_{15}H_{26}O_4$, obtained earlier¹ by the chromic acid oxidation of jatamansone. With excess benzaldehyde, either under acid or base catalysis, jatamansone formed only a monobenzylidene derivative, which yielded jatamansic acid on ozonolysis. It can be concluded that the formation of jatamansic acid does not involve any prior rearrangement of the carbon skeleton of jatamansone.

Jatamansone showed infra-red absorption at 1699 cm^{-1} , which could be ascribed to a 2,2-dialkylcyclohexanone system.² With one mole of bromine, a monobromojatamansone, $C_{15}H_{25}OBr$, m.p. 105° , was formed (infra-red absorption at 1729 cm^{-1} , equatorial α -bromine). With excess bromine, only a dibromojatamansone, $C_{15}H_{24}OBr_2$, b.p. $145^{\circ}/0.6$ mm was formed (infra-red absorption at 1724 cm^{-1}). Since the presence of a $-CO-CH_2-$ group has been established, these results indicate that the other carbon adjacent to the carbonyl group is fully substituted.

Pyrolysis of jatamansic acid yielded norjatamansone, $C_{14}H_{24}O$, b.p. $110^{\circ}/4$ mm, showing carbonyl absorption at 1735 cm^{-1} (cyclopentanone). With excess benzaldehyde, norjatamansone yielded a monobenzylidene

² E. J. Corey, T. H. Topie and W. A. Wozniak, J. Amer. Chem. Soc. **77**, 5415 (1955).

derivative, b.p. $160^{\circ}/0.2$ mm (carbonyl band at 1709 cm^{-1}), yielding on ozonolysis a diketone, $\text{C}_{14}\text{H}_{22}\text{O}_2$, b.p. $140^{\circ}/0.3$ mm, oxidized by sodium metaperiodate to norjatamansic acid, $\text{C}_{14}\text{H}_{24}\text{O}_4$, m.p. 143° , forming an anhydride, m.p. $85-86^{\circ}$, having carbonyl bands at 1757 and 1805 cm^{-1} (glutaric anhydride). Norjatamansic anhydride yielded, with excess bromine, a monobromo derivative, $\text{C}_{14}\text{H}_{21}\text{O}_3\text{Br}$, m.p. 143° , converted by treatment with dimethylaniline to dehydronorjatamansic anhydride, $\text{C}_{14}\text{H}_{20}\text{O}_3$, m.p. 153° ($\lambda_{\text{max}}\ 225\ \mu$, $\log \epsilon$, 3.67 , infra-red bands at 1786 , 1672 and 1595 cm^{-1}). Dehydronorjatamansic anhydride was recovered unreacted after treatment with ozone and no volatile product like formaldehyde or acetone could be detected in the reaction mixture. A terminal methylene group or an isopropylidene group was not likely to be present in this compound. Dehydronorjatamansic anhydride dissolved in alkali but acidification of the alkaline solution yielded the anhydride directly, the intermediate acid not being isolable.

Oxidation of jatamansic acid (or jatamansone) with manganese dioxide - sulphuric acid (60 per cent) yielded trimellitic acid, whose formation should not have involved any rearrangement prior to dehydrogenation, since jatamansic acid was recovered unchanged together with some norjatamansone under the same conditions, in the absence of manganese dioxide.

Dehydrogenation of norjatamansic acid with Pd-C yielded a benzenoid hydrocarbon ($\lambda_{\text{max}}\ 265\ \mu$), oxidized by manganese dioxide - sulphuric acid to trimellitic acid.

The degradation results outlined establish that:

(1) jatamansone has a carbonyl-containing ring, which is six-membered, and that this ring includes the structural feature

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