(VIII). Catalytic debenzylation of VIII over Pd/C yielded the required glucoside (I). The spectral data of the synthetic sample agreed with the reported values. A direct comparison could not be made because of the nonavailability of the authentic sample.

5,7,3',4',5'-Pentaacetyl-3-methylmyricetin (IV) — The flavone (III, 1·2 g) in anhyd. pyridine (5 ml) was treated with acetic anhydride (5 ml) and solution was kept at room temperature for 48 hr. The reaction contents were diluted with ice-cold water and the precipitated pentaacetoxy flavone (IV) filtered, washed with water and dried. It crystallized from ethanol as long white silky needles (1 g); m.p. 229-30° (Found: C, 57·8; H, 4·0. $C_{26}H_{22}O_{13}$ requires C, 57·6; H, 4·1%); UV (EtOH) nm: 260, 320; NMR ($CDCl_3$): 2·4, 2·5 (*s*, 15H, 5 × =OCOCH_3), 3·9 (*s*, 3H, C_3-OCH_3), 6·9 (*m*, 2H, C_6-*H* and C_8-H), 8·1 (*s*, 2H, $C_{2'}$-*H* and $C_{6'}$-*H*).

5,3',5'-Triacetyl-7,4'-dibenzyl-3-methylmyricetin (V) — To a solution of IV (800 mg) dissolved in acetone (25 ml) was added anhyd. KI (0·2 g), benzyl chloride (4·9 ml) and anhyd. potassium carbonate (2 g). The reaction mixture was refluxed on a water-bath for 10 hr. The potassium salts were filtered off and the acetone solution was concentrated. The product crystallized from ethyl acetate-pet.-ether as colourless needles (750 mg); m.p. 180-81° (Found: C, 67·5; H, 4·6. $C_{36}H_{30}O_{11}$ requires C, 67·7; H, 4·7%); NMR ($CDCl_3$): 2·3, 2·5 (*s*, 9H, 3 × =OCOCH_3), 4·0 (*s*, 3H, C_3-OCH_3); 5·2 (s, -CH_2 of benzyls at C_7 and $C_{4'}$); 6·8 (*d*, 1H, C_6-*H*); 7·0 (*d*, 1H, C_8-*H*); 8·0 (2H, C_2-*H* and C_6-*H*).

7,4'-Dibenzyl-3-methylmyricetin (VI) — To a suspension of V (700 mg) in ethanol (15 ml) was added aq. sodium carbonate (10%, 15 ml) and the mixtue boiled for ½ hr. Acidification of the clear solution gave the impure hydroxyflavone (VI). It was chromatographed over silica gel using benzene with increasing amounts of ethyl acetate as eluant. The fraction eluted with ethyl acetate-benzene (1: 19) afforded a yellow solid which crystallized from ethyl acetate-pet.-ether to give VI as yellow cubes (500 mg), m.p. 126-27° (Found: C, 70·0; H, 5·0. $C_{30}H_{24}O_8$ requires C, 70·3; H, 4·7%).

7,4'-Dibenzyloxy-5,5'-dihydroxy-3-methoxyflavone-3'-β-D-glucoside (VIII) — VI (400 mg) in dry pyridine (10 ml) was shaken with silver carbonate (600 mg) and anhyd. calcium sulphate (400 mg) for 1 hr. To this tetraacetylglucosyl bromide (700 mg) was added and the mixture shaken for another 3 hr. Inorganic salts were filtered off and the pyridine solution acidified with dil. acetic acid and subsequently extracted with ethyl acetate. The extract was washed with water and dried (Na_2SO_4). The acetyl glucoside (VII, 100 mg) obtained after the evaporation of ethyl acetate was taken up in absolute methanol (5 ml) and sodium methoxide (3 drops) added to it. It was neutralized with methanolic acetic acid after half an hour and the evaporation of this to half of its volume and cooling gave a solid that was filtered, dried *in vacuo* over P_2O_5. It was chromatographed over silica gel using benzene with increasing amounts of ethyl acetate as eluant. The fraction eluted with ethyl acetate-benzene (1:3) afforded a yellow solid which was further purified by preparative TLC (silica gel, toluene-ethyl formate-formic acid, 5: 4: 1). The product crystallized from ethyl acetate-pet.-ether as pale yellow needles (50 mg); m.p. 207° (Found: C, 63·9; H, 5·2. $C_{36}H_{34}O_{13}$ requires C, 64·1; H, 5·0%; UV (MeOH) nm (log ε): 264 (4·00), 268 (4·00), 344 (3·95); + $AlCl_3$ 275, 350-55, 395; + $AlCl_3$/HCl 280, 305, 340; + NaOAc 265, 340-45; + NaOAc/H_3BO_3 265, 330-35.

