($CHCl_3$) (lit [9] $-36°$); UV λ_{max} 224, 282, 5 et 291 nm; IR: 3390 cm^{-1}; SM:$M^{+\cdot}$ ($C_{19}H_{24}N_2$) 280 (95%), principaux pics à 265, 195, 156, 149, 136 (100%), 122; RMN (δ): *t* (3H) 0,89 (Me_{18}).

(f) (*19S*) *hydroxy*-19 *ibogamine*. **12**: Par la technique indiquée en (e) l'heyneanine **3** a fourni, par cristallisation dans Me_2CO le dérivé décarbométhoxylé **12**: F 195–205°; $(\alpha)_D$ $-8°$ ($CHCl_3$, C: 0,48); UV λ_{max} 225, 288, 291 nm; IR: 3390 cm^{-1}; SM=$M^{+\cdot}$ ($C_{19}H_{24}ON_2$) 296 (100%), principaux pics à 281 (67%), 278 (32,5%) 251 (14%), 195 (30%), 165, 156, 152 (58%) 138, 122; RMN (δ): *s* (1H) 7,85 (N-H), q.*d* (1H) 4,16 (C<u>H</u>OH), *d* (3H) 1,11 (Me_{18}).

(g) (*19R*)*hydroxy*-*19 ibogamine*. **13**: Par la technique indiquée en (e) l'épi-19 heyneanine **4** a fourni par cristallisation dans Me_2CO (Rdt 88%) le dérivé décarbométhoxylé **13**: F 168–173°; $(\alpha)_D$ $-29°$ ($CHCl_3$, C: 1); UV λ_{max} 225, 283, 291 nm; IR: 3410, 3240 cm^{-1}; SM:$M^{+\cdot}$ ($C_{19}H_{24}ON_2$) 296 (100%) principaux pics à *m/e*: 281 (66%), 278 (50%), 251, 195 (30%), 165, 156 (24%), 152 (51%), 138, 122; RMN: *s* (1H) 8,0 (N-H), *s* (1H) 5,18 (CHO<u>H</u>), q.*d* (1H) 3,89 (C<u>H</u>OH), *d* (3H) 1,27 (Me_{18}).

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TERPENOIDS AND ALKALOIDS OF THE LEAVES OF *TABERNAEMONTANA CORONARIA*

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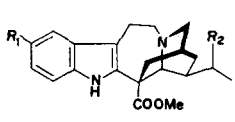
Key Word Index—*Tabernaemontana coronaria*; Apocynaceae; coronaridine; voacristine; tabernaemontanine; dregamine; α-amyrin acetate; lupeol acetate; α-amyrin; lupeol; sitosterol.

Tabernaemontana coronaria R.Br. *syn. Ervatamia coronaria* Stapf (*syn. Ervatamia divartica* (L) Burkill) is a glabrous, evergreen, dichotomously branched shrub or small tree with milky juice, cultivated all over India primarily for the ornamental value of its fragrant white flowers and for medicinal use. The root is prescribed for biliousness, diseases of the blood, epilepsy, paralysis and scorpion stings and its charcoal is considered a remedy for ophthalmia. The wood is used as a refrigerant and the milky juice is rubbed into the head to cure pain in the eyes. The root is chewed to relieve toothache [1].

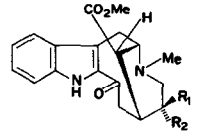
The stems and barks of this plant were investigated previously and have been found to produce indole alkaloids [2], terpenoids [3] and sterol [3]. However, there seems to be no report on the chemical constituents of the leaves of this plant. The present chemical investigation of the leaves has resulted in the isolation of coronaridine (**1**) [2, 4], voacristine (**2**) [5], tabernaemontanine (**3**) [2, 5] and dregamine (**4**) [2, 5] from the basic fraction, and lupeol acetate, α-amyrin acetate, lupeol, α-amyrin and sitosterol from the neutral fraction—successively eluted out from the respective columns. Identity of each compound was established by direct comparison (mmp determination, co-TLC, superimposable IR and similar UV) with respective authentic samples. The alkaloids **1**, **3** and **4** were previously found [2] in the stem and bark of this plant. The isolation of voacristine, however, constitutes its first report from this plant.

While pharmacological studies have shown voacristine [6] and dregamine [7] to be pharmacologically active, there seems to be no such

report to our knowledge on coronaridine and tabernaemontanine.



(1) Coronaridine $R_1 = R_2 = H$
(2) Voacristine $R_1 = OMe$, $R_2 = OH$



(3) Tabernaemontanine $R_1 = H$, $R_2 = Et$
(4) Dregamine $R_1 = Et$, $R_2 = H$

EXPERIMENTAL

Dried and ground leaves (600 g) of *Tabernaemontana coronaria* were extracted with $CHCl_3$ in a Soxhlet for 25 hr. From the extract concentrate, the neutral and basic components were separated in the usual way. EtOH extract of the marc showed positive alkaloid test, but yielded no characterizable product.

Isolation of coronaridine (**1**), *voacristine* (**2**), *tabernaemontanine* (**3**) *and dregamine* (**4**). The basic fraction (1·8 g) was chromatographed over Brockmann alumina (Neutral, grade I) elution being carried out with solvents and solvent mixtures of increasing polarity. The eluted fractions showing identical TLC behaviour were combined. The earlier C_6H_6 eluates afforded an amorphous base which formed a hydrochloride (20 mg), mp 231–4° (d) (MeCOMe) and was identified as coronaridine (**1**). The latter C_6H_6 eluates afforded a base (130 mg) mp 108–10° and 155–60° (ether), identified as voacristine (**2**). Further elution of the same chromatogram with C_6H_6–$CHCl_3$ (1:1) mixture yielded from the earlier fractions tabernaemontanine (**3**) mp 216–8° (MeOH) (16 mg). Dregamine (**4**) mp 181–3° (MeOH) (8 mg) was isolated from the later fractions of the same solvent mixture.

Isolation of α-amyrin acetate, lupeol acetate, α-amyrin, lupeol and sitosterol. The non-basic fraction was chromatographed over Brockmann alumina (Neutral, Grade I) in a similar manner. Earlier petrol eluate fractions showing identical spot in TLC were combined and concentrated to afford an amorphous residue (~3 g) which could not be induced to crystallize. The residue (mp 170–80°), showing single spot in TLC, positive Liebermann Burchardt (L.B.) test for triterpene and IR bands for acetate (ν_{max} (nujol) 1737 and 1242 cm^{-1}) was hydrolysed with 10% alcoholic alkali (50 ml). The amorphous material obtained (2·2 g) although showed single spot in TLC, could not be crystallized. The substance was benzoylated and then chromatographed over alumina. Evaporation of the early petrol eluates gave a pure benzoate (60 mg) crystallizing from $CHCl_3$–MeOH in fine needles, mp 190–2° which upon hydrolysis with alcoholic alkali afforded α-amyrin, mp 185–6°, $[\alpha]_D$ +79° ($CHCl_3$). Further elution with petrol furnished another pure benzoate (80 mg) from the later fractions crystallizing in tiny flakes from $CHCl_3$–MeOH, mp 257–9°. Alkaline hydrolysis of this benzoate furnished lupeol, mp 210, $[\alpha]_D$ +24° ($CHCl_3$). The middle fractions gave a mixture (~1·8 g) of the above benzoates. Thus the triterpene acetate mixture was found to contain α-amyrin acetate and lupeol acetate.

The later petrol eluate fractions of the main chromatogram afforded an amorphous triterpene alcohol mixture (400 mg, single spot in TLC and positive L.B. test for terpenes). Attempts to separate through acetylation of the material, repeated chromatography and fractional crystallizations met with failure. The alcohol mixture was then benzoylated and the product chromatographed over alumina. From the petrol eluates two compounds, mp 191–3° (10 mg) and 246–8° (6 mg), both crystallizing from $CHCl_3$–MeOH, were obtained. Middle fractions gave a mixture (~450 mg) of the two. They were identified as α-amyrin benzoate and lupeol benzoate respectively. Thus α-amyrin lupeol were present in the mixture.

Further elution with a mixture of petrol–C_6H_6 (1:2) yielded a compound crystallizing from $CHCl_3$–MeOH in flakes (260 mg) mp 138° $[\alpha]_D$ −36° ($CHCl_3$) (positive L.B. test for sterol) identified as sitosterol.

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