

extract was used for the qualitative and quantitative analysis of inorganic constituents of the seeds. Elements were detected by semi-micro and micro analysis. Blank tests were also carried out for comparison.

The following are the results of analysis expressed in percentages of the seed :

(1) Oorganic matter : 78.7%, (2) Silica : 0.0155%, (3) Ca : 0.225%, (4) Mg : 0.131% and (5) Mn : 0.0013%. The atomic absorption spectrophotometric analysis was carried out for nickel, cobalt, bismuth, silver, zinc and iron and the results are as follows in ppm :

Ni : 220, CO : 30, Bi : 50, Ag : 15, Zn : 190 and Fe : 120.

Generally, silver is not obtainable even in trace amount in any Indian plant⁶. Deb *et al.*⁶ have reported 5 ppm silver in edible algae of Manipur. The present studies, however, indicate the presence of 15 ppm silver in Nirmali Seeds. The presence of 220 ppm of nickel seems to be quite high.

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Nagpur, March 12, 1976. V. V. DESHPANDE.

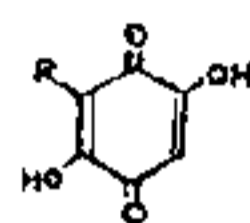
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SYNTHESIS OF A NEW PHENAZINE

PHENAZINE systems are well known for their utility as dyes. Several studies have been made to establish their pharmacological utility. *Streptomyces griseoluteus* is known to produce phenazine compounds having carboxyl group or alkyl group¹. Hydroxy, methoxy and aminophenazines have been thoroughly studied for their insecticidal value². It is therefore proposed to synthesize a hydroxyphenazine with an alkyl side chain, which may have useful physiological action.

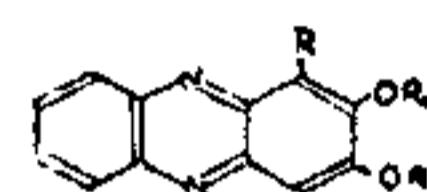
2, 5-Dihydroxy-1 : 4-benzoquinone [I] reacts with orthophenylenediamine forming 2, 3-dihydroxyphenazine [II]³. Embelin, 2, 5-dihydroxy-6-undecyl-1 : 4-benzoquinone [III] has been condensed with orthophenylenediamine in 1 : 1 molar proportion in acetic acid as solvent. The reaction mixture on working up gave a red crystalline substance

m.p. 225° C. It gave a positive ferric reaction and it developed a yellow coloration in aqueous sodium-hydroxide. Mass spectrum indicated the M⁺ peak (366) which is in agreement with the molecular formula C₂₃H₃₀O₂N₂. I.R. spectra data 3200 cm⁻¹ (—OH), 1625 cm⁻¹ (—C=N—) and uv absorptions at 253.5 nm (log ε, 5.24), 260 nm (log ε, 5.24) 391 nm (log ε, 4.84), showed the compound to be a phenazine derivative.