3'-O-β-D-Glucoside (I) *of myricetin-3-O-methylether* — The dibenzylated glucoside (VIII, 30 mg) was dissolved in ethyl acetate (20 ml) and Pd/C (10%, 15 mg) was added. The mixture was stirred under H-atmosphere for 4 hr. The catalyst was filtered, the solvent removed and the product crystallized from ethanol as yellow cubes (15 mg); m.p. > 300° (Found: C, 53·6; H, 4·2. $C_{22}H_{22}O_3$ requires C, 53·4; H, 4·5%). It gave brown colour with alc. $FeCl_3$ solution and gave response to Mg/HCl and Molisch's tests; UV (MeOH) nm (log ε): 252 (4·07), 302 (3·82), 356 (4·03); + $AlCl_3$ 275, 345, 435; + $AlCl_3$/HCl 270, 305, 355; + NaOAc 265, 320-30, 340, 410; + NaOAc/H_3BO_3 260, 380. IR (KBr): 3450, 1640, 1600, 1490, 1360, 1305, 1175, 1075(b), 1050, 805 cm^{-1}.

References

1. Howard, G. & Mabry, T. J., *Phytochemistry*, **9** (1970), 2413.
2. Sharma, C. S., *Synthesis of some naturally occurring flavonoid partial methyl ethers*, Ph.D. thesis, Delhi University, 1974, 114.
3. Koenings, W. & Knorr, E., *Ber. dt. chem. Ges.*, **34** (1901), 957.

Alkaloids of *Tabernaemontana wallichiana**

S. K. Talapatra, S. Sen Gupta, M. Bhattacharya & B. Talapatra

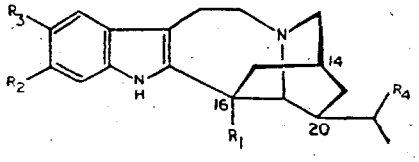
Department of Chemistry, University College of Science Calcutta 700009

Received 29 *May* 1975; *accepted* 28 *July* 1975

The stem bark of *Tabernaemontana wallichiana* Steud (Fam : Apocynaceae) furnishes three iboga alkaloids, voacangine (I) (0·09%), coronaridine (III) (0·04%) and voacristine (V) (0·06%). The leaves of the same plant afford I (0·02%), V (0·0006%) and isovoacangine VI (0·0003%). Decarbomethoxylation of I and III gives ibogaine (II) and ibogamine (IV) respectively. The crude decarboxymethylation product of I upon keeping in chloroform solution suffers autoxidation to yield ibogaine hydroxyindolenine (VII), the mass fragments of which have been rationalized.

THE present paper, in continuation of our previous communication[1] reporting the neutral constituents of *Tabernaemontana wallichiana* (syn.[2]

*Formed part of the Ph.D. thesis, Calcutta University, 1970, of S. Sen Gupta; major part of this work was presented at the 56th Session of the Indian Science Congress, 1967.



