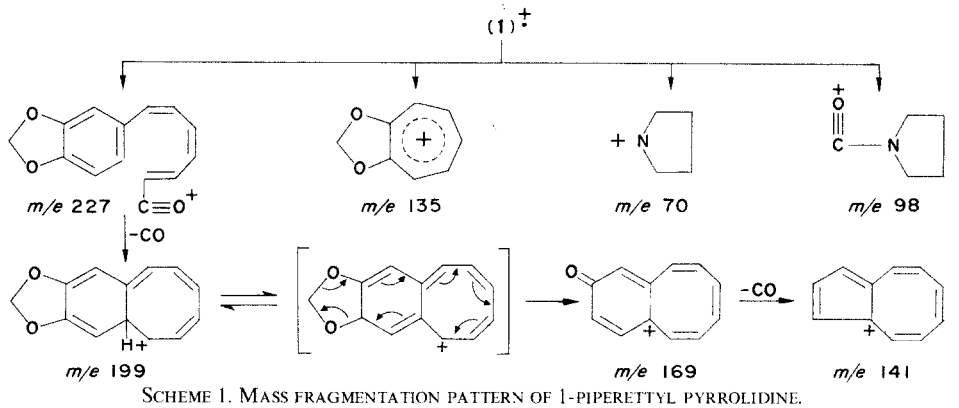
yielded piperettic acid, m.p. 221–223°, λ_{max}^{MeOH} 360 nm and the base pyrrolidine. Further chemical evidence on its structure could not be obtained due to paucity of the compound.



SCHEME 1. MASS FRAGMENTATION PATTERN OF 1-PIPERETTYL PYRROLIDINE.

EXPERIMENTAL

Extraction and isolation procedure. The air dried coarsely powdered stems (1250 g) *P. trichostachyon* were extracted (Soxhlet) with petrol. (60–80°) for 70 hr. The residue (20 g) after the removal of the solvent was extracted with C_6H_6 to yield a yellow semisolid (0·55 g). This semisolid was chromatographed over a column of neutral alumina. Elution with a mixture of EtOAc and petrol. (60–80°) yielded I. (105 mg), which was crystallized from EtOAc–petrol. mixture, m.p. 147–149°; R_f 0·42 (EtOAc C_6H_6, 1:1).

Hydrolysis. The compound in 10% alcoholic KOH (1·25 ml/10 mg) was heated under reflux for 50 hr. The crystalline K salt was collected by filtration, dissolved in H_2O (10 μml^3) and acidified with dil.HCl. The yellow ppt. was extracted with $CHCl_3$. After removal of the solvent the residue crystallized from alcohol into yellow crystals of piperattic acid, m.p. 221–223°, λ_{max}^{MeOH} 360 nm (lit.[2] m.p. 224°, λ_{max}^{MeOH} 360 nm).

The alcoholic filtrate was treated with dil. HCl and evaporated to dryness. This agreed on mixed and co-TLC with an authenic sample of pyrrolidine. R_f 0·65 (phenol–H_2O; 8·3).

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STEROIDAL ESTROGENS OF *PRUNUS ARMENIACA* SEEDS

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Estrone has been recently identified in several plants including seeds of *Elaeis guineensis*,[1] Phoenix dactylifera,[2,3] *Punica granatum*,[4] and apple.[5] It has also been

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obtained from roots of *Clossostemon brugiueri*[6] (Moghat) and from date palm pollen[2,6,8] (*Phoenix dactylifera*).

The sterol isolated from the non-saponifiable fraction of $CHCl_3$–MeOH extract of apricot seeds and as an insoluble precipitate in the acetone–H_2O fraction of the MeOH extract, was identified as Δ^{24} cholesterol, by m.m.p., $[\alpha]_D$, UV, IR and NMR spectroscopy. It was present as 0·91% of the dry weight of the seed. Sitosterol was not found.

The estrogenic fraction (0·09%) contained estrone (free and conjugated) in both the petrol. and Et_2O extracts. α-Estradiol (estradiol-β-17-ol) was identified in the MeOH extract. Purification of both estrogens was accomplished by saponifying for 10 min with 6% KOH in EtOH. The estrogens were obtained in highly purified crystalline forms by TLC.

When treated with Brown's reagent[7] the Et_2O extracts showed absorption at 423–428 nm similar to that given by estradiol dipropionate (410–430 nm) indicating that an esterified estrogen may be present.

Bioassays showed that the ether and methanol extracts produced similar effects to those obtained by injection of authentic estrone or α-estradiol.

EXPERIMENTAL

Methods. Silica gel G (0·3 mm) was used for TLC. Following development with C_6H_6–5% EtOAc, the compounds were eluted with $CHCl_3$–MeOH (1:1) and evaporated under N_2 for NMR, R_fs, IR and UV determinations, and Liebermann–Burchard reaction. Brown's reagent[9] was used before and after hydrolysis, and optical rotations were used for partial identification of the sterols extracted. The sterol acetate was prepared and chromatogramed on a silica gel–$AgNO_3$ column followed by TLC using C_6H_6–5% EtOAc and 6% H_2SO_4 for location. The steroid was also identified by preparation of *p,p'*-nitrophenylazobenzoyl chloride derivatives.[5]

For bioassays of estrogenic material extracted from apricot seeds, two methods were used; the first was Marrians' method[8] using ovarectomized young adult female rats; the second used rabbit uterus and Kreb's cycle acids.[10]

Isolation of estrone from seeds. The phenolic fractions were isolated from 500 g of peeled seeds of apricot according to the method of Bennett *et al.*[3] The petrol. and Et_2O extract both gave a yellow oil. The Et_2O extract was hydrolyzed[3] in 3 N methanolic HCl and fractionated with petrol. By TLC this fraction gave a main spot with R_f = 0·85, $[\alpha]_D$ + 165° and m.p. 259°. It showed maximum absorption at 420 and 520 nm with Brown's reagent[7] and gave IR spectrum identical with that of estrone.

The MeOH extract gave a brownish oil which dried to an amorphous material which was fractionated with petrol. (b.p. 30–50°) in the cold and gave white suspension, which precipitated to give a white solid which on purification and recrystallization from acetone had $[\alpha]_D$ × 81°, m.p. 179° and R_f = 0·35 by TLC. It showed maximum absorption at 300, 370 and 470 nm with Brown's reagent[7] with fluorescence when heated with H_2SO_4. It gave IR spectrum identical with that of estradiol.

Isolation of sterols of apricot seeds. The finely ground peeled dried seeds were extracted with $CHCl_3$–MeOH (2:1). Sterols were isolated,[9] acetylated overnight and chromatogramed on a silica gel–$AgNO_2$ column followed by TLC, and recrystallized from MeOH. The major cpd. gave a +ve Liebermann–Burchard reaction, has m.p. 122° (acetate m.p. 119°). When $[\alpha]_D$ and its acetate were −40° and −38° respectively in $CHCl_3$ at 23°, typical of Δ^5 sterols. Its UV and IR spectra were similar to that of cholesterol (IR) bands at 3200–3600 cm^{-1}, QH, and at 3030, 1660 cm^{-1} (double bond). It showed no conjugated double bonds. The NMR of the isolated sterol was identical of desmosterol (24-dehydrocholesterol).

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