CHAPTER II

HISTORICAL

1.Chemical Constituents of Asclepiadaceae

Plants in the Asclepiadaceae are found to contain a wide range of chemical constituents: steroids, triterpenoids, alkaloids, flavonoids and miscellaneous compounds. The main groups are pregnane steroids, cardenolides and phenanthroindolizidine alkaloids.

List of compounds found in various species of the family Asclepiadaceae is shown in Table 2.1.

Table 2.1 Chemical constituents of Asclepiadaceae

Botanical Origin	Plant Part	Chemical Substance	Category	Reference
1. *Antitoxicum*				
Antitoxicum funebre	unclassified part	antofine	alkaloid	Platonova, Kuzovkov, and Massagetov, 1958
	"	2 unidentified alkaloids	"	"
	"	antoside[3(7)-*O*-glucosyl-7 (3)-rhamnosylquercetin]	flavonoid (glycoside)	Utkin, and Serebryakova, 1966
Antitoxicum sibiricum	unclassified part	2 alkaloids	alkaloid	Blinova, Mitroshina, and Shatokhina, 1968

Antitoxicum sibiricum	unclassified part	five coumarins	coumarin	"
		four flavonoids	flavonoid	"
2. *Araujia*				
Araujia sericifera	leaf, fruit & stem	serotonin	amine	Federici, Galeffi,and Nicoletti, 1988
	leaf & stem	7-*O*-β-*D*-glucoluteolin	miscellaneous	"
3. *Asclepias*				
Asclepias amplexicaulis	root	amplexoside A	steroid	Piatak *et al.*, 1985
	"	amplexoside B	"	"
	"	amplexoside C	"	"
Asclepias asperula subsp. *capricornu*	aerial part	coroglaucigenin	cardenolide	Martin *et al.*, 1991
	"	5,6-dehydrocalotropin	"	"
	"	5,6-dehydrouscharidin	"	"
	"	desglucouzarin	"	"
	"	6'-*O*-(*E*-4-hydroxycinna-moyl)-desglucouzarin	"	"
Asclepias cordifolia	leaf & latex	calactin	cardenolide	Seiber, Nelson, and Lee, 1982
	"	calotoxin	"	"
	"	calotropagenin	"	"
	"	calotropin	"	"
	"	uscharidin	"	"
	"	uscharin	"	"
Asclepias cornuti	seed	linoleic	fatty acid	Krivenchuk, 1957
	"	linolenic	"	"
	"	oleic	"	"
	"	palmitic	"	"

Asclepias curassavica	leaf	asclepogenin	cardenolide	Tschesche, Forstmann, and Rao, 1958
	"	ascurogenin	"	"
	"	clepogenin	"	"
	"	coroglaucigenin	"	"
	"	corotoxigenin	"	"
	"	curassavogenin	"	"
	"	uzarigenin	"	"
	unclassified part	curassavicin	"	Lo et al., 1964
	leaf	asclepin	"	Singh, and Rastogi, 1969
	"	calotropin	"	"
	"	uzarin	"	"
	leaf & latex	calactin	"	1.Singh, and Rastogi, 1969, 2.Seiber *et al* , 1982
	"	calotropagenin	"	"
	"	calotoxin	"	Seiber *et al.*, 1982
	"	uscharin	"	"
	leaf, latex & aerial part	uscharidin	"	1.Seiber *et al.*, 1982; 2.Groeneveld *et al.*, 1990
	latex & aerial part	voruscharin	"	"
Asclepias eriocarpa	ground part	eriocarpin	cardenolide	Seiber, Roeske, and Benson, 1978
	leaf, latex & ground part	labriformidin	"	Seiber *et al.*, 1978
	"	labriformin	"	Seiber *et al.*, 1982
	leaf & latex	desglucosyrioside	"	"

Asclepias fruticosa (*Gomphocarpus fruticosus*)	aerial part	afroside	cardenolide	1.Watson, 1966; 2.Cheung, Nelson, and Watson, 1988
	"	gomphoside	"	"
	"	3'-epi-afroside	"	Cheung *et al.*, 1988
	"	3'-epi-afroside-3'-acetate	"	"
	"	3'-didehydroafroside	"	"
	"	asclepin	"	"
	"	calactin	"	"
	"	3'-didehydrogomphoside	"	"
	"	3'-epi-gomphoside	"	"
	"	3'-epi-gomphoside-3'-4'β-hydroxygomphoside	"	"
	"	uscharidin	"	"
	"	uscharin	"	"
	"	19-deoxyuscharin	"	"
Asclepias glaucescens	latex & aerial part	labriformin	cardenolide	Fonseca *et al.*, 1991
	"	taraxasterol	triterpenoid	"
	"	ω-taraxasterol acetates	"	"
Asclepias glaucophylla	root	β-anhydrouszarigenin	cardenolide	Nasciments *et al.*, 1964_b
	"	ascleposide (6-deoxy-α-*D*-alloside of uzarigenin)	"	"
	"	coroglaucigenin	"	"
	"	linelone	"	"
	"	sarcostin	"	"
	"	uzarigenin	"	"
	"	digitalose	sugar	"
	"	digitoxose	"	"
	"	glucose	"	"

Asclepias glaucophylla	root	thevetose	sugar	"
	"	new butenolide mp. 251 - 253°C	butenolide	Nasciments *et al.*, 1996[4a]
	"	new butenolide mp. 275 - 282°C	"	"
Asclepias incarnata	leaf	C_{23}-C_{33} alkanes	alkane	Piatak & Eichmeier, 1972
Asclepias labriformis	aerial part	eriocarpin	cardenolide	Seiber *et al.*, 1978
	"	labriformidin	"	"
	"	labriformin	"	"
Asclepias lanuginosa	leaf	C_{23}-C_{33} alkanes	alkane	Piatak & Eichmeier, 1972
Asclepias latifolia	aerial part	β-amyrin acetate	triterpenoid	Doninguez, and Torres, 1972
	"	β-amyrin benzoate	"	"
	"	β-sitosterol acetate	sterol	"
Asclepias lilacina	root	campesterol	sterol	Sawlewicz, Weiss, and Reichstein, 1967[a]
	"	β-sitosterol	"	"
	"	stigmasterol	"	"
	"	*p*-hydroxyacetophenone	Miscellaneous	"
	"	lilacinoside-α	cardenolide	"
	"	uzarigenin	"	"

Asclepias lilacina	unclassified part	asclepobiose	sugar	Sawlewicz, Weiss, and Reichstein, 1967b
	"	cymarose	sugar	"
	"	lilacinoside-3	cardenolide	"
	"	genin B, C, D	"	"
	rhizome	drebyssobiose	sugar	Allgeier, 1968
	"	viminose	"	"
Asclepias linaria	aerial part	calactin	cardenolide	Rodriguez-Hahn, and Fonseca, 1991
	"	calotoxin	"	"
	"	6'-*p*-coumaroyl-desglucouzarin	"	"
	"	desglucouzarin	"	"
	"	gomphoside	"	"
	"	proceroside	"	"
	"	oleanolic acid	fatty acid	Dominguez, 1974
	"	sitosterol	sterol	"
	"	Ψ-taraxasteryl acetate	triterpenoid	"
	"	triacontane	alkane	"
Asclepias mellodora	unclassified part	uzarigenin	cardenolide	Petricic, 1967
Asclepias ruthiae	seed	uzarin	cardenolide	Sady, and Seiber, 1991
Asclepias speciosa	leaf	desglucosyrioside	cardenolide	Seiber *et al.*, 1982
	aerial part	aspecioside (7β, 8β-epoxy cardenolide glycoside)	"	Cheung, and Watson, 1986
	"	syriobioside	"	"

Asclepias subulata	aerial part	calactin	cardenolide	Jolad *et al.*, 1986
	"	calotropin	"	"
	"	coroglaucigenin 3β-*D*-glucoside	"	"
	"	corotoxigenin 3β-*D*-glucoside	"	"
	"	frugoside 4' β-*D*-glucoside	"	"
	"	3β-(β-*D*-glucopyranosyl-oxy)-19-carboxy-14β-hydroxycard20(22)enolide	"	"
	"	16α-hydroxycalactin	"	"
	"	uzarigenin 3β-*D*-glucoside	"	"
	"	uscharidin	"	"
	"	uscharin	"	"
	"	4(β-*D*-glucopyranosyloxy) -larciresinol	lignan (glycoside)	"
	"	lupeol	triterpenoid	"
Asclepias syriaca	unclassified part seed	hemicellulose	miscellaneous	Barth, 1958
		11,12-dihydroxystearic acid	fatty acid	Chisholm, and Hopkins, 1960
	"	9,12-hexadecadienoic acid	"	"
	"	9-hexadecenoic acid	"	"
	"	linoleic acid	"	"
	"	linolenic acid	"	"
	"	*cis*-11-octadecenoic acid	"	"
	"	oleic acid	"	"
	"	palmitic acid	"	"
	"	stearic acid	"	"
	unclassified part	resin	miscellaneous	Gomez *et al*, 1960
	"	rubber hydrocarbon	"	"
	"	desglucouzarin	cardenolide	Baver *et al.*, 1961

Asclepias syriaca	unclassified part	uzarigenin	cardenolide	Baver *et al.*, 1961
	root & leaf	nicotine	alkaloid	Kowalewski, and Drost, 1966
	"	unidentified pyridine alkaloid	"	"
	root	syriobiside	cardenolide	Petricic, 1967
	"	syriogenin glycosides	"	"
	"	syrioside	"	"
	"	uzarigenin-*D*-glucoside	"	"
	leaf	isorhamnetin	flavonoid	Gonnet, Kozjek, and Favre-Bonvin, 1973
	"	kaempferol	"	"
	"	3,5,3',4' tetrahydroxy-	"	"
	"	7,8-(2",2"-dimethyl-4"-methyl-5",6")pyranoflavone		"
	aerial part	aspeciside	cardenolide	Cheung, and Watson, 1986
	"	syriobioside	"	"
	latex	lysozyme	miscellaneous	Lynn, 1989
Asclepias tuberosa	root	glucofrugoside	cardenolide	Petricic, 1966
	unclassified part	uzarigenin	"	Petricic, 1967
	"	coroglaucigenin	"	"
Asclepias verticillata	leaf	C_{23}-C_{33} alkanes	alkane	Piatak & Eichmeier, 1972
Asclepias vestita subsp. *parishii*	leaf & latex	calactin	cardenolide	Seiber *et al.*, 1982
	"	calotropagenin	"	"
	"	calotropin	"	"

Asclepias vestita subsp. *parishii*	leaf & latex	calotoxin	cardenolide	Seiber *et al.*, 1982
	"	uscharidin	"	"
	"	calactin	"	"
	"	calotropagenin	"	"
	"	calotropin	"	"
	"	calotoxin	"	"
	"	uscharidin	"	"
	"	uscharin	"	"
Asclepias viridiflora	leaf	C_{23}-C_{33} alkanes	alkane	Piatak & Eichmeier, 1972
Asclepias viridis	aerial part	5,6-dehydroasclepin	cardenolide	Martin et al., 1991
Asclepias viridis	"	5,6-dehydrouscharidin	"	"
4. *Boucerosia*				
Boucerosia aucheriana	whole plant	boucerin	steroid	Nikaido, Shimizu, and Mitsuhashi, 1967
	"	dihydroboucerin	"	"
	aerial part	12-*O*-benzoyl-20-*O*-acetyl-boucerin	"	Hayashi et al., 1988
	"	12-*O*-benzoyl-20-*O*-acetyl--dihydroboucerin	"	"
	"	12-*O*-benzoyl-boucerin	"	"
	"	12-*O*-benzoyl-dihydro-boucerin	"	"
	"	boucerosides AI	"	"
	"	boucerosides AII	"	"
	"	boucerosides BI	"	"
	"	boucerosides BII	"	"

Boucerosia aucheriana	aerial part	bouceroides ANC	steroid	Tanaka, Tsukamoto, and Hayashi, 1990
	"	bouceroides ADC	"	"
	"	bouceroides ANO	"	"
	"	bouceroides ADO	"	"
	"	bouceroides BNO	"	"
	"	bouceroides BDO	"	"
	"	bouceroides BNC	"	"
	"	bouceroides BDC	"	"
	"	bouceroides CNO	"	"
	"	bouceroides CNC	"	"
5. *Calotropis*				
Calotropis gigantea	flower & seed	hyperoside	flavonoid (glycoside)	Subramanian, and Nair, 1968_a
	"	quercetin	flavonoid	"
	flower	kaempferol	flavonoid (glycoside)	"
	"	rutin	flavonoid	"
	root bark	α-amyrin benzoate	titerpenoid	Anjansyula, and Row, 1968
	"	β-amyrin benzoate	"	"
	"	ψ-taraxasterol benzoate	"	"
	root bark&latex	α-amyrin	"	1 Anjansyula& Row, 1968 2 Thakur *et al.*, 1984
	"	β-amyrin	"	"
	"	ψ-taraxasterol	"	"
	"	ψ-taraxasterol acetate	"	"
	latex	3'-methylbutanoate of ψ-taraxasterol	"	Thakur *et al.*, 1984
	"	lupeol	"	"
	"	lupeol acetate	"	"

Calotropis gigantea	latex	3'-methylbutanoate of lupeol	triterpenoid	Thakur *et al.*, 1984
	"	24-methylenecyclo artanol	"	"
	root & latex	α-amyrin acetate	"	1.Thakur *et al.*, 1984 2.Kitagawa *et al.*, 1992
	"	β-amyrin acetate	"	"
	"	α-amyrin-methylbutanoate	"	"
	"	β-amyrin-methylbutanoate	"	"
	root	calotroposide A-G	steroid	Kitagawa *et al.*, 1992
	"	frugoside	"	"
	"	4'-β-*D*-glucofrugoside	"	"
Calotropis procera	root bark	benzoylisolineolone	steroid	Chandler, Coombe, and Watson, 1968
	"	benzoyllineolone	"	"
	"	isolineolone	"	"
	"	lineolone	"	"
	leaf	α-amyrin	triterpenoid	Saber, and Mahran, 1968
	"	β-amyrin	"	"
	"	β-sitosterol	sterol	"
	leaf & latex	calactin	cardenolide	Seiber *et al.*, 1982
	"	calotropagenin	"	"
	"	calotropin	"	"
	"	calotoxin	"	"
	"	uscharidin	"	"
	"	uscharin	"	"
	latex	voruscharin	thiazolidine derivative	Seiber *et al.*, 1982

Calotropis procera	flower	calotropenyl acetate	triterpenoid	Khan *et al.*, 1988
	"	procesterol	sterol	Khan, and Malik, 1989
6. *Caralluma*				
Caralluma buchardii	whole plant	guimarenol	triterpenoid	Castro *et al.*, 1980
	"	lupenone	"	"
	"	lupeol	"	"
	"	lupeol acetate	"	"
	"	3,4-seco-lup20(29)-en-3-oic-acid methyl ester	"	"
	"	sitosterol	sterol	"
	"	sitosterol acetate	"	"
Caralluma tuberculata (*Boucerosia aucheriana*)	whole plant	caratubersides A	steroid	Admad, Usmanghani, and Rizwani, 1988
	"	caratubersides B	"	"
	"	boucerin	"	"
	"	dihydroboucerin	"	"
7. *Ceropegia*				
Ceropegia juncea	whole plant	cerpegin	alkaloid	Adibatti *et al.*, 1991
	"	lupeol	triterpenoid	"
Ceropegia woodii	leaf	hexacosane	alkane	Salgues, 1958
8. *Chlorocodon*				
Chlorocodon sp.	root	*p*-methoxysalicylaldehyde	miscellaneous	Mascre, and Paris, 1947
	root & seed	unidentified alkaloids	alkaloid	"
Chlorocodon whiteii	root	*p*-methoxysalicylaldehyde	miscellaneous	Gailly, 1947

9. Cryptolepis				
Cryptolepis buchanani	stem	buchananine	alkaloid	Dutta, Sharma B.N., and Sharma P.V., 1978
Cryptolepis buchanani	"	1,3,6-*O*-trinicotinoyl-α-*D*-glucopyranose	" (glycoside)	Dutta, Sharma B.N., and Sharma P.V., 1980
	root	sarmentocymarin	cardenolide	Shah, and Khare, 1981
	"	sarmentogenin	"	"
	"	buchanin	"	Khare, and Shan, 1983
	"	cryptanoside C-D	"	Purushothaman *et al.*, 1988
	"	germanicol doconosate	Miscellaneous	"
	leaf	cryptanoside A-B	cardenolide	"
	"	cryptosin	"	Venkateswara *et al.*, 1989
Cryptolepis sanguinolenta	leaf	cryptosine	alkaloid	Raymond-Hamlet,1937
	root	cryptolepine	"	Gellert, Raymond-Hamet, and Schlittler, 1951
	"	quinaline	"	Dwuma-Badu *et al.*, 1978
10. *Cryptostegia*				
Cryptostegia grandiflora	leaf & stem	cryptograndoside A	cardenolide	Aebi, and Reichstein, 1950
	"	cryptograndoside B	"	"
	leaf	cryptograndoside C	"	"

Cryptostegia grandiflora	leaf	16-desacetylanhydro cryptograndoside A	cardenolide	"
	"	16-desacetylanhydro cryptograndoside B	"	"
	leaf & stem	16-anhydrogitoxigenin	"	Doskotch*et al.*, 1972
	"	gitoxigenin	"	"
	"	oleandrigenin	"	"
	"	oleandrigenin-3-rhamnoside	"	"
	"	propionylgitoxigenin	"	"
Cryptostegia madagascariensis	leaf & stem	16-anhydrogitoxigenin	cardenolide	Sanduja *et al.*, 1984
	"	16-anhydrogitoxigenin-3 -rhamnoside	"	"
	"	digitoxigenin	"	"
	"	14,16-dianhydrogitoxi-genin-3-rhamnoside	"	"
	"	oleandrigenin	"	"
	"	16-propionylgitoxigenin -3-rhamnoside	"	"
	"	3β-hydroxyurs-12-en-28-oic acid	triterpenoid	Douis *et al.*, 1985
	"	lup-20(29)-en-3β-ol	"	"
	"	lup-20(29)-en-3-one	"	"
	"	β-sitosterol	sterol	"
11. *Cynanchum*				
Cynanchum africanum	unclassified part	methyl-α-cymaropyranose	miscellaneous	Tsukamoto *et al.*, 1986$_b$
	"	methyl-β-cymaropyranose	"	"
	"	cynafogenin	cardenolide	Tsukamoto *et al.*, 1986$_a$

Cynanchum africanum	leaf & stem	cynafoside A-D	cardenolide	Tsukamoto, Hayashi, and Kaheko, 1988
Cynanchum atratum	root	14,15-seco-pregnanes	steroid	Zhang *et al.*, 1988
	root & rootstock	atratosides A-D	cardenolide	1.Zhang *et al.*, 1988 2.Tang & Eisenbrand, 1992
	rootstock	atrotogenin A-B	"	Tang & Eisenbrand, 1992
	"	cynajapogenin A	"	"
	"	cynatratosides A-F	"	"
	"	glaucogenin A,C,H	"	"
Cynanchum boerhavifolium	aerial part	β-amyrin	triterpenoid	Mitsuhashi, and Mizuta, 1969
	"	benzoylisolineolone	steroid	"
	"	isolineolone	"	"
	"	isoramanone	"	"
	"	lineolone	"	"
Cynanchum caudatum	root	cynanchogenin	cardenolide	Mitsuhashi, and Shimizu, 1959
	"	cynanchotoxin	"	Mitsuhashi, and Shimizu, 1960
	"	*D*-cymarose	Sugar	"
	"	lupeol acetate	triterpenoid	"
	"	β-sitosterol	sterol	"
	tuberous root	penupogenin	cardenolide	Mitsuhashi *et al.*, 1962

Cynanchum caudatum	leaf & stem	deacetylcynanchogenin	cardenolide	Mitsuhashi *et al.*, 1962
	"	sarcostin	"	"
	unclassified part	deacylmetaplexigenin	"	Yamagishi, and Mitsuhashi, 1972_a
	"	isolineolon	"	"
	"	lineolon	"	"
	rhizome	caudatin	"	Yamagishi, and Mitsuhashi, 1972_b
	"	ikemagenin	"	"
	"	isoikemagenin	"	"
	"	glycocynanchogenin	"	Yamagishi *et al* 1972
Cynanchum japonicum	leaf	cynajaponin	cardenolide	Hayashi *et al.*, 1986
Cynanchum glaucescens	rhizome	glaucogenin A-C	cardenolide	Tang & Eisenbrand, 1992
	"	glaucogeninC-3-*O*-β-*D*-thevetopyranoside	"	"
	"	glaucoside A-I	"	"
Cynanchum haneockianum	aerial part	antofine	alkaloid	Li, Peng, and Ohda, 1989
	"	de-6-*O*-methyl antofine	"	"
	leaf	hancokinol	triterpenoid	Takayanaki, *et al.*, 1991
	"	hancolupenol	"	"
	"	hancolupenone	"	"
	root	glaucogenin A,C	cardenolide	Konda *et al.*, 1992

Cynanchum haneockianum	root	hancopregnane	steroid	Konda *et al.*, 1992
	"	1-*p*-menthene-8,9-diol	monoterpene	"
	"	*p*-menthane-1,7,8-triol	"	"
	"	*p*-menthene-1,8,9-triol	"	"
	"	2-acetylphenol-1-β-*D*-glucopyranosyl-(1->6)-β-*D*-xylpyranoside	glycoside	Lou *et al.*, 1993
	"	β-*D*-fructofuranosyl-α-*D*-(6-*O*-*E*-sinapoylgluco pyranoside)	"	"
	"	6-*O*-[*E*]-sinapoyl-(α-and β)-*D*-glucopyranoside	"	"
Cynanchum otophyllum	root	caudatin	steroid (ester)	Tang & Eisenbrand, 1992
	"	otophylloside A-B	steroid	"
	"	qingyangshengenin	steroid (ester)	"
	"	rostratamine	"	"
	"	β-sitosterol	sterol	"
	"	methyl palmitate	miscellaneous	"
	"	vanillic acid	"	"
	"	digitoxose	sugar	"
Cynanchum paniculatum	whole plant	cynapanosides A-C	cardenolide	Sugama *et al.*, 1986
	"	cynatratoside B	"	"
	"	glaucogenin B,D	"	"
	"	3β,14-dihydroxy-14β-pregn-5-en-20-one	steroid	"
	root	neocynapanoside A	cardenolide	Sugama, and Hayashi, 1988

Cynanchum sibirium	unclassified part	cinnamoyl ester of sarcostin	cardenolide	Maslennikova, Tursunova, and Abukakirov, 1969
Cynanchum sibirium	unclassified part	cinnamoyl ester of sibicoside	"	"
	"	sibirigenin	"	"
Cynanchum versicolor	root	cynaversicoside A-E	steroid	1.Qiu, Zhang, and Zhou, 1989 2.Qui *et al.*, 1991
	"	glaucogenin C-D	cardenolide	"
Cynanchum vincetoxicum	unclassified part	vincetoxin	cardenolide (glycoside)	Mitsuhashi, and Shimizu, 1960
	root	chlorogenic acid	miscellaneous	Haznagy, and Toth, 1967
	"	sinaptic acid	"	"
	"	6,7,-(trimethoxy)-9,10-dehydro-9,10-phenanthroindolizidin	alkaloid	Haznagy, and Toth, and Szendrei, 1967
	aerial part	tylophorine	"	Wiegrebe *et al.*, 1969
	"	alkaloid II	"	"
	"	alkaloid III	"	"
	"	α-amyrin	triterpenoid	Toth, Haznagy, and Makay, 1969
	"	friedelin	"	"
	"	sitosterol	sterol	"
	root	2,4-dihydroxyacetophenone	miscellaneous	"
	"	3-methoxy and 4-hydroxyacetophenone	"	"
	leaf	antofine	alkaloid	Li *et al.*, 1989

Cynanchum vincetoxicum	leaf	de-6-*O*-methylantofine	alkaloid	Li *et al.*, 1989
Cynanchum wallichii	root	caudatin	cardenolide	Tang, Eisenbrand, 1992
	"	deacetylmetaplexigenin	"	"
	"	gagaminine	"	"
	"	qingyangshengenin	"	"
	"	rostratamine	"	"
	"	wallicoside	"	"
Cynanchum wilfordi	leaf	cynanchogenin	steroid	Mitsuhashi, and Shimizu, 1962
	"	caudatin	"	Hayashi, and Mitsuhashi, 1972
	"	deacylmetaplexigenin	"	"
	"	kidjolanin	"	"
	"	lineolon	"	"
	"	penupogenin	"	"
	"	sarcostin	"	"
	"	wilforine	"	"
	"	glaucobiose	sugar	Hayashi *et al.*, 1983
	"	wilfoside	cardenolide	Tsukamoto *et al.*, 1988
12. *Daemia*				
Daemia extensa (*Pergularia extensa*)	stem	hyperoside	flavonoid (glycoside)	Subramanian, and Nair, 1968a
	"	kaempferol	"	"
	"	quercetin	"	"
	root	α-amyrin	triterpenoid	Seshadri, and Vydeeswaran, 1971

Daemia extensa	root	α-amyrin acetate	triterpenoid	Seshadri, and Vydeeswaran, 1971
	"	lupeol	"	"
	"	lupeol acetate	"	"
	"	β-sitosterol	sterol	"
	"	β-sitosterol-β-D-glucopyranoside	"	"
	"	calactin	cardenolide	"
	"	calotropin	"	"
	"	coroglaucigenin	"	"
	"	uzarigenin	"	"
13. ***Decalepis***				
Decalepis hamiltonii	root	4-methoxyresorcylaldehyde	miscellaneous	1. Roa, and Iyengar, 1923 2.Murti, and Seshadri, 1941$_a$
	"	inositol	triterpenoid	Murti and Seshadri,1941$_b$
	"	α-amyrin	"	Murti and Seshadri, 1941$_c$
	"	β-amyrin	"	"
	"	β-amyrin acetate	"	"
	"	lupeol	"	"
14. ***Dregea***				
Dregea lanceolata (*Marsdenia lanceolata*)	root	α-amyrin acetate	triterpenoid	Krishna *et al.*, 1990$_a$
	"	β-amyrin	"	"
	"	β-sitosterol	sterol	"
	"	ceolin	steroid	"
	"	drelin	"	"
	"	dregealin	"	Krishna *et al.*, 1990$_b$

Dregea lanceolata	root	dregenin	steroid	Krishna *et al.*, 1990b
Dregea sinensis var. *corrugata*	rhizome	dregeoside A-C	steroid	Jin, Zhou, and Mu, 1989
	"	12-*O*-benzoyl-drevogenin-3-*O*-β-*D*-oleandropyranosyl-(1->4)- -*O*-β-*D*-cymaro-pyranosyl-(1->4)--*O*-β-*D*-cymaropyranoside	"	"
	"	drevogenin	cardenolide	"
Dregea volubilis	leaf	drevoside A	cardenolide	Mitsuhashi, and Shimizu, 1960
	seed	drevogenin A,B,D,P	"	Hayashi, Kakao, and Mitsuhashi, 1969
	stem	dregoside A	"	"
	"	drebyssogenin G	"	"
	"	isodrevogenin P	"	"
	leaf	dregeatriose	sugar	Hayashi *et al.*, 1983
15. ***Finlaysonia***				
Finlaysonia obovata	leaf	α-amyrin acetate	triterpenoid	Pradhan, and Mukhopadhyay, 1985
	"	β-amyrin acetate	"	"
	bark	lupeol acetate	"	"
	leaf & bark	ursolic acid	"	"
	"	β-sitosterol	sterol	"
	leaf	stigmasterol	"	"

16. *Glossostelma*				
Glossostelma carsoni	unclassified part	β-amyrin	triterpenoid	Reichstein *et al.*, 1967
	"	3-*O*-acetyl-β-amyrin	"	"
	"	3-*O*-isovaleryl-β–amyrin	"	
	"	luepol	"	"
	"	campesterol	sterol	"
	"	chloresterol	"	"
	"	β-sitosterol	"	"
	"	stigmasterol	"	"
	"	deacetylmetaplexigenin	cardenolide	"
	"	lineolone	"	"
	"	perioplogenin	"	"
	"	sarcostin	"	"
	"	strophanthidin	"	"
	"	xysmalogenin	"	"
	"	6-unidentified cardenolides	"	"
	"	xysmalogenin-β-D-sarmentoside	"	"
Glossastelma spathulatum	whole plant	strophanthidin	cardenolide	Mauli, Tamm, and Reichstein, 1957
	"	strophanthidin-β-D-glucoside	"	"
17. *Gomphocarpus*				
Gomphocarpus fruticosus	leaf	β-anhydrogomphogenin	cardenolide	Carman, Combe, and Watson, 1964
	"	gomphoside	cardenolide (glycoside)	"
Gomphocarpus sp.	root	xysmalogenin	cardenolide	1.Tschesche & Brathg, 1952

				2.Tschesche, Ruhsen, and Snatzke, 1955
Gomphocarpus sp	"	allouzarigenin	cardenolide	Tschesche, Freytag, and Snatzke, 1959
	"	uzaron	"	"
	"	5α-pregnanol-(3β)-one(20)	"	Tschesche, and Snatzke, 1960
	"	Δ^5-pregnenol-(3β)-one(20)	"	"
	"	β-sitosterol	sterol	"
18. ***Gymnena***				
Gymnena sylvestre	leaf	conduritol A	miscellaneous	Manni, and Sinsheimer, 1965
	"	hentriacontane	alkane	"
	"	nonacosane	"	"
	"	tritiacontane	"	"
	"	viburnitol	cyclic alcohol	"
	"	gymnemagenin	triterpenoid	Rao, and Sinsheimer, 1968
	"	gymnemic acid	"	"
	"	gymnestrogenin	"	Rao, and Sinsheimer, 1971
	"	gymnanine	alkaloid	Sinsheimer, and McIlhenny, 1972
19. ***Hemidesmus***				
Hemidesmus indicus	root	2-hydroxy-4-methoxy-benzaldehyde	miscellaneous	Dutta, Ghosh, and Chopra, 1938

Hemidesmus indicus	root	hemidesmol	sterol	Dutta, Ghosh, and Chopra, 1938
	"	hemidosterol	"	"
	"	β-sitosterol	"	Chatterjec, and Bhattacharyya, 1955
	leaf & flower	hyperoside	flavonoid (glycoside)	Subramanian, and Nair, 1968a
	"	quercetin	flavonoid	"
	"	rutin	flavonoid (glycoside)	"
	flower	isoquercitrin	flavonoid	"
	root	α-amyrin	triterpenoid	Padhy, Mahato, and Dutta, 1973
	"	β-amyrin	"	"
	"	β-amyrin acetate	"	"
	"	hexatriacontane	alkane	"
	"	lupeol	triterpenoid	"
	"	lupeol acetate	"	"
	root, leaf, stem	campesterol	sterol	Heble, and Chadha, 1978
	"	cholesterol	"	"
	"	16-dehydrogregnenolone	steroid	"
	twig	desinine	"	Oberai, Khare, M.P., and Khare, A., 1985
	stem	hemidine	"	Prakash *et al.*, 1991
	"	indicine	"	"
20. *Heterostemma*				
Heterostemma tanjorense	pericarp	quercetin	flavonoid	Subramanian, and Nair, 1968a

Heterostemma tanjorense	stem & follicle	rutin	flavonoid (glycoside)	Subramanian, and Nair, 1968a
21. ***Hoya***				
Hoya angustifolia	leaf	vitexin	flavonoid (glycoside)	Niemann, 1980
Hoya australis	leaf	apigenin-7-ferulyl glucoside	flavonoid (glycoside)	Niemann, 1980
	"	apigenin-7-glucoside	"	"
	"	apigenin-7-rutinoside	"	"
	"	chlorogenic acid	miscellaneous	"
	"	chrysoeriol-7-rutinoside	flavonoid	"
Hoya imperialis	leaf	kaempferol-3-diglucoside	flavonoid (glycoside)	Niemann, 1980
Hoya lacunosa	leaf	6,8,-di-*C*-arbinosyl-apigenin	flavonoid	Niemann, 1980
	"	ferulic acid	miscellaneous	"
	"	di-*C*-glycosides-isoschaftoside	flavonoid	"
	"	schaftoside	"	"
	leaf	dihydronyctanthic acid - methyl ester	miscellaneous	Baas, 1983
Hoya latifolia	leaf	chlorogenic acid	miscellaneous	Niemann, 1980
	"	isovitexin	flavonoid	"
Hoya naumanii	leaf	n-hydrocarbons (mainly n-C_{31} & n-C_{33})	alkane	Baas, and Ivonne, 1991
	"	α-amyrin	triterpenoid	"
	"	β-amyrin	"	"
	"	lupeol	"	"
	"	methyl-3,4-seco-olean-12-ene-3-oate	"	"

Hoya naumanii	leaf	3,4-seco-3-acid-methyl-ester of lupeol	triterpenoid	Baas, and Ivonne, 1991
	"	methyl-3,4-seco-urs-12-en-3-oate	"	"
Hoya obovata	leaf	chlorogenic acid	miscellaneous	Neimann, 1980
	"	isovitexin	flavonoid	"
22. *Leptadenia*				
Leptadenia pyrotechnica	aerial part	fernenol	triterpenoid	Manavalan, and Mithal, 1980
	"	β-sitosterol	sterol	"
	"	taraxerol	triterpenoid	"
	whole plant	leptadenol	"	Noor *et al.*, 1993
Leptadenia reticulata	latex	quercetin	flavonoid	Subramanian, and Nair, 1968_a
	latex & seed	hyperoside	flavonoid (glycoside)	"
	follicle & pericarp	isoquercetrin	"	"
	"	kaempferol	flavonoid	"
	"	rutin	flavonoid (glycoside)	"
	seed	mesoinositol	triterpenoid	Subramanian, and Nair, 1968_b
	"	mesoinositol - monomethyl ether	"	"
	"	γ–sitosterol	sterol	"
23. *Margaretta*				
Margaretta rosea subsp. *rosea*	root	ascleposide	cardenolide	Sierp, Stoecklin, and Reichstein, 1970

Margaretta rosea subsp. *rosea*	root	coroglaucigenin	cardenolide	Sierp, Stoecklin, and Reichstein, 1970
	"	corotoxigenin	"	"
	"	frugoside	"	"
	"	gofruside	"	"
	"	uzarigenin	"	"
	"	*O*-acetyl-β-amyrin	triterpenoid	"
24. *Marsdenia*				
Marsdenia cundurango	unclassified part	condurangin	cardenolide	Mitsuhashi, and Shimizu, 1960
	"	conduritol A	"	Manni, and Sinsheimer, 1965
	cortex	dihydrodrevogenin-D	"	Hayashi, and Mitsuhashi, 1968
	"	drevogenin-D	"	"
	"	marsdenin	"	"
	"	sarcostin	"	"
	bark	kondurangoglycoside A,C	"	"
	"	kandurangogenin A,C	"	"
	"	condurangoglycoside	steroid	Berger, Junior, and Kopanski, 1988
	"	condurangogenin	"	"
Marsdenia erecta	unclassified part	marsectobiose	sugar	Saner, and Allgeier, 1969
	"	drevogenin-P	steroid	Saner, Stockel and Reichstein, 1972
	"	marsectohexol	"	"

Marsdenia erecta	root	marsdenin	steroid	Baytop *et al.*, 1959
Marsdenia pringlei	dried plant	β-amyrin juarezate (β-amyrin-5-phenyl-pentadien-2,4-ate)	triterpenoid	Dominguez *et al.*, 1974
Marsdenia rostrata	dried plant	anabasine	alkaloid	Summons, Ellis, and Gellert, 1972
	"	dihydrorostratine	steroidal alkaloid	"
	"	rostratine	"	"
	"	metaplexigenin	steroid	"
Marsdenia tenacissima	seed	cissogenin	steroid	Singhal, Khare, M.P., and Khare, A., 1980_a
	"	tenasogenin	"	Singhal, Khare, M.P., and Khare, A., 1980_b
	stem	tenacissosides A-E	steroid	Miyakawa *et al.*, 1986
Marsdenia tomentosa	whole plant	sarcostin	steroid	Mitsuhashi *et al.*, 1962_a
	"	tomentogenin	"	"
	unclassified part	dehydrotomentogenin	"	Mitsuhashi, Sato, and Nomura, 1965
	stem	kidjolanin	"	Horii, Ohkawa, and Iwata, 1972
	"	penupogenin	"	"

Marsdenia tomentosa	stem	utendin	steroid	Horii,Ohkawa, and Iwata, 1972
Marsdenia volubilis	follicle & hair	hyperoside	flavonoid (glycoside)	Subramanian, and Nair, 1968$_a$
	"	quercetin	flavonoid	"
	"	rutin	flavonoid (glycoside)	"
	bark	β-sitosterol	sterol	Rao, D.V., and Rao, E.V., 1969
	stem, leaf, bark	kaemferol	flavonoid	1.Subramanian, and Nair, 1968 2.Rao, D.V., and Rao, E.V., 1969
	"	kaemferol glycoside	flavonoid (glycoside)	"
25. *Menabea*				
Menabea venenata	root	menabein	cardenolide	Raymond-Hamet, 1936
	"	menabegenin	"	Frerejacque, 1959
26. *Metaplexis*				
Metaplexis japonica (*Pergularia japonica*)	stem & leaf	sarcostin	cardenolide	Mitsuhashi *et al.*, 1962$_b$
	leaf	benzoylramanone	-	Mitsuhashi, and Nomura, 1964
	"	deacylcynanchogenin	cardenolide	"
	"	metaplexigenin	"	"
	stem & leaf	pergularin	"	"
	"	utendin	"	"

Metaplexis japonica	unclassified part	stephanol	-	Fukuoka, and Mitsuhashi, 1968
	"	dibenzoylgagaimol	-	Nomura, and Mitsuhashi, 1972
	root	7α-OH-12-*O*-benzoyl-deacylmetaplexigenin	cardenolide	Nomura, Fukai and,Kuramochi, 1981
27. *Mondia*				
Mondia whytei	tuberous root	2-hydroxy-4-methoxy-benzaldehyde	miscellaneous	Msonthi *et al.*, 1989
28. *Orthenthera*				
Orthenthera viminea	dried twig	orgogenin	steroid	Tiwari, Khare, A. and Khare, M.P.,1985
	"	orthenin	"	"
	"	penupogenin	"	Kaur, and Khare, 1985
	"	sarcostin	"	"
	"	sarcogenin	"	Kaur, and Khare, 1988
	"	α-amyrin acetate	triterpenoid	"
	"	β-amyrin	"	"
	"	β-sitosterol	sterol	"
	"	therogenin	cardenolide	"
29. *Oxystelma*				
Oxystelma esculentum	root	oxystine	steroid	Trivedi, and Khare, 1988
	"	oxysine	"	Trivedi, and Khare, 1989
	"	esculentin	"	Trivedi, and Khare, 1990

Oxystelma esculentum	root	oxylin	cardenolide	Srivastava, and Khare, 1991
	"	oxystelmoside	"	Srivastava, and Khare, 1993
	"	oxystelmine	"	"
30. *Pachycarpus*				
Pachycarpus concolor	unclassifeid part	bulloside	cardenolide	Golab, Jager,and Reichstein, 1960
Pachycarpus distinctus	root	pachygenin	cardenolide	Schmid *et al.*, 1939
	"	pychygenol	"	"
	"	bulloside	"	Golab, Jager, and Reichstein, 1960
	"	cannodioxide	"	"
	"	cannogenin	"	"
	"	digitoxigenin	"	"
	"	sarmentogenin	"	"
	"	xysmalogenin	"	"
Pachycarpus linelatus (P. schweinfurthii)	root	lineolon	cardenolide	Avisch, Tamm, andReichstein, 1959
	"	mono-*O*-benzoyl-lineolon	"	"
	"	sarcostin	"	"
	"	utendin	"	"
Pachycarpus schinziamus	root & seed	carpogenin	cardenolide	Schmid *et al.*, 1959
	"	digitoxigenin	"	"
	"	3-epi-digitoxigenin	cardenolide	"
	"	pachomonoside	"	"

Pachycarpus schinziamus	root & seed	pachygenin	cardenolide	Schmid *et al.*, 1959
	"	pachygenol	"	"
	"	uzarin	"	"
	"	xysmalogenin	"	Polonia *et al.*, 1959
31. *Parquetina*				
Parquetina nigrescens (*Peliploca nigrescens*)	unclassified part	sarmentosigenin A	cardenolide	Schenker, Hunger, and Reichstein, 1954
	"	nigrescigenin	"	Reichstein, 1963
	wood	convallatoxin	"	Berthold, Wehri, and Reichstein, 1965
	"	strophadogenin	"	"
	"	strophanthidin	"	"
	unclassified part	16-β-acetoxystrophanthidin	"	Idem, 1965
	"	16-dehydrostrophanthidin	"	"
	"	16-dehydrostrophanthidol	"	"
	"	monodigitoxigenin of 16-dehydrostrophanthidin	"	"
	"	rhamnoside of 16-acetoxy-strophanthidin	"	"
	unclassified part	cymarin	cardenolide (glycoside)	Reinhold, Harborne, and Swain, 1978
32. *Pentatropis*				
Pentatropis spiralis (*Asclepias spiralis ; Pentatropis cynanchoides*)	freshy plant	cycloart-22-ene-3 α,25-diol	triterpenoid	Rasool *et al.*, 1991
	"	cycloeucalenol	"	"

Pentatropis spiralis	freshy plant	24-methylenecycloartanol	triterpenoid	Rasool *et al.*, 1991
	"	*cis*-phyltyl-1-palmitate	diterpenoid	Rasool, Ahmad, and Malik, 1991
	"	squalene	triterpenoid	"
	"	taraxasterol	"	"
	"	ψ-taraxasterol	"	"
33. *Pentopetia*				
Pentopetia androsaemifolia	bark	cymarin	cardenolide	Golab *et al.*, 1959
	"	digitoxigenin	"	"
	"	periplocymarin	"	"
	"	periplogenin	"	"
34. *Pergularia*				
Pergularia pallida	root	desoxypergularine	alkaloid	Mulchandani, and Venkatachalam, 1976
	"	pergularinine	"	"
	"	tylophorine	"	"
	"	tylophorinidine	"	"
	"	tylophorinicine	"	Mulchandani, and Venkatachalam, 1984
	twig	pallidine	steroid	Khare, 1984
	"	pallidinine	"	"
Pergularia tomentosa	unclassified part	coroglaucigenin	cardenolide	Chopra *et al.*, 1937
	root	calactin	"	Al-Said *et al.*, 1988
	"	ghalakinoside	"	"

35. *Periploca*				
Periploca aphylla	unclassified part	$C_{25}H_{42}O_3$	resin alcohol	Chopra *et al.*, 1937
	above ground part	lupeol	triterpenoid	Mitsuhashi, and Tomimota, 1971
	"	maslinic acid	"	"
	"	oleanoic acid	"	"
	"	β-sitosterol-β-*O*-glucopyranoside	sterol (glycoside)	"
Periploca calophylla	twig	calocin	steroid	Srivastava, and Khare, 1982
	stem	periplogenin	"	"
	twig	α-amyrin acetate	triterpenoid	Srivastava, and Khare, 1983
	"	β-amyrin	"	"
	"	dihydroxy olean-12-ene-28-carboxylic acid	"	"
	"	monohydroxy-olean-12-ene-28-carboxylic acid	"	"
	"	2,3,23-trihydroxy-olean-12-ene-28 carboxylic acid	"	"
	"	phyllacin	steroid	"
	twig	plocigenin	"	Deepak, and Khare, 1985_a
	"	plocinine	"	Deepak, and Khare, 1985_b
	"	calocinin	"	Sethi *et al.*, 1988
	"	locin	"	"
	"	plocin	"	"
	"	plocinin	"	"

Periploca graeca	bark	periplocymarin	cardenolide	Solacula, and Herrmann, 1934
	wood, bark, leaf&seed	periplocin	"	1.Stoll, and Renz, 1939 2.Komissarenko, and Bagirov, 1969
	twining part	quercetin glycoside	flavonoid (glycoside)	Tronchet, and Melin, 1962
	leaf & stem	rutin	"	1.Melin, 1963 2.Melin, 1964
	leaf	astragalin	flavonoid	Komissarenko, and Bagirov, 1969
	"	isoquercitin	"	"
	"	esculentin glycoside	flavonoid (glycoside)	Melin, 1964
	stem	cyanidin	flavonoid	Melin, 1975
	"	peonidin	"	"
	bark	4-methyoxysalicylaldehyde	miscellaneous	Solacuta *et al.*, 1935
	leaf & stem	chlorogenic acids	"	1.Melin, 1963 2.Melin, 1964
	leaf	isochlorogenic acid	"	Melin, 1964
	"	neochlorogenic acid	"	"
	stem	ursolic acid	triterpenoid	Zorina, Matyukhina, and Ryabinin, 1966
	bark	scopoletin	coumarin	Komissarenko, and Bagirov, 1969
	"	unidentified coumarin	coumarin	"

Periploca laevigata	stem & root	α-amyrin	triterpenoid	Askri, Bui, and Mighri, 1982
	stem	β-amyrin	"	"
	root	α-amyrin acetate	"	"
	stem & root	lupeol	"	"
	"	β-sitosterol	sterol	"
	root	periplocadiol	sesquiterpene	Askri *et al.*, 1989
Periploca nigrescens	wood	strophanthidol	cardenolide	Schenker, Hunger, and Reichstein, 1954
	"	convallotoxin	"	Berthold *et al.*, 1965_a
	"	16β-hydroxystrophanthidin	"	"
	"	16-acetoxystrophanthidin	"	Berthold *et al.*, 1965_b
	"	16-dehydrostrophanthidin	"	"
	"	3-*O*-digitoxosyl-16-dehydrostrophanthidin	"	"
	"	3-*O*-rhamnosyl-16-acetoxystrophanthidin	"	"
	root	cymarin	"	Marks et al., 1975
	"	strophanthidin	"	"
	"	strophanthidin glycoside	"	"
	wood	α-amyrin	triterpenoid	"
	"	β-amyrin	"	"
	"	β-sitosterol-β-*D*-glucoside	sterol (glycoside)	"
	leaf	apigenin	flavonoid	Ogundaini, and Okafor, 1987
	"	isorhoifolin	"	"
	"	ursolic acid	triterpenoid	"

Periploca sepium	unclassified part	periplogenin	cardenolide	Sakuma *et al.*, 1968
	"	Δ^5-pregnene-3β-20α-diol	"	"
	"	Δ^5-pregnene-3β,16α, 20α-triol	"	"
	"	Δ^5-pregnene-3β,17α, 20α-triol	"	"
	"	β-sitosterol	sterol	"
	"	β-sitosterol-β-*D*-glucoside	sterol (glycoside)	"
	"	7-methoxysalicylaldehyde	miscellaneous	"
	"	4-*O*-(2-*O*-acetyl-β-*D*-digitalosyl)-*D*-cymarose	cardenolide	Shoji *et al.*, 1968
	"	methyl-4-*O*-(2-*O*-acetyl-β-*D*-digitalosyl)-β-D-cymaroside	"	"
	cortex	periplocin	"	Sakuma *et al.*, 1971
	"	Δ^5-pregnene-3β-20α-diol-(20)-β-*D*-glucopyranosyl-(1glu->6glu)-β-*D*-glucopyranosyl-(1glu->2glu)-β-D-digitalopyranoside	"	"
	cortex & young seedling	scopoletin	coumarin	Komissarenko *et al.*, 1983
	root bark	3-*O*-[2-*O*-acetyl-β-*D*-digitalopyranosyl (1->4)-β-*D*-cymaropyranoside]-20-*O*-[β-*D*-glucopyranosyl (1->6)-β-D-Dglucopyranosyl (1->2)-β-D-digitalopyranoside] of preg-5-ene-3β-16α, 20(S)-triol and preg-5-ene-3β,20(S)-diol	steroid	Itokawa, Xu, and Takeya, 1988_a

Sarcostemma brevistigma (*S. acidum*)	stem	α-amyrin	triterpenoid	Tabulated phytochem reports,1975
	"	β-amyrin	"	"
	"	octacosane	alkane	"
	twig	brivinine	steroid	Oberai, and Khare, 1985_a
	"	brevine	"	Oberai, and Khare, 1985b
	"	bregenin	"	Khare *et al.*, 1987
	aerial part	sarcogenin	"	"
	"	brevebiose	sugar	"
	"	tigmobiose	"	"
	"	sarcobiose	"	"
Sarcostemma viminale	twig	viminose	sugar	Allgeir, 1968
	twig & stem	metaplexigenin	cardenolide	Schaub *et al.*, 1968
	"	mono-*O*-acetyl-mono-*O*-benzoylsarcostin	cardenolide (glycoside)	"
	"	12,20,di-O-benzoyl-sarcostin	"	"
	"	genin G	cardenolide	Schaub, Stoecklin, and Reichstein, 1968
	"	genin H	"	"
Sarcostemma sp.	stem & leaf	C_{29},C_{31},C_{33} alkanes	*n*-alkanes	Keetan, and Keogh, 1975
	"	germanicol	triterpenoid	"
	"	germanicol acetate	"	"
	"	germanicol butyrate	"	"
	"	lupeol	"	"
	"	taraxerol	"	"

Periploca sepium	root bark	Preg-5-ene-3-β,16-β,20(*R*)-triol-20-*O*-β-*D*-glucopyranosyl-(1->6)-β-*D*-glucopyranosyl-(1->2)--β-*D*-glucopyranoside	steroid	Itokawa, Xu and Takeya, 1988_a
	"	Preg-5-ene-3β,20(*S*)-diol-3-O-[β-*D*-digitalopyranosyl-(1->4)-β-*D*-cymaropyranoside]-20-O-[β-D-glucopyranosyl-(1->6)-β-D-glucopyranoside]	"	"
	antitumor fraction	periplocosides A,B, and C	"	Itokawa *et al.*, 1988_b
	"	periplocosides M,D,E,L,N	"	Itokawa *et al.*, 1988_c
	"	periplocosides J,K,F,O	"	Itokawa *et al.*, 1988_d
	root bark (antitumor-fraction)	21-*O*-methyl-5-pregnene-3β,14β,17β,20,21-pentaol	"	Xu, Takeya, and Itokawa *et al.*, 1990
	"	21-*O*-methyl-5,14-pregndiene-3β,17β,20,21-tetraolxysmalogenin	"	"
	"	xysmalogenin	"	"
36. *Raphinoacme*				
Raphinoacme burkei	bulb	JB 9	cardenolide	Binkert, Schindler, and Reichstein, 1960
	"	JB 11,15,20	"	"
37. *Sarcostemma*				
Sarcostemma australe	unclassified part	sarcostin	cardenolide	Cornforth, 1959

38. *Secamone*				
Secamone afzelii	root	friedelin	triterpenoid	El-Said *et al.*, 1971
39. *Stapelia*				
Stapelia gigantea	seed	stapelogenin	cardenolide	Eppenberger *et al.*, 1966
40. *Stephanotis*				
Stephanotis japonica	whole plant	deacylmetaplexigenin	cardenolide	Fukuoka, and Mitsuhashi, 1968
	"	lineolon	"	"
	"	sarcostin	"	"
	"	stephanol	"	"
	aerial part	5α-dihydrosarcostin	"	Fukuoka, and Mitsuhashi, 1969
41. *Solenostemma*				
Solenostemma argel	unclassified part	argelin	-	Mahran, Wanba, and Saber, 1967
	"	argeloside	-	"
42. *Telosma*				
Telosma minor	flower	hyperoside	flavonoid (glycoside)	Subramanian, and Nair, 1968
	"	isoquercitrin	"	"
	"	quercitin	flavonoid	"
43. *Tylophora*				
Tylophora asthmatica	unclassified part	tylophorine	alkaloid	1.Govindachari *et al.*, 1960 2.Govindachari, Pai *et al.*, 1960

Tylophora asthmatica	unclassified part	tylophorinine	alkaloid	Govindachari, Pai *et al.*, 1960
	root	tylophorinidine	"	Mulchandani, Iyer, and Badheka, 1971
	root & aerial part	γ-fagarine	"	Etherington, Herberr, and Jackson, 1977
	"	skimmianine	"	"
Tylophora crebriflora	dried plant	alkaloid A-E	alkaloid	Rao *et al.*, 1970
	"	septicine	"	Rao *et al.*, 1971
	"	tylocrebrine	"	"
	"	tylophorine	"	"
	unclassified part	tylophorinine	"	Reinhold *et al.*, 1978
Tylophora dalzellii	unclassified part	desmethyltylophorinine	alkaloid	Rao *et al.*, 1971
Tylophora hirsuta	unclassified part	tylocrebrine	alkaloid	Reinhold *et al.*, 1978
	aerial part	tylohirsutinine	"	Bhutani, Ali, and Atal, 1984
	"	13α-methyltylohirsutine	"	"
	"	13α-methyltylo-hirsutinidine	"	"
	"	tylohirsutinidine	"	"
	"	13α-hydroxysepticine	"	"
	unclassified part	14-desoxy-13α-methyltylo-hirsutinidine	alkaloid	Ali, and Bhutani, 1987
	"	5-hydroxy-*O*-methyltylo-phorinidine	"	"

Tylophora hirsuta	unclassified part	tylohirsuticine	Alkaloid	Ali, and Bhutani, 1987
	"	14-hydroxyisotylocrebrine	"	"
	"	(+)-isotylocrebrine	"	"
	"	(-)-tylophorine	"	"
	"	4-desmethylisotylocrebrine	"	"
	"	13α-hydroxytylophorine	"	Bhutani, Sharma, and Ali, 1987
Tylophora indica	unclassified part	α-amyrin	triterpenoid	Chandrashekar, and Seshadri, 1968
	"	kaempferol	flavonoid	"
	"	quercetin	"	"
	"	desmethyltylophorine	alkaloid	Rao *et al.*, 1971
	"	desmethyltylophorinine	"	"
	"	tylophorine	"	1.Rao *et al.*, 1971 2.Bhutani *et al.*, 1987
	"	tylophorinine	"	"
	leaf	acetyl-*O*-methyltylo-phorinidine/acetyl-tyloprorinine	"	Van *et al.*, 1985
	"	demethyltylophorine	"	"
	"	4-methoxy-14-hydroxy-tylophorine	"	"
	"	*d*-septicine	"	"
	aerial part	tyloindicines A-E	"	Ali, and Bhutani, 1989
	"	(+)-14-hydroxyiso-tylocrebrine	"	"

Tylophora indica	aerial part	4,6-desdimethyliso	alkaloid	Ali, and Bhutani, 1989
	"	tylocrebrine		
	"	5-hydroxy-*O*-methyltylophorinidine	"	Ali, and Bhutani, 1989
Tylophora kerrii	unclassified part	tylolupenols A (*D:C*-friedolup-8(9)-en-3β-ol)	triterpenoid	Kawanishi *et al.*, 1985
	"	tylolupenols B (*D:C* friedolup-(9)11en-3β-ol)	"	"
Tylophara mollissima	whole plant	caffeine	alkaloid	Viswanathan, and Pai, 1985
	"	tylophorine	"	"
	"	tylophorinine	"	"
44. *Vincetoxicum*				
Vincetoxicum hirundinaria	root	hirundigenin	steroid	Kennard *et al.*, 1968
	"	anhydrohirundigenin	"	"
	"	vincetogenin	"	"
	"	hirundoside A	"	1.Stoeckel, and Reichstein, 1969_a 2.Stoeckel, and Reichstein, 1969_b
Vincetoxicum nigrum	aerial part	antofine	alkaloid	Capro, and Saa, 1989

Vincetoxicum officinale	root	antofine	alkaloid	Pailer, and Streicher, 1965
	"	3,6,7-or2,3,6-trimethoxy-9,11,12,13α,14-hexahydro-bibenzo[*f,h*]pyrrolo[1,2-6]-isoquinoline	"	"
	"	tylophorine	"	"
	leaf	vincetoxicosides A-B	"	1.Kozjek, and Lebreton, 1967 2.Kozjek, 1969
	"	isoquercitrin	flavonoid	Koziek, 1969
	"	quercifrin	"	"
	"	quercetin	"	"
	"	kaempferol	"	"
	"	chlorogenic acid	miscellaneous	"
Vincetoxicum sp.	unclassified part	α-amyrin	triterpenoid	Toth, Haznagy, and Snatzke, 1969
	"	friedelin	"	"
45. *Xysmalobium*				
Xysmalobium undulatum	unclassified part	xysmalogenin	cardenolide	Huber *et al.*, 1951
	root	uzarin	"	Ghorbani *et al.*, 1990
	"	urezin (3-epi-uzarin)	"	"
	"	uzarosid (gluco-uzarin)	"	"
	"	xysmalorin	"	"

2.Triterpenoids (C30)

2.1 Introduction to Triterpenoids

Triterpenoids are the most ubiquitous non-steroidal secondary metabolites in terrestrial, marine flora and fauna (Mahato, Nandy, and Roy, 1992). Traditionally, C30 isoprenoid compounds were viewed as triterpenes. Triterpenes are produced from two molecules of farnesyl pyrophosphate (FPP) condensed head to head (Figure 2.1). The acyclic hydrocarbon squalene is the first triterpene formed, and evidence indicates that it is the precursor of all other triterpenes, as well as of steroids.

The majority of natural triterpenes are pentacyclic compounds. The next largest groups are the tetracyclic triterpenes. There is also a smaller number of triterpenes with various other cyclic structures. The only important acyclic triterpene is squalene (and its 2,3- oxide as a metabolic intermediate). Most triterpenes are alcohol (3-OH). They are found free and as glycosides (saponins) or esters. Free triterpenes are often components of resins, latex, or cuticle (Stumpf and Conn, 1980). There are probably upward of 750 naturally occuring triterpenes of known compounds (Devon and Scott, 1972), and new compounds and new structural types are still being discovered.

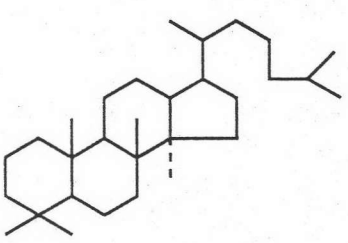
2.2 Classification of triterpenoids

(Richards and Hendrickson, 1964; Devon and Scott, 1972)

The triterpenes consist of three large groups: tetracyclic, pentacyclic and miscellaneous groups. The naturally occuring triterpenes can be suitably placed into 29 main skeleta.

1.2.1 Tetracyclic Triterpenoids

a) Damarane type *1* such as: dammarenediol *2*, dipterocarpol *3*



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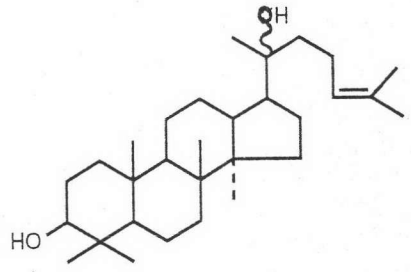

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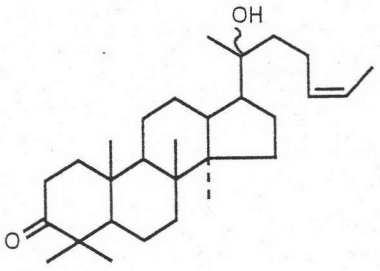
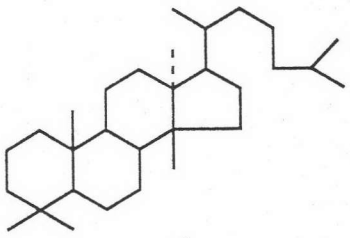


3

b) Euphane type *4* such as euphol *5*



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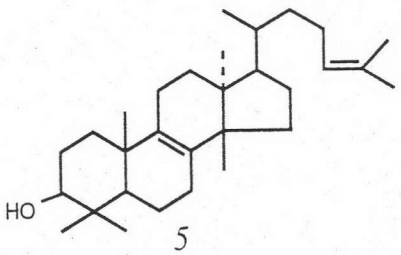
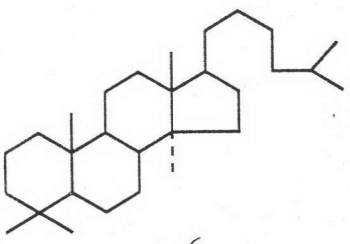


5

c) Lanostane type *6* such as lanosterol *7*



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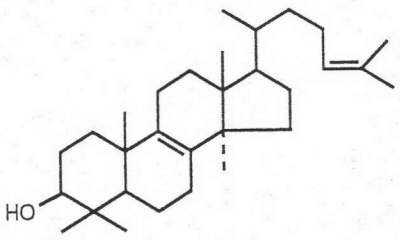
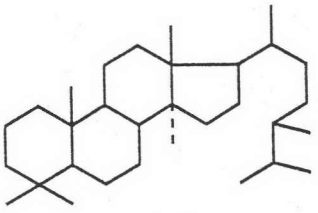


7

d) Eburicane type *8* such as eburicoic acid *9*



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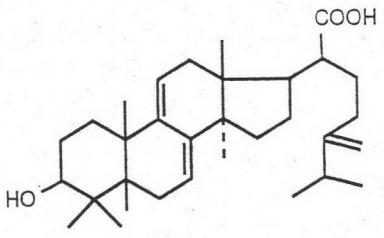

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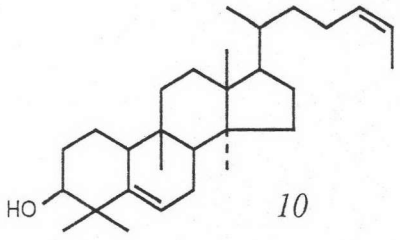
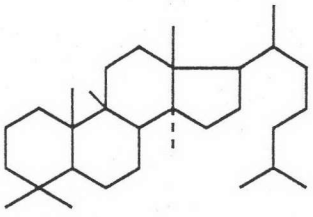
e) Cucurbitacin type *10*



10

f) Cycloartane type *11* such as cycloartenol *12*



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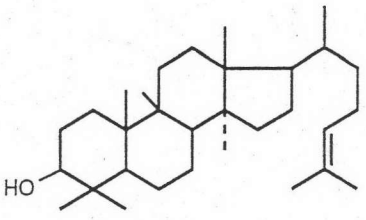
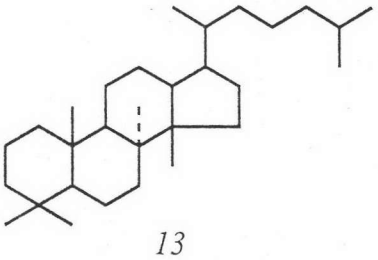


12

g) Protostane type *13* such as protosterol *14*



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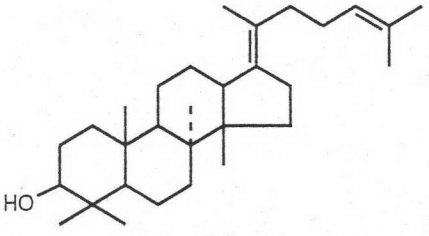
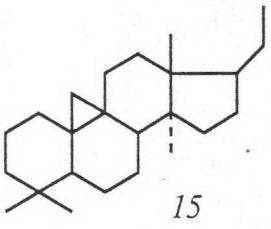


14

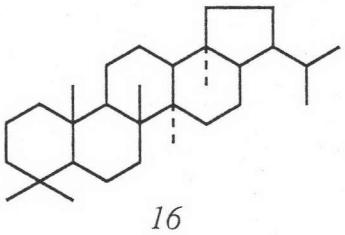
h) Buxane type *15*



15

1.2.2 Pentacyclic Triterpenoids

a) Hopane type *16* such as hopene *17*



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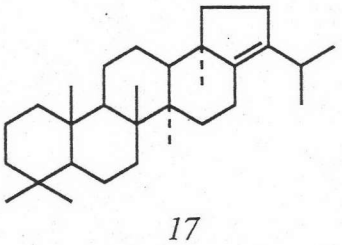
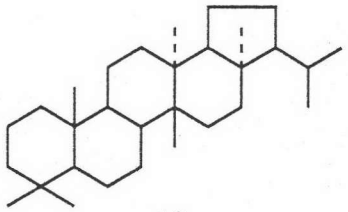


17

b) Fernane type *18* such as fernene *19*



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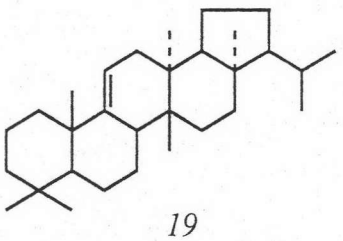

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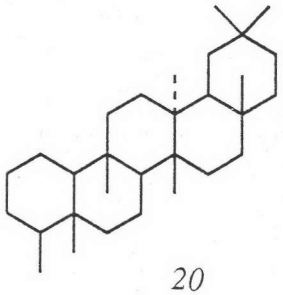
c) Friedelane type *20* such as friedelin *21*



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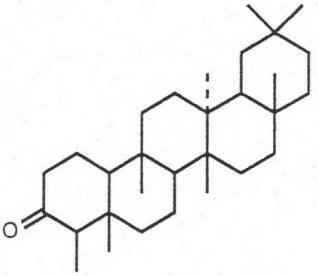
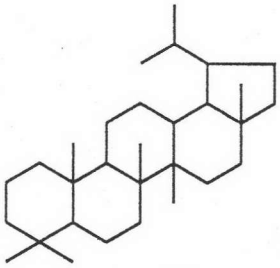


21

d) Lupane type *22* such as lupeol *23*



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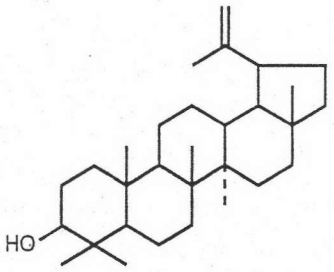
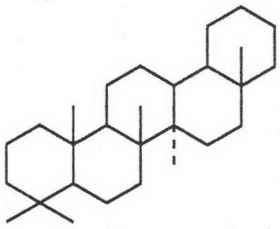


23

e) Germanicane type *24* such as germanicol *25*



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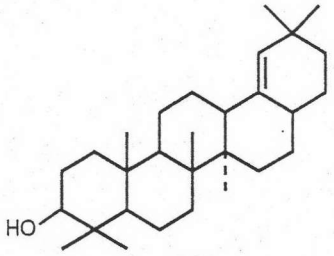
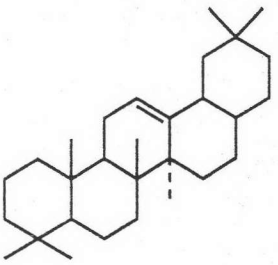


25

f) Oleanene type *26* such as β-amyrin *27*, oleanoic acid *28*



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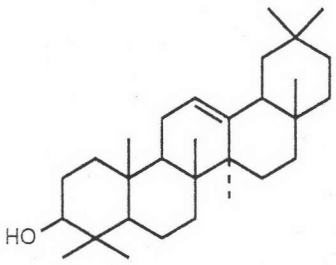

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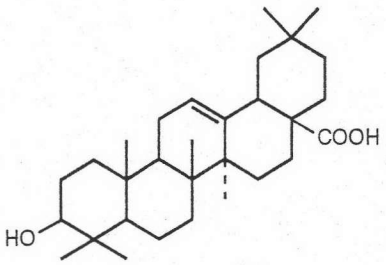
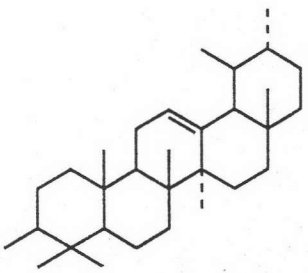


28

g) Ursane type 29 such as α-amyrin *30*, ursolic acid *31*



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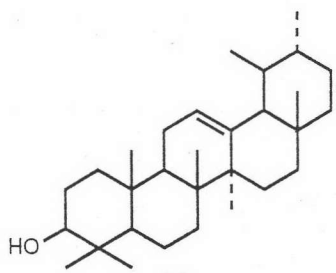

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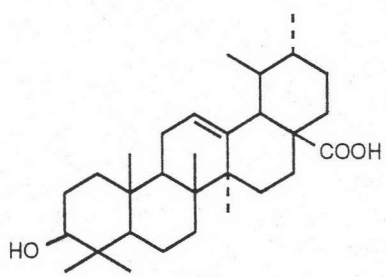
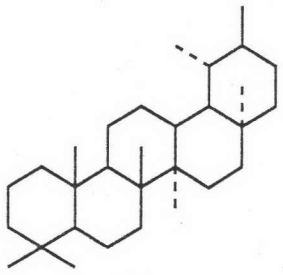


31

h) Taraxasterane type *32* such as γ- taraxasterol *33*



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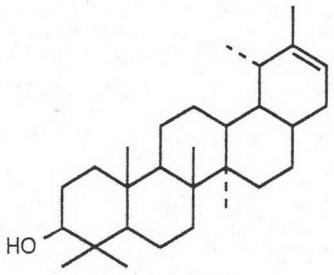

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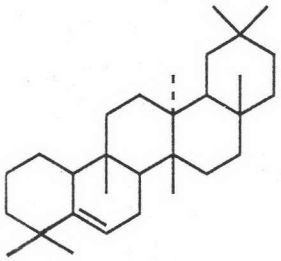
i) Glutinane type *34* such as glutinone *35*



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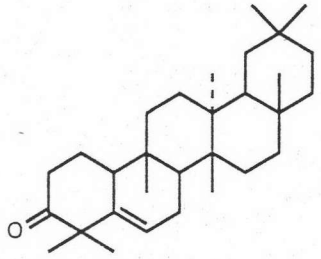
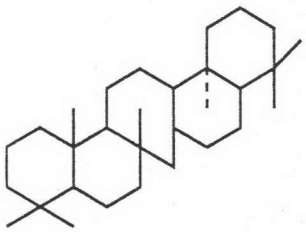


35

j) Serratane type *36* such as serratane *37*



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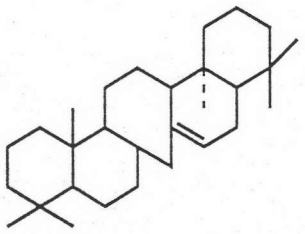
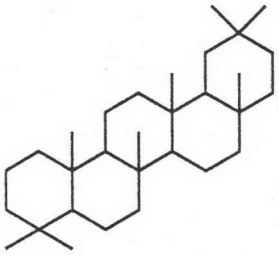


37

k) Taraxerane type *38* such as taraxerol *39*



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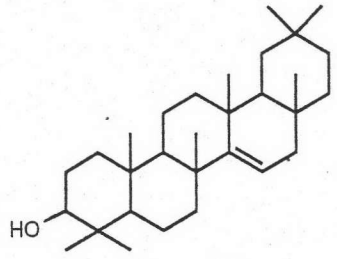

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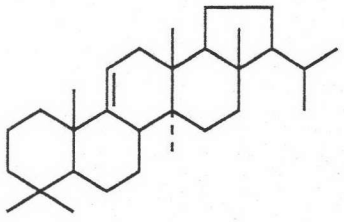
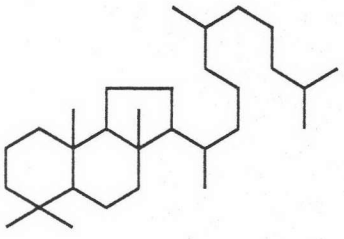
l) Arborene type *40*



40

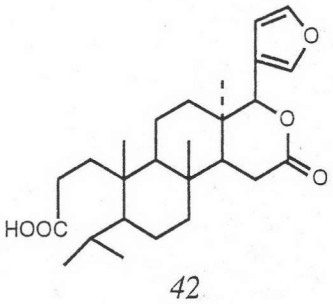
1.2.3 Miscellaneous

a) Malabaricane type *41*



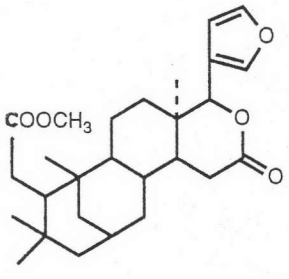
41

b) Limonin type *42*



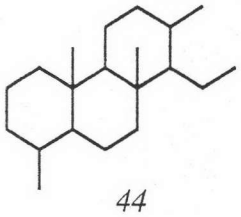
42

c) Swietenine type *43*



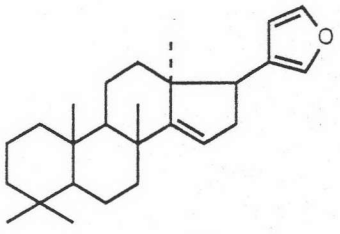
43

d) Quassin type *44*



44

e) Meliacane type *45*



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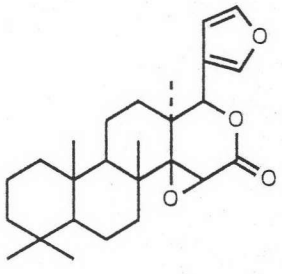
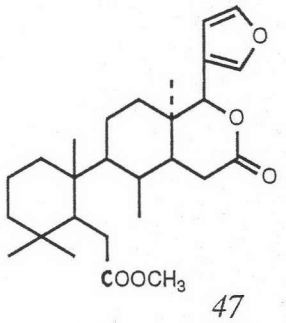
f) Gedunin type *46*



46

g) Andirobin type *47*



47

This group is included other structures of which represent secondary transformation (such as oxidation) on a presumably performed triterpene skeleton. Nyctanthic acid (Fig.2.2 a) is a member of the oleanane type which has suffered an oxidative opening of ring A. Another interestingly altered triterpene is ceanothic

acid(Fig. 2.2 b) a lupeol-type triterpene that has undergone a ring-A contraction analogous to that postulated for the diterpene giberellic acid.

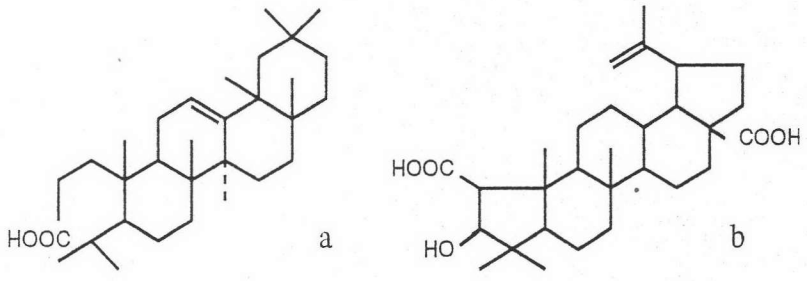


Figure 2.2 Structure of Nyctanthic acid and Ceanothic acid

2.3 Biosynthesis of Pentacyclic triterpenes

All types of cyclic triterpenes originate from squalene. The formation of squalene is as follows (Miller, 1973; Herbert, 1981).

The formation of squalene is through the familiar pathway of acetyl Co A *48* , acetoacetyl Co A*49* , 3-hydroxymethylglutaryl CoA *50* , mevalonic acid *51*, mevalonic acid pyrophosphate *52*, isopentenyl pyrophosphate *53*, 3,3-dimethylallylpyrophosphate *54*, geranyl pyrophosphate *55*, farnesyl pyrophosphate *56* and squalene *57* (Figure 2.3).

In plants as well as in animals and microorganisms the pentacyclic triterpenes are derived from squalene -2,-3-epoxide, which is formed from squalene by a monoxygenase. The cyclization of a proton (or an electron-accepting group of the enzyme) which causes the formation of a hydroxy group at position 3. This leaves a positive charge at position 2. Ring formation proceeds by addition of double bonds to this positively charged C-atom. The number and configuration of the ring built depends on the folding of the squlene chain, which is determined by the enzyme. The positive charge that remain in the molecule after the cyclization is lost by elimination of a proton. It may , however, migrate within the molecule prior to proton elimination by the shift of hydride ions and methyl anions while maintaining the spatial orientation of these groups in front of and behind the plane of the ring system (Z-anionotropy). Cyclization, Z-anionotropy, and elimination of the proton proceed in a concerted manner. (Intermediates are given for didactic reasons only)

The pentacyclic triterpenes are derived from 3(S)-2,3-squalene epoxide in chair-chair-boat-unfolded conformation. In pentacyclic triterpenes, ring D of the

steroid cation I (Fig. 2.4) formed as an intermediate, may be enlarged by a Wagner-Meerwein rearrangement, and an addittional five-membered ring may be formed (Figure 2.4) (biosynthesis of lupeol-type compounds).

Enlargement of ring E by a further Wagner-Meerwein rearrangement leads to the cation II, from which a large number of different amyrin-type compounds are derived by Z-anionotropy and elimination of a proton (Figure 2.5) (Porter and Spurgeon, 1981; Richards and Hendrickson, 1964; Luckner, 1990).

2.4 Some Aspects of Lupeol (Simomsen and Ross,1957 ; Gibbs,1974; Wiondholz, 1989)

Lupeol (Lupenol), $C_{30}H_{50}O$, m.p. 215-216°C, $(\alpha)_D$ +27.2°, +33° (in benzene), +45.7° (in ethylene dibromide), which was readily soluble in ether, benzene and light petroleum but sparingly so in water. The melting point of lupeol acetate was 220 °C

Lupeol would appear to be the most widely distributed of all the triterpenes, being encountered in more plant species than the α and β-amyrins with which it is frequently associated. It has been isolated from representatives of the following families of plants: Apocynaceae, Asclepiadaceae, Capparidaceae, Celastraceae, Compositae, Labiatae, Leguminosae, Linaceae, Loganiaceae, Loranthaceae, Moraceae, Rosaceae, Rutaceae and Sapotaceae. In addition to the sources already mentioned lupeol occurs free in the roots of *Phyllanthus distichus*, of *Fagara zanthoxyloides*, of *Decalepis hamiltonii*, of *Hemidesmus indicus*, in the bark of *Zanthoxylum macrophyllum*, of *Holarrhena antidysenterica*, of *Crataegus oxycantha*, of *Lophopetalum toxicum*, of the Chinese plant "Shikeihi" and of *Alstonia verticillosa*, in the leaves of *Mentha aquatica* and of *Viscum album*, and also in the flowers of *Anthemis nobilis*. The acetate has been isolated from the oils and exudates of many plants, including *Ficus variegata*, *Ficus vogelii*, *Ficus glomerata*, *Alstonia scholaris* , *Achras sapota*, *Artocarpus elastica*, *Maclura aurantiaca* and *M. pomifera* .

2.5 Some Aspects of Amyrin (Simonsen and Ross, 1957; Gibbs , 1974 ; Windholz, , 1989)

α–Amyrin (α-amyrenol, 3-hydroxy-$\Delta^{12:13}$-ursene), $C_{30}H_{50}O$, m.p. 186.5-187°C, b.p. 243°C/0.7 mm., $(\alpha)_D$+91.6° (in benzene) ,+91.4°, was soluble in benzene, ether, acetic acid and hot ethanol, but only sparingly so in light petroleum and

cold ethanol. In general α-amyrin derivatives were more soluble than the corresponding dervatives of β-amyrin. The m.p. of α-amyrin acetate was 227°C.

β–Amyrin (β-amyrenol,3-hydroxy olean-$\Delta^{12:13}$-ene), $C_{30}H_{50}O$,m.p. 199-200°C, $(\alpha)_D$ +89°, +99.8° (in benzene) was reasonably soluble in benzene from which solvent it separated as fine needles- ether ,acetic acid and hot alcohol, but only sparingly soluble in cold alcohol and petroleum ether. Its acetates m.p. was 241°C·.

Both α- and β- amyrins are very widely distributed in the vegetable kingdom, occuring in the free state but more frequently as esters, particularly as acetates in the families of plants, Burseraceae, Rutaceae, Moraceae, Sapotaceae, Apocynaceae, Asclepiadaceae, and several others. The two amyrins occur together in many plant exudates especially in the latex of *Castilloa elastica* , of *Ficus glomerata*, of *Achras sapota* (chicle gum), of *Alstonia scholaris*, of *Tabernaemontana sphaerocarpa*, of *Artocarpus communis*, and of *Asclepias cornuti*, and also in the resins of *Canarium commune*, of *Canarium schweinfurtii* ,of *Aucoumea klaineana*, and of *Icica heptaphylla* (*Amyris ambrosiaca*).

α- Amyrin or its acetate has been isolated from the latex of the following: *Madhuca butyracea*; *Alstonia* sp., *Ervatamia* sp., *Plumeria* sp., and *Daemia* sp.

β– Amyrin or its acetate has been isolated from the latex of the following: *Ficus toxicaria*, *F. fulva*, *Plumeria acutifolia*, *Asclepias syriaca.*, *Calotropis gigantea*, *Euphorbia* sp., *Artocarpus elastica*, *Stauntonia hexaphylla*, *Machaerium incorruptible*, *Cannarium strictum*, *Madhuca butyraceae*, *Lactuca virosa* and *Mimosops globosa*.

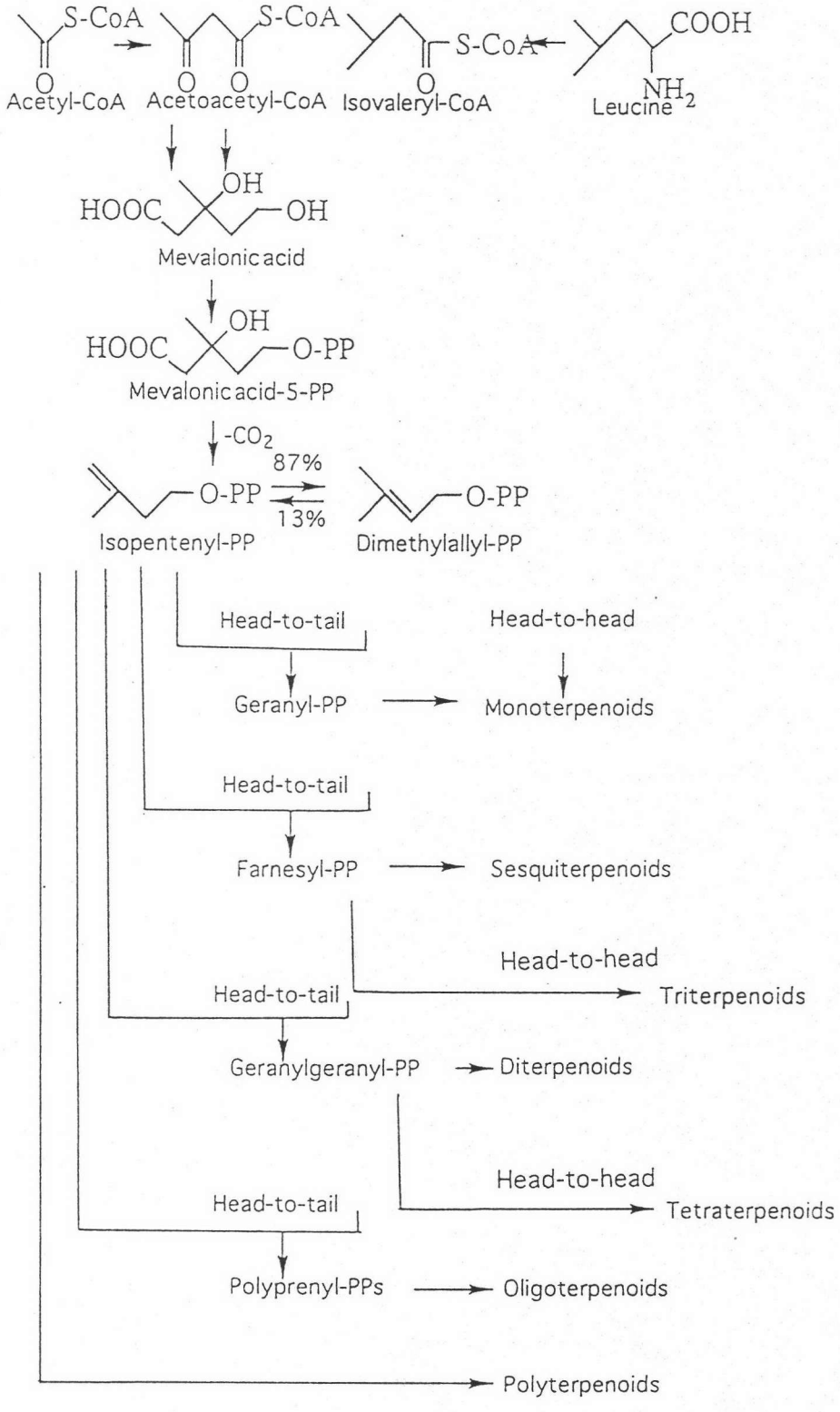


Figure 2.1 Biosynthesis scheme of terpenoids

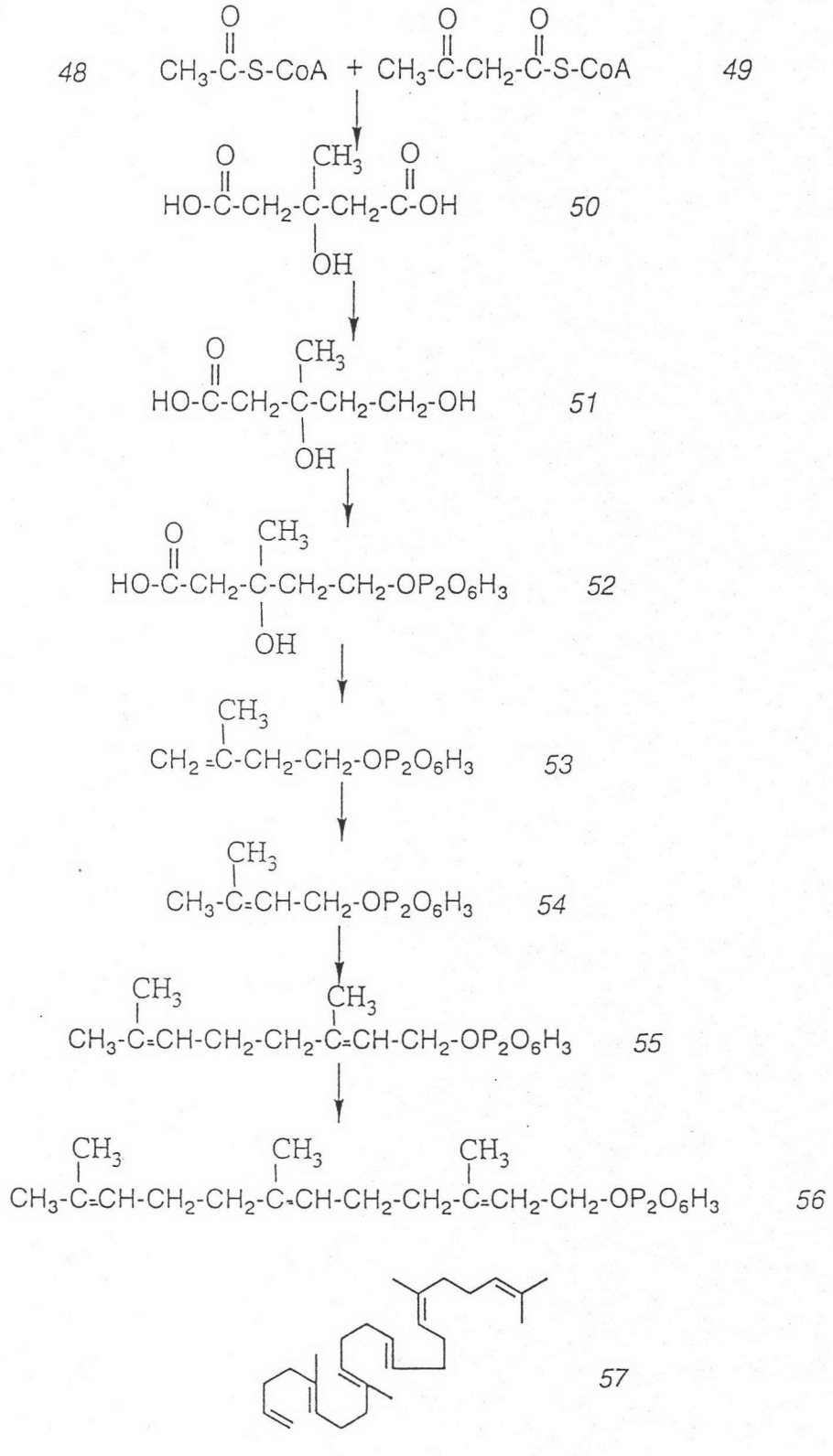


Figure 2.3 Squalene biosynthesis

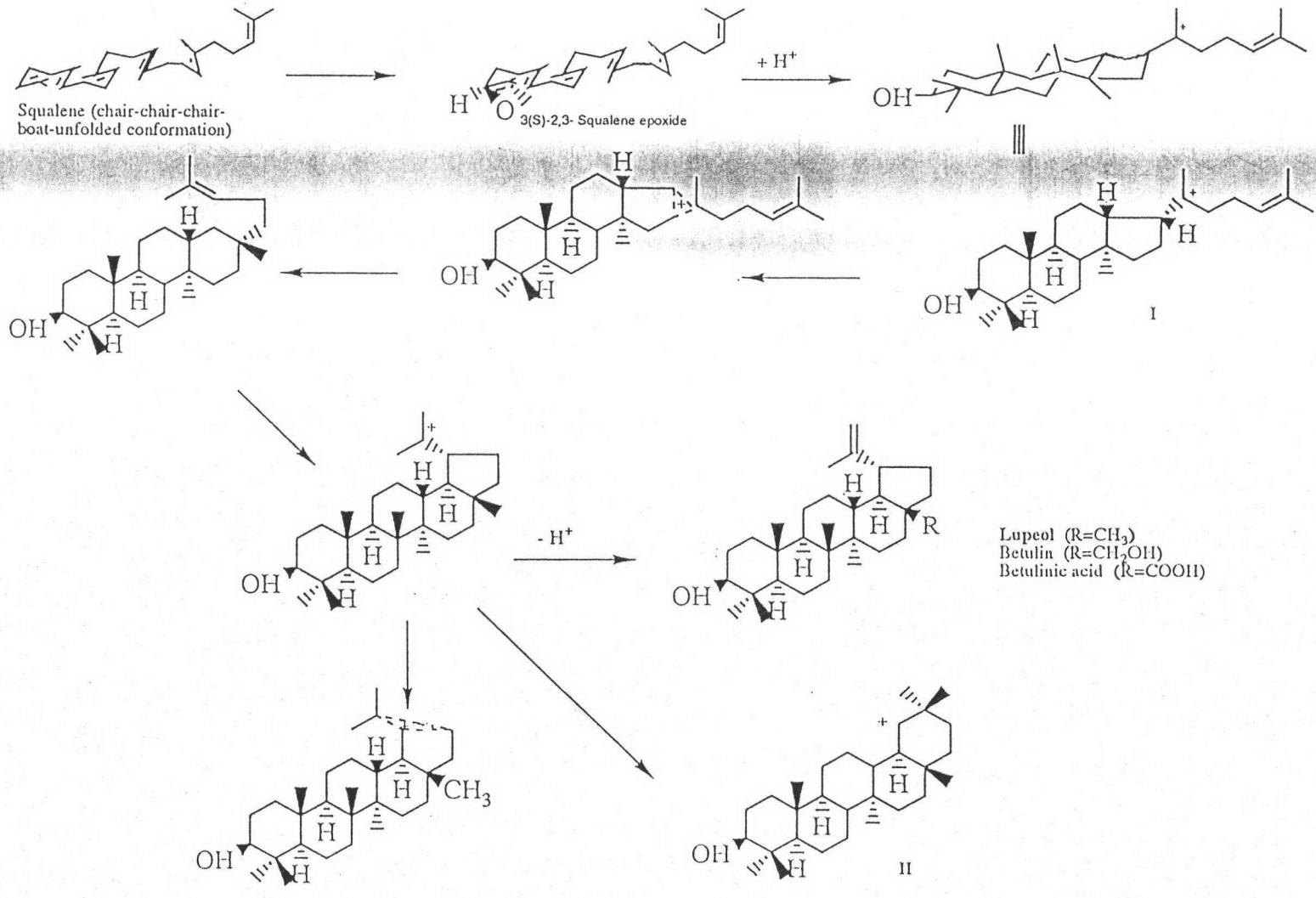


Figure 2.4 Biosynthesis of pentacyclic triterpenoids, part I

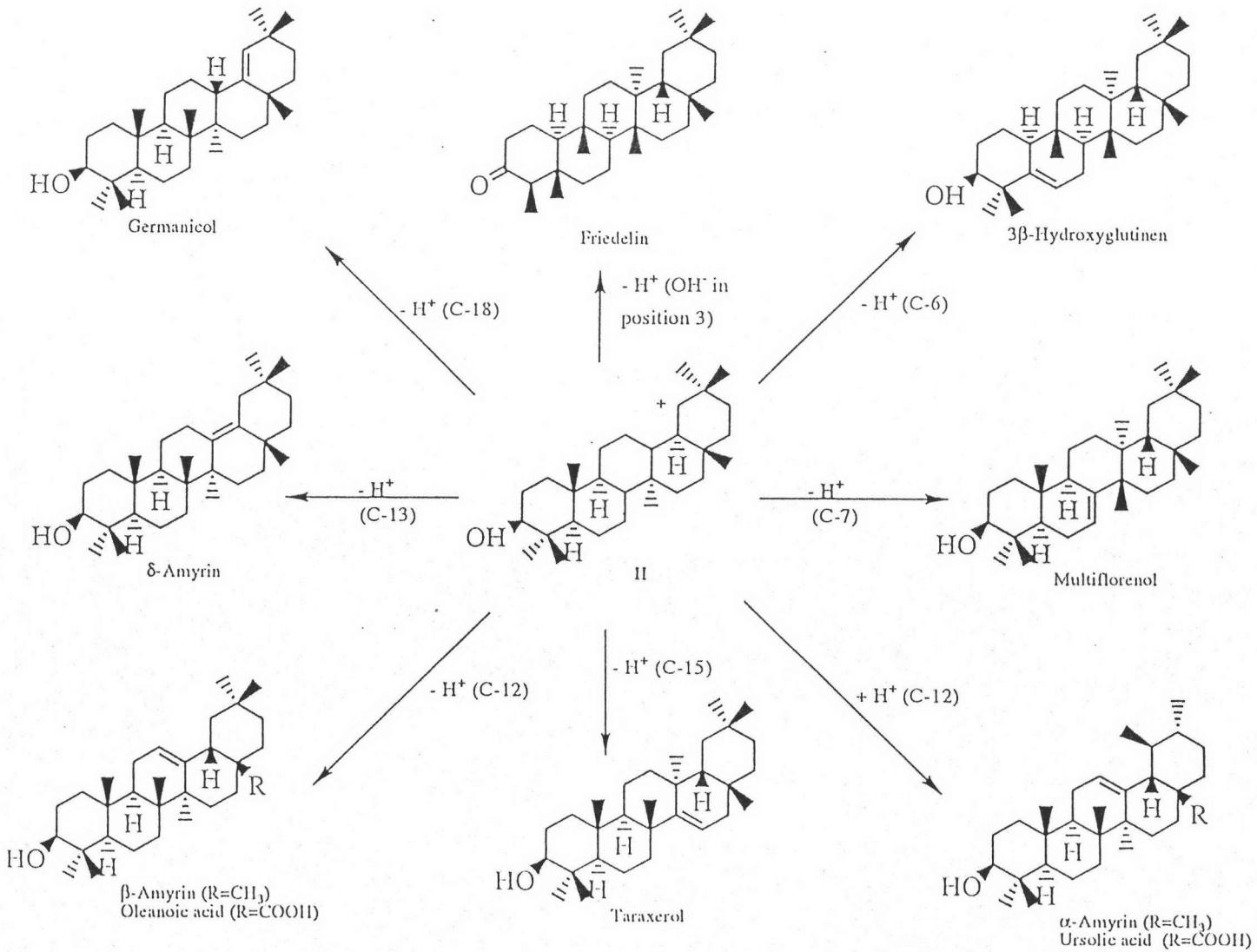


Figure 2.5 Biosynthesis of pentacyclic triterpenoids, part II

3 Aromatic aldehydes

3.1 Introduction to Aromatic aldehydes

The aromatic and aliphatic aldehydes are a most important asset in the preparation of synthetic perfumes. Many of them occur naturally and in varying proportions in essential oils (Poucher, 1974). The simplest of the aromatic aldehydes is benzaldehyde. C_6H_5CHO (benzoic aldehyde, benzoyl hydride), formula weight 106.12 (Kirk and Othmer, 1948).

The distribution of aromatic aldehydes is so fragmentary that we can use it but little in chemotaxnomy.

3.2 Naturally Occuring Aromatic aldehydes

Aromatic aldehydes are of plants of economic value, such as *Cinnamomum* and *Vanilla*. In this group, there are two points of interest. (Gibbs, 1974)

a) The order Magnoliales is represented in the following list by Magnoliaceae, Annonaceae, Illiciaceae , Monimiaceae, and Lauraceae. The Ranunculales is without representation.

b) The occurrence of 4-methoxy-salicylic aldehyde in the order Gentianales might prove of real interest. It has been reported from Apocynaceae and from Asclepiadaceae (several genera, mostly closely related).

A list of aromatic aldehydes found in various families is shown in Table 2.2

Table 2.2 Naturally Occuring Aromatic aldehydes.

Aldehyde compound	Botanical origin	Family	Plant part	Reference
1 *p*- Anisaldehyde	*Magnolia salicifolia*	Magnoliaceae	leaf-oil	Gibbs, 1974
	Acacia farnesiana	Leguminosae	flower-oil	"
	Pelea madagascariensis	Rutaceae	-	"
1. *p*- Anisaldehyde	*Protium carana*	Burseraceae	-	Gibbs, 1974

1. *p*- Anisaldehyde	*Protium carana*	Burseraceae	-	Gibbs, 1974
	Erica arborea	Ericaceae	-	"
	Agastache rugosa	Labiatae	essential oil	"
	Vanilla spp.	Orchidaceae	-	"
	Pimpinella anisum	Umbelliferae	-	Leung, 1980
	Illicium verum	Illiciaceae	dried ripe fruit	"
	Forniculum vulgare	Umbelliferae	dried fruit	"
	Pinus mugo var.*pumilio*	Pinaceae	-	"
	Agropyrum repens	Poaceae	rhizome	Boesel, and Schilcher, 1989
2. *o*-Anisaldehyde	*Cinnamomum cassia*	Lauraceae	-	Gibbs, 1974
3. Asaronaldehyde	*Asarum europaeum*	Aristolochiaceae	root-oil	Gibbs, 1974
	Daucus carota	Umbelliferae	-	"
	Acorus calamus	Araceae	-	"
	Atalantia ceylanica	Rutaceae	leaf	"
4. Benzaldehyde	*Cananga odorata*	Annonaceae	flower-oil	Gibbs, 1974
	Rubus idaeus	Rosaceae	fruit	"
	Rosa spp.	"	-	"
	Acacia farnesiana	Leguminosae	flower-oil	"
	Citrus spp	Rutaceae	-	"
	Ruta spp.	"	-	"
	Eucalyptus spp.	Myrtaceae	-	"
	Melaleuca leucadendron	"	-	"
	Hyacinthus spp.	Liliaceae	flower-oil	"
	Narcissus spp.	Amaryllidaceae	-	"
	Prunus amygdalus var.*amara*	Rosaceae	seed	Leung,1980
	P. serotina	"	-	"
	Styrax sp.	Styracaceae	-	"
	Cinnamomum verum	Lauraceae	bark	"
	C. zeylanicum	"	-	"
	Salvia sclarea	Labiatae	-	"

4. *benzaldehyde*	*Syzygium aromaticum*	Myrtaceae	-	Leung,1980
	Citrus ladaniferus & other spp.	Cistaceae	-	"
	Glycyrrhiza glabra	Leguminosae	root	"
	Pogostemon cablin	Labiatae	-	"
	Acinos suaveolens	Lamiaceae	-	Kokkalou, 1988
	Agropyrum repens	Poaceae	-	Boesel, Schilcher, 1989
	Dennettia tripetala	Annonaceae	-	Ekundayo *et al*, 1992
	Elsholtzia polystachya	Labiatae	-	Mathela *et al*, 1992
	Thapsia garganica	Umbelliferae	-	Avato, 1991
5. *p* (4)-Hydroxy benzaldehyde	*Papaver somniferum*	Papaveraceae	-	Gibbs, 1974
	Xanthorrhoea australis	Xanthorrhoeceae	resin	"
	X. hastilis	"	resin	"
	Andropogon spp.	Gramineae	-	"
	Ocimum sanctum	Labiatae	-	Leung, 1980
	Vanilla planifolia	Orchidaceae	-	"
	V. tanitensis	"	-	"
	Onopordon macracanthum	Compositae	-	Cardona *et al.* ,1987
6. 3,4-Dihydroxy-benzaldehyde	*Cichorium intybus*	Compositae	seed	Gibbs,1974
	Musa spp.	Musaceae	green fruit	"
7. Dihydro-benzaldehyde	*Erythroxylum coca* var.*coca*	Erythroxylaceae	-	Novak, Salemink, 1987
8. 3-Acetyl-6-methoxy-benzaldehyde	*Encelia farinosa*	Compositae	leaf	Gibbs, 1974

9. 2-Hydroxy-4-methoxy-benzaldehyde	*Periploca graeca*	Asclepiadaceae	bark	Solacula *et al*, 1935
	Hemidesmus indicus	"	root	Dutta *et al*,1938
	Chlorocodon sp.	"	"	Mascre & Paris,1947
	C. whiteii	"	"	Gailly, 1947
	P. sepium	"	seedling	Shoji *et al*, 1967
	Tylophora indica	"	"	Gibbs, 1974
	Decalepis hamiltonii	"	"	"
	Hanghomia marseillii	Apocynaceae	"	"
	Decalepis hamiltonii	"	"	Guenther, 1957
10. Caniferylaldehyde	*Santalum album*	Santalaceae	-	Leung, 1980
	S. spicatum	"	-	"
11. Cinnamaldehyde	*Cinnamomum* spp.	Lauraceae	essential oil	Gibbs, 1974
	Cassia spp.	Leguminosae	-	"
	Melaleuca spp.	Myrtaceae	-	"
	Lavandula spp.	Labiatae	-	"
	Pogostemon cablin	"	-	"
	Hyacinthus spp.	Liliaceae	flower-oil	"
	Narcissus spp.	Amaryllidaceae	"	"
	Cinnamomum verum	Lauraceae	bark	Leung, 1980
	C. aromaticum	"	"	"
	C. osmophloeum	"	leaf	Hussain *et al.* ,1986
	Commiphora molmol	Burseraceae	-	Leung, 1980
12. *o*-Methoxy-cinnamaldehyde	*Cinnamomum cassia*	Lauraceae	oil of bark and leaf	Gibbs,1974
	C. aromaticum	"	bark	Leung, 1980

13. *p*-Methoxy-cinnamaldehyde	*Artemisia dracunculus*	Compositae	essential oil	Gibbs, 1974
14. 3,4-Methylene dioxy-cinnamal-dehyde	*Cinnamonum* sp.	Lauracece	-	Gibbs, 1974
15.Phenyl-propionaldehyde	*Cinnamomum cassia* *C. zeylanicum*	Lauracece "	- -	Gibbs, 1974 "
16. Cumene aldehyde	*Salvia sclarea*	Labiatae	-	Leung, 1974
17. Cuminaldehyde	*Cinnamomum verum* *Cuminum cyminum* *Lavandula stoechas* *Achillea grandifolia*	Lauraceae Umbelliferae Lamiaceae Compositae	bark - - -	Leung, 1980 " Kakkalou, 1988 Hanlidou, Kokkalou, and Kokkini, 1992
18. Coniferaldehyde	*Sassafras albidum* (*S. variifolium*)	Lauraceae	-	Leung, 1980
19. Cumaldehyde	*Cuminum cyminum*	Umbelliferae	-	Leung, 1980
20. Hydro-cinnamaldehyde	*Cinnamomum verum*	Lauraceae	-	Leung, 1980
21. Ferulaldehyde	*Santalum album* *S. spicatum*	Santalaceae "	- -	Leung, 1980 "
22. Phenylacetal-dehyde	*Rosa* spp. *Cynara scolymus*	Rosaceae Compositae	- -	Gibbs, 1974 Leung, 1980

23. Piperonal	*Doryphora sassafras*	Atherosperma-taceae	tree	Gibbs, 1974
	Cinnamomum sp.	Lauraceae	-	"
	Spiraea spp.	Rosaceae	-	"
	Robinia pseudacacia	Leguminosae	flower-oil	"
	Viola odorata	Violaceae	flower	"
	Eryngium spp.	Umbelliferae	essential oil	"
	Vanilla spp.	Orchidaceae	bean	Leung, 1980
	Spiraea ulmaria	Rosaceae	flower	"
24. 4-methoxy-resorcylaldehyde	*Decalepis hamiltonii*	Asclepiadaceae	root	Rao and Iyengar, 1983
25. Salicylaldehyde	*Cinnamomum cassia*	Lauraceae	-	Gibbs, 1974
	Filipendula (Spiraea) ulmaria	Rosaceae	-	"
	Prunus avium	"	-	"
	Ceanothus velutinus	Rhamnaceae	leaf	"
	Homalium tomentosum	Flacourtiaceae	-	"
	Rauwolfia caffra	Apocynaceae	bark	"
	Cordia asperrima	Boraginaceae	-	"
	Nicotiana tabacum	Solanaceae	leaf	"
	Cinnamomum aromaticum	Lauraceae	-	Leung, 1980
	Tagetes erecta	Compositae	-	"
	T. patula	"	-	"
	T. minuta	"	-	"
26. Methyl-salicylaldehyde	*Cinnamomum aromaticum*	Lauraceae	-	Leung, 1980
27. Sinaptic aldehyde	*Juglans cinerea*	Juglandaceae	heart wood	Gibbs, 1974
	J. nigra	"	"	"
	Quercus spp.	Fagaceae	"	"
	Acer saccharinum	Aceraceae	"	"
28. Sinaptyl aldehyde	*Santalum album*	Santalaceae	-	Leung, 1980
	S. spicatum	"	-	"

	Vanilla planifolia	"	fruit	"
	Ferula assa-foetida	Umbelliferae	-	Leung, 1980
	Ferula spp.	"	-	"
	Styrax spp.	Styracaceae	-	"
	Agropyron repens	Gramineae	-	"
	Liquidambar styraciflua	Hamamelidaceae	-	"
	L. orientalis	"	-	"
	Vanilla tanitensis	Orchidaceae	pod	"
	Ferula sinkiangensis	Umbelliferae	gum resin	"
	F. fukanensis	"	-	"
	Myroxylon pereirae	Leguminosae	-	"
	M. balsamum	"	-	"
30. Methylvanillin	*Eryngium poterium*	Umbelliferae	-	Gibbs, 1974
	Cymbopogon javanensis	Graminae	-	"
	Melaleuca leucadendron	Myrtaceae	-	Leung, 1980
31. Syringic aldehyde	*Santalum album*	Santalaceae	-	Leung, 1980
	S. spicatum	"	-	"

3.3 Biosynthesis of Benzaldehyde derivatives

(Goodwin and Mercer, 1983; Luckner, 1990)

Benzaldehyde derivatives derive from dihydrocinnamic acid. Dihydrocinnamic acids (phenylpropionic acids) are formed from cinnamic acids by hydrogenation of the side chain. In plants and microorganisms cinnamic acid is formed from L-phenylalanine by phenylalanine ammonia-lyase (PAL). This enzyme catalyzes the antiperiplanar elimination of the pro 3 (S)-hydrogen atom and the NH_2 group to yield *E*- cinnamic acid.

The biosynthesis of benzaldehyde derivatives is through dihydrocinnamic acids which are cleaved with the formation of a two-carbon fragment and an aromatic aldehyde. Aromatic aldehyde may be oxidized to the corresponding acids or reduced to the alcohols (Figure 2.6).

In the nature, aromatic aldehydes are produced from lignins. The lignins of monocotyledonous angiosperms, dicotyledonous angiosperms and gymnosperms are structurally different from one another. This difference stems from the structure of phenylpropane building units. This is apparent from the different aromatic aldehydes produced when native lignin from this sources is subjected to mild oxidation with nitrobenzene in alkaline medium. Gymnosperm lignin yields mostly vanillin *61* but also a little *p*-hydroxybenzaldehyde *62* , dicotyledonous lignin