(I) R_1=COOCH$_3$, R_2=R_4=H; R_3=OCH$_3$ (16S,20S)

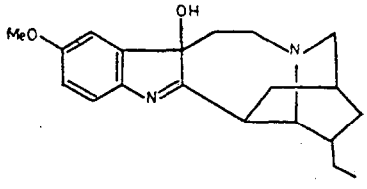
(II) R_1=R_2=R_4=H, R_3=OCH$_3$ (16R,20S)

(III) R_1=COOCH$_3$, R_2=R_3=R_4=H (16S,20S)

(IV) R_1=R_2=R_3=R_4=H (16R,20S)

(V) R_1=COOCH$_3$, R_2=H, R_3=OCH$_3$, R_4=OH (16S,20R)

(VI) R_1=COOCH$_3$, R_2=OCH$_3$, R_3=R_4=H (16S,20S)



(VII)

Ervatamia wallichiana) is concerned with the isolation and characterization of the alkaloidal constituents of the stem bark and leaves of the same.

The alkaloidal fraction obtained from the light petrol and chloroform extracts of the stem bark upon chromatography over neutral alumina furnished one amorphous and two crystalline alkaloids. The crystalline alkaloids were identified as voacangine[3,4] (I) and voacristine[5-7] (V) (= voacangarine) from their physical and spectral data[8]. I was smoothly decarbomethoxylated to ibogaine[5] (II) which when kept in chloroform solution for weeks, underwent auto-oxidation to ibogaine hydroxyindolenine[6] (VII), identified by direct comparison with an authentic sample prepared by peracid oxidation of II.

The mass spectrum of VII displayed diagnostic peaks at *m/e* 326 (M^+, 100%), 311 (M^+—Me, 30), 309 (M^+—OH, 40), 297 (M^+—Et, 5), 203 (*a*, 10), 202 (*b*, 30), 189 (*c*, 10), 188 (*d*, 5), 138 (*e*, 20), 136 (*f*, 10), 122 (*g*, 15). The formation of each ion (Chart 1) can be rationalized on the basis of well-known fragmentation pathways[8]. Genesis of the ion at *m/e* 202 has been reported earlier[9].

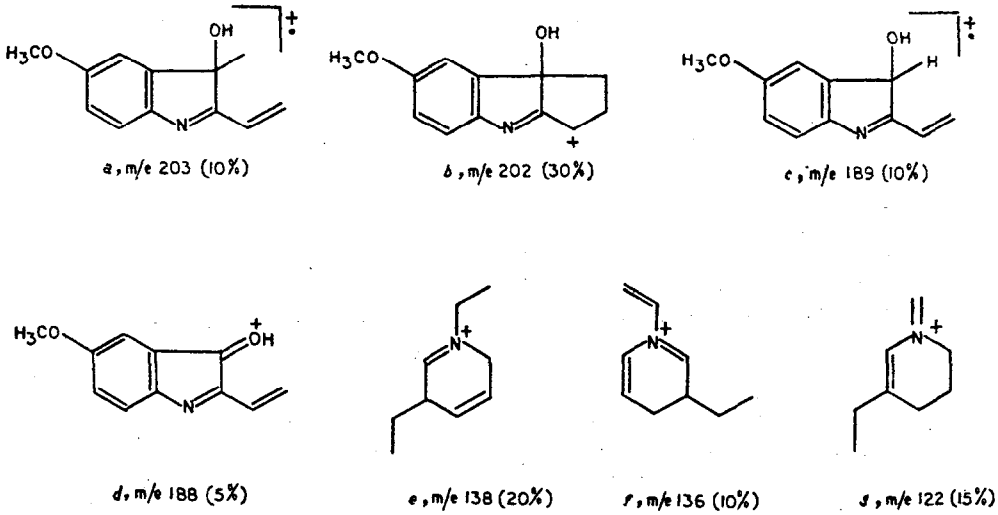
The amorphous alkaloid, characterized as coronaridine[7,10] (III) from physical and spectral characteristics of its hydrochloride, upon decarbomethoxylation formed ibogamine (IV). The alcoholic extract of the dried leaves afforded the fourth iboga alkaloid, characterized as isovoacangine (VI)[11], in addition to small amounts of I, III and V.

The structures shown in this paper represent the absolute configuration of the iboga and voacanga alkaloids as determined by Blaha *et al.*[12] by chiro-optical approach.