I R=H

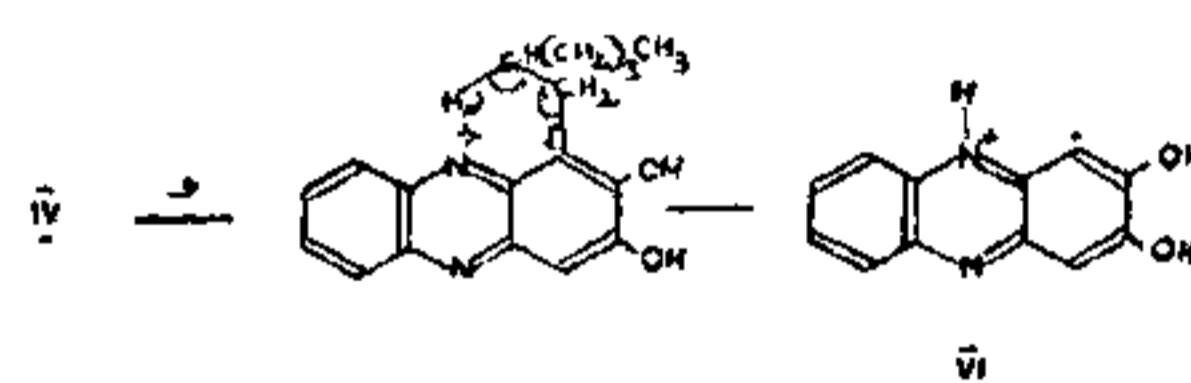
III R=-(CH₂)₁₀CH₃



II R=R₁, H

IV R=-(CH₂)₁₀CH₃, R₁=H

V R=-(CH₂)₁₀CH₃, R₁=-COCH₃



III

V

The presence of hydroxyl groups has been evidenced by the formation of acetate [V], m.p. 118° C, by refluxing the compound with acetic anhydride-sodium acetate. [V] showed the uv absorptions 253.5 nm (log ε, 5.13) and 365 nm (log ε, 4.22) characteristic of phenazine derivatives. Proton-magnetic resonance spectrum recorded on Bruker WH 90 in deuterodimethyl sulfoxide as solvent showed 7.23 δ (H, aromatic) 7.72 δ (2 H, aromatic) and 8.02 δ (2 H, aromatic) which is in agreement with the structure [IV]. Protons of the aliphatic side chain were observed in the region 2.5 δ to 3.5 δ. prominent peaks recorded in the mass spectrum (70 ev) 366 (M⁺, 5.8%) ; 226 (M⁺ - 140, 12.5%) ; 212 (M⁺ - 154, 100%) and 184 (212-28, 90.5%), confirm the structure [IV] for the condensation product of embelin with orthophenylenediamine. Intense peak at m/e 212 is attributed to the formation of radical ion [VI]. Aliphatic side chain fragment C₁₁H₂₂⁽⁺⁾ (154) has also been recorded.

More conclusive evidence for the structure of the condensation product [IV] has been obtained through the NMR spectrum of the acetate [V] in deuteriochloroform, which showed signals 0.95 δ (3 H, t, aliphatic CH₃) ; 1.36 δ (18 H aliphatic protons) ; 3.45 δ (2 H, t, benzylic protons) ; 2.47 δ (3 H, s, -COCH₃) ; 2.52 δ (3 H, s, -COCH₃) ; and 8.13 δ (1 H, s, aromatic H). Four aromatic protons were indicated by signals at 7.92 δ and 8.31 δ.

Further work in the field is in progress. Author is thankful to Prof. B. Franck for N.M.R., I.R.

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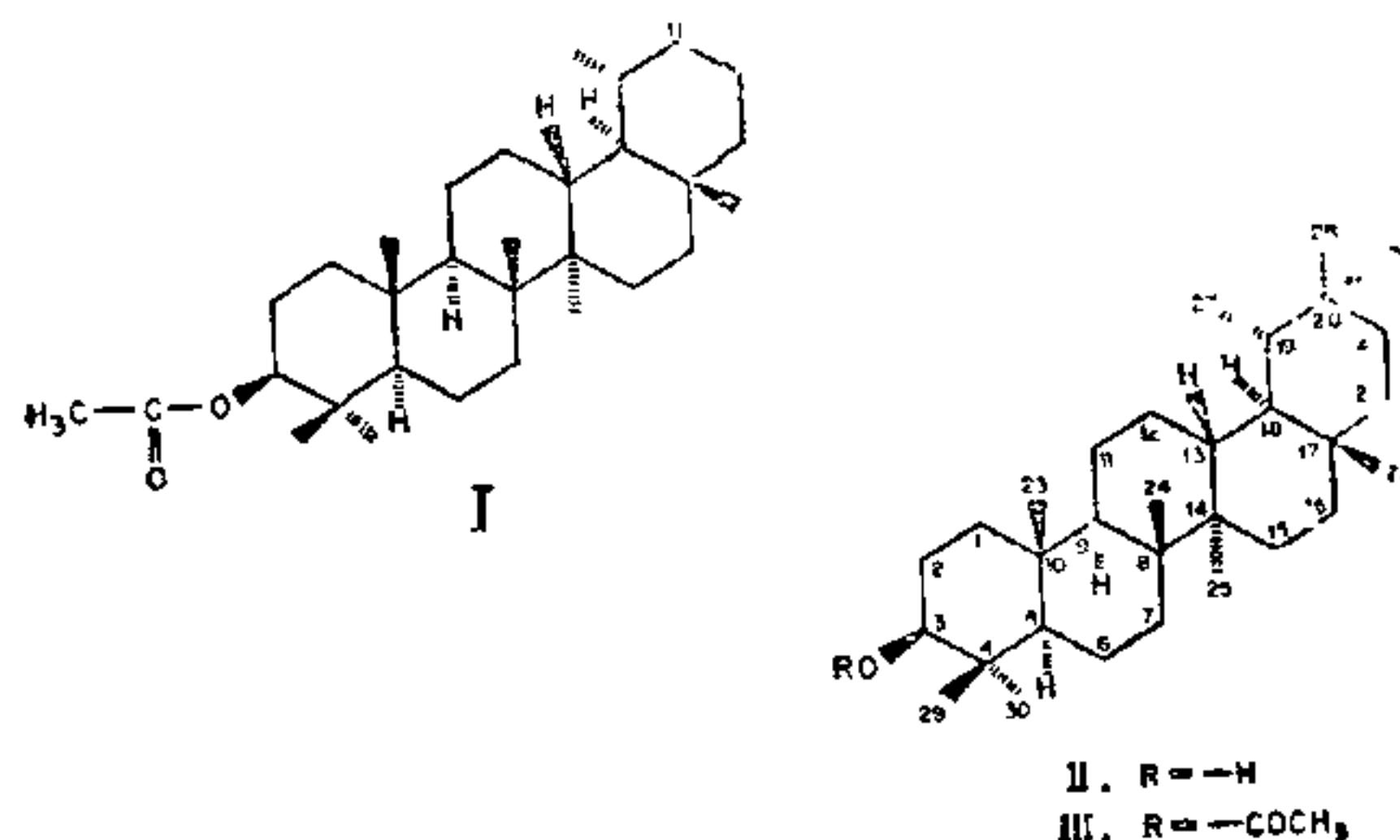
CONVERSION OF TARAXASTERYL ACETATE INTO TARAXASTANE 3 β -20 DIOL

