

8.2. *PANCRATIUM* L.

Alkaloids

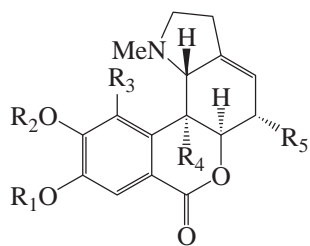
Amaryllidaceae, including *Pancratium* (Piozzi *et al.*, 1969). *Pancratium* species are rich and important sources of Amaryllidaceae alkaloids e.g. *Pancratium canariense* bulbs, from which sixteen alkaloids have been isolated (Cedrón *et al.*, 2009). The chemistry and biology of *Pancratium* alkaloids have been reviewed by Cedrón *et al.* (2010). In this review, the alkaloids have been classified according to their following 4 skeleton types:

1. Lycorenine and Lycorine Types

From the genus *Pancratium* four alkaloids with this skeleton have been isolated *viz.* hippeastrine (**110**), (+)-9-*O*-demethylhomolycorine (**111**), 10-norneronine (**112**) and pancratinine A (**113**). All of the alkaloids contain a lactone ring, due to the oxidation of the hydroxyl group at C-6. Pancritatin A, which has an unusual oxygenated function at position 10*b*, has only been detected in a few species (Latvala *et al.*, 1995; Cedrón *et al.*, 2009). Seventeen lycorine-type alkaloids (**1**, **19**, **41**, **57**, **64**, **76**, **114-124**) have been identified in *Pancratium* species (Rangaswami and Rao, 1966; Cedrón *et al.*, 2009). Several of them have been isolated as *N*-oxides (**123**, **124**) (Vazquez-Tato *et al.*, 1988; Cedrón *et al.*, 2009), as zwitterionic compounds (**57**, **122**), in a chiral form (**64**, **118**, **119**) (Ghosal *et al.*, 1986d; Amarasekara and Gottlieb, 1993) or with glycosidic substituents (**115**, **116**) (Ghosal *et al.*, 1984; Cedrón *et al.*, 2010).

2. Montanine, Narciclasine, and Tazettine Types

Alkaloids belonging to the montanine (**5**), narciclasine (**4**), and tazettine (**3**) groups are unusual in the *Pancratium* genus. Only three alkaloids with a montanine-type skeleton have been identified: pancracine (**65**) from *Pancratium maritimum* (Ali *et al.*, 1984c) and *Pancratium sickenbergeri* (Sener *et al.*, 1998b), and pancratinine B (**125**) and pancratinine C (**126**) from *Pancratium canariense* (Cedrón *et al.*, 2009). From *Pancratium maritimum* three narciclasine-type alkaloids have been isolated: pancratistatin (**127**) (Pettit *et al.*, 1995b), narciclasine (**4**) (Fuganti and Mazza, 1972) and its glycosidic derivative (**128**) (Abou-Donia *et al.*, 1991). The tazettine type alkaloids in the *Pancratium* genus are tazettine (**3**) and deoxytazettine (**129**) isolated from *Pancratium maritimum* (Berkov *et al.*, 2004b), and pretazettine (**89**) from *Pancratium biflorum* (Ghosal *et al.*, 1986d).

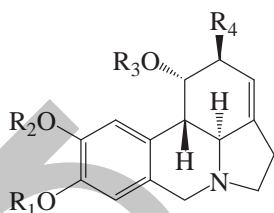


110 Hippastrine $R_1+R_2=CH_2, R_3=R_4=H, R_5=OH$

111 (+)-9-O-demethylhomolycorine $R_1=H, R_2=Me, R_3=R_4=R_5=H$

112 10-Norneronine $R_1+R_2=CH_2, R_3=OH, R_4=H, R_5=OH$

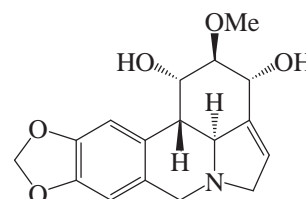
113 Pancratinine A $R_1+R_2=CH_2, R_3=H, R_4=R_5=OH$



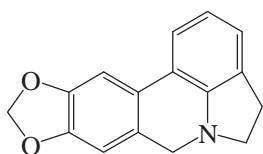
114 9-Norpluviine $R_1=Me, R_2=H, R_3=H, R_4=OH$

