CHAPTER II

HISTORICAL

1. Chemical Constituents of *Murraya* Linn.

Chemically, the Clauseneae are characterized by the occurrence of carbazole alkaloids. In addition to carbazoles *Murraya* species have been reported to contain furoquinoline and acridone alkaloids and are also a good source of coumarins (Kong *et al.*, 1986a).

List of the compounds found in various species of *Murraya* is shown in the following tables:-

Table 1 Chemical constituents of *Murraya alata* Drake

Chemical substance	Category	Plant part	Reference
Yuehchunene	Indole alkaloid	Roots	(Kong *et al.*, 1986b)

Table 2 Chemical constituents of *Murraya crenulata* (Turcz.) Oliver

Chemical substance	Category	Plant part	Reference
Girinimbine(37)	Carbazole alkaloid	Roots	(Kong *et al.*, 1986b)
Murrayafoline-A(5)	Carbazole alkaloid	Roots	(Kong *et al.*, 1986b)

Table 3 Chemical constituents of *Murraya elongata* Alph. DC.

Chemical substance	Category	Plant part	Reference
Murralongin(190)	Coumarin	Leaves	(Talapatra, Dutta, and Talapatra, 1973a)
Murrangatin(196)	Coumarin	Leaves	(Talapatra, Dutta, and Talapatra, 1973b)

Table 4 Chemical constituents of *Murraya euchrestifolia* Hayata

Chemical substance	Category	Plant part	Reference
Bismurrayafoline-A(66)	Carbazole alkaloid	+	(Furukawa, Wu, and Ohta, 1983)
Bismurrayafoline-B(67)	Carbazole alkaloid	+	(Furukawa, Wu, and Ohta, 1983)
Bismurrayafolinol(65)	Carbazole alkaloid	Stem bark	(Ito, Wu, and Furukawa, 1987)
Dihydroxygirinimbine(47)	Carbazole alkaloid	Root bark	(Furukawa, Wu, and Kuoh, 1985a)
3-Formylcarbazole(2)	Carbazole alkaloid	Root bark	(Ito, Wu, and Furukawa, 1988)
Girinimbine(37)	Carbazole alkaloid	Roots	(Kong *et al.*, 1986b)
Isomurrayafoline(36)	Carbazole alkaloid	Stem bark	(Ito, Wu, and Furukawa, 1987)

Table 4 (Continue)

Chemical substance	Category	Plant part	Reference
N-Methoxy-3-formylcarbazole(25)	Carbazole alkaloid	Root bark	(Ito, Wu, and Furukawa, 1988)
Murrafoline-A(68)	Carbazole alkaloid	Root bark	(Wu, Ohta, and Furukawa, 1983)
Murrafoline-B(69)	Carbazole alkaloid	+	(Furukawa, Wu, and Kuoh, 1985b)
Murrafoline-C(70)	Carbazole alkaloid	+	(Furukawa, Wu, and Kuoh, 1985b)
Murrafoline-D(71)	Carbazole alkaloid	+	(Furukawa, Wu, and Kuoh, 1985b)
Murrafoline-E(72)	Carbazole alkaloid	Root bark	(Ito, Wu, and Furukawa, 1988)
Murrafoline-F(73)	Carbazole alkaloid	Root bark	(Ito, Wu, and Furukawa, 1988)
Murrayafoline-A(5)	Carbazole alkaloid	Root bark	(Wu, Ohta, and Furukawa, 1983)
Murrayafoline-B(35)	Carbazole alkaloid	Root bark	(Furukawa, Wu, and Ohta, 1983)
Murrayaline(23)	Carbazole alkaloid	Stem bark	(Furukawa *et al.*, 1986)
Murrayaquinone-A	Carbazolequinone	Root bark	(Wu, Ohta, and Furukawa, 1983)
Murrayaquinone-B	Carbazolequinone	Root bark	(Wu, Ohta, and Furukawa, 1983)
Murrayaquinone-C	Carbazolequinone	Root bark	(Wu, Ohta, and Furukawa, 1983)
Murryastine(22)	Carbazole alkaloid	Stem bark	(Furukawa *et al.*, 1986)
Oxydimurrayafoline(74)	Carbazole alkaloid	Stem bark	(Ito, Wu, and Furukawa, 1987)
Pyrayafoline(49)	Carbazole alkaloid	Stem bark	(Furukawa *et al.*, 1986)
Pyrayaquinone-A	Carbazolequinone	Root bark	(Furukawa *et al.*, 1985)
Pyrayaquinone-B	Carbazolequinone	Root bark	(Furukawa *et al.*, 1985)
Pyrayaquinone-C	Carbazolequinone	Root bark	(Ito, Wu, and Furukawa, 1988)

Table 5 Chemical constituents of *Murraya exotica*

Chemical substance	Category	Plant part	Reference
Semi-α-carotenone	Carotenoid	Fruits	(Yokoyama and Guerrero, 1970)
3-(1,1-Dimethylallyl) xanthyletin(234)	Coumarin	Stem bark	(Ahmad and Begum, 1986)
Exoticin	Flavonoid	Leaves	(Joshi and Kamat, 1969)
Exozoline(57)	Carbazole alkaloid	Leaves	(Ganguly and Sarkar, 1978)
3,5,6,8,3',4',5'-Heptamethoxyflavone	Flavonoid	Fruits	(Chowdhury and Chakraborty, 1971b)
Peroxymurraol(182)	Coumarin	Leaves	(Ito and Furukawa, 1989)
Yuehchunene	Indole alkaloid	Roots	(Kong *et al.*, 1985)

Table 6 Chemical constituents of *Murraya exotica* L.

Chemical substance	Category	Plant part	Reference
Aurantiamide acetate	Unclassified	Stem bark	(Kong *et al.*, 1987)
Auraptenol(178)	Coumarin	Leaves Leaves	(Barik *et al.*, 1983) (Bishay *et al.*, 1988)
Casegravol(186)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Chloticol(184)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Dehydroosthol(173)	Coumarin	Leaves Leaves	(Ito and Furukawa, 1987a) (Ito and Furukawa, 1987b)
3-Epi-cyclolaudenol	Cycloartenol	Leaves	(Bishay *et al.*, 1988)
Exoticin	Flavonoid	Leaves	(Bishay *et al.*, 1987)
3-Formylindole	Indole alkaloid	Stem bark	(Chowdhury and Chakraborty, 1971a)
Girinimbine(37)	Carbazole alkaloid	Stem bark	(Roy and Bhattacharyya, 1981)
Hainanmurpanin(2[illegible])	Coumarin	Leaves	(Ito and Furukawa, 1987a)
3,5,6,7,3',4',5'-Heptamethoxyflavone	Flavonoid	Leaves Leaves	(Barik *et al.*, 1983) (Bishay *et al.*, 1987)

Table 6 (Continue)

Chemical substance	Category	Plant part	Reference
3,5,6,8,3',4',5'-Heptamethoxyflavone	Flavonoid	Leaves	(Barik *et al.*, 1983)
3,5,7,8,3',4',5'-Heptamethoxyflavone	Flavonoid	Leaves	(Joshi and Kamat, 1970) (Bishay *et al.*, 1987)
3,5,7,3',4',5'-Hexamethoxyflavone	Flavonoid	Leaves	(Bishay *et al.*, 1987)
5,6,7,3',4',5'-Hexamethoxyflavone	Flavonoid	Leaves	(Bishay *et al.*, 1987)
Isomeranzin(175)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Isomurralonginol acetate (191)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Isomurranganon senecioate (193)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Koenimbine(40)	Carbazole alkaloid	Stem bark	(Roy and Bhattacharya, 1981)
Lupeol	Cycloartenol	Leaves	(Bishay *et al.*, 1988)
Mahanimbine(51)	Carbazole alkaloid	Tissues	(Bhattacharyya *et al.*, 1978)
Meranzin(180)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Meranzin hydrate(183)	Coumarin	Leaves	(Manandhar, 1980) (Barik *et al.*, 1983)
7-Methoxy-8-(2'-methoxy-3'-hydroxy-3'-methylbutyl) coumarin(185)	Coumarin	Leaves	(Manandhar, 1980)
Mexoticin(218)	Coumarin	Stem bark	(Chakraborty and Chowdhury, 1967)
Minumicrolin(196)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Murracarpin(199)	Coumarin	Leaves	(Manandhar, 1980)
Murralongin(190)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Murranganon(195)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Murrangatin(196)	Coumarin	Leaves Leaves	(Barik *et al.*, 1983) (Ito and Furukawa, 1987a)
Murrangatin acetate(197)	Coumarin	Leaves	(Ito and Furukawa, 1987a)

Table 6 (Continue)

Chemical substance	Category	Plant part	Reference
Murraol(181)	Coumarin	Leaves Leaves	(Ito and Furukawa, 1987a) (Ito and Furukawa, 1987b)
Murraxocin(201)	Coumarin	Leaves	(Barik and Bundu, 1987)
Murraxonin	Cinnamic acid derivative	Leaves	(Barik and Bundu, 1987)
Murrayatin(189)	Coumarin	Leaves Leaves	(Barik, Dey, and Chatterjee,, 1983) (Ito and Furukawa, 1987a)
Murrayazoline(63)	Carbazole alkaloid	Tissues	(Bhattacharyya *et al.*, 1978)
Murrayone(176)	Coumarin	Leaves	(Lakshmi, Ratnam, and Subba Rao, 1972)
Osthenon(177)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Osthol(172)	Coumarin	Leaves Leaves	(Ito and Furukawa, 1987a) (Bishay *et al.*, 1988)
5,6,7,3',4'-Pentamethoxyflavone	Flavonoid	Leaves	(Bishay *et al.*, 1987)
Peroxyauraptenol(179)	Coumarin	Leaves Leaves	(Ito and Furukawa, 1987a) (Ito and Furukawa, 1987b)
Phebalosin(194)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Sibiricol(207)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Sitosterol-β-D-galactoside	Stearoid	Stem bark	(Ahmad, Tripathi, and Begum, 1987)
Umbelliferone(119)	Coumarin	Leaves	(Ito and Furukawa, 1987a)
Yuehchunene	Indole alkaloid	Roots	(Kong *et al.*, 1986b)

Table 7 Chemical constituents of *Murraya gleinei*

Chemical substance	Category	Plant part	Reference
Bulnesol	Sesquiterpene	Roots	(Kumar *et al.*, 1987)
Coumarrayin(213)	Coumarin	Root bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)
Exoticin	Flavonoid	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
Gleinadiene(212)	Coumarin	Roots	(Kumar *et al.*, 1987)
Gleinene(211)	Coumarin	Roots	(Kumar *et al.*, 1987)
Guaiol	Sesquiterpene	Roots	(Kumar *et al.*, 1987)
α-Gurjunene	Sesquiterpene	Roots	(Kumar *et al.*, 1987)
Herniarin(155)	Coumarin	Stem bark	(Kumar, 1985)
Meranzin(180)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
Meranzin hydrate(183)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
Mexoticin(218)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
		Root bark	(Kumar, 1985)
		Stem bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)
Murpanidin(196)	Coumarin	Root bark	(Kumar, 1985)
Murragleinin(221)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
Murralongin(190)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
		Root bark	(Kumar, 1985)
		Stem bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)

Table 7 (Continue)

Chemical substance	Category	Plant part	Reference
Murrangatin(196)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
		Root bark	(Kumar, 1985)
		Stem bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)
Omphamurin(214)	Coumarin	Root bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)
Osthol(172)	Coumarin	Root bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)
Phebalosin(194)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
		Root bark	(Kumar, 1985)
		Stem bark	(Kumar, 1985)
		Roots	(Kumar *et al.*, 1987)
Scopoletin(160)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
Sibiricin(216)	Coumarin	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Leaves	(Kumar, 1985)
		Root bark	(Kumar, 1985)
		Stem bark	(Kumar, 1985)
		Roots	(Kumar *et al.*,1987)
Skimmianine	Quinoline alkaloid	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
Stigmasterol	Sterol	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
		Roots	(Kumar *et al.*, 1987)
Toddalenone(217)	Coumarin	Roots	(Kumar *et al.*, 1987)

Table 8 Chemical constituents of *Murraya koenigii*

Chemical substance	Category	Plant part	Reference
Currayangine(63)	Carbazole alkaloid	+	(Dutta, Quasim, and Wadia, 1969a)
Curryangin(60)	Carbazole alkaloid	+	(Dutta, Quasim, and Wadia, 1969b)
Cyclomahanimbine(58)	Carbazole alkaloid	Stem bark	(Narasimhan and Kelkar, 1976)
Girinimbine(37)	Carbazole alkaloid	Stem bark Stem bark	(Das, Chakraborty, and Bose, 1965) (Dutta and Quasim, 1969)
Glycozoline(16)	Carbazole alkaloid	+	(Adesina *et al.*, 1988)
Isomurrayazoline(64)	Carbazole alkaloid	Stem bark	(Bhattacharya, Roy, and Chakraborty, 1982)
Koenidine(44)	Carbazole alkaloid	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
Koenigine(43)	Carbazole alkaloid	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
Koenimbin(40)	Carbazole alkaloid	Fruits	(Narasimhan, Paradkar, and Chitguppi, 1968)
Koenine(39)	Carbazole alkaloid	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
Koenoline(7)	Carbazole alkaloid	Root bark	(Fiebig *et al.*, 1985)
Mahanimbin(51)	Carbazole alkaloid	Stem bark	(Narasimhan, Paradkar, and Chitguppi, 1968)
Mahanimbine(51)	Carbazole alkaloid	Stem bark Stem bark	(Das, Chakraborty, and Bose, 1965) (Dutta and Quasim, 1969)
Mahanimbinol(50)	Carbazole alkaloid	Stem wood	(Rama Rao, Bhide, and Mujumdar, 1980)
Mahanine(53)	Carbazole alkaloid	Leaves Leaves	(Narasimhan, Paradkar, and Kelkar, 1970) (Atta, Zaidi, and Firdous, 1988)
2-Methoxy-3-methylcarbazole(14)	Carbazole alkaloid	Seeds	(Bhattacharyya and Chowdhury, 1985b)
3-Methylcarbazole(3)	Carbazole alkaloid	+	(Adesina *et al.*, 1988)
Mukoeic acid(8)	Carbazole alkaloid	Stem bark	(Chowdhury and Chakraborty, 1969)
Mukonal(12)	Carbazole alkaloid	Stems	(Bhattacharyya and Chakraborty, 1984b)
Mukonidine(13)	Carbazole alkaloid	+	(Chakraborty, Roy, and Guha, 1978)
Murrayanine(6)	Carbazole alkaloid	Stem bark	(Das, Chakraborty, and Bose, 1965)

Table 9 Chemical constituents of *Murraya koenigii* (L.) Spreng.

Chemical substance	Category	Plant part	Reference
Murrayanine(6)	Carbazole alkaloid	Leaves	(Gupta and Nigam, 1971)

Table 10 Chemical constituents of *Murraya koenigii* Spreng.

Chemical substance	Category	Plant part	Reference
Bicyclomahanimbicine(62)	Carbazole alkaloid	Leaves	(Kureel, Kapil, and Popli, 1970b)
Bicyclomahanimbine(61)	Carbazole alkaloid	Leaves	(Kureel, Kapil, and Popli, 1969b)
Cyclomahanimbine(58)	Carbazole alkaloid	Leaves	(Kureel, Kapil, and Popli, 1969b)
3-(1,1-Dimethylallyl) xanthyletin(234)	Coumarin	Stem bark	(Bhattacharyya and Chakraborty, 1984a)
Girinimbine(37)	Carbazole alkaloid	Leaves and roots Roots	(Joshi, Kamat, and Gawad, 1970) (Kong *et al.*, 1985b)
2-Hydroxy-3-methylcarbazole(11)	Carbazole alkaloid	Roots	(Bhattacharyya, Jash, and Chowdhury, 1986)
Isomahanimbine(54)	Carbazole alkaloid	Leaves and roots +	(Joshi, Kamat, and Gawad, 1970) (Narasimhan *et al.*, 1975)
Koenidine(44)	Carbazole alkaloid	+	(Narasimhan *et al.*, 1975)
Koenigine(43)	Carbazole alkaloid	+	(Narasimhan *et al.*, 1975)
Koenimbidine(44)	Carbazole alkaloid	Leaves and roots	(Joshi, Kamat, and Gawad, 1970)
Koenimbin(40)	Carbazole alkaloid	Leaves +	(Kureel, Kapil, and Popli, 1969a) (Narasimhan *et al.*, 1975)
Koenine(39)	Carbazole alkaloid	+	(Narasimhan *et al.*, 1975)
Mahanimbicine(54)	Carbazole alkaloid	Leaves	(Kureel, Kapil, and Popli, 1970b)
Mahanimbidine(63)	Carbazole alkaloid	Leaves	(Kureel, Kapil, and Popli, 1969b)
Mahanimbine(51)	Carbazole alkaloid	Leaves Leaves and roots Stem bark +	(Kureel, Kapil, and Popli, 1969b) (Joshi, Kamat, and Gawad, 1970) (Roy and Chakraborty, 1974) (Narasimhan *et al.*, 1975)
Mahanimbinine(56)	Carbazole alkaloid	Leaves	(Kureel, Kapil, and Popli, 1970a)

Table 10 (Continue)

Chemical substance	Category	Plant part	Reference
Mahanine(53)	Carbazole alkaloid	+	(Narasimhan *et al.*, 1975)
Mukoeic acid(8)	Carbazole alkaloid	Barks	(Chowdhury and Chakraborty, 1971a)
Mukolidine(9)	Carbazole alkaloid	+	(Roy, Bhattacharyya, and Chakraborty, 1982)
Mukoline(10)	Carbazole alkaloid	+	(Roy, Bhattacharyya, and Chakraborty, 1982)
Mukonicine(45)	Carbazole alkaloid	Leaves	(Mukherjee *et al.*, 1983)
Murrayacine(38)	Carbazole alkaloid	Leaves and roots	(Joshi, Kamat, and Gawad, 1970)
Murrayacinine(52)	Carbazole alkaloid	Barks	(Chakraborty *et al.*, 1974)
Murrayanine(6)	Carbazole alkaloid	Stem bark	(Chakraborty, Barman, and Bose, 1965)
Murrayazolidine(58)	Carbazole alkaloid	Stem bark	(Chakraborty *et al.*, 1970)
Murrayazolinine(59)	Carbazole alkaloid	Stem bark	(Chakraborty *et al.*, 1973)
Scopolin(167)	Coumarin	Leaves	(Gupta and Nigam, 1971)

Table 11 Chemical constituents of *Murraya kwangsiensis*

Chemical substance	Category	Plant part	Reference
Geranial	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Geraniol	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Geranyl acetate	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Limonene	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Linalool	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Neral	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Nerol	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
Neryl acetate	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)
γ-terpinene	Monoterpene	Leaves	(Li, Zhang, and Zhu, 1988)

Table 12 Chemical constituents of *Murraya microphylla* (Merr. and Chun)

Chemical substance	Category	Plant part	Reference
Girinimbine(37)	Carbazole alkaloid	Roots	(Kong *et al.*, 1986b)

Table 13 Chemical constituents of *Murraya omphalocarpa*

Chemical substance	Category	Plant part	Reference
Coumurrayin(213)	Coumarin	Fruits	(Wu *et al.*, 1980)
5,7-Dimethoxy-8-(3'-methyl-2'-oxobutyl) coumarin(215)	Coumarin	Fruits	(Wu *et al.*, 1980)
3,5,6,7,3',4',5'-Heptamethoxyflavone	Flavonoid	Fruits	(Wu *et al.*, 1980)
Mexoticin(218)	Coumarin	Fruits	(Wu *et al.*, 1980)
Murrayanol	Flavonoid	Fruits	(Wu *et al.*, 1980)
Omphamurin(214)	Coumarin	Leaves	(Wu, 1981)
Sitosterol	Sterol	Fruits	(Wu *et al.*, 1980)

Table 14 Chemical constituents of *Murraya paniculata*

Chemical substance	Category	Plant part	Reference
Coumurrin(188)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
Glucose	Sugar	Flowers Fruits Leaves	(Wu *et al.*, 1975) (Wu *et al.*, 1975) (Khosa, 1975)
Imperatorin(226)	Coumarin	Leaves	(Ganguly, Ghosh, and Basak, 1977)
Isomurralonginol nicotinate(192)	Coumarin	Leaves	(Ito and Furukawa, 1987c)
Murpaniculol(195)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
Osthenon(177)	Coumarin	Leaves	(Ito and Furukawa, 1987c)

Table 14 (Continue)

Chemical substance	Category	Plant part	Reference
Panial(198)	Coumarin	Leaves	(Ito and Furukawa, 1987c)
Panicula1(168)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
Paniculin(171)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
Paniculonol isovalerate(187)	Coumarin	Leaves	(Ito and Furukawa, 1989c)
Scopoletin(160)	Coumarin	Flowers Fruits	(Wu *et al.*, 1975) (Wu *et al.*, 1975)
Scopolin(167)	Coumarin	Flowers Fruits	(Wu *et al.*, 1975) (Wu *et al.*, 1975)

Table 15 Chemical constituents of *Murraya paniculata* Jack

Chemical substance	Category	Plant part	Reference
Hentriacontane	Unclassified	Leaves	(Khosa, 1975)
Phebalosin(194)	Coumarin	Leaves	(Khosa, 1975)

Table 16 Chemical constituents of *Murraya paniculata* (Linn.)

Chemical substance	Category	Plant part	Reference
Myricyl alcohol	Alcohol	Leaves	(Positong, 1980)
Phebalosis	Unclassified	Leaves	(Positong, 1980)

Table 17 Chemical constituents of *Murraya paniculata* (Linn.) Jack

Chemical substance	Category	Plant part	Reference
Auraptenol(178)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Bannamurpanisin	Flavonoid	Leaves	(Yang and Du, 1984a)

Table 17 (Continue)

Chemical substance	Category	Plant part	Reference
		Root bark Leaves	(Imai *et al.*, 1989) (Imai, Kinoshita, and Sankawa, 1989)
Coumarrayin(213)	Coumarin	Foliages Foliages	(Dreyer, 1968) (Steck, 1972)
Coumurrin(188)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
5,7-Dimethoxy-8-(3'-methyl-2'-oxobutyl) coumarin(215)	Coumarin	Leaves Root bark	(Yang and Su, 1983) (Imai *et al.*, 1989)
Eduline	Quinoline alkaloid	Root bark	(Imai *et al.*, 1989)
Exoticin	Flavonoid	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Hainanmurpanin(200)	Coumarin	Leaves and branches Leaves	(Yang and Du, 1984b) (Imai, Kinoshita, and Sankawa, 1989)
3,5,6,7,3',4',5'-Heptamethoxyflavone	Flavonoid	Foliages	(Dreyer, 1968)
3,5,7,8,3',4',5'-Heptamethoxyflavone	Flavonoid	Leaves	(Yang and Du, 1984a)
4'-Hydroxy-3,5,6,7,3,'5'-hexamethoxyflavone	Flavonoid	Leaves	(De Silva *et al.*, 1980)
Isomeranzin(175)	Coumarin	Leaves and branches Leaves	(Yang and Du, 1984b) (Imai, Kinoshita, and Sankawa, 1989)
Isomexoticin(218)	Coumarin	Leaves	(Yang and Su, 1983)
Meranzin hydrate(183)	Coumarin	Leaves Leaves Leaves	(Raj *et al.*, 1976) (Yang and Du, 1984a) (Imai, Kinoshita, and Sankawa, 1989)
7-Methoxy-8-(2'-formyl-2'-methylpropyl)coumarin (170)	Coumarin	Leaves and branches Leaves	(Yang and Du, 1984b) (Imai, Kinoshita, and Sankawa, 1989)
de-N-Methylacronycine	Acridone alkaloid	Roots	(Fauvel *et al.*, 1978)
de-N-Methylnoracronycine	Acridone alkaloid	Roots	(Fauvel *et al.*, 1978)
Methyl N-methylanthranylate	Alkaloid	Root bark	(Imai *et al.*, 1989)
Mexoticin(218)	Coumarin	Root bark	(Imai *et al.*, 1989)

Table 17 (Continue)

Chemical substance	Category	Plant part	Reference
Microminutin(203)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murpanicin(201)	Coumarin	Leaves Leaves and branches	(Yang and Su, 1983) (Yang and Du, 1984b)
Murpaniculol(195)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murpanidin(196)	Coumarin	Leaves Leaves	(Yang and Su, 1983) (Yang and Du, 1984a)
Murralongin(190)	Coumarin	Leaves Leaves Leaves Root bark Root bark	(Raj *et al.*, 1976) (Yang and Su, 1983) (Imai, Kinoshitaa, and Sankawa, 1989) (Imai *et al.*, 1989) (Kinoshita *et al.*, 1989)
Murrangatin(196)	Coumarin	Leaves Leaves Root bark	(Raj *et al.*, 1976) (Imai, Kinoshita, and Sankawa, 1989) (Imai *et al.*, 1989)
Murrangatin acetate(197)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murrayatin(189)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Noracronycin	Acridone alkaloid	Roots	(Fauvel *et al.*, 1978)
Osthol(172)	Coumarin	Foliages Root bark	(Steck, 1972) (Kinoshita *et al.*, 1989)
Paniculatin(202)	Coumarin	Foliages	(Steck, 1972)
Paniculidine-A	Indole alkaloid	Root bark Root bark	(Kinoshita, Tatara, and Sankawa, 1985) (Kinoshita *et al.*, 1989)
Paniculidine-B	Indole alkaloid	Root bark Root bark	(Kinoshita, Tatara, and Sankawa, 1985) (Kinoshita *et al.*, 1989)
Paniculin(171)	Coumarin	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
5,7,3',4',5'-Pentamethoxyflavone	Flavonoid	Leaves and branches Root bark	(Yang and Du, 1984b) (Imai *et al.*, 1989)
Scopoletin(160)	Coumarin	Root bark	(Imai *et al.*, 1989)
Sibiricin(216)	Coumarin	Root bark	(Imai *et al.*, 1989)
Skimmianine	Quinoline alkaloid	Roots	(Fauvel *et al.*, 1978)
Yuehchunene	Indole alkaloid	Roots	(Kong *et al.*, 1986b)

Table 18 Chemical constituents of *Murraya paniculata* var. *omphalocarpa*

Chemical substance	Category	Plant part	Reference
5,7-Dimethoxy-8-(3'-methyl-2'-oxobutyl) coumarin(215)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Mupanidin(196)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Murracarpin(199)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Murraculatin(210)	Coumarin	Leaves	(Wu, 1988)
Murrayacarpin-A(169)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Murrayacarpin-B(208)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Murrayanone(220)	Coumarin	Leaves	(Wu, 1988)
Omphalocarpin(219)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Paniculatin(202)	Coumarin	Leaves	(Wu, 1988)
Scopoletin(160)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Scopolin(167)	Coumarin	Flowers	(Wu, Liou, and Kuoh, 1989)
Seselinal(209)	Coumarin	Leaves	(Wu, 1988)
Yuehchunene	Indole alkaloid	Roots	(Kong *et al.*, 1986b)

Table 19 Chemical constituents of *Murraya siamensis* Craib

Chemical substance	Category	Plant part	Reference
Girinimbine(37)	Carbazole alkaloid	Roots	(Kong *et al.*, 1986b)
Murrayanine(6)	Carbazole alkaloid	Roots	(Fiebig *et al.*, 1985)

+ = Unclassified part

2. Carbazole Alkaloids

2.1 Introduction

A wide variety of structurally different alkaloids are known to be present in the Rutaceae family e.g. alkaloids belonging to the quinoline, furoquinoline, pyrrolidine, quinazoline, protoberberine, imidazole, oxazole and aporphine types have been obtained. A number of alkaoids which are carbazole derivatives have been isolated in recent years. Carbazole (1) was first isolated in 1872 from coal tar by Graebe and Glazer. Its occurrence in plants was not reported until 1964-65 when the structure of murrayanine (6) the first member of carbazole alkaloids was reported (Chakraborty, 1980). From plant sources almost all of carbazole alkaloids have been reported in the family Rutaceae, subfamily Aurantioideae in tribe Clauseneae. There is found only one carbazole alkaloids `ekeberginine' (32) from stem bark of *Ekebergia senegalensis* family Meliaceae (Lontsi *et al.*, 1985). Over the past ten years a number of carbazole alkaloids, such as carbazomycin-B (24) (Kaneda *et al.*, 1981), has been found in marine sources and microorganisms.

2.2 Classification

Whereas most groups of indole alkaloids have been known for many years, the carbazole alkaloids are a relatively recent addition in this area and included in tryptophan-derived alkaloids, there is at present no evidence to support this classification. However carbazole alkaloids have been described into three basic types. All are based on the parent carbazole nucleus(1), but they differ in the number of carbon atoms attached to nucleus. The groups are better analyzed however in terms of the number of isoprene units linked to an indole nucleus. The first group, represented by murrayanine(6), has an indole unit plus one isoprene unit, the second group e.g. heptaphylline(26) has an indole unit plus two isoprene units, and the third group e.g. mahanimbine(51) has an indole unit plus three isoprene units (Cordell, 1981).

Similar to Cordell, Chakraborty (1980) classified carbazole alkaloids into three main groups as below:-

Members with C-13 carbon skeleton.

Members with C-18 carbon skeleton.

Members with C-23 carbon skeleton.

From dictionary of alkaloids (Southon and Buckingham, 1989) they have been classified carbazoles as alkaloids derived from tryptophan and sub-divided into:-

2.2.1 Simple carbazoles, there is simple groups substitute on carbazole nucleus(1).

2.2.2 Carbazoles with an additional dimethylallyl substituent.

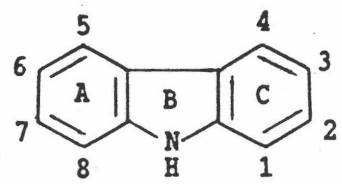
2.2.3 Pyranocarbazoles, in which a prenyl residue has cyclized on to a phenolic hydroxy groups.

2.2.4 Other alkaloids , in which a complete monoterpene unit has been introduced into the carbazole nucleus(1).

2.2.5 A number of bis-carbazole alkaloids.

The carbazole alkaloids that have been reported from natural sources are listed below:-

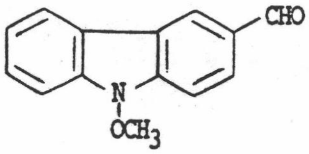
2.2.1 Simple carbazoles



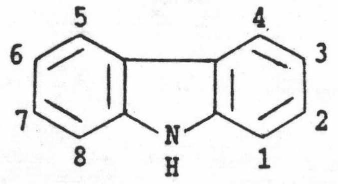
Carbazole nucleus(1)

Compound	Substituent	Reference
Carbazole(1)	-	(Chowdhury *et al.*, 1987)
3-Formylcarbazole(2)	3-CHO	(Ito, Wu, and Furukawa, 1988)
3-Methylcarbazole(3)	3-CH_3	(Roy, Bhattacharyya, and Chakraborty, 1974) (Joshi and Gawad, 1974) (Chowdhury *et al.*, 1987) (Adesina *et al.*, 1988) (Ngadjui *et al.*, 1989a)
3-Formyl-1-hydroxycarbazole(4)	1-OH 3-CHO	(Ngadjui *et al.*, 1989c)
Murrayafoline-A(5)	1-OCH_3 3-CH_3	(Wu, Ohta, and Furukawa, 1983) (Kong *et al.*, 1986b)
Murrayanine(6)	1-OCH_3 3-CHO	(Chakraborty, Barman, and Bose, 1965) (Bhattacharyya and Chakraborty, 1973)
Koenoline(7)	1-OCH_3 3-CH_2OH	(Fiebig *et al.*, 1985)
Mukoeic acid(8)	1-OCH_3 3-COOH	(Chowdhury and Chakraborty, 1969)
Mukolidine(9)	1-OCH_3 6-CHO	(Roy, Bhattacharyya, and Chakraborty, 1982)

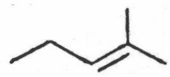
Mukoline(10)	1-OCH_3 6-CH_2OH	(Roy, Bhattacharyya, and Chakraborty, 1982)
2-Hydroxy-3-methylcarbazole(11)	2-OH 3-CH_3	(Bhattacharyya, Jash, and Chowdhury, 1986)
Mukonal(12)	2-OH 3-CHO	(Bhattacharyya and Chakraborty, 1984b)
Mukonidine(13)	2-OH 3-$COOCH_3$	(Chakraborty, Roy, and Guha, 1978)
2-Methoxy-3-methylcarbazole(14)	2-OCH_3 3-CH_3	(Bhattacharyya and Chowdhury, 1985b)
Glycozolinol(15)	3-CH_3 6-OH	(Bhattacharyya *et al.*, 1984)
Glycozoline(16)	3-CH_3 6-OCH_3	(Chakraborty, 1966) (Rastogi, Kapil, and Popli, 1980) (Adesina *et al.*, 1988)
Lansine(17)	2-OH 3-CHO 6-OCH_3	(Prakash *et al.*, 1980)
2-Hydroxy-3-formyl-7-methoxycarbazole(18)	2-OH 3-CHO 7-OCH_3	(Chaichantipyuth *et al.*, 1988)
Glycozolidol(19)	2-OCH_3 3-CH_3 6-OH	(Bhattacharyya, Chakrabartty, and Chowdhury, 1985)
Glycozolidine(20)	2-OCH_3 3-CH_3 6-OCH_3	(Chakraborty and Das, 1966) (Anwer, Kapil, and Popli, 1972) (Rastogi, Kapil, and Popli, 1980)
Glycozolidal(21)	2-OCH_3 3-CHO 6-OCH_3	(Bhattacharyya and Chowdhury, 1985a)

Murrayastine(22)	1-OCH_3 3-CH_3 7-OCH_3 8-OCH_3	(Furukawa *et al.*, 1986)
Murrayaline(23)	2-OCH_3 3-CH_3 7-OCH_3 8-CHO	(Furukawa *et al.*, 1986)
Carbazomycin-B(24)	1-CH_3 2-CH_3 3-OCH_3 4-OH	(Kaneda *et al.*, 1981)
N-Methoxy-3-formylcarbazole (25)		(Ito, Wu, and Furukawa, 1988)

2.2.2 Carbazoles with an additional dimethylallyl substituent



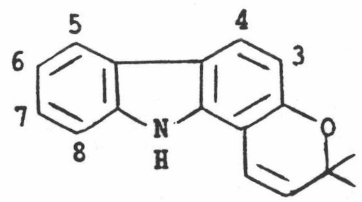
Carbazole nucleus(1)

R = 

Compound	Substituent	Reference
Heptaphylline(26)	1=R 2-OH 3-CHO	(Joshi *et al.*, 1967) (Anwer *et al.*, 1977) (Prakash *et al.*, 1980) (Wu and Furukawa, 1982) (Wangboonskul, Pummangura, and Chaichantipyuth, 1984) (Ngadjui *et al.*, 1989c)

6-Methoxyheptaphylline (27)	1=R 2-OH 3-CHO 6-OCH_3	(Joshi, Gawad, and Kamat, 1972)
7-Methoxyheptaphylline (28)	1=R 2-OH 3-CHO 7-OCH_3	(Chaichantipyuth *et al.*, 1988)
Heptazoline (29)	1=R 2-OH 3-CHO 8-OH	(Chakraborty, Das, and Islam, 1970)
Clausenapin (30)	1-OCH_3 2=R 3-CH_3	(Bhattacharyya, 1984)
Indizoline (31)	1-OCH_3 2=R 3-CHO	(Joshi and Gawad, 1974)
Ekeberginine (32)	1-OCH_3 3-CHO 4=R	(Lontsi *et al.*, 1985) (Ngadjui *et al.*, 1989c)
Clausanitin (33)	2-OH 3-CHO 7=R	(Okorie, 1975)
Atanisatin (34)	2-OCH_3 3-CHO 8=R	(Okorie, 1975)
Murrayafoline-B (35)	1-OH 3-CH_3 7-OCH_3 8=R	(Furukawa, Wu, and Ohta, 1983)
Isomurrayafoline (36)	2-OH 3-CH_3 7-OCH_3 8=R	(Ito, Wu, and Furukawa, 1987)

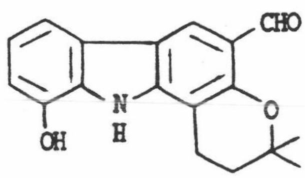
2.2.3 Pyranocarbazoles



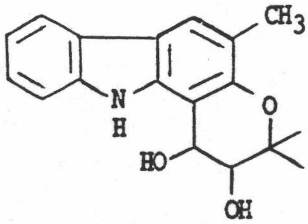
Compound	Substituent	Reference
Girinimbine(37)	3-CH_3	(Das, Chakraborty, and Bose, 1965) (Joshi, Kamat, and Gawad, 1970) (Kong *et al.*, 1986b) (Adesina *et al.*, 1988)
Murrayacine(38)	3-CHO	(Joshi, Kamat, and Gawad, 1970) (Ray and Chakraborty, 1976)
Koenine(39)	3-CH_3 6-OH	(Narasimhan, Paradkar, and Kelkar, 1970)
Koenimbin(40)	3-CH_3 6-OCH_3	(Narasimhan, Paradkar, and Chitguppi, 1968)
Koenimbine(40)		(Roy and Bhattacharyya, 1981)
Mupamine(41)	3-CH_3 8-OCH_3	(Mester and Reisch, 1977) (Kamaruzzman, Roy, and Chakraborty, 1989)
Heptazolidine(42)	3-OCH_3 6-CH_3	(Chakraborty *et al.*, 1985)
Koenigine(43)	3-CH_3 6-OCH_3 7-OH	(Narasimhan, Paradkar, and Kelkar, 1970) (Bowen and Perera, 1982)
Koenidine(44)	3-CH_3 6-OCH_3 7-OCH_3	(Narasimhan, Paradkar, and Kelkar, 1970)
Koenigicine(44)		(Kureel, Kapil, and Popli, 1969a)
Koenimbidine(44)		(Joshi, Kamat, and Gawad, 1970)

Mukonicine(45) — 3-CH_3, 6-OCH_3, 8-OCH_3 — (Mukherjee *et al.*, 1983)

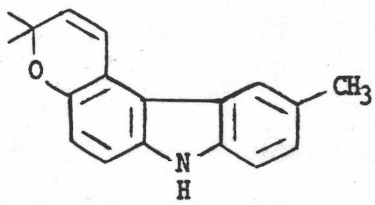
Heptazolicine(46) — (Bhattacharyya, Chakraborty, and Chowdhury, 1984)



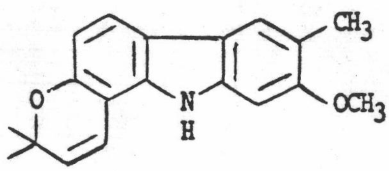
Dihydroxygirinimbine (47) — (Furukawa, Wu, and Kuoh, 1985a)



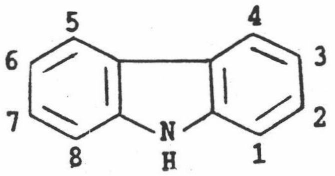
5,6-Pyranoglycozoline (48) — (Kong *et al.*, 1988)



Pyrayafoline(49) — (Furukawa *et al.*, 1986)



2.2.4 Other alkaloids, in which a complete monoterpene units



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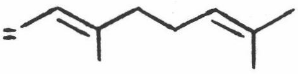
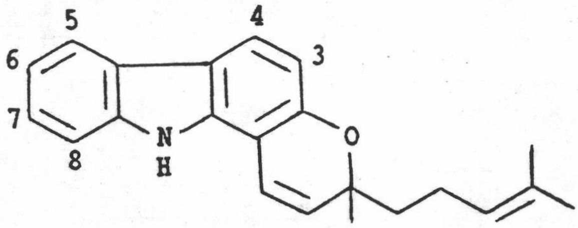
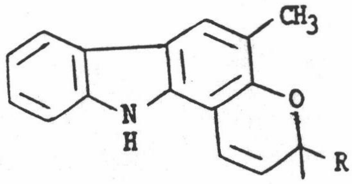


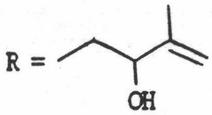
Carbazole nucleus (1)

Compound	Substituent	Reference
Mahanimbinol (50)	1-R 2-OH 3-CH_3	(Rama Rao, Bhide, and Mujumdar, 19[illegible])

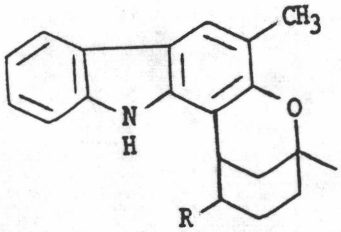


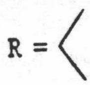
Compound	Substituent	Reference
Mahanimbine (51)	3-CH_3	(Das, Chakraborty, and Bose, 1965) (Bhattacharyya *et al.*, 1978)
Mahanimbin (51)		(Narasimhan, Paradkar, and Chitguppi, 1968)
Murrayacinine (52)	3-CHO	(Chakraborty *et al.*, 1974)
Mahanine (53)	3-CH_3 7-OH	(Narasimhan, Paradkar, and Kelkar, 1970)
Mahanimbicine (54)	6-CH_3	(Kureel, Kapil, and Popli, 1970b)
Isomahanimbine (54)		(Joshi, Kamat, and Gawad, 1970)

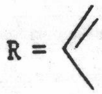


Mahanimboline (55)  (Gosh and Chakraborty, 1979)

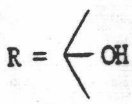
Mahanimbinine (56)  (Kureel, Kapil, and Popli, 1970a)



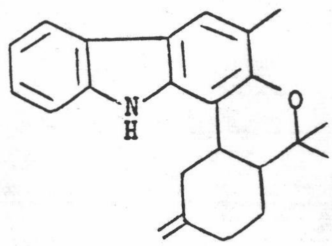
Exozoline (57)  (Ganguly and Sarkar, 1978)

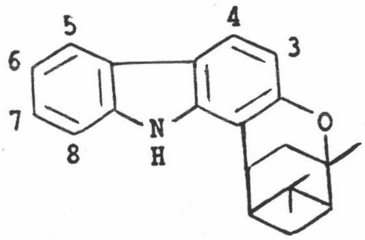
Cyclomahanimbine (58)  (Kureel, Kapil, and Popli, 1969b)

Murrayazolidine (58) (Chakraborty, Bhattacharya, and Mitra, 1974)

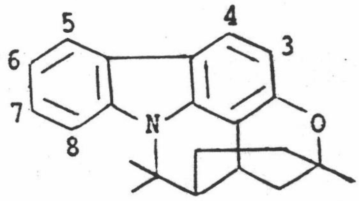
Murrayazolinine (59)  (Chakraborty *et al.*, 1973)

Curryangin (60) (Dutta, Quasim, and Wadia, 1969a)



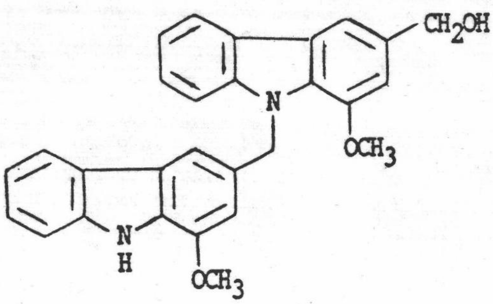


Bicyclomahanimbine(61)	3-CH_3	(Kureel, Kapil, and Popli, 1969b)
Bicyclomahanimbicine (62)	6-CH_3	(Kureel, Kapil, and Popli, 1970b)

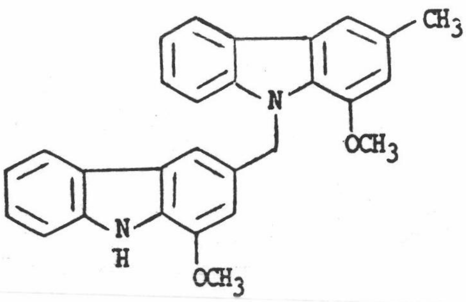


Currayangine(63)	3-CH_3	(Dutta, Quasim, and Wadia, 1969b)
Mahanimbidine(63)		(Kureel, Kapil, and Popli, 1969b)
Murrayazoline(63)		(Bhattacharyya *et al.*, 1978)
Isomurrayazoline(64)	6-CH_3	(Bhattacharya, Roy, and Chakraborty, 1982)

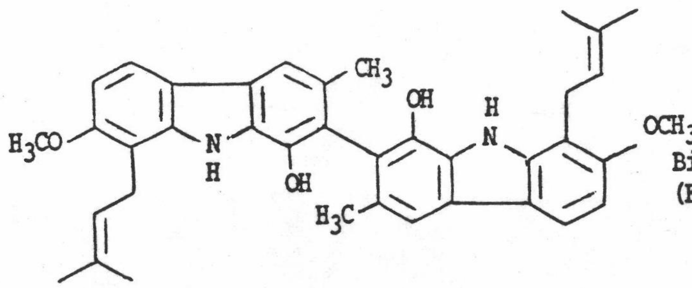
2.2.5 A number of bis-carbazole alkaloids



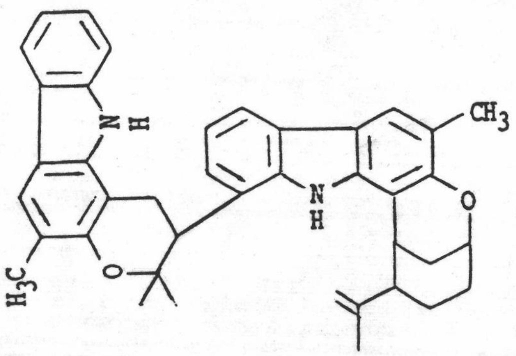
Bismurrayafolinol(65)
(Ito, Wu, and Furukawa, 1987)



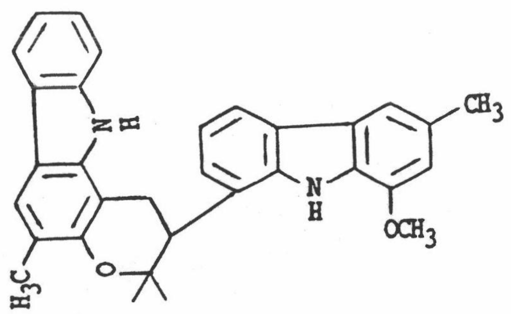
Bismurrayafoline-A(66)
(Furukawa, Wu, and Ohta, 1983)



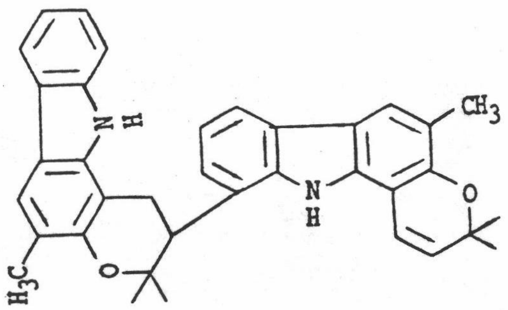
Bismurrayafoline-B(67)
(Furukawa, Wu, and Ohta, 1983)



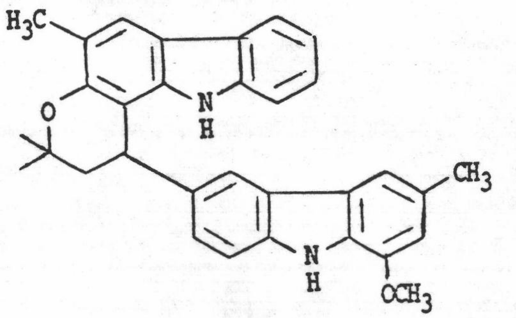
Murrafoline-A(68)
(Mc Phail *et al.*, 1983)



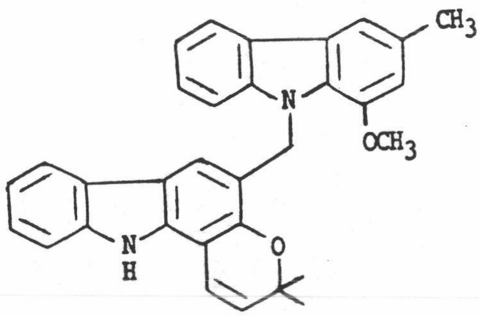
Murrafoline-B(69)
(Furukawa, Wu, and Kuoh, 1985b)



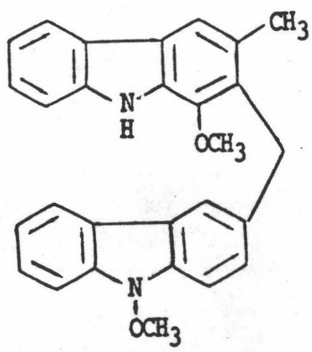
Murrafoline-C(70)
(Furukawa, Wu, and Kuoh, 1985b)



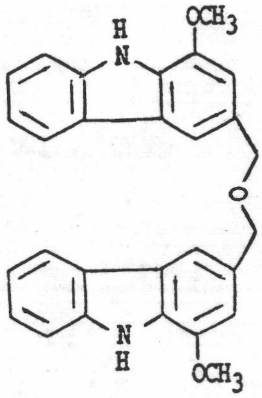
Murrafoline-D(71)
(Furukawa, Wu, and Kuoh, 1985b)



Murrafoline-E(72)
(Ito, Wu, and Furukawa, 1988)



Murrafoline-F(73)
(Ito, Wu, and Furukawa, 1988)



Oxydimurrayafoline(74)
(Ito, Wu, and Furukawa, 1987)

2.3 Biosynthesis

Little is known concerning the biosynthesis of the carbazole alkaloids, an important group that displays widely varied structural features. Several working hypothesis have been proposed for the origin of the carbazole nucleus(1), possible precursors include anthranilic acid, mevalonic acid, and tryptophan (Husson, 1985).

There have been postulated that the indole ring could arise from anthranilic acid *via* dimethylallyl quinolines and subsequent ring contraction. However consideration that tryptophan is the substrate to which the C_5-units initially attacks the 3-position of the heterocyclic system. Subsequently cyclization and loss of serine residue in presence of pyridoxal coenzyme give a dihydrocarbazole which on dehydrogenation yields a 3-methylcarbazole(3). Further steps in the biogenesis would include aromatization, incorporation of a hydroxyl group at 2-position, introduction of terpene chain at 1-position and cyclization to give the fused pyranocarbazole ring (figure 2) (Narasimhan *et al.*, 1975 ; Chakraborty, 1980).

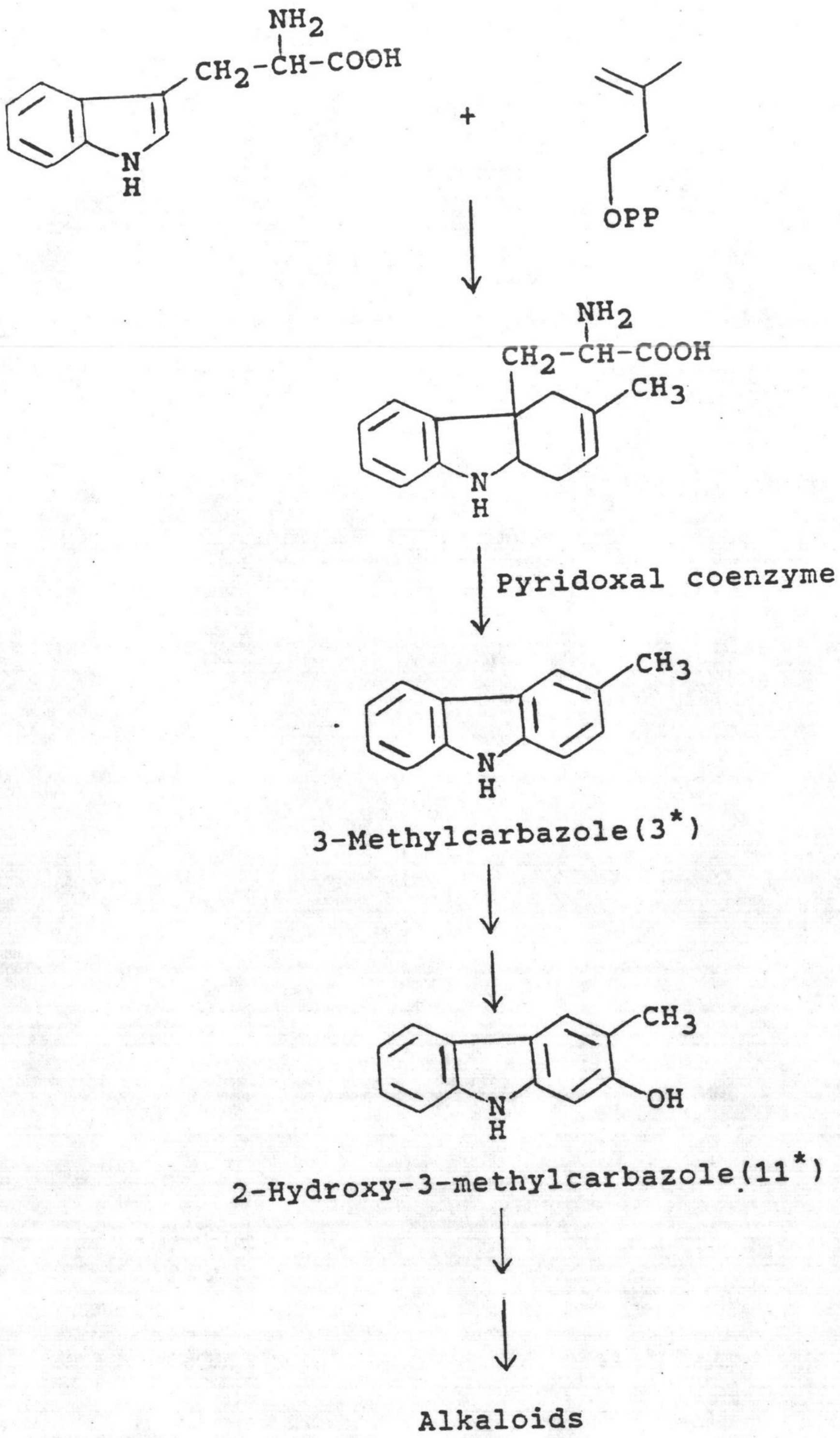


Figure 2 Biosynthesis of carbazole alkaloids

3-Methylcarbazole (3) isolated from *Clausena heptaphylla* (Roy, Bhattacharyya, and Chakraborty, 1974) has been postulated to be the key intermediate for the biogenesis of carbazole alkaloids and that this compound may then be the object of hydroxylation and prenylation reaction (figure 3) (Cordell, 1981). The addition of a mevalonate at the C-1 position interact to the phenol group at C-2 provides a route to C-18 carbazole alkaloids group (pyranocarbazoles). The incorporation of a monoterpene unit would give C-23 alkaloids whose cyclization affords, for example, murrayazolidine (58) (Husson, 1985). The isolation of 2-hydroxy-3-methylcarbazole (11) from the root of *Murraya koenigii* is of significance biogenetically (Bhattacharyya, Jash, and Chowdhury, 1986).

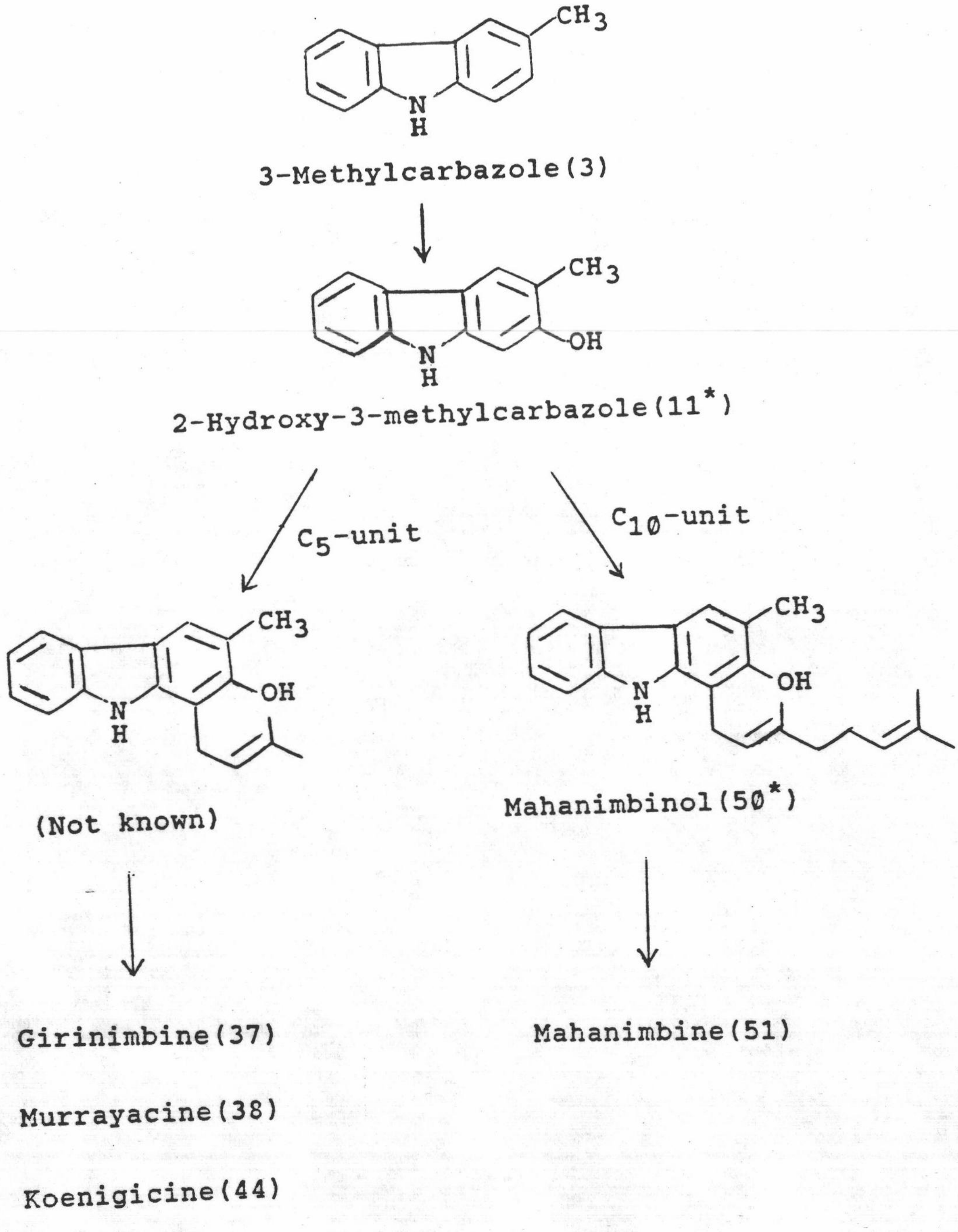


Figure 3

Biosynthesis of carbazole alkaloids from 3-methylcarbazole(3)

2.4 Biological Activity

The antibiotics from higher plants have been subject of numerous investigation. It is still a matter of experience that few compounds from these sources have been found substantially promising as compare with the antibiotics of microbial origin. Since carbazole alkaloids formed a new group of plant products, the examination of antibiotic action have been reported.

Das, Chakraborty, and Bose (1965) reported the antifungal action of murrayanine(6), girinimbine(37), and mahanimbine (51) on some human pathogenic fungi. The compounds were tested against the fungi *Microsporum gypseum*, *Microsporum audouini*, *Trichophyton rubrum*, *Nocardia asteroids*, *Epidermophyton floccosum*, and *Candida albicans*. The experiments were carried out by the usual agar-cup assay method using Sabouraud's agar medium. The results of assay are presented in table 20. The minimum inhibitory concentration (MIC) was determined, using dilute solution of the materials in the assay procedure. This data is shown in table 21.

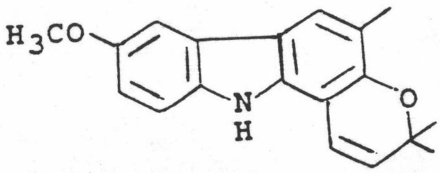
Table 20 The antifungal action of murrayanine(6), girinimbine(37) and mahanimbine(51)

Test organisms	Zone of inhibition (mm)		
	Girinimbine	Murrayanine	Mahanimbine
Microsporum gypseum	20	14	12
Microsporum audouini	18	-	-
Trichophyton rubrum	16	10	12
Nocardia asteroids	24	-	20
Epidermophyton floccosum	-	-	-
Candida albicans	9	9	9

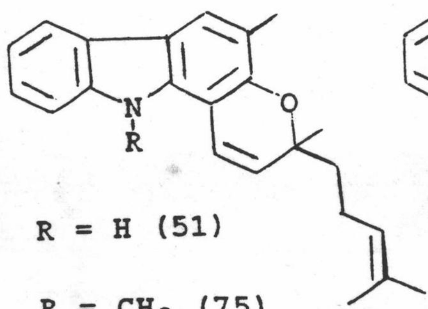
Table 21 MIC (μg/ml) of girinimbine(37), murrayanine(6), and mahanimbine(51)

Test organisms	Girinimbine	Murrayanine	Mahanimbine
Microsporum gypseum	300	3000	3000
Microsporum audouini	300	-	-
Trichophyton rubrum	300	3000	3000
Nocardia asteroids	30	3000	300

The structure of mahanimbine(51), koenimbine(40), and N-methylmahanimbine (75) are of close similarity to acronycine (76) which is known for its antitumour activity. So three carbazole alkaloids were tested for their anticancer, preliminary reports indicated that all of them were inactive. Mahanimbine (51) was also tested for its antimalarial activity. The result was negative (Narasimhan *et al.*, 1975).

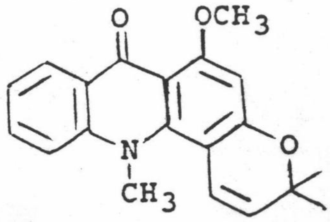


(40)



R = H (51)

R = CH_3 (75)



(76)

Chakraborty (1980), again examined the antibiotic action of carbazole alkaloids. These compounds were tested by the agar cup assay method using Sabourad's medium against *Microsporum gypseum*, *Trichophyton rubrum*, *Epidermophyton floccosum*, *Candida albicans*, *Candida tropicalis*, *Staphylococcus aureus*, and *Escherichia coli*. Glycozoline (16), glycozolidine (20), murrayanine (6), girinimbine(37), mahanimbine(51), and heptazoline(29) were active at a concentration of 10 µg/ml. The most significant activity was observed with 6-hydroxy-3-methylcarbazole(15) which could inhibit the growth of *Trichophyton rubrum* at 10 µg/ml. Girinimbine (37) was active against *Nocardia asteroids* at a concentration of 30 µg/ml.

Glycozolidol (19) was screened for antibacterial activity against both Gram-positive and Gram-negative bacteria using the standard cup assay method at a concentration of 200 µg/ml. The bacteria used were *Staphylococcus aureus*, *Bacillus firmis*, *Sarcina lutea*, *Escherichia coli*, *Agrobacterium tumefacients*, and *Proteus vulgaris*. Glycozolidol (19) was active against all the organisms tested except *Escherichia coli*. Gram-positive strains are more susceptible to the compound than Gram-negative ones (Bhattacharyya, Chakrabartty, and Chowdhury, 1985).

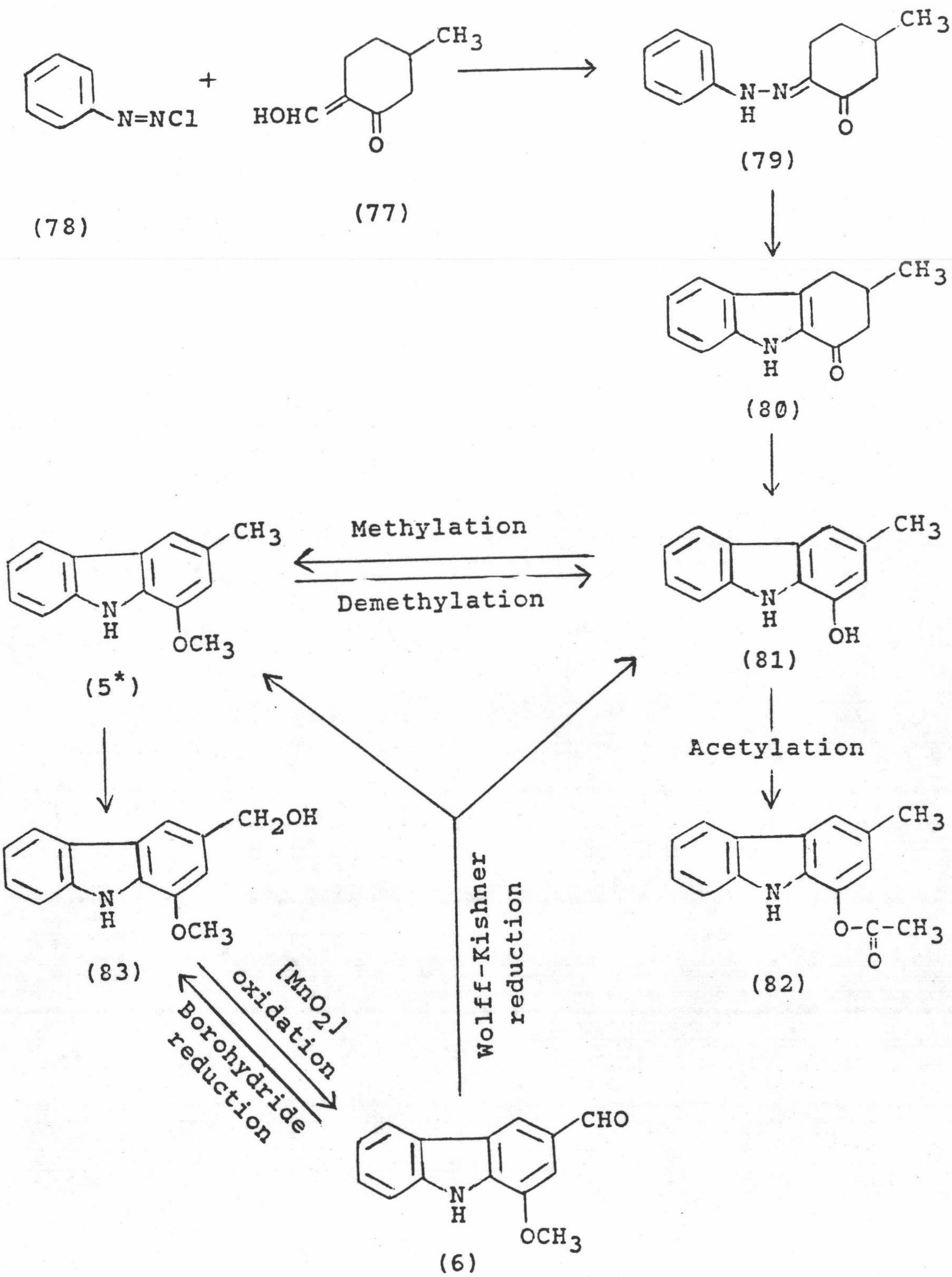
2-Hydroxy-3-formyl-7-methoxycarbazole (18) and 7-methoxyheptaphylline(28) were tested for biological activity in several bioassays including the brine shrimp lethality assay, and cytotoxicity in murine leukemia (9PS), human nasopharyngeal carcinoma (9KB and KBMRI), human lung carcinoma (A-549), and human colon adenocarcinoma (HT-29). Compound 18 was found to be toxic to brine shrimp at an LC_{50} value of 35.1 ppm with a 95 % confidence interval of 21.2-51.4 ppm. Compound 28 was found to have an LC_{50} value > 500 ppm. Both compounds were inactive on 9PS with ED_{50} value > 10 µg/ml, but slightly active in 9KB, KBMRI, A-549, and HT-29 cell lines, with compound 28 showing stronger activity (table 22) (Chaichantipyuth *et al.*, 1988).

Table 22 Biological activity of 2-hydroxy-3-formyl-7-methoxycarbazole(18) and 7-methoxyheptaphylline(28)

Compound	Brine shrimp	9KB	KBMRI	A-549	HT-29
	LC_{50}(ppm)	ED_{50}(μg/ml)	ED_{50}(μg/ml)	ED_{50}(μg/ml)	ED_{50}(μg/ml)
18	35(51/21)	5.70	4.48	2.74	4.00
28	>500	3.01	2.87	2.16	1.30

2.5 Synthesis

Murrayanine(6) was obtained from the stem bark of *Murraya koenigii* (Chakraborty, Barman, and Bose, 1965). The UV spectrum of murrayanine (6) was similar to that of 3-formylcarbazole, but after potassium borohydride reduction was similar to that of 1-methoxycarbazole. This structure has been confirmed by synthesis (figure 4). The hydrazone necessary for the present synthesis was obtained by the condensation of 2-hydroxymethylene-5-methylcyclohexanone(77) with phenyldiazonium chloride(78) under Japp-Klingemann condition. The resulting 4 -methylcyclohexane- 1,2- dione-1-phenylhydrazone (79), was cyclized to 1-oxo-3-methyl-1,2,3,4-tetrahydrocarbazole(80) using a mixture of acetic acid and concentrated hydrochloric acid as the condensing agent. The dehydrogenation of 1-oxo-3 -methyl -1,2,3,4-tetrahydrocarbazole(80) with Pd-C (10 %) in a seal tube under evacuated condition instead of chloranil furnished 1-hydroxy-3-methylcarbazole(81). This was found to be identical with the phenol (81) obtained by demethlylation of the Wolff-Kishner reduction product of murrayanine(6). 1-Acetoxy-3-methylcarbazole (82), obtained by acetylation of phenol(81) with pyridine and acetic anhydride, was identical with the phenol acetate derived from murrayanine (6). Compound 81 on methylation with diazomethane in the presence of methanol furnished 1- methoxy-3- methylcarbazole (5^*) identical with the Wolff- Kishner reduction product of murrayanine(6). This eventually confirms the structure of the Wolff-Kishner reduction product of murrayanine (6) as 1-methoxy-3-methylcarbazole(5^*). Compound 5^* was brominated with N-bromosuccinimide in the presence of traces of benzoyl peroxide to 1- methoxy- 3- hydroxymethylcarbazole (83). Compound 83 was found to be identical with the borohydride reduction product of murrayanine(6). The benzylic alcohol (83) was oxidized with manganese dioxide in carbon tetrachloride to 1-methoxy-3-formylcarbazole (6) which was found to be identical with natural murrayanine(6) in all respects. (Chakraborty and Chowdhury, 1968).



<u>Figure 4</u> Synthesis of murrayanine(6)

Heptaphylline (26) was obtained from the roots of *Clausena heptaphylla* (Joshi *et al.*, 1967) and again the UV spectrum was similar to that of carbazole-3-aldehyde(2*). The structure was confirmed by the reaction of compound 2* with 3,3-dimethylallyl bromide at 25°C in presence of potassium hydroxide or treatment of compound 2* with 2-methyl-3-buten-2-ol in presence of BF_3-etherate in dioxane (Joshi *et al.*, 1972).

The synthesis of murrayacine(38) (figure 5) has been accomplished by the treatment of 4-hydroxymethyl-3-hydroxyaniline(84) with formylcyclohexanone(85) under Japp-Klingemann condition furnished cyclohexane-1,2-dione-4-hydroxymethyl-3-hydroxyphenylhydrazone(86). Compound 86, on indolization with a mixture of glacial acetic acid and hydrochloric acid, furnished the indole-2-hydroxy-3-hydroxymethyl-8-oxol-5,6,7,8-tetrahydrocarbazole(87). Wolff-Kishner reduction of the keto alcohol (87) furnished 2-hydroxy- 3-hydroxymethyl- 5,6,7,8- tetrahydrocarbazole (88). Compound 88 was acetylated with 2,2- dimethylacroylyl chloride at 5°C in the presence of pyridine and compound (89) was obtained. The phenol ester(89) on Fries migration and subsequent treatment with hydrochloric acid furnished the chromanone(90). Compound 90 was dehydrogenated with palladized charcoal when the indolochromanone (91) was obtained. The chromone derivative was reduced with sodium borohydride when the alcohol (92) was obtained.

Dehydrotosylation of the tosyl derivative(92) in the presence of collidine furnished chromenoindole (93), which had the characteristic UV spectrum of a pyranocarbazole like girinimbine(37). Oxidation of chromenoindole(93) with active MnO_2 furnished murrayacine(38) (Chakraborty, Islam, and Bhattacharyya, 1973).

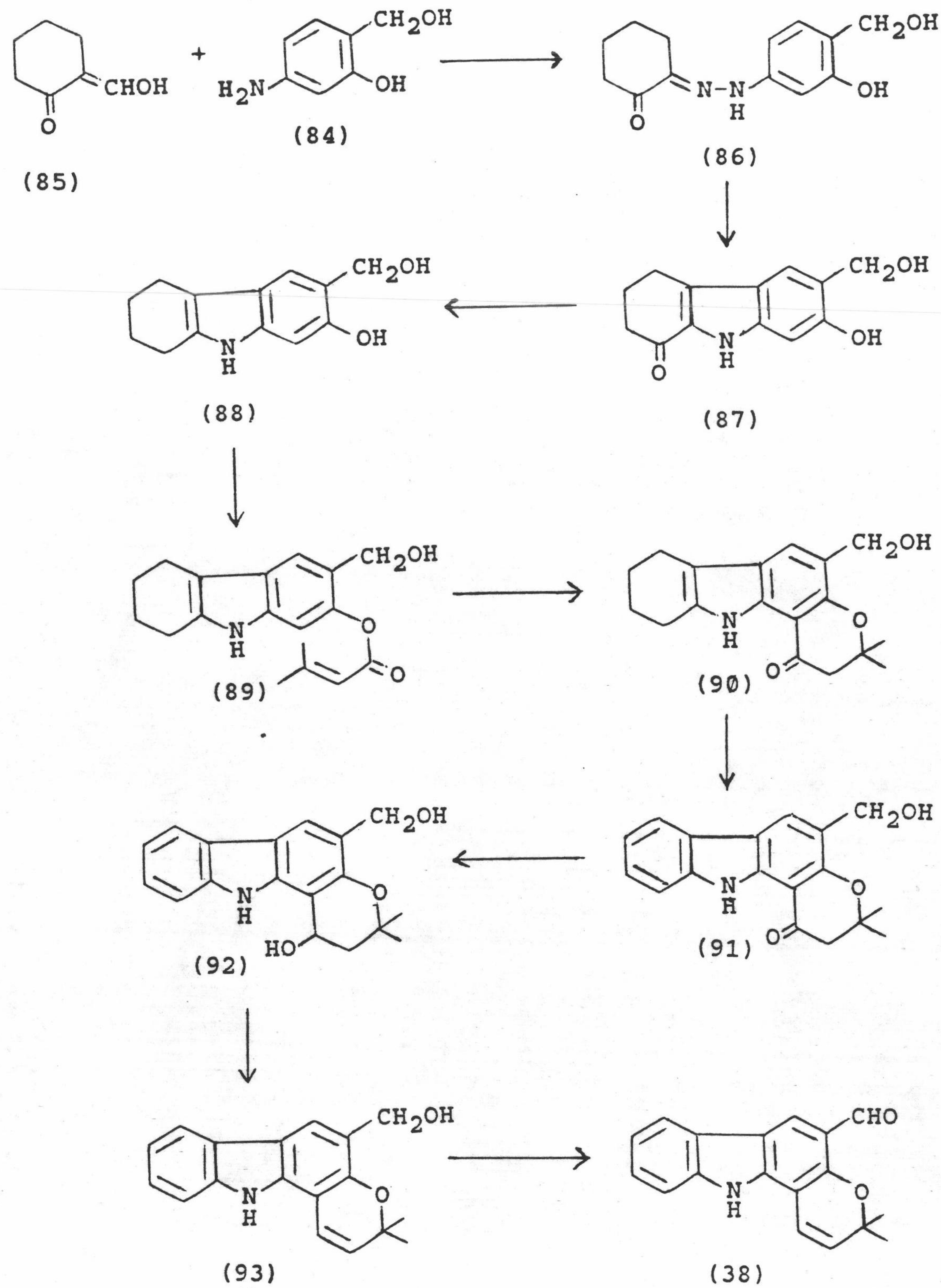


Figure 5 Synthesis of murrayacine(38)

The most complex alkaloids are those derived from indole and three isoprene units or carbazole nucleus(1) plus monoterpene. Mahanimbine (51) from the stem bark of *Murraya koenigii* (Das, Chakraborty, and Bose, 1965) was the first alkaloid of this type to be isolated. Its UV spectrum was similar to that of girinimbine (37). As in the synthesis of heptaphylline(26), 2-hydroxy-3-methylcarbazole(11*) is a key intermediate in synthesis of mahanimbine(51) too (figure 6). By Ullmann condensation of 2-nitrobromobenzene (94) with 4-bromo-2-methylanisole(95) gave the biphenyl(96), which could be cyclized to the carbazoles 14* and 97 with triethyl phosphite. Demethylation of the major component afforded compound 11*. Condensation with citral can be carried out in the presence of anhydrous ferric chloride or pyridine with 2 % benzoic acid to afford mahanimbine(51) (Cordell, 1981).

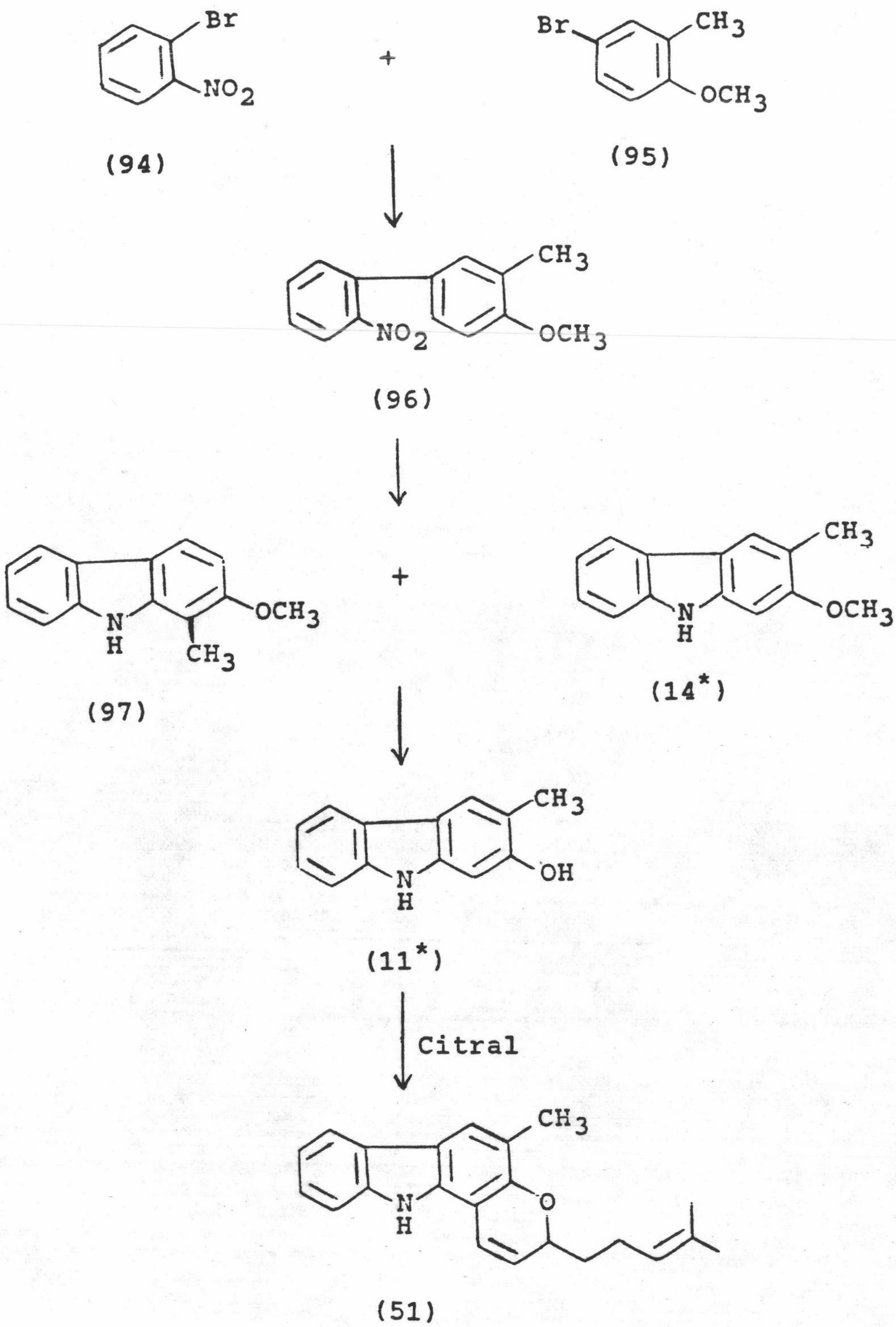


Figure 6 Synthesis of mahanimbine(51)

Note The compounds with asterisks (*) are also found as natural products.

Table 23 Distribution of carbazole alkaloids in Clauseneae

Compound	Botanical origin	Plant part	Reference
Atanisatin(34)	*Clausena anisata*	Stems	(Okorie, 1975)
Bicyclomahanimbicine(62)	*Murraya koenigii*	Leaves	(Kureel, Kapil, and Popli, 1970b)
Bicyclomahanimbine(61)	*Murraya koenigii*	Leaves	(Kureel, Kapil, and Popli, 1969b)
Bismurrayafoline-A(66)	*Murraya euchrestifolia*	+	(Furukawa, Wu, and Ohta, 1983)
Bismurrayafoline-B(67)	*Murraya euchrestifolia*	+	(Furukawa, Wu, and Ohta, 1983)
Bismurrayafolinol(65)	*Murraya euchrestifolia*	Stem bark	(Ito, Wu, and Furukawa, 1987)
Carbazole(1)	*Glycosmis pentaphylla*	Root bark	(Chowdhury *et al.*, 1987)
Clausanitin(33)	*Clausena anisata*	Roots	(Okorie, 1975)
Clausenapin(30)	*Clausena heptaphylla*	Leaves	(Bhattacharyya, 1984)
Currayangine(63)	*Murraya koenigii*	+	(Dutta, Quasim, and Wadia, 1969b)
Curryangin(60)	*Murraya koenigii*	+	(Dutta, Quasim, and Wadia, 1969a)
Cyclomahanimbine(58)	*Murraya koenigii* *Murraya koenigii*	Leaves Stem bark	(Kureel, Kapil, and Popli, 1969b) (Narasimhan and Kelkar, 1976)
Dihydroxygirinimbine(47)	*Murraya euchrestifolia*	Root bark	(Furukawa, Wu, and Kuoh, 1985a)
Ekeberginine(32)	*Clausena anisata*	Stem bark and roots	(Ngadjui *et al.*, 1989c)
Exozoline(57)	*Murraya exotica*	Leaves	(Ganguly and Sarkar, 1978)
3-Formylcarbazole(2)	*Murraya euchrestifolia*	Root bark	(Ito, Wu, and Furukawa, 1988)
3-Formyl-1-hydroxycarbazole(4)	*Clausena anisata*	Stem bark and roots	(Ngadjui *et al.*, 1989c)
Girinimbine(37)	*Murraya koenigii* *Murraya koenigii* *Murraya koenigii* *Clausena heptaphylla* *Clausena heptaphylla* *Murraya crenulata* *Murraya euchrestifolia* *Murraya koenigii* *Murraya microphylla* *Murraya siamensis* *Clausena anisata* *Clausena anisata*	Stem bark Stem bark Leaves and roots Roots Roots Roots Roots Roots Roots Roots + Stem bark and roots	(Das, Chakraborty, and Bose, 1965) (Dutta and Quasim, 1969) (Joshi, Kamat, and Gawad, 1970) (Joshi *et al.*, 1972) (Ray and Chakraborty, 1976) (Kong *et al.*, 1986b) (Kong *et al.*, 1986b) (Kong *et al.*, 1986b) (Kong *et al.*, 1986b) (Kong *et al.*, 1986b) (Adesina *et al.*, 1988) (Ngadjui *et al.*, 1989c)

Table 23 (Continue)

Compound	Botanical origin	Plant part	Reference
Glycozolidal(21)	*Glycosmis pentaphylla*	Roots	(Bhattacharyya and Chowdhury, 1985a)
Glycozolidine(20)	*Glycosmis pentaphylla*	+	(Chakraborty and Das, 1966)
	Glycosmis pentaphylla	Root bark	(Anwer, Kapil, and Popli, 1972)
	Glycosmis pentaphylla	+	(Chakraborty, Das, and Basak, 1974)
	Glycosmis mauritiana	Roots	(Rastogi, Kapil, and Popli, 1980)
Glycozolidol(19)	*Glycosmis pentaphylla*	Roots	(Bhattacharyya, Chakrabartty, and Chowdhury, 1985)
Glycozoline(16)	*Glycosmis pentaphylla*	+	(Chakraborty, 1966)
	Glycosmis pentaphylla	Root bark	(Chakraborty, 1969)
	Glycosmis mauritiana	Roots	(Rastogi, Kapil, and Popli, 1980)
	Murraya koenigii	+	(Adesina *et al.*, 1988)
Glycozolinol(15)	*Glycosmis pentaphylla*	Roots	(Bhattacharyya *et al.*, 1984)
Heptaphylline(26)	*Clausena heptaphylla*	Roots	(Joshi *et al.*, 1967)
	Clausena pentaphylla	Roots	(Anwer *et al.*, 1977)
	Clausena lansium	Leaves	(Prakash *et al.*, 1980)
	Clausena excavata	Root bark	(Wu and Furukawa, 1982)
	Clausena harmandiana	Root bark	(Wangboonskul, Pummangura, and Chaichantipyuth, 1984)
	Clausena anisata	Stem bark and roots	(Ngadjui *et al.*, 1989c)
Heptazolicine(46)	*Clausena heptaphylla*	Roots	(Bhattacharyya, Chakraborty, and Chowdhury, 1984)
Heptazolidine(42)	*Clausena heptaphylla*	+	(Chakraborty *et al.*, 1985)
Heptazoline(29)	*Clausena heptaphylla*	Stem bark	(Chakraborty, Das, and Islam, 1970)
2-Hydroxy-3-formyl-7-methoxycarbazole(18)	*Clausena harmandiana*	Root bark	(Chaichantipyuth *et al.*, 1988)
2-Hydroxy-3-methylcarbazole(11)	*Murraya koenigii*	Roots	(Bhattacharyya, Jash, and Chowdhury, 1986)
Indizoline(31)	*Clausena indica*	Roots	(Joshi and Gawad, 1974)
Isomahanimbine(54)	*Murraya koenigii*	Leaves and roots	(Joshi, Kamat, and Gawad, 1970)
	Murraya koenigii	+	(Narasimhan *et al.*, 1975)
Isomurrayafoline(36)	*Murraya euchrestifolia*	Stem bark	(Ito, Wu, and Furukawa, 1987)
Isomurrayazoline(64)	*Murraya koenigii*	Stem bark	(Bhattacharya, Roy, and Chakraborty, 1982)
Koenidine(44)	*Murraya koenigii*	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
	Murraya koenigii	+	(Narasimhan *et al.*, 1975)

Table 23 (Continue)

Compound	Botanical origin	Plant part	Reference
Koenigicine(44)	*Murraya koenigii*	Leaves	(Kureel, Kapil, and Popli, 1969a)
Koenigine(43)	*Murraya koenigii*	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
	Murraya koenigii	+	(Narasimhan *et al.*, 1975)
	Micromelum zeylanicum	Leaves	(Bowen and Perera, 1982)
Koenimbidine(44)	*Murraya koenigii*	Leaves and roots	(Joshi, Kamat, and Gavad, 1970)
Koenimbine(40)	*Murraya koenigii*	Fruits	(Narasimhan, Paradkar, and Chitguppi, 1968)
	Murraya koenigii	Leaves	(Kureel, Kapil, and Popli, 1969a)
	Murraya koenigii	+	(Narasimhan *et al.*, 1975)
	Murraya exotica	Stem bark	(Roy and Bhattacharya, 1981)
Koenine (39)	*Murraya koenigii*	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
	Murraya koenigii	+	(Narasimhan *et al.*, 1975)
Koenoline(7)	*Murraya koenigii*	Root bark	(Fiebig *et al.*, 1985)
Lansine(17)	*Clausena lansium*	Leaves	(Prakash *et al.*, 1980)
Mahanimbicine(54)	*Murraya koenigii*	Leaves	(Kureel, Kapil, and Popli, 1970b)
Mahanimbidine(63)	*Murraya koenigii*	Leaves	(Kureel, Kapil, and Popli, 1969b)
Mahanimbin(51)	*Murraya koenigii*	Stem bark	(Narasimhan, Paradkar, and Chitguppi, 1968)
Mahanimbine(51)	*Murraya koenigii*	Stem bark	(Das, Chakraborty, and Bose, 1965)
	Murraya koenigii	Stem bark	(Dutta and Quasim, 1969)
	Murraya koenigii	Leaves	(Kureel, Kapil, and Popli, 1969b)
	Murraya koenigii	Leaves and roots	(Joshi, Kamat, and Gavad, 1970)
	Murraya koenigii	Stem bark	(Roy and Chakraborty, 1974)
	Murraya koenigii	+	(Narasimhan *et al.*, (1975)
	Murraya exotica	Tissues	(Bhattacharyya *et al.*, 1978)
Mahanimbinine(56)	*Murraya koenigii*	Leaves	(Kureel, Kapil, and Popli, 1970a)
Mahanimbinol(50)	*Murraya koenigii*	Stem wood	(Rama Rao, Bhide, and Mujumdar, 1980)
Mahanimboline(55)	*Murraya koenigii*	Roots	(Gosh and Chakraborty, 1979)
Mahanine(53)	*Murraya koenigii*	Leaves	(Narasimhan, Paradkar, and Kelkar, 1970)
	Murraya koenigii	+	(Narasimhan *et al.*, 1975)
	Murraya koenigii	Leaves	(Atta, Zaidi, and Firdous, 1988)
N-Methoxy-3-formylcarbazole(25)	*Murraya euchrestifolia*	Root bark	(Ito, Wu, and Furukawa, 1988)
6-Methoxyheptaphylline(27)	*Clausena indica*	Roots	(Joshi, Gavad, and Kamat, 1972)

Table 23 (Continue)

Compound	Botanical origin	Plant part	Reference
7-Methoxyheptaphylline(28)	*Clausena harmandiana*	Root bark	(Chaichantipyuth *et al.*, 1988)
2-Methoxy-3-methylcarbazole(14)	*Murraya koenigii*	Seeds	(Bhattacharyya and Chowdhury, 1985b)
3-Methylcarbazole(3)	*Clausena indica*	Roots	(Joshi and Gawad, 1974)
	Clausena heptaphylla	Roots	(Roy, Bhattacharyya, and Chakraborty, 1974)
	Clausena pentaphylla	Root bark	(Chowdhury *et al.*, 1987)
	Murraya koenigii	+	(Adesina *et al.*, 1988)
	Clausena anisata	Stem bark and roots	(Ngadjui *et al.*, 1989c)
Mukoeic acid1(8)	*Murraya koenigii*	Stem bark	(Chowdhury and Chakraborty, 1969)
	Murraya koenigii	Barks	(Choudhury and Chakraborty, 1971)
Mukolidine(9)	*Murraya koenigii*	+	(Roy, Bhattacharyya, and Chakraborty, 1982)
Mukoline(10)	*Murraya koenigii*	+	(Roy, Bhattacharyya, and Chakraborty, 1982)
Mukonal(12)	*Murraya koenigii*	Stems	(Bhattacharyya and Chakraborty, 1984b)
Mukonicine(45)	*Murraya koenigii*	Leaves	(Mukherjee *et al.*, 1983)
Mukonidine(13)	*Murraya koenigii*	+	(Chakraborty, Roy, and Guha, 1978)
Mupamine(41)	*Clausena anisata*	Root bark	(Mester and Reisch, 1977)
	Glycosmis pentaphylla	Leaves	(Kamaruzzaman, Roy, and Chakraborty, 1989)
Murrafoline-A(68)	*Murraya euchrestifolia*	Root bark	(Mc Phail *et al.*, 1983)
Murrafoline-B(69)	*Murraya euchrestifolia*	+	(Furukawa, Wu, and Kuoh, 1985b)
Murrafoline-C(70)	*Murraya euchrestifolia*	+	(Furukawa, Wu, and Kuoh, 1985b)
Murrafoline-D(71)	*Murraya euchrestifolia*	+	(Furukawa, Wu, and Kuoh, 1985b)
Murrafoline-E(72)	*Murraya euchrestifolia*	Root bark	(Ito, Wu, and Furukawa, 1988)
Murrafoline-F(73)	*Murraya euchrestifolia*	Root bark	(Ito, Wu, and Furukawa, 1988)
Murrayacine(38)	*Murraya koenigii*	Leaves and roots	(Joshi, Kamat, and Gawad, 1970)
	Clausena heptaphylla	Roots	(Ray and Chakraborty, 1976)
Murrayacinine(52)	*Murraya koenigii*	Barks	(Chakraborty *et al.*, 1974)
Murrayafoline-A(5)	*Murraya euchrestifolia*	Root bark	(Wu, Ohta, and Furukawa, 1983)
	Murraya crenulata	Roots	(Kong *et al.*, 1986)
Murrayafoline-B(35)	*Murraya euchrestifolia*	Root bark	(Furukawa, Wu, and Ohta, 1983)

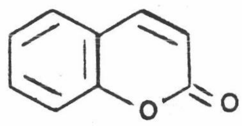
Table 23 (Continue)

Compound	Botanical origin	Plant part	Reference
Murrayaline(23)	*Murraya euchrestifolia*	Stem bark	(Furukawa *et al.*, 1986)
Murrayanine(6)	*Murraya koenigii*	Stem bark	(Chakraborty, Barman, and Bose, 1965)
	Murraya koenigii	Stem bark	(Das, Chakraborty, and Bose, 1965)
	Murraya koenigii	Leaves	(Gupta and Nigam, 1971)
	Clausena heptaphylla	Roots	(Bhattacharyya and Chakraborty, 1973)
	Murraya siamensis	Roots	(Fiebig *et al.*, 1983)
Murrayastine(22)	*Murraya euchrestifolia*	Stem bark	(Furukawa *et al.*, 1986)
Murrayazolidine(58)	*Murraya koenigii*	Stem bark	(Chakraborty, Bhattacharyya, and Mitra, 1974)
Murrayazoline(63)	*Murraya exotica*	Tissues	(Bhattacharyya *et al.*, 1978)
Murrayazolinine(59)	*Murraya koenigii*	Stem bark	(Chakraborty *et al.*, 1973)
Oxydimurrayafoline(74)	*Murraya euchrestifolia*	Stem bark	(Ito, Wu, and Furukawa, 1987)
5,6-Pyranoglycozoline(48)	*Micromelum falcatum*	Roots	(Kong *et al.*, 1988)
Pyrayafoline(49)	*Murraya euchrestifolia*	Stem bark	(Furukawa *et al.*, 1986)

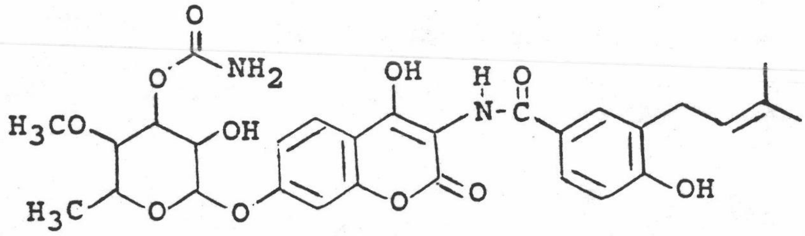
3. Coumarins

3.1 Introduction

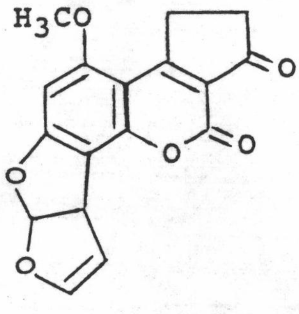
Coumarins were discovered originally in plants; the name of the groups derived from `coumarona' the common name of *Coumarouna odorata* (syn. *Dipteryx odorata*), from which coumarin itself was isolated first by Vogel in 1820 (Soine, 1964 ; Seshadri and Vishwapaul, 1973). The term of coumarin is applied, collectively, to a large group of naturally occurring compounds possessing benzopyran-2-one (coumarin nucleus) (98) (Gray and Waterman, 1978). Coumarins are a class of secondary plant and microbial products whose members exhibit a considerable range of physiological effects in animals. The least complex member of the class structurally is toxic to mammals, and at the other end of the scale the highly substituted coumarin, novobiocin (99) is a commercial antibiotic. Another group of coumarin-type is the aflatoxins (100, 101) which microbial metabolites are potent hepatotoxins and are among the most potent carcinogens yet discovered . Several coumarins hydroxylated at C-4, including the well known dicoumarol(102) function as anticoagulants (Brown, 1979). Now the naturally occurring coumarins are doubtful that their full range of physiological actions, so there has been a continuing effort and a build up of literature in this area with certain coumarins that have caught the wider interest of scientists especially to the pharmacologists and phytochemists.



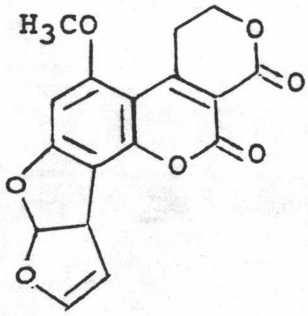
Coumarin nucleus(98)



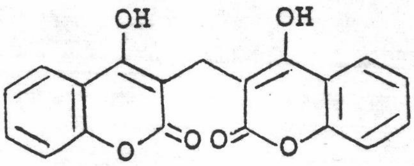
Novobiocin(99)



Aflatoxin B_1(100)



Aflatoxin G_1(101)



Dicoumarol(102)

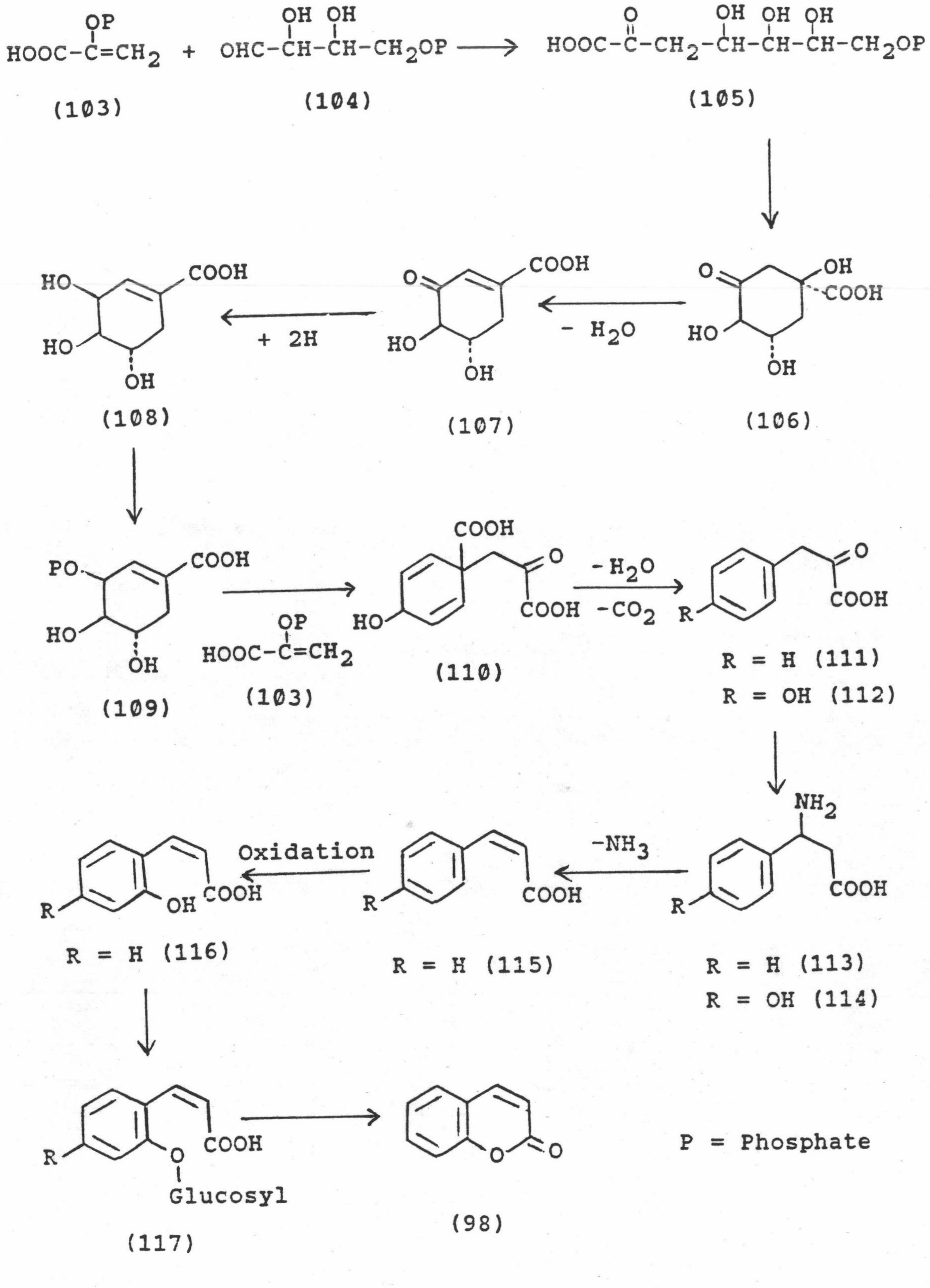
3.2 Natural occurrence and biosynthesis

Coumarins are a widely distributed and important class of natural compounds. Most of them have been isolated from Graminae, Orchidaceae, Leguminosae, Umbelliferae, Guttiferae, Rutaceae, Labiatae, Compositae and other families of lesser importance such as Caryophyllaceae, Euphorbiaceae, Hippocastanaceae, Oleaceae and Thymelaeaceae (Soine, 1964 ; Murry, Méndez, and Brown, 1982). More recently a few complex coumarins have been found as metabolic products of bacteria and fungi, the most recent being the aflatoxins (100, 101) which are the result of *Aspergillus flavus* infection of oil-seed cake derived from peanuts. Only a few coumarins have been obtained from animal sources.

At present the total number of coumarins reported from natural sources is well known to be in excess of eight hundred (Murray, Méndez, and Brown, 1982) and is still rising steadily. Most coumarins probably derive their benzopyran nucleus from the cyclization of a C-2-oxygenated cis-cinnamic acid, simple structures such as umbelliferone (119), angelicin (120) are known to occur in many plant families. On the other hand, coumarins that have undergone elaboration of the basic structure by the addition of C_5-units originating from mevalonic acid have been noted in relatively few families. The resulting simple prenyl coumarins and derived furano- and pyranocoumarins have been reported. It is now apparent that simple coumarins are of common occurrence in the Umbelliferae and Rutaceae

(Gray and Waterman, 1978).

A complete consideration of the biosynthesis is still in its infancy and much can be expected in the future. Being phenylpropanoid compounds, it has been of considerable interest to researchers to determine which of the two known major pathways is involved in coumarin biosynthesis. These are the Birch-Donovan acetate pathway and the shikimic acid pathway. The acetate route involves head-to-tail condensation of acetate units to build up hydroxylated aromatic rings and has been shown not to be the major pathway to coumarins. On the other hand, the shikimic acid pathway (figure 6) has been demonstrated as definited involved. The initial step is a condensation of phospho enolpyruvic acid (103) with D-erythrose phosphate (104) to form 2-keto-3-deoxy-D-arabo-heptonic acid 7-phosphate (105) which cyclizes to 5-dehydroquinic acid (106). This, in turn, proceeds to 5-dehydroshikimic acid(107) and then to shikimic acid (108) which, by way of its 5-phosphate (109), condenses with another mole of phosphoenolpyruvic acid (103) to form prephenic acid(110). The latter aromatizes to yield phenylpyruvic acid(111) (or its p-hydroxy derivative(112)), then proceeds to phenylalanine(113) (or tyrosine(114)). Enzymatic deamination of phenylalanine , for example , provides cinnamic acid(115) which has been shown to undergo o-hydroxylation(116) followed by glucoside formation(117). The glucoside, in some manner, is finally converted to coumarin(98) (Soine, 1964).

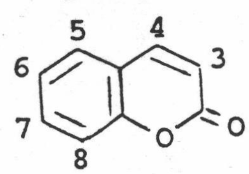


<u>Figure 7</u> Shikimic acid pathway to coumarins

3.3 Classification

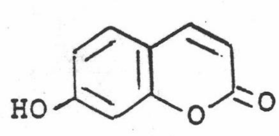
There are several structural categories into which coumarins could be divided based on the desires and needs of the classifier. No completely satisfactory classification is possible at present. From representation NMR data for natural coumarins of over 100 spectra, Steck and Mazurek (1972) have divided coumarins into `normal' and `abnormal' types. The normal type have an oxygen function at C-7 and this type of coumarins comprises the great majority of natural derivatives. The compounds which either lack the C-7 oxygen or possess pyrone ring substituents, are thus abnormal type in this respect. Seshadri and Vishwapaul (1973); Tandon and Rastogi (1979) have classified coumarins into five groups as below.

3.3.1 Simple coumarins. From coumarin nucleus (98) there are side chains substituted at the various position and 7-oxygenated coumarins are the most common in this type. For example umbelliferone(119) and angelical(120) which were isolated from the leaves of *Micromelum ceylanicum* and the root bark of *Glycosmis cyanocarpa* Spreng, respectively (De Silva *et al.*, 1983; Talapatra, Chaudhury, and Talapatra, 1975).



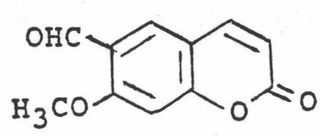
Coumarin nucleus

(98)



Umbelliferone

(119)

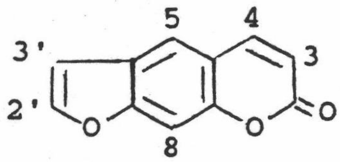


Angelical

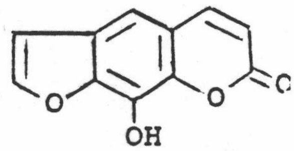
(120)

3.3.2 Furanocoumarins. Structurally, this group of coumarins concists a furan ring which is fused onto the coumarin nucleus (98) at the various positions to form linear or angular furanocoumarins and can be classified into six subtypes.

3.3.2.1 Psoralene type (linear) (121). The furan ring with C-2', C-3' double bond is fused with benzene ring at C-6 and C-7 to form linear structure. For example xanthotoxal (122) which was isolated from *Clausena indica* Oliv. (Rakash *et al.*, 1978).

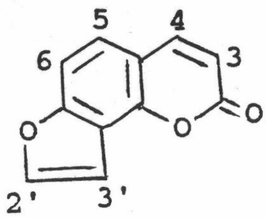


Psoralene type (linear) (121)



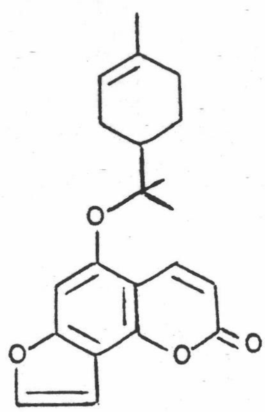
Xanthotoxol (122)

3.3.2.2 Angelicin type (angular) (123). The furan ring with C-2', C-3' double bond is fused with the benzene ring at C-7 and C-8. The example of this type archangelin(124) which was found in the root of *Angelica archangelica* L. (Chatterjee and Gupta, 1964) has substituent at C-5 as below:-



Angelicin type (angular)

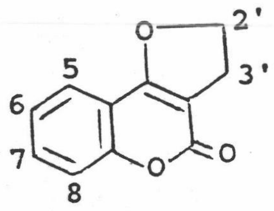
(123)



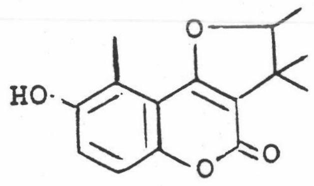
Archangelin (124)

3.3.2.3 Dihydrofuranocoumarin[4,3](125)

The furan ring is fused at C-4 and C-3 of the coumarin nucleus(98), while C-2' and C-3' is saturated. The sample of compound glaupalol (126) isolated from the rhizome of *Glaucidium palmatum* (Irie *et al.*, 1967).



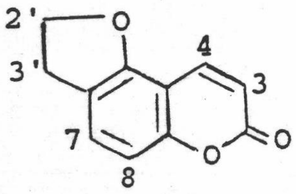
Dihydrofuranocoumarin [4,3] (125)



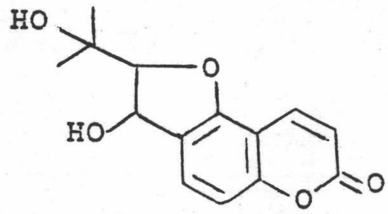
Glaupalol (126)

3.3.2.4 Dihydrofuranocoumarin [5,6](127)

The furan ring is fused at C-5 and C-6, while C-2', C-3' is saturated. For example of this type xanthoarnol (128) isolated from *Xanthoxylum arnottianum* Maxim (Ishii *et al.*, 1973).



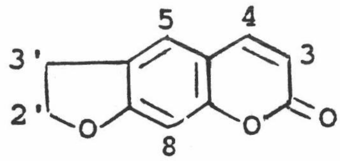
Dihydrofuranocoumarin [5,6] (127)



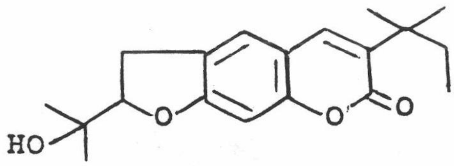
Xanthoarnol (128)

3.3.2.5 Dihydrofuranocoumarin[7,6](129)

Similar to psoralene type (121) but C-2', C-3' is saturated. For example chalepin(130) or heliettin has been reported to be found in the root of *Clausena indica* Oliv. (Joshi and Gawad, 1971) and *Clausena anisata* (Willd.) (Okorie, 1975).

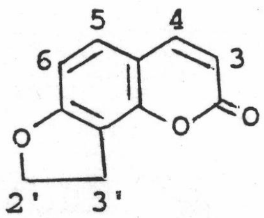


Dihydrofuranocoumarin [7,6]
(129)

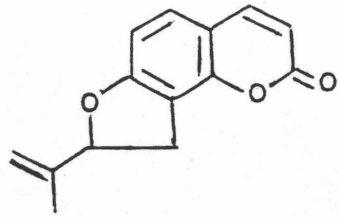


Chalepin or Heliettin
(130)

3.3.2.6 Dihydrofuranocoumarin[7,8](131) Similar to angelicin type (123) but C-2', C-3' is saturated. For example angenomalin(132) or masquin, a coumarin from *Pimpinella rupicola* roots (Martinez *et al.*, 1967).



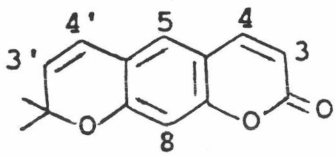
Dihydrofuranocoumarin [7,8]
(131)



Angenomalin or Masquin
(132)

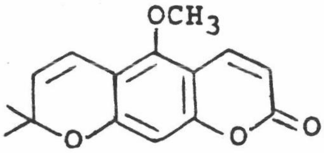
3.3.3 Pyranocoumarins. The pyran ring is fused with the coumarin nucleus(98) at various positions to form linear or angular pyranocoumarins. This group of coumarins can be classified into four subtypes.

3.3.3.1 Xanthyletin type (linear)(133). The pyran ring is fused at C-6 and C-7 , the hydrogen at C-2' is substituted with gem dimethyl group , while between C-3' and C-4' have one double bond. Xanthoxyletin(134) is the sample of this type which was isolated from the root bark of *Clausena anisata* (Willd.) Oliv. (Mester, Szendrei, and Reisch, 1977).



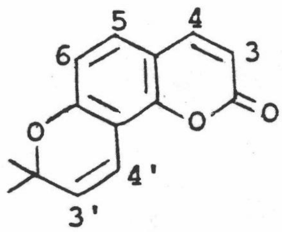
Xanthyletin type (linear)

(133)



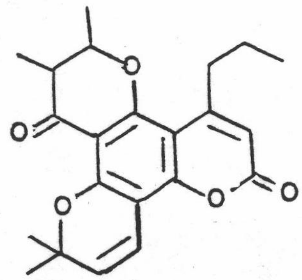
Xanthoxyletin (134)

3.3.3.2 Seselin type (angular) (135). The pyran ring with C-3', C-4' double bond is fused at C-7, C-8 and substituted with gem dimethyl group at C-2'. The sample of this compound is tomentolide-B(136) which isolated from *Calophyllum tomentosum* (Nigam *et al.*, 1967).



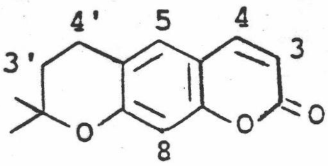
Seselin type (angular)

(135)



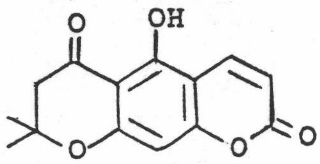
Tomentolide-B (136)

3.3.3.3 Dihydroxanthyletin type(linear) (137). The structure of this type is as same as xanthyletin type (linear)(133) but at C-3' and C-4' is saturated. Clausenin(138) is the sample of this type which isolated from the root of *Clausena heptaphylla* Wight & Arn. (Joshi, Kamat, and Saksena, 1967).



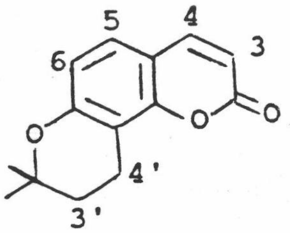
Dihydroxanthyletin type (linear)

(137)

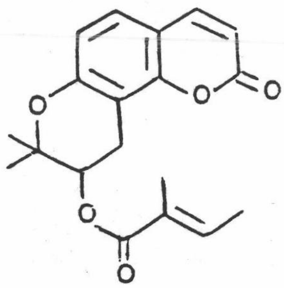


Clausenin (138)

3.3.3.4 Dihydroseselin type (angular) (139). Just the same as seselin type (angular) (135) but at C-3' and C-4' is saturated. For example selinidin (140) which was extracted from *Selinum vaginatum* (Seshadri *et al.*, 1967).



Dihydroseselin type (angular)
(139)



Selinidin (140)

3.3.4 Phenylcoumarins . There is phenyl substituted at C-3 or C-4 of coumarin nucleus(97). They can be divided into six subtypes.

3.3.4.1 3-Phenylcoumarins(141)

3.3.4.2 4-Phenylcoumarins(143)

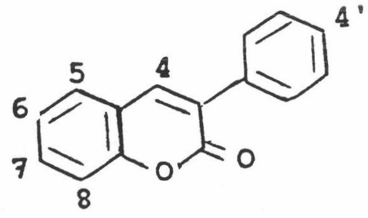
3.3.4.3 4-Phenyldihydroangelicin(145)

3.3.4.4 3-Phenylxanthyletin(147)

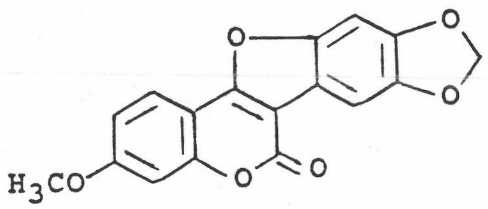
3.3.4.5 3-Phenylseselin(149)

3.3.4.6 4-Phenylseselin (angular)(151)

The structures and some examples of compounds in each subtype are listed below:-



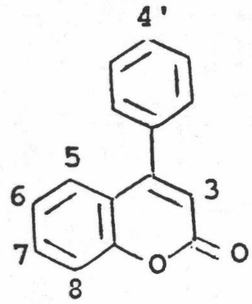
3.3.4.1 3-Phenylcoumarin(141)



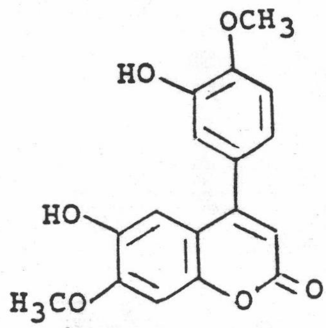
Flemichapparin(142)

From *Flemingia chapper* Ham.(roots)

(Adityachaudhury and Gupta, 1970)



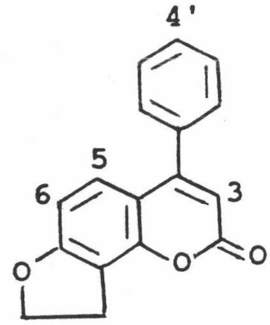
3.3.4.2 4-Phenylcoumarin(143)



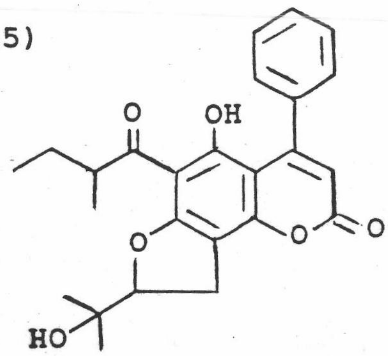
Melannein(144)

From *Dalbergia baroni* Baker (heartwood)

(Donnelly, Donnelly, and O'Sullivan, 1968)



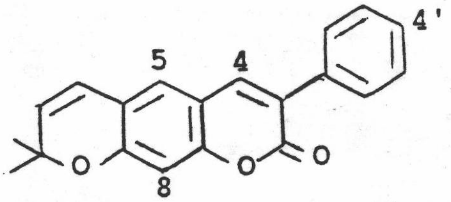
3.3.4.3 4-Phenyldihydroangelicin(145)



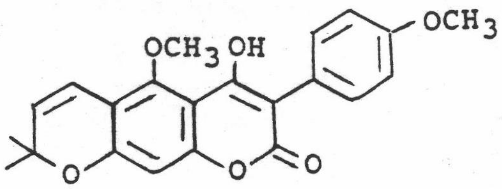
MAB-3(146)

From *Mammea africana* G. Don (barks)

(Carpenter, Mc Garry, and Scheinmann, 197Ø)



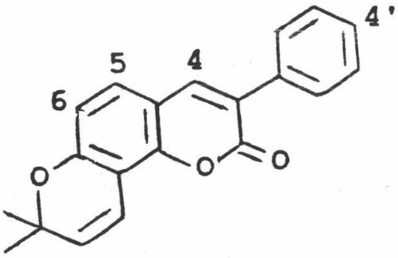
3.3.4.4 3-Phenylxanthyletin(147)



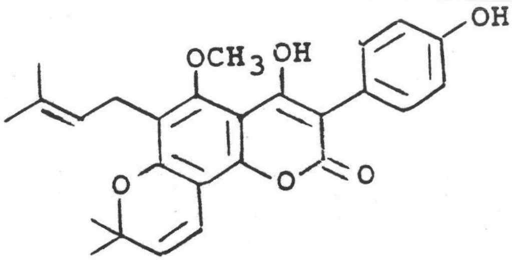
Robustic acid(148)

From *Derris robusta* (Roxb.) Benth.(roots)

(Johnson and Pelter, 1964)



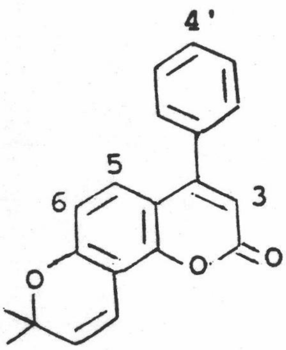
3.3.4.5 3-Phenylseselin(149)



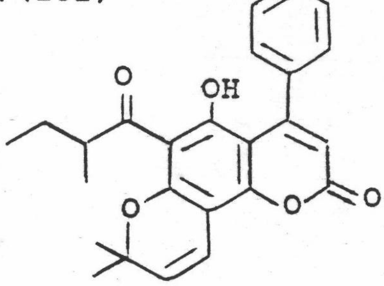
Scandenin(150)

From *Derris scandens* (Roxb.) Benth.(roots)

(Pelter and Johnson, 1964)



3.3.4.6 4-Phenylseselin(angular)(151)

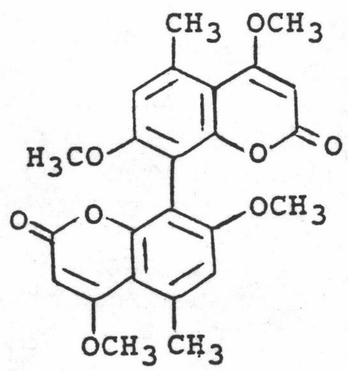


MAB-5(152)

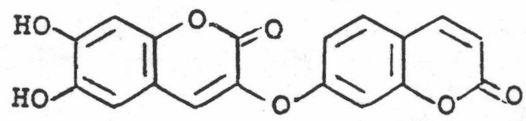
From *Mammea africana* G. Don (barks)

(Carpenter, Mc Garry, and Scheinmann, 1970)

3.3.5 Bicoumarins. Coumarins in this group possess two coumarin-nuclei in their structures. Some examples of this type are kotamine (153) and edgeworthin (154) which have been isolated as a metabolite of *Aspergillus glaucus* cultures and from stem bark of *Edgeworthia gardneri*, respectively (Bϋchi *et al.*, 1971; Majumder *et al.*, 1974).



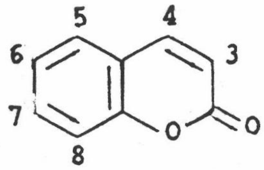
Kotamine (153)



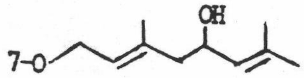
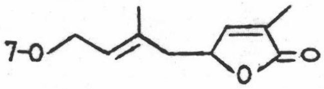
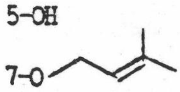
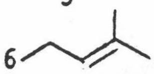
Edgeworthin (154)

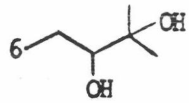
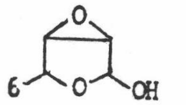
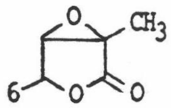
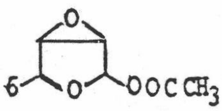
Up to date, the previously reported coumarins in Clauseneae were classified into three groups ; simple, furanocoumarins, and pyranocoumarins. The compounds isolated are listed below.

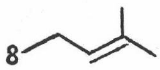
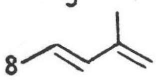
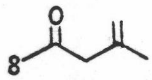
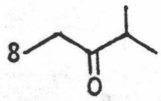
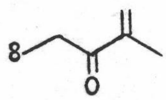
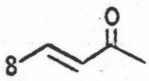
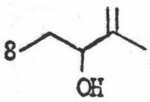
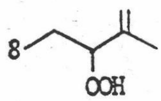
3.3.1 Simple coumarins

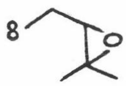
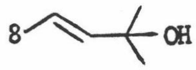
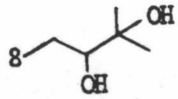
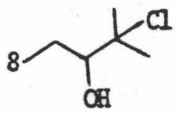
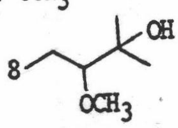
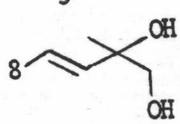
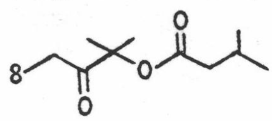
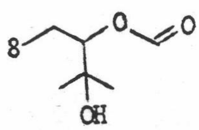


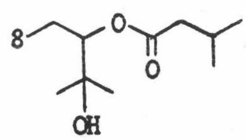
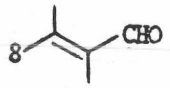
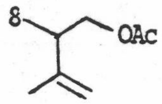
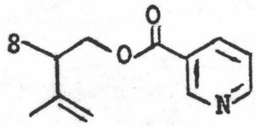
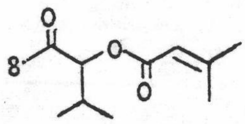
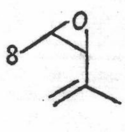
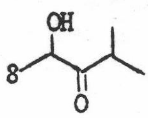
Coumarin nucleus (98)

Compound	Substituent	Reference
Umbelliferone (119)	7-OH	(De Silva *et al.*, 1983)
Herniarin (155)	7-OCH_3	(Kumar, 1985)
Anisocoumarin-H (156)		(Ngadjui *et al.*, 1989b)
Capnolactone (157)		(Ngadjui *et al.*, 1989b)
Anisocoumarin-B (158)	5-OH 	(Ngadjui *et al.*, 1989a)
Limettin (159)	5-OCH_3 7-OCH_3	(Talapatra, Chaudhuri, and Talapatra, 1975)
Scopoletin (160)	7-OH 6-OCH_3	(Wu *et al.*, 1975)
Angelical (120)	7-OCH_3 6-CHO	(Talapatra, Chaudhuri, and Talapatra, 1975)
Suberosin (161)	7-OCH_3 	(Rakash *et al.*, 1978)

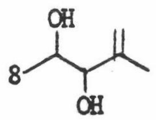
6-(2,3-Dihydroxy-3-methylbutyl)-7-methoxycoumarin (162)	7-OCH_3 	(Joshi *et al.*, 1975)
Dihydromicromelin (163)	7-OCH_3 	(Das *et al.*, 1984)
Micromelin (164)	7-OCH_3 	(Lamberton, Price, and Redcliffe, 1967)
Micromelumin (164)		(Chatterjee, Dutta, and Bhattacharyya, 1967)
Acetyldihydromicromelin (165)	7-OCH_3 	(Das *et al.*, 1984)
Anisocoumarin-A (166)	7-OCH_3  6 CHO	(Ngadjui *et al.*, 1989a)
Scopolin (167)	7-O-glucosyl 6-OCH_3	(Gupta and Nigam, 1971)
Panicular (168)	7-OCH_3 8-CHO	(Imai, Kinoshita, and Sankawa, 1987)
Murrayacarpin-A (169)	7-OCH_3 8-CH_2OH	(Wu, Liou, and Kuoh, 1989)
7-Methoxy-8-(2'-formyl-2'-methylpropyl) coumarin (170)	7-OCH_3 	(Yang and Du, 1984b)

Paniculin (171)	7-OCH_3 	(Imai, Kinoshita, and Sankàwa, 1987)
Osthol (172)	7-OCH_3 	(Steck, 1972) (Bishay *et al.*, 1988)
Dehydroosthol (173)	7-OCH_3 	(Ito and Furukawa, 1987a) (Ito and Furukawa,1987b)
Micropubescin (174)	7-OCH_3 	(Chatterjee, Dutta, and Bhattacharyya, 1967)
Isomeranzin (175)	7-OCH_3 	(Yang and Du, 1984b)
Murrayone (176)	7-OCH_3 	(Lakshmi, Ratnam, and Subba Rao, 1972)
Osthenon (177)	7-OCH_3 	(Ito and Furukawa, 1987a) (Ito and Furukawa, 1987c)
Auraptenol (178)	7-OCH_3 	(Barik *et al.*, 1983) (Bishay *et al.*, 1988)
Peroxyauraptenol (179)	7-OCH_3 	(Ito and Furukawa, 1987a) (Ito and Furukawa, 1987b)

Meranzin (180)	7-OCH_3 	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
Murraol (181)	7-OCH_3 	(Ito and Furukawa, 1987a) (Ito and Furukawa, 1987b)
Peroxymurraol (182)	7-OCH_3 	(Ito and Furukawa, 1989)
Meranzin hydrate (183)	7-OCH_3 	(Raj *et al.*, 1976)
Chloticol (184)	7-OCH_3 	(Ito and Furukawa, 1987a)
7-Methoxy-8-(2'-methoxy -3'-hydroxy-3'-methyl butyl) coumarin (185)	7-OCH_3 	(Manandhar, 1980)
Casegravol (186)	7-OCH_3 	(Ito and Furukawa, 1987a)
Paniculonol isovalerate (187)	7-OCH_3 	(Ito and Furukawa, 1989)
Coumurrin (188)	7-OCH_3 	(Imai, Kinoshita, and Sankawa, 1987)

Murrayatin(189)	7-OCH_3 	(Barik, Dey, and Chatterjee, 1983)
Murralongin(190)	7-OCH_3 	(Talapatra, Dutta, and Talapatra, 1973a)
Isomurralonginol acetate(191)	7-OCH_3 	(Ito and Furukawa, 1987a)
Isomurralonginol nicotinate(192)	7-OCH_3 	(Ito and Furukawa, 1987c)
Isomurranganon senecioate(193)	7-OCH_3 	(Ito and Furukawa, 1987a)
Phebalosin(194)	7-OCH_3 	(Khosa, 1972)
Murpaniculol(195)	7-OCH_3 	(Imai, Kinoshita, and Sankawa, 1987)
Murranganon(195)		(Ito and Furukawa, 1987a)

Murrangatin (196) — 7-OCH3 — (Talapatra, Dutta, and Talapatra, 1973b)

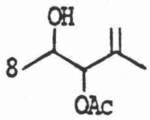


Mupanidin (196) — (Wu, Liou, and Kuoh, 1989)

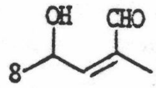
Murpanidin (196) — (Yang and Su, 1983)

Minumicrolin (196) — (Ito and Furukawa, 1987a)

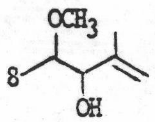
Murrangatin acetate (197) — 7-OCH3 — (Ito and Furukawa, 1987a)



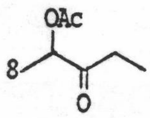
Panial (198) — 7-OCH3 — (Ito and Furukawa, 1987c)



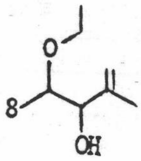
Murracarpin (199) — 7-OCH3 — (Manandhar, 1980) (Wu, Liou, and Kuoh, 1989)



Hainanmurpanin (200) — 7-OCH3 — (Yang and Du, 1984b)

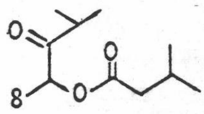


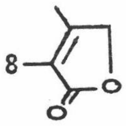
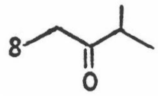
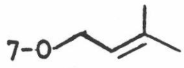
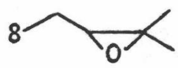
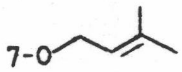
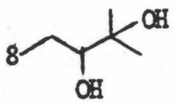
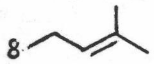
Murpanicin (201) — 7-OCH3 — (Yang and Su, 1983)



Murraxocin (201) — (Barik and Bundu, 1987)

Paniculatin (202) — 7-OCH3 — (Steck, 1972)

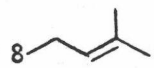


Microminutin(203)	7-OCH_3 	(Tantivatatana *et al.*, 1983)
Anisocoumarin-E(204)	 	(Ngadjui *et al.*, 1989b)
Anisocoumarin-F(205)	 	(Ngadjui *et al.*, 1989b)
Anisocoumarin-G(206)	 	(Ngadjui *et al.*, 1989b)
Sibiricol(207)	5-OH 7-OCH_3 	(Ito and Furukawa, 1987a)
Murrayacarpin-B(208)	5,7-$(OCH_3)_2$ 8-CH_2OH	(Wu, Liou, and Kuoh, 1989)
Seselinal(209)	5,7-$(OCH_3)_2$ 	(Wu, 1988)
Murraculatin(210)	5,7-$(OCH_3)_2$ 	(Wu, 1988)

Gleinene(211) — 5,7-$(OCH_3)_2$ — (Kumar *et al.*, 1987)

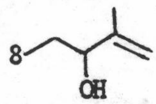
Gleinadiene(212) — 5,7-$(OCH_3)_2$ — (Kumar *et al.*, 1987)

Coumarrayin(213) — 5,7-$(OCH_3)_2$ — (Abe and Taylor, 1971)

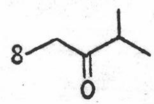


Coumurrayin(213) — (Steck, 1972)

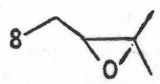
Omphamurin(214) — 5,7-$(OCH_3)_2$ — (Wu, 1981)



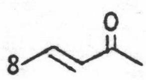
5,7-Dimethoxy-8-(3'-methyl-2'oxobutyl) coumarin(215) — 5,7-$(OCH_3)_2$ — (Wu *et al.*, 1980)



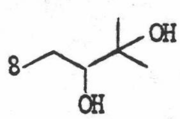
Sibiricin(216) — 5,7-$(OCH_3)_2$ — (Wickramaratne, Kumar, and Balasubramaniam, 1984)



Toddalenone(217) — 5,7-$(OCH_3)_2$ — (Kumar *et al.*, 1987)

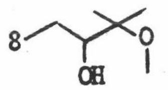


Mexoticin(218) — 5,7-$(OCH_3)_2$ — (Chakraborty, Chowdhury, and Das, 1967)

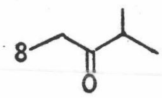


Isomexoticin(218) — (Yang and Du, 1983a)

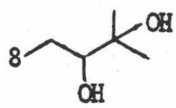
Omphalocarpin(219) $5,7-(OCH_3)_2$ (Wu, Liou, and Kuoh, 1989)



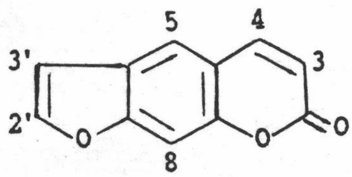
Murrayanone(220) $5,6,7-(OCH_3)_3$ (Wu, 1988)



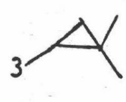
Murragleinin(221) $5,6,7-(OCH_3)_3$ (Wickramaratne, Kumar, and Balasubramaniam, 1984)

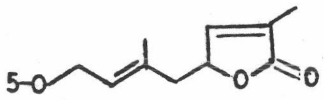


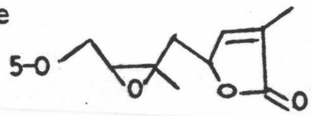
3.3.2 Furanocoumarins



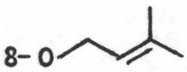
Psoralene type(121)

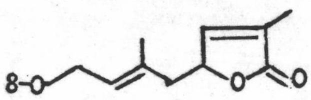
Compound	Substituent	Reference
Chalepensin(222)		(Joshi and Gawad, 1971)
Clausindine(223)		(Joshi, Kamat, and Gawad, 1974)

Anisolactone(224)  (Lakshmi *et al.*, 1984)

2'3'-Epoxyanisolactone (225)  (Lakshmi *et al.*, 1984)

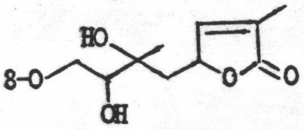
Xanthotoxol(122) 8-OH (Rakash *et al.*, 1978)

Imperatorin(226)  (Govindachari *et al.*, 1968)

Wampetin(227)  (Khan, Naqvi, and Ishratullah, 1983)

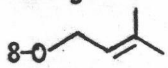
Dehydroindicolactone (227) (Kong *et al.*, 1983)

Indicolactone(227) (Lakshmi *et al.*, 1984)

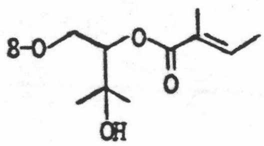
Indicolactonediol (228)  (Rakash *et al.*, 1978)

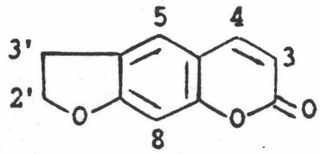
8-Hydroxy-5-methoxypsoralen(229) 5-OCH_3 8-OH (Rakash *et al.*, 1978)

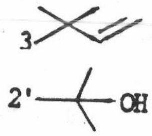
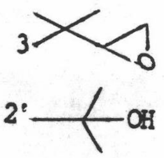
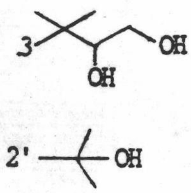
Phellopterin(230) 5-OCH_3 (Joshi and Gawad, 1971)



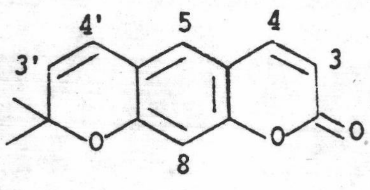
Byakangelicin(231) 5-OCH_3 (Rakash *et al.*, 1978)

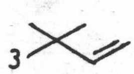




Chalepin(130)		(Joshi and Gawad, 1971)
Heliettin(130)		(Adesina and Ette, 1982)
Anisocoumarin-C (232)		(Ngadjui *et al.*, 1989a)
Anisocoumarin-D (233)		(Ngadjui *et al.*, 1989a)

3.3.3 Pyranocoumarins



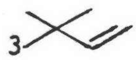
Compound	Substituent	Reference
Xanthyletin(133)	-	(Talapatra, Chaudhuri, and Talapatra, 1975)
3-(1,1-Dimethylallyl) xanthyletin(234)		(Mester, Szendrei, and Reisch, 1977)

Xanthoxyletin (134) 5-OCH_3 (Mester, Szendrei, and Reisch, 1977)

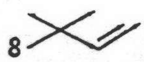
Nordentatin (235) 5-OH (Govindachari *et al.*, 1968)

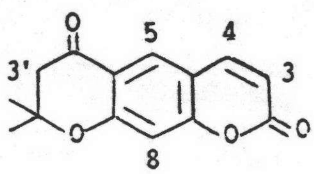
Dentatin (236) 5-OCH_3 (Govindachari *et al.*, 1968)

Clausarin (237) (Anwer *et al.*, 1977)



5-OH

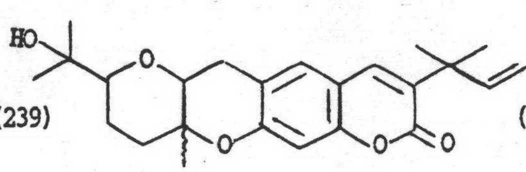




Clausenin (138) 5-OH (Joshi and Kamat, 1966)

Clausenidin (238) 5-OH (Joshi and Kamat, 1966)

Clausmarin (239)



(Shoeb *et al.*, 1978)

Table 24 Distribution of coumarins in Clauseneae

Compound	Botanical origin	Plant part	Reference
Acetyldihydromicromelin-A (165)	*Micromelum minutum*	Stems	(Das *et al.*, 1984)
Angelical (120)	*Glycosmis cyanocarpa* *Micromelum zeylanicum*	Root bark Stems	(Talapatra, Chaudhuri, and Talapatra, 1975) (Bowen and Perera, 1982)
Anisocoumarin-A (166)	*Clausena anisata*	Stem bark and roots	(Ngadjui *et al.*, 1989a)
Anisocoumarin-B (158)	*Clausena anisata*	Stem bark and roots	(Ngadjui *et al.*, 1989a)
Anisocoumarin-C (232)	*Clausena anisata*	Stem bark and roots	(Ngadjui *et al.*, 1989a)
Anisocoumarin-D (233)	*Clausena anisata*	Stem bark and roots	(Ngadjui *et al.*, 1989a)
Anisocoumarin-E (204)	*Clausena anisata*	Leaves	(Ngadjui *et al.*, 1989b)
Anisocoumarin-F (205)	*Clausena anisata*	Leaves	(Ngadjui *et al.*, 1989b)
Anisocoumarin-G (206)	*Clausena anisata*	Leaves	(Ngadjui *et al.*, 1989b)
Anisocoumarin-H (156)	*Clausena anisata*	Leaves	(Ngadjui *et al.*, 1989b)
Anisolactone (224)	*Clausena anisata* *Clausena anisata*	Stem +	(Lakshmi *et al.*, 1984) (Lakshmi *et al.*, 1987)
Auraptenol (178)	*Murraya exotica* *Murraya paniculata* *Murraya exotica*	Leaves Leaves Leaves	(Barik *et al.*, 1983) (Imai, Kinoshita, and Sankawa, 1989) (Bishay *et al.*, 1988)
Byakangelicin (231)	*Clausena indica*	Aerial part	(Rakash *et al.*, 1978)
Capnolactone (157)	*Clausena anisata*	Leaves	(Ngadjui *et al.*, 1989b)
Casegravol (186)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
Chalepensin (222)	*Clausena indica*	Roots	(Joshi and Gawad, 1971)
Chalepin (130)	*Clausena indica* *Clausena anisata* *Clausena anisata*	Roots Roots Root bark	(Joshi and Gawad, 1971) (Okorie, 1975) (Mester, Szendrei, and Reisch, 1977)
Chloticol (184)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
Clausarin (237)	*Clausena pentaphylla* *Clausena excavata* *Clausena harmandiana*	Roots Root bark Root bark	(Anwer *et al.*, 1977) (Wu and Furukawa, 1982) (Wangboonskul, Prawangura, and Chaichantipyuth, 1984)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
Clausenidin(238)	*Clausena heptaphylla*	Roots	(Joshi and Kamat, 1966)
	Clausena heptaphylla	Roots	(Joshi, Kamat, and Saksena, 1967)
	Clausena heptaphylla	Roots	(Joshi *et al.*, 1972)
	Clausena pentaphylla	Roots	(Anwer *et al.*, 1977)
	Clausena excavata	Root bark	(Wu and Furukawa, 1982)
Clausenin(138)	*Clausena heptaphylla*	Roots	(Joshi and Kamat, 1966)
	Clausena heptaphylla	Roots	(Joshi, Kamat, and Saksena, 1967)
	Clausena heptaphylla	Roots	(Joshi *et al.*, 1972)
Clausindin(223)	*Clausena indica*	Roots	(Joshi, Kamat, and Gavad, 1974)
Clausmarin(239)	*Clausena pentaphylla*	+	(Shoeb *et al.*, 1978)
Coumarrayin(213)	*Murraya paniculata*	Foliages	(Dreyer, 1968)
	Clausena anisata	Roots	(Abe and Taylor, 1971)
	Clausena anisata	Roots	(Okorie, 1975)
	Murraya gleinei	Root bark	(Kumar, 1985)
Coumurrayin(213)	*Murraya paniculata*	Foliages	(Steck, 1972)
	Murraya omphalocarpa	Fruits	(Wu *et al.*, 1980)
	Murraya gleinei	Root	(Kumar *et al.*, 1987)
Coumurrin(188)	*Murraya paniculata*	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Dehydroindicolactone(227)	*Clausena lansium*	+	(Kong *et al.*, 1983)
Dehydroosthol(173)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Ito and Furukawa, 1987b)
Dentatin(236)	*Clausena dentata*	Root bark	(Govindachari *et al.*, 1968)
	Clausena heptaphylla	Roots	(Reddy, Ayengar, and Rangaswami, 1973)
	Clausena pentaphylla	Roots	(Anwer *et al.*, 1977)
	Clausena harmandiana	Root bark	(Wangboonskul, Pummangura, and Chaichantipyuth, 1984)
Dihydromicromelin(163)	*Micromelum minutum*	Stems	(Das *et al.*, 1984)
6-(2,3-Dihydroxy-3-methylbutyl)-7-methoxycoumarin(162)	*Micromelum pubescens*	Stems and leaves	(Joshi *et al.*, 1975)
5,7-Dimethoxy-8-(3'-methyl-2'-oxobutyl) coumarin(215)	*Murraya omphalocarpa*	Fruits	(Wu *et al.*, 1980)
	Murraya paniculata	Leaves	(Yang and Su, 1983)
	Murraya paniculata var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
3-(1,1-Dimethylallyl) xanthyletin(234)	*Clausena anisata*	Root bark	(Mester, Szendrei, and Reisch, 1977)
	Clausena willdenovii	Barks	(Subba Rao, Raj, and Kumar, 1981)
	Murraya koenigii	Stem bark	(Bhattacharyya and Chakraborty, 1984)
	Murraya exotica	Stem bark	(Ahmad and Begum, 1986)
2',3'-Epoxyanisolactone (225)	*Clausena anisata*	Stems	(Lakshmi *et al.*, 1984)
Gleinadiene(212)	*Murraya gleinei*	Roots	(Kumar *et al.*, 1987)
Gleinene(211)	*Murraya gleinei*	Roots	(Kumar *et al.*, 1987)
Hainanmurpanin(200)	*Murraya paniculata*	Leaves and branches	(Yang and Du, 1984b)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Heliettin(130)	*Clausena anisata*	Roots	(Adesina and Ette, 1982)
Herniarin(155)	*Murraya gleinei*	Stem bark	(Kumar, 1985)
8-Hydroxy-5-methoxypsoralene(229)	*Clausena indica*	Aerial part	(Rakash *et al.*, 1978)
Imperatorin(226)	*Clausena dentata*	Root bark	(Govindachari *et al.*, 1968)
	Clausena anisata	Roots	(Abe and Taylor, 1971)
	Clausena indica	Roots	(Joshi and Gawad, 1971)
	Clausena anisata	Roots	(Okorie, 1975)
	Murraya paniculata	Leaves	(Ganguly, Ghosh, and Basak, 1977)
	Clausena anisata	Roots	(Adesina and Ette, 1982)
	Clausena anisata	+	(Gebreyesus and Chapya, 1983)
	Clausena anisata	Stems	(Lakshmi *et al.*, 1984)
	Clausena anisata	Leaves	(Ngadjui *et al.*, 1989b)
Indicolactone(227)	*Clausena anisata*	Stems	(Lakshmi *et al.*, 1984)
	Clausena anisata	+	(Lakshmi *et al.*, 1987)
Indicolactonediol(228)	*Clausena indica*	Aerial part	(Rakash *et al.*, 1978)
Isomeranzin(175)	*Murraya paniculata*	Leaves and branches	(Yang and Du, 1984b)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Isomexoticin(218)	*Murraya paniculata*	Leaves	(Yang and Du, 1983a)
Isomurralonginol acetate(191)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
Isomurralonginol nicotinate(192)	*Murraya paniculata*	Leaves	(Ito and Furukawa, 1987c)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
Isomurranganon senecioate(193)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
Limettin(159)	*Glycosmis cyanocarpa*	Root bark	(Talapatra, Chaudhuri, and Talapatra, 1975)
Meranzin(180)	*Murraya gleinei*	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
Meranzin hydrate(183)	*Murraya paniculata*	Leaves	(Raj *et al.*, 1976)
	Murraya exotica	Leaves	(Manandhar, 1980)
	Murraya exotica	Leaves	(Barik *et al.*, 1983)
	Murraya gleinei	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya paniculata	Leaves	(Yang and Du, 1984a)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
7-Methoxy-8-(2'-formyl-2'-methylpropyl) coumarin(170)	*Murraya paniculata*	Leaves and branches	(Yang and Du, 1984b)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
7-Methoxy-8-(2'-methoxy-3'-hydroxy-3'-methylbutyl) coumarin(185)	*Murraya exotica*	Leaves	(Manandhar, 1980)
Mexoticin(218)	*Murraya exotica*	Stem bark	(Chakraborty, Chowdhury, and Das, 1967)
	Murraya omphalocarpa	Fruits	(Wu *et al.*, 1980)
	Murraya gleinei	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya gleinei	Stem bark	(Kumar, 1985)
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
	Murraya paniculata	Root bark	(Imai *et al.*, 1989)
Micromelin(164)	*Micromelum minutum*	Leaves	(Lamberton, Price, and Redcliffe, 1967)
	Micromelum integerrimum	+	(Cassady *et al.*, 1979)
	Micromelum zeylanicum	Leaves	(Bowen and Perera, 1982)
	Micromelum minutum	Stem	(Das *et al.*, 1984)
	Micromelum minutum	Stem bark	(Tantishaiyakul *et al.*, 1986)
	Micromelum integerrimum	Roots	(Kong *et al.*, 1988)
Micromelumin(164)	*Micromelum pubescens*	Stem bark	(Chatterjee, Dutta, and Bhattacharyya, 1967)
Microminutin(203)	*Micromelum minutum*	Leaves	(Tantivatana *et al.*, 1983)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
Micropubescin(174)	*Micromelum pubescens*	Stem bark	(Chatterjee, Dutta, and Bhattacharyya, 1967)
Minumicrolin(196)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
Mupanidin(196)	*Murraya paniculata* var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Murpanicin(201)	*Murraya paniculata*	Leaves	(Yang and Su, 1983)
	Murraya paniculata	Leaves and branches	(Yang and Du, 1984b)
Murpaniculol(195)	*Murraya paniculata*	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murpanidin(196)	*Murraya paniculata*	Leaves	(Yang and Su, 1983)
	Murraya paniculata	Leaves	(Yang and Du, 1984a)
	Murraya gleinei	Root bark	(Kumar, 1985)
Murracarpin(199)	*Murraya exotica*	Leaves	(Manandhar, 1980)
	Murraya paniculata var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Murraculatin(210)	*Murraya paniculata* var. *omphalocarpa*	Leaves	(Wu, 1988)
Murragatin(196)	*Murraya paniculata*	Leaves	(Yang and Su, 1983)
	Murraya paniculata	Leaves	(Yang and Du, 1984)
Murragleinine(221)	*Murraya gleinei*	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
Murralongin(190)	*Murraya elongata*	Leaves	(Talapatra, Dutta, and Talapatra, 1973a)
	Murraya paniculata	Leaves	(Raj *et al.*, 1976)
	Murraya paniculata	Leaves	(Yang and Su, 1983)
	Micromelum minutum	Stems	(Das *et al.*, 1984)
	Murraya gleinei	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya gleinei	Stem bark	(Kumar, 1985)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
	Murraya paniculata	Root bark	(Imai *et al.*, 1989)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
	Murraya paniculata	Root bark	(Kinoshita *et al.*, 1989)
Murranganon(195)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
Murrangatin(196)	*Murraya elongata*	Leaves	(Talapatra, Dutta, and Talapatra, 1973)
	Murraya paniculata	Leaves	(Raj *et al.*, 1976)
	Murraya exotica	Leaves	(Barik *et al.*, 1983)
	Micromelum minutum	Stems	(Das *et al.*, 1984)
	Murraya gleinei	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya gleinei	Stem bark	(Kumar, 1985)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
	Murraya paniculata	Root bark	(Imai *et al.*, 1989)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murrangatin acetate (197)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murraol(181)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Ito and Furukawa, 1987b
Murraxocin(201)	*Murraya exotica*	Leaves	(Barik and Bundu, 1987)
Murrayacarpin-A(169)	*Murraya paniculata* var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Murrayacarpin-B(208)	*Murraya paniculata* var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Murrayanone(220)	*Murraya paniculata* var. *omphalocarpa*	Leaves	(Wu, 1988)
Murrayatin(189)	*Murraya exotica*	Leaves	(Barik, Dey, and Chatterjee, 1983)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Murrayone(176)	*Murraya exotica*	Leaves	(Lakshmi, Ratnam, and Subba Rao, 1972)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya gleinei	Roots	(Kumar *et al* ., 1987)
Nordentatin(235)	*Clausena dentata*	Root bark	(Govindachari *et al.*, 1968)
	Clausena excavata	Root bark	(Wu and Furukawa, 1982)
	Clausena harmandiana	Root bark	(Wangboonskul, Pummangura, and Chaichantipyuth, 1984)
Omphalocarpin(219)	*Murraya paniculata* var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Omphamurin(214)	*Murraya omphalocarpa*	Leaves	(Wu, 1981)
	Murraya gleinei	Root bark	(Kumar, 1985)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
Osthenon(177)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Ito and Furukawa, 1987c)
Osthol(172)	*Murraya paniculata*	Foliages	(Steck, 1972)
	Clausena anisata	Roots	(Okorie, 1975)
	Clausena anisata	Root bark	(Mester, Szendrei, and Reisch, 1977)
	Micromelum minutum	Stems	(Das *et al.*, 1984)
	Clausena harmandiana	Root bark	(Wangboonskul, Pummangura, and Chaichantipyuth, 1984)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
	Murraya paniculata	Root bark	(Kinoshita *et al.*, 1989)
	Murraya exotica	Leaves	(Bishay *et al.*, 1988)
Panial(198)	*Murraya paniculata*	Leaves	(Ito and Furukawa, 1987c)
Paniculal(168)	*Murraya paniculata*	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
Paniculatin(202)	*Murraya paniculata*	Foliages	(Steck, 1972)
	Murraya paniculata var. *omphalocarpa*	Leaves	(Wu, 1988)
Paniculin(171)	*Murraya paniculata*	Leaves	(Imai, Kinoshita, and Sankawa, 1987)
	Murraya paniculata	Leaves	(Imai, Kinoshita, and Sankawa, 1989)
Paniculol isovalerate (187)	*Murraya paniculata*	Leaves	(Ito and Furukawa, 1989)
Peroxyauraptenol(179)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Leaves	(Ito and Furukawa, 1987b)
Peroxymurraol(182)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1989)
Phebalosin(194)	*Murraya paniculata*	Leaves	(Khosa, 1972)
	Murraya gleinei	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya gleinei	Stem bark	(Kumar, 1985)
	Micromelum minutum	Stem bark	(Tantishaiyakul *et al.*, 1986)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
	Micromelum integerrimum	Roots	(Kong *et al.*, 1988)
Phellopterin(230)	*Clausena indica*	Roots	(Joshi and Gawad, 1971)

Table 24 (Continue)

Compound	Botanical origin	Plant part	Reference
Scopoletin(160)	*Murraya paniculata*	Flowers and fruits	(Wu *et al.*, 1975)
	Micromelum integerrimum	+	(Cassady *et al.*, 1979)
	Murraya gleinei	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
	Murraya paniculata	Root bark	(Imai *et al.*, 1989)
	Murraya paniculata var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Scopolin(167)	*Murraya koenigii*	Leaves	(Gupta and Nigam, 1971)
	Murraya paniculata	Flowers and fruits	(Wu *et al.*, 1975)
	Murraya paniculata var. *omphalocarpa*	Flowers	(Wu, Liou, and Kuoh, 1989)
Seselinal(209)	*Murraya paniculata* var. *omphalocarpa*	Leaves	(Wu, 1988)
Sibiricin(216)	*Murraya gleinei*	Leaves	(Wickramaratne, Kumar, and Balasubramaniam, 1984)
	Murraya gleinei	Leaves	(Kumar, 1985)
	Murraya gleinei	Root bark	(Kumar, 1985)
	Murraya gleinei	Stem bark	(Kumar, 1985)
	Murraya gleinei	Roots	(Kumar *et al.*, 1987)
	Murraya paniculata	Root bark	(Imai *et al.*, 1989)
Sibiricol(207)	*Murraya exotica*	Leaves	(Ito and Furukawa, 1987a)
Suberosin(161)	*Clausena indica*	Aerial part	(Rakash *et al.*, 1978)
Toddalenone(217)	*Murraya gleinei*	Roots	(Kumar *et al.*, 1987)
Umbelliferone(119)	*Micromelum ceylanicum*	Leaves	(De Silva *et al.*, 1983)
	Murraya exotica	Leaves	(Ito and Furukawa, 1987a)
Wampetin(227)	*Clausena wampi*	Root bark	(Khan, Naqvi, and Ishratullah, 1983)
Xanthotoxol(122)	*Clausena indica*	Aerial part	(Rakash *et al.*, 1978)
	Clausena anisata	Stem	(Lakshmi *et al.*, 1984)
	Clausena anisata	+	(Lakshmi *et al.*, 1987)
Xanthoxyletin(134)	*Clausena anisata*	Root bark	(Mester, Szendrei, and Reisch, 1977)
	Clausena excavata	Root bark	(Wu and Furukawa, 1982)
	Clausena anisata	+	(Gebreyesus and Chapya, 1983)
	Clausena harmandiana	Root bark	(Wangboonskul, Pummangura, and Chaichantipyuth, 1984)
Xanthyletin(133)	*Glycosmis cyanocarpa*	Root bark	(Talapatra, Chaudhuri, and Talapatra, 1975)