The yield of products and recovered oxide accounted for 86 to 95% of the starting material except in the case of 4-bromostyrene oxide (55% yield) in which there was a large pot residue.

4-Bromoethylbenzene and 3,4-Dichloroethylbenzene. 4-Bromoacetophenone[10] and 3,4-dichloroacetophenone were reduced by the Clemmensen method. 3,4-Dichloroethylbenzene was distilled at 64° at 2 mm.; n_D^{34} 1.5363.

Anal. Calc'd for $C_8H_8Cl_2$: C, 54.9; H, 4.6. Found: C, C, 55.1; H, 4.6.

Hydrogenation of 2-(3,4-Dichlorophenyl)ethanol. A sample of 2-(3,4-dichlorophenyl)ethanol[5] was hydrogenated under the conditions used for the oxides. The product was 2-cyclohexylethanol, b.p. 50–57° at 0.5 mm. (reported[11] 88–90° at 7 mm.). The 3,5-dinitrobenzoate melted at 69.5–70.5° (reported[11] 70.5°).

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Alkaloids from *Rauwolfia Schueli*

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Rauwolfia schueli is the only species of this genus which grows in Argentina. It is a tree with roots of rather large diameter and the cortex of the root contains alkaloids which were found pharmacologically active in the ptosis test.[1]

An investigation of the alkaloids present in the bark revealed the presence of aricine, reserpiline, isoreserpiline, and reserpine and of the stronger base, ajmaline.

The amount of aricine found in several batches was around 0.5% of the cortex. It is very interesting to observe that the same alkaloid was found in another South American species, *Rauwolfia sellowii*,[2] but in larger amounts.

Reserpiline and isoreserpiline were both identified by Stoll, Hofmann, and Brunner[3] in the leaves of *R. canescens* and although reserpiline was first isolated from *R. serpentina* by Klohs, Draper, Keller, and Malesh,[4] the isomeric base was not found in this species.

EXPERIMENTAL

The cortex of the root was well ground and the bases were extracted with methanol. The solvent was evaporated and the residue extracted with 10% acetic acid. To the acetic acid solution 10% sodium hydroxide solution was added to bring it to *p*H 9, when most of the bases precipitated. The crude precipitate was extracted with chloroform and the solution was filtered. Practically all the sedative activity passed into the chloroform.

Ajmaline. The chloroform solution was then extracted with 10% acetic acid and the extract alkalinized to *p*H 9 and extracted with benzene. After washing with water and drying, the benzene solution was evaporated to dryness and the residue dissolved in methanol after which crystals soon appeared. Recrystallization from methanol yielded material melting at $[\alpha]_D^{21}$ +129.2° (chloroform). It was transformed into isoajmaline, m.p. 260–262°, $[\alpha]_D^{20}$ +71.4° (chloroform). These data agree substantially with the constants of ajmaline and isoajmaline.[5]

Aricine. The acid-washed chloroform solution was evaporated to dryness and the residue dissolved in ten times its weight of methanol containing 10% of acetic acid. A crystalline precipitate appeared in a few minutes. It was filtered and washed with the same solvent. Recrystallization from methanol containing 1% of acetic acid yielded rhombic plates melting at 148–149°, which contained about one mole of acetic acid.

Anal. Calcd. for $C_{22}H_{26}N_2O_4 \cdot C_2H_4O_2$: acetyl (1) 9.67. Found: 8.20.

From this acetate, aricine was prepared by shaking the crystals with a mixture of ether and dilute ammonium hydroxide, washing with water, evaporating the dried ether solution, dissolving the residue in ethanol, and seeding with a sample of the base. Recrystallization from the same solvent yielded long prisms melting at 189°. A mixed melting point with authentic aricine was unchanged. $[\alpha]_D^{25}$ −58.6 ± 1° (*c*, 0.54, ethanol). *Hydrochloride*, m.p. 255°; *hydrobromide*, m.p. 263–264°; *oxalate*, m.p. 243–245°; and *picrate*, m.p. 222–223°.

Isoreserpiline. The methanolic acetic acid solution remaining after the isolation of aricine was evaporated to dryness and the residue treated with chloroform and ammonia water, whereupon all the bases passed again into chloroform. This solution was washed, dried, and evaporated and the residue was dissolved in benzene. The solution was submitted to chromatography on a column of aluminium oxide. Elution with benzene and evaporation of the first fractions yielded a residue which was dissolved in 60% methanol. Dilute nitric acid (1:10) was added to the solution. The crystalline nitrate of the base precipitated in a few minutes. Upon recrystallization from methanol needles, m.p. 264–265° (vac.), $[\alpha]_D^{20}$ −46.3 ± 3° (*c*, 0.08, water) were obtained.

Anal. Calcd. for $C_{23}H_{28}N_2O_5 \cdot HNO_3$: C, 58.09; H, 6.15; N, 8.84. Found: C, 58.22; H, 5.93; N, 8.77.

The base was separated by dissolving the nitrate in water and adding sodium hydroxide solution to *p*H 10.5. The amorphous solid was collected, washed with water, and dried. It was dissolved in benzene-hexane and when the solution was evaporated, isoreserpiline crystallized in hexagonal plates, m.p. 208°, $[\alpha]_D^{20}$ −84.7 ± 2° (pyridine); $[\alpha]_D^{21}$ −112.0 ± 2° (chloroform); $[\alpha]_D^{21}$ −84.2 ± 2° (ethanol). Stoll *et al.*[3] give m.p. 211–212°.