115 1-O-β-D-Glycosilylcorine $R_1=Me, R_2=R_3=R_4=H$

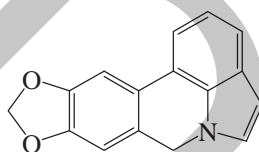
116 1-O-β-D-Glycosilpseudolycorine $R_1+R_2=CH_2, R_3=β-D-glc, R_4=OH$



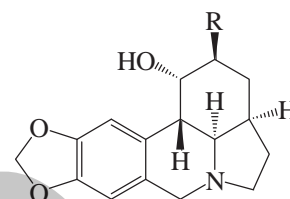
117



118 Galanthane

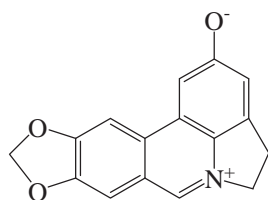


119 3,4-Dihydroanhydrolycorine

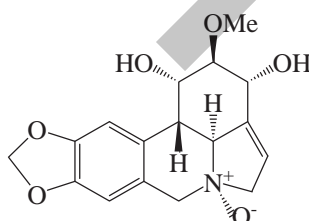


120 Dihydrocaranine $R=H$

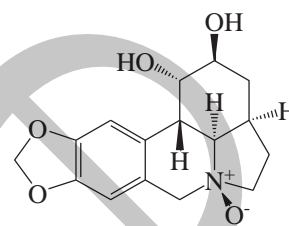
121 Dihydrolycorine $R=OH$



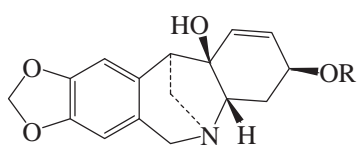
122 Ungeremine



123 Ungiminorine N-oxide

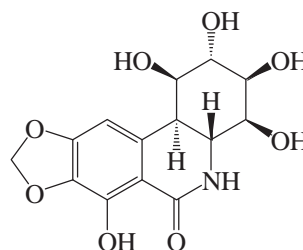


124 Pancratinine D

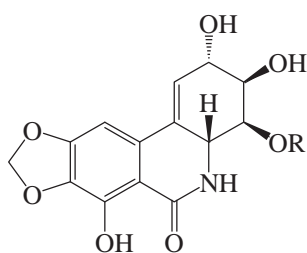


125 Pancratinine B $R=Me$

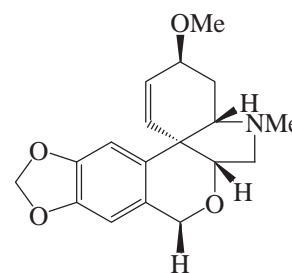
126 Pancratinine C $R=H$



127 Pancratistatin



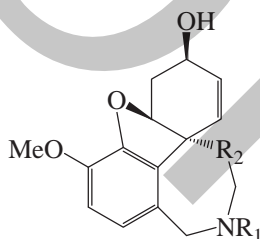
128 R=β-D-glc 4-O-β-D-glycosylnarciclasine



129 6-Deoxytazettine

3. Galanthamine Type

The galanthamine-type alkaloids are characterized by the presence of two *ortho* aromatic hydrogen. The galanthamine-type alkaloids are less common in this genus in comparison with other genera such as *Galanthus* or *Narcissus*. Seven different alkaloids (**2**, **130-135**) have been found in *Pancratium maritimum*, *Pancratium biflorum* and *Pancratium foetidum* (Abou-Donia *et al.*, 1991; Amarasekara and Gottlieb, 1993; Sarg *et al.*, 1996; Berkov *et al.*, 2004b; Cedrón *et al.*, 2010). The more abundant alkaloids are galanthamine (Sarg *et al.*, 1996) and lycoramine (Youssef and Frahm, 1998; Youssef, 1999).



