CHEMICAL CONSTITUENTS OF CAPPARIS APHYLLA

Part II.—Isolation of Capparin, Capparilin and Capparinin

M. MANZOOR-I-KHUDA* and N.A. JEELANI

Drugs, Pharmaceuticals and Pesticides Research Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

(Received January 5, 1958)

New water-soluble indole bases designated as capparin, m.p. 236–38°, α_D^{20}–17° (*c* 1.05%, ethanol,) capparilin, m.p. 188–91°, α_D^{29}–43°(*c* 0.58%, ethanol) and capparinin, m.p. 229–31°C, α_D^{29}–12° (*c* 1.3%, ethanol) have been isolated from the roots of *Capparis aphylla*.

Capparis aphylla (synonym *Capparis decidua*)[1] grows wild in and around Karachi. The root bark of the plant has been used in the indigenous system of medicine for the treatment of rheumatism, phthisis, heart ailments, gout, cough, dropsy, palsy etc. and externally applied for the treatment of malignant ulcers, boils, eruption and diseases of the joints.[2]

In an earlier communication[3] isolation of β-sitosterol from the fresh undried root material was reported. The ethanolic extract of the root material on concentration gave a mainly aqueous concentrate which was extracted with ethyl acetate. The aqueous layer on evaporation gave a dark residue which was leached out with dry methanol. The methanol-soluble portion on column chromatography over alumina with progressive elution by chloroform, and mixtures of methanol–chloroform gave crystalline materials. The 10% methanol in chloroform elutes when freshly charcoaled gave deep violet solution which on heating became pale yellow. The crystalline residue on crystallisation from methanol–acetone gave capparin, m.p. 236–38°C, α_D^{29}–17° (*c* 1.05%, ethanol). Subsequent elution with the same solvent gave capparilin, m.p. 188–91°C, α_D^{29}–43° (*c*, 0.58°, ethanol). The 30% methanol in chloroform on evaporation followed by crystallisation gave capparinin, m.p. 229–31°C, α_D^{29}-°15° (*c*, 0.925%; ethanol). All the three crystalline compounds were highly hygroscopic and readily absorbed moisture from atmosphere.

Capparin, capparilin and capparinin had very similar IR spectrum and R_f values on paper and thin layer chromatography. The R_f values being 0.35, 0.33 and 0.35 on paper chromatographic run with n-butanol, acetic acid and water (4:1:1) solvent on Selectra Filter Paper No. 2045 (equivalent to Whatman No. 1 filter paper). The UV spectrum differred mainly in the end absorption characteristics, capparin had strong end absorption below 228 mμ., whereas capparinin had strong absorption below 245 mμ. The major absorption peaks were at 276i, 274, 270, 267, 263.5, 261.5, 259, 257, 254, 250 and 244 mμ (E_1^1 18.7, 21.0, 25.3, 27.8, 25.3, 25.3, 21.2, 19.0, 15.9, 13.1) for capparin and 275i, 273.6, 269.5, 266.5, 263, 261.5, 258.5, 256.5 and 253.5 mμ (E_1^1 16.9, 17.7, 20.7, 22.7, 20.8, 20.7, 19.4, 17.8, 17.7) for capparinin. Capparilin was isolated in very small quantity and no analytical figures were obtained. Capparin analysed for $C_{15}H_{37}N_3O_6$ and capparinin for $C_{15}H_{35}N_3O_6$ with some molecules of water of crystallisation. The colour reactions for indole nucleus on the compounds were inconclusive. capparin gave peaks at 6.47(29H), 6.59(1H), 7.40, 7.44 and 7.50 (three peaks total 7H) τ and capparinin at 6.54 (15H), 6.67, 6.93 (3H), 7.35, 7.38, 7.41, 7.44, 7.48i and 7.50i (total 17H) τ in the NMR spectra.

Experimental

IR spectra were determined in KBr disc on a Perkin Elmer Model 137 IR Spectrophotometer. Optical rotation was determined in ethanol solution on a Schmidt–Haensch polarimeter. All m.ps are uncorrected. NMR spectra were recorded by Dr. S.H. Zaidi of these Laboratories on a Varian A-60 NMR Spectrophotometer using tetramethyl silane as external standard and using deuterated dimethyl sulphoxide as solvent. Mass spectra were taken with a MS-9 Mass Spectrophotometer by probe injection of sample.

Isolation of Capparin, Capparilin and Capparinin.—Fresh roots of *Capparis aphylla* (3.85 kg; moisture 30%) were cut into small pieces and soaked in ethanol (7 l.). After 4 days the extract was taken out and the extraction repeated twice with dilute ethanol (density 0.82, 6 l.; followed by ethanol density 0.826,6.15 l.) for 4 days each. The combined extract was evaporated in a cyclone evaporator to a small, mainly aqueous concentrate (1.5 l.). This concentrate was extracted with

* Now at Technological Research Board, Jute Research Institute, Tejgaon, Dacca.

ethyl acetate, finally leaving behind an aqueous layer (A; 800 ml) containing about 15% solid. The ethyl acetate extract on evaporation gave 28.0 g gummy solid.

The aqueous solution (A, 300 ml) was evaporated to dryness under reduced pressure. The residue was leached with hot methanol. Evaporated methanol extractive (10.37 g) was redissolved in a small volume of methanol and evaporated to dryness under reduced pressure with a small amount of neutral chromatographic alumina (50 g). The powdery material was transferred on to a column of alumina (250 g) and first eluted with chloroform followed by successive elutions with 10%, 20%, 50% and 80% methanol in chloroform giving 2.348 g, 0.272 g, 0.544 g. and 0.836 g of eluted materials, respectively. The total residue (4g) was rechromatographed as before on a column of alumina (100 g) by elutions with 50% ether in chloroform followed by 25% ether–chloroform, chloroform, 0.5%, 1%, 2%, 3%, 5%, 10%, 20% and 50% methanol in chloroform. Crystalline materials were collected in 92 fractions of 125 ml each by elutions with 5% and above methanol in chloroform. Earlier fractions of 10% methanol in chloroform elute gave an intense purple solution on charcoaling. After evaporation under reduced pressure a colourless crystalline highly hygroscopic solid was obtained 0.44 g). This fraction on crystallisation from methanol–acetone mixture gave *capparin*, m.p. 236–38°C, α_D^{29} −17° (*c* 0.5%, ethanol) (Found: C, 45.81; H, 9.95; N, 10.32%; mass mol wt, 355. $C_{15}H_{37}N_3O_6.2H_2O$ requires C, 46.00; H, 10.55; N, 10.73%; mol wt, 355. $C_{15}H_{35}N_3O_6.2H_2O$ requires C, 46.24; H, 10.09; N, 10.8%; mol wt, 353).

Subsequent elutions with methanol in 10% chloroform gave another crystalline product by

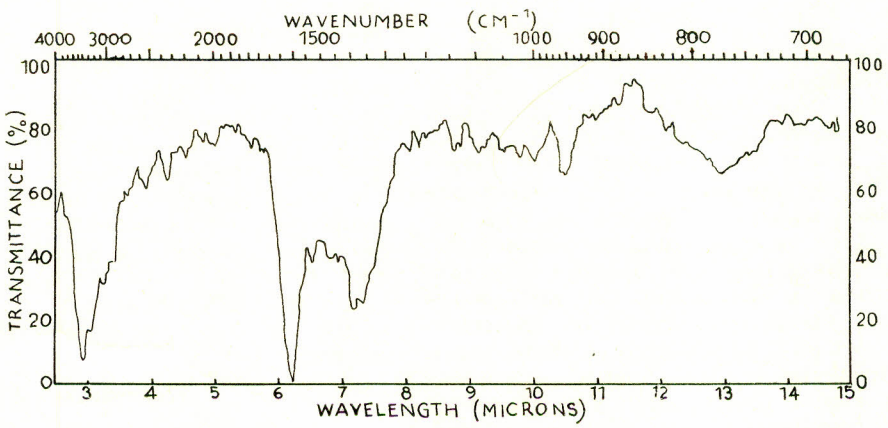

Fig. 1.—Capparin.

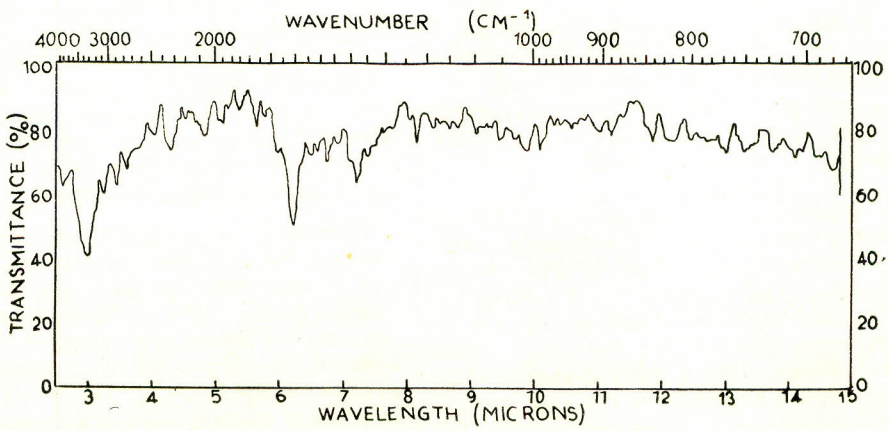

Fig. 2.—Capparinin.

crystallisation from methanol–acetone mixture giving *capparilin* 23 mg m.p. 188–91°C, α_D^{29} –43° (*c* 0.58%, ethanol) (Found: C, 49.86; H, 10.32% $C_{15}H_{35}N_3O_6.O.5H_2O$ requires C, 49.96; H, 10.07%).

The subsequent elutions with 10% methanol in chloroform produced 0.29 g of impure products. The 50% methanol in chloroform elution gave a small quantity of crystalline product in the earlier elutes (82 mg) which did not exhibit the intense purple coloration in charcoaling as in the case of capparin and capparilin. It was somewhat less hygroscopic. On crystallisation from methanol–accetone it gave *capparinin*, m.p. 229–31°C, α_D^{29} –12° (*c* 1.3%, ethanol).

Acknowledgement.—The authors wish to thank Dr. M. Barbier of the Institute of Chemistry for Natural Products, Gif-Sur-Yuette, France, and Dr. M. Salaque of these Laboratories for their help with the mass mol wt and elemental analysis.

References

1. M.H. Jafri, *The Flora of Karachi* (The Book Corporation, Karachi), p. 131.
2. K.M. Nadkarani, *Indian Materia Medica* (Popular Book Depot, Bombay), p. 265.
3. M. Manzoor-i-Khuda and Z. Kapadia, Pakistan J. Sci. Ind. Res., **11,** 108 (1968).