Dried and powdered stem bark (0·8 kg) of *T. wallichiana* was extracted with light petrol (b.p. 60-80°), chloroform and ethanol successively. The petrol and chloroform extracts were separately extracted with 2*N* hydrochloric acid and basified with a saturated solution of sodium carbonate (*p*H 7·5). The liberated base in each case was repeatedly extracted with ether. The ether extract was washed, dried and concentrated to afford a basic residue-A (1·5 g) from the petrol extract and B (2·5 g) from the chloroform extract.

Isolation of voacangine (I) — The residue-A was chromatographed over neutral alumina (80 g). The benzene eluates upon evaporation and crystallization of the residue from methanol furnished I, m.p. 134-35°; $[\alpha]_D$ —39° (chloroform), λ_{max} nm (log ϵ): 226 (4·40), 286 (3·89), 299 (3·85).

Conversion of I *to ibogaine* (II) — A solution of I (0·13 g) in 20 ml of 60% aq. ethanol containing 1·2 g of potassium hydroxide was refluxed for 6 hr



a, m/e 203 (10%) *b*, m/e 202 (30%) *c*, m/e 189 (10%)

d, m/e 188 (5%) *e*, m/e 138 (20%) *f*, m/e 136 (10%) *g*, m/e 122 (15%)

Chart 1

on a steam-bath. Ethanol was removed under reduced pressure and the residue warmed on a steam-bath with 5*N* hydrochloric acid (35 ml) for 1 hr. The solution was cooled, basified with ammonium hydroxide and extracted with ether. Chromatography over neutral alumina afforded ibogaine as colourless needles (methanol), m.p. 154° (d); $[\alpha]_D$ −53° (chloroform) from benzene eluates.

Isolation of coronaridine (III) — The mother liquor remaining after the isolation of I was twice chromatographed over alumina (15 g) and benzene-ether (3:1) fractions of the second chromatography furnished III. It gave crystalline hydrochloride, m.p. 234° (dec.); $[\alpha]_D$ −7° (chloroform); λ_{max} nm (log ϵ): 233 (4·47), 285 (3·87), 289 (3·84), characteristics of 2,3-disubstituted indole chromophore; IR (hydrochloride of III) 5·81 μ (COOMe); MS (M^+ 338, 100%), 253 (9), 214 (26), 154 (20), 130 (20), 148 (11), 136 (99), 122 (41).

Conversion of III *to ibogamine* (IV) — The base hydrochloride (0·03 g) was decarbomethoxylated by the same method as in the case of the conversion of I to IV. The product was chromatographed over neutral alumina and benzene eluents furnished IV crystallizing from methanol in needles, m.p. 160-61°; $[\alpha]_D$ −36° (chloroform).

Isolation of voacristine (V) — The basic residue-B was chromatographed over neutral alumina (120 g). Benzene-ether (1:2) eluated the base V, crystallizing from methanol in needles, m.p. 92-93° and 164-66°; $[\alpha]_D$ −24° (chloroform); λ_{max} nm (log ϵ): 225 (4·40), 285 (3·91), 301 (3·84), characteristics of 5-methoxyindole chromophore; IR 3·01 μ broad (indole NH, overlapped with H-bonded OH peak), 5·82 (COOMe), 6·19, 6·32 (5-methoxyindole moiety); MS (M^+ 384, 100%), 283 (27), 244 (53), 184 (73) and 160 (53).

Isolation of isovoacangine (VI) — The basic fraction (1·8 g) of the alcoholic extract (room temperature, 7 days) of the dried leaves (1·5 kg) of the plant on chromatography over neutral alumina (100 g) furnished VI (0·15 g) from benzene eluate fractions. It crystallized from methanol in fine needles, m.p. 155-57°; $[\alpha]_D$ −52°; λ_{max} nm (log ϵ): 227 (4·55), 278 (3·60), 300 (3·82), characteristics of 5-methoxyindole base; IR 3·0 μ (indole NH), 5·83 (COOMe), 6·18, 6·30 (5-methoxy indole moiety); MS (M^+ 368, 100%), 283 (7), 244 (18), 184 (31), 160 (53), 136 (85) and 122 (32).