EPOXIDATION (PBA) of taraxasteryl acetate¹ (I) gives a mixture of two stereoisomeric epoxides (TLC) (C₂₀-epimers). One of these epoxides (less polar), C₃₂H₅₂O₃, M⁺ 484, m.p. 236–38° (hexane + 10% benzene) has been isolated in the TLC pure state by chromatography. It shows IR absorptions at 1724, 1250 cm⁻¹ (acetate) and NMR (CCl₄) signals at τ : 9.17, 9.14, 9.07, 9.04, 8.97, 8.9 (21 H, methyls at C₄, C₈, C₁₀, C₁₄, C₁₇ and C₁₉); 8.07 (3 H, s, acetate methyl at C₃); 7.4 (2 H, s, CH₂ protons at C₂₈) and 5.6 (1 H, t, C₃-proton).

LAH reduction of the epoxide gives a diol (II), C₃₀H₅₂O₂, M⁺ 444, m.p. 266–68°, (α)_D - 9° (c, 1.5). It shows IR absorptions at 3344 (OH) and NMR (CHCl₃) signals at τ : 9.2, 9.14, 9.0, 8.93, 8.9 (21 H, methyls at C₄, C₈, C₁₀, C₁₄, C₁₇ and C₁₉); 8.8 (3 H, s, methyl at C₂₀) and a triplet at 6.8 (1 H, C₃-proton). Acetylation of (II) (Ac₂O/Py) affords a monoacetate (III), C₃₄H₅₄O₃, M⁺ 486, m.p. 276–80° (hexane), (α)_D \pm 0°. It shows IR absorptions at 3448 (OH), 1718, 1266 cm⁻¹ (acetate) and NMR (CCl₄) signals at τ : 9.18, 9.15, 9.0, 8.9 (21 H, methyls at C₄, C₈, C₁₀, C₁₄, C₁₇ and C₁₉); 8.86 (3 H, s, methyl at C₂₀); 8.0 (3 H, s, acetate methyl at C₃) and a triplet centred at 5.57 (1 H, C₃-proton).

Two taraxastane 3 β -20 diols which are epimeric at C₂₀ have been described in literature^{2,3}. A comparison of the IR spectrum of diol (II) with that of 20-epi- ψ -taraxastane, 3 β -20 diol³, isolated from black dammar resin, suggests a close relationship between the two compounds. However, some differences were observed in the NMR spectra of their monoacetates³ especially in the methyl region signals. In addition, the physical constants especially, the optical rotation of the two diols and their monoacetates are found to be

different [Lit.³ records for 20-epi- ψ -taraxastane-3 β -20 diol, m.p. 261–63°, (α)_D \pm 0°; monoacetate, m.p. 266–67°, (α)_D + 23°].



However, the physical constants of both (II) and (III) are in close agreement with those reported for ψ -taraxastane 3 β -20 diol² and its monoacetate. [Lit.² records for ψ -taraxastane 3 β -20 diol, m.p. 270–72°, (α)_D - 10.9°, monoacetate, m.p. 281–84°, (α)_D - 1.5°].

It therefore appears that diol (II) is identical with ψ -taraxastane 3 β -20 diol, isolated from manila elemi resin. A direct comparison between the two, however, could not be made due to the non-availability of the sample of ψ -taraxastane 3 β -20 diol.

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STUDIES ON PESTICIDES

Part I. Some Halogeno-polynitro Phenyl, Toly and Naphthyl Thiocyanates

Nitro phenyl, thiocyanates have been claimed to be toxicants for fungi^{1,2}, bacteria, moulds and other pests^{3,4}. The pesticides also show some tuberculostatic and acaricidal activity⁵. Incorporation of one or more substituents of electrophilic character in the ortho or para positions to the thiocyanate group results in an increase of both bacteriostatic and fungistatic activity⁵. It has been suggested that these compounds exert their anti-microbial