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Anal. Calcd. for $C_{23}H_{28}N_2O_5$: C, 66.90; H, 6.84; N, 6.79; CH_3O—(3), 22.54; CH_3—C (1); 3.6. Found: C, 67.35; H, 6.68; N, 6.62; CH_3O—, 22.84; CH_3—C, 3.26.

The infrared spectrum was identical with that of isoreserpiline.

The *hydrochloride* was prepared in the usual way. Recrystallization from absolute ethanol gave long needles, m.p. 280–281° (vac., fast heating); $[\alpha]_D^{26}$ −36.4 ± 2° (*c*, 0.37, ethanol 96%).

Anal. Calcd. for $C_{23}H_{28}N_2O_5 \cdot HCl$: C, 61.53; H, 6.51; Cl, 7.89. Found: C, 61.37; H, 6.26; Cl, 7.63.

The *methanesulfonate* prepared according to Stoll *et al.*,[3] melted at 282–283° alone and when mixed with an authentic specimen.

Reserpine. Subsequent elution of the column with benzene-acetone (2:1) gave several fractions, the first of which were pharmacologically active. They were united, evapoated to dryness in vacuum, and the residue was dissolved in boiling methanol when a spontaneous crystallization took place. After filtration and recrystallization from chloroform-methanol, needles melting 263–265° were obtained, showing no depression when mixed with pure reserpine. $[\alpha]_D^{28}$ −122 ± 3° (chloroform). By hydrolysis according to Dorfmann *et al.*,[6] *reserpic acid hydrochloride*, m.p. 255–257°, could be prepared.

Reserpiline. The mother liquors from the preparation of reserpine were evaporated, and the residue was dissolved in benzene and rechromatographed on aluminium oxide. After washing with benzene, an elution with benzene containing 0.5% of ethanol gave a small amount of reserpine.

Subsequent elution with benzene containing 1% of ethanol gave fractions which by evaporation yielded an amorphous residue. This, on solution in ethanol containing 10% of oxalic acid, gave a crystalline oxalate which was recrystallized from 70% ethanol. Long prisms, m.p. 248–250° (vac.). Klohs *et al.*[4] give m.p. 244–245°.

From the oxalate, decomposed in the usual way, the phosphate was prepared, m.p. 200–201° (vac.), $[\alpha]_D^{23}$ −50.4 ± 0.5° (water). Stoll *et al.*[3] give m.p. above 200°; $[\alpha]_D^{20}$ −52°.

The *hydrochloride*, short prisms from absolute ethanol, melted at 221–223° (vacuum, fast heating). $[\alpha]_D^{25}$ −44.7 ± 2° (ethanol 96%).

Anal. Calcd. for $C_{23}H_{28}N_2O_5 \cdot HCl$: C, 61.53; H, 6.51; N, 6.24; CH_3O (3) 20.74. Found: C, 61.58; H, 6.19; N, 5.76; CH_3O, 20.46.

The *picrate*, red needles from 50% ethanol, melted 174° (vac.).

Anal. Calcd for $C_{23}H_{28}N_2O_5 \cdot C_6H_3N_3O_7$: C, 51.32; H, 4.57. Found: C, 51.25; H, 5.29.

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Chemical Investigation of Roots of *Carissa Congesta*,[1] Santapau. I. Isolation of Carissone and D-Glucoside of β-Sitosterol

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The plant *Carissa congesta* (Apocynaceae) has been long known in Ayurveda (Indian system of medicine) as an anthelmintic and as a bitter stomachic.[6] The only reported work on this plant is the preliminary investigation by Dymock,[7] wherein the presence of an alkaloid, based on qualitative nonspecific tests, was reported. However, it was not possible to isolate any alkaloid from the roots of this plant in the present investigation.

The roots of *Carissa congesta* were collected in 1952 after the monsoon from a number of marked bushes growing on the hills of Western Ghats near Janjira, Bombay. They were sun-dried and powdered to 20 mesh. For large scale extraction the powdered roots were percolated with 96% ethyl alcohol and the extract was concentrated under reduced pressure. On working up the extract two crystalline compounds, D-glucoside of β-sitosterol (A) and carissone (B), together with a noncrystallizable bitter oil, were isolated.

Chemical investigation of (A). The white crystalline substance was obtained in very low yields of about 370 mg. per 180 lb. of the dry root. It was found to be insoluble in most of the organic solvents. On crystallization from glacial acetic acid it melted at 272–275°. On the basis of the carbon and hydrogen analysis and a molecular weight determination, it was assigned the molecular formula $C_{35}H_{60}O_6$. The Liebermann-Burchard test and the reduction of Fehling's solution indicated that the substance was a steroidal glucoside. From its infrared spectrum (Fig. 1)[8] and from the melting

(1) According to Cooke's Flora[3] this plant was thought to be *Carissa carandas* but later it was learned[4] that from the more recent critical studies of Santapau[5] this species should be called *Carissa congesta*. It has been pointed out that normally *Carissa carandas* has eight seeds in its fruit, whereas *Carissa congesta* has only four. There is also a difference in the shape of the leaves.

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