The authors thank Dr B. C. Das (CNRS, France) for mass spectral measurements, Dr M. Gorman (Eli Lilly & Co., USA) for IR spectra of voacristine, voacangine and their authentic samples, Dr S. C. Pakrashi (IIEM, Calcutta) for IR spectra of other compounds and rotations. Thanks are also due to Dr T. K. Bose, Royal Agri-Horticultural Society, Calcutta, for the gift of the plant materials.

References

1. Talapatra, S. K., Sen Gupta, S. & Talapatra, B., *J. Indian chem. Soc.*, **44** (1967), 416.
2. *Index kewensis, plantarum phanerogamarum*, edited by G. Taylor (Clarendon Press, Oxford).
3. Hwang, B., Weisbach, J. A., Douglas, B., Raffauf, R., Cava, M. P. & Bessho, K., *J. org. Chem.*, **34** (1969), 412.
4. Taylor, W. I., *The alkaloids*, edited by R. H. F. Manske, Vol. 8 (Academic Press, New York), 1965, 203.
5. Percheron, F., Le Hir, A., Goutarel, R. & Janot, M. W., *C.r. Acad. Sci.*, **245** (1957), 1141.
6. Dickel, D. F., Holden, C. L., Maxfield, R. C., Foszek, L. E. & Taylor, W. I., *J. Am. chem. Soc.*, **80** (1958), 123.
7. Talapatra, B., Patra, A. & Talapatra, S. K., *Phytochem.*, **14** (1975), 1652.
8. Budzikiewicz, H., Djerassi, C., Puisieux, F., Percheron, F. & Poisson, J., *Bull. Soc. chim. Fr.*, (1963), 1899.
9. Thomas, D. W. & Biemann, K., *Tetrahedron*, **24** (1968), 4223.
10. Gorman, M., Neuss, N., Cone, N. J. & Deyrup, J. A., *J. Am. chem. Soc.*, **82** (1960), 11.
11. Renner, U., Prins, D. A. & Stoll, W. G., *Helv. chim. Acta*, **42** (1959), 1572.
12. Blaha, K., Koblicova, Z. & Trojanek, J., *Tetrahedron Lett.*, (1972), 2763.

Essential Oil of *Elsholtzia pilosa*

R. K. Thappa, S. G. Agarwal, V. N. Vashist & C. K. Atal

Regional Research Laboratory, Jammu-Tawi 180001

and

B. C. Gulati

Central Indian Medicinal Plants Organization Jammu Tawi

and

S. P. S. Duhan

Central Indian Medicinal Plants Organization, Haldwani

Received 12 *May* 1975; *accepted* 26 *July* 1975

The essential oil of *Elsholtzia pilosa* is composed of 21 mono and sesquiterpenes. These are α-pinene, β-pinene, phellandrene, limonene, 1:8-cineole, *p*-cymene, γ-terpinene, terpinolene, linalool, caryophyllene, α-terpineol, terpinene-4-ol, terpinyl acetate, geranyl acetate, geraniol, elemol, β-caryophyllene oxide and four unidentified compounds.

As a part of our programme[1,2] on the essential oils of various *Elsholtzia* species, we report in this paper the results of the chemical examination of the essential oil of *E. pilosa*, collected at flowering stage during August-September around Nainital (U.P.).

The oil was obtained in 0·12% yield by hydrodistillation of the fresh flowering plants. The oil was examined[3] for its physico-chemical characteristics: d_{20}^{20} 0·9010; n_D^{25} 1·4695; $(\alpha)_D$ +4·13°; acid value 3·38; ester value 43·40; ester value after acetylation 77·61; carbonyl value 14·03%. The oil was analysed both on simple and silver nitrate impregnated[4] silica gel 'G' thin layer plates followed by gas-liquid chromatography. The GLC was done on Perkin Elmer-881 using Reoplex 400 stainless steel column of 6 ft length, column temperature 150°, FID detector, chart speed 15 mm/min. and nitrogen as the carrier gas. The peak areas were determined by the triangulation method. The compounds identified by comparison of their reten-