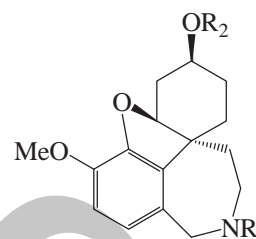
130 N-Norgalanthamine

R₁=R₂=H

131 N-Formylgalanthamine

R₁=CHO, R₂=H

132 Habranthine

R₁=Me, R₂=OH

133 Lycoramine

R₁=Me, R₂=H

134 N-Norlycoramine

R₁=R₂=H

135 3-O-Acetylycoramine

R₁=Me, R₂=Ac

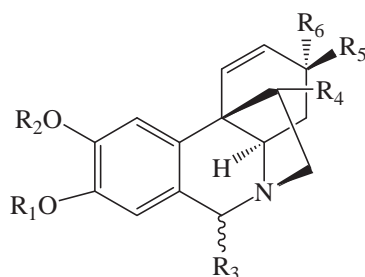
4. Crinine and Haemanthamine Type

The crinine- and haemanthamine-type alkaloids, together with the lycorine-type alkaloids, are the most abundant alkaloids in *Pancratium* genus. Six different alkaloids have been found in *Pancratium maritimum* (**8**, **1**, **136-139**) (Sener *et al.*, 1993c, 1994). The most common type of alkaloid is haemanthamine-type. Ten of these alkaloids have been isolated from *Pancratium maritimum* (**7**, **75**, **140**, **145**), *Pancratium sickenbergeri* (**142-144**) (Abou-Donia *et al.*, 2002b), *Pancratium foetidum* (**37**, **77**, **142-144**) (Sarg *et al.*, 1997), and *Pancratium tortuosum* (**141**) (Toaima, 2007).

Examples of the alkaloids isolated from some *Pancratium* species are shown in Table 5.

Other Secondary Metabolites

7,4'-Dihydroxy-8-methylflavan was isolated from *Pancratium littorale* stem (Ioset *et al.*, 2001). Two polyoxygenated chromones, 5,7-dihydroxy-2-methylchromone and 5,6-dihydroxy-7-methoxy-2-methylchromone and a glucosyloxychromone (7-glucosyloxy-5-hydroxy-2-methylchromone) were isolated from the bulbs of *Pancratium biflorum* (Ghosal *et al.*, 1982). Biflorin (**146**, a chromone C-glucoside) was identified from the roots of the same species (Ghosal *et al.*, 1983c). The bulbs of *Pancratium biflorum* contain the following free

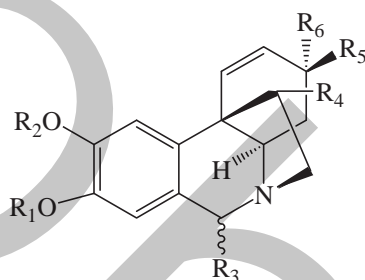


136 Crinan-3-one $R_1+R_2=CH_2, R_3=R_4=H, R_5+R_6=O$

137 Buphanisine $R_1+R_2=CH_2, R_3=R_4=R_5=H, R_6=OMe$

138 (-)-3 β -Methoxy-6,11-dihydroxycrine $R_1+R_2=CH_2, R_3=R_4=R_5=OH, R_6=H$

139 (-)-3 β ,11-Dihydroxycrine $R_1+R_2=CH_2, R_3=H, R_4=R_5=OH, R_6=H$



140 11-Hydroxyvittatine

$R_1+R_2=CH_2, R_3=H, R_4=OH, R_5=H, R_6=OH$

141 Maritidine

$R_1=R_2=Me, R_3=R_4=R_5=H, R_6=OH$

142 ent-6-Hydroxybuphanisine

$R_1+R_2=CH_2, R_3=OH, R_4=R_5=H, R_6=OMe$

143 8-Demethylmaritidine

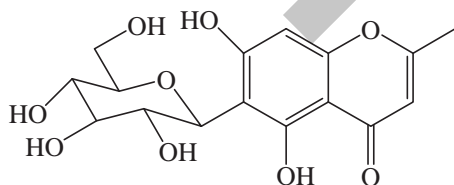
$R_1=H, R_2=Me, R_3=R_4=R_5=H, R_6=OH$

144 9-Demethylmaritidine

$R_1=Me, R_2=H, R_3=R_4=R_5=H, R_6=OH$

145 6-O-Methylhaemanthidine

$R_1+R_2=CH_2, R_3=\beta, OMe, R_4=OH, R_5=H, R_6=OMe$



146 Biflorin

and glucosyloxy acetophenones: 2,4,6-trimethoxyacetophenone, 4,6-dimethoxyacetophenone-2-*O*- β -D-glucoside and 2,6-dimethoxyacetophenone-4-*O*- β -D-glucoside (Ghosal *et al.*, 1989c).

α -Amyrin acetate and β -amyrin acetate were isolated from *Pancratium zeylanicum* (Amarasekara and Gottlieb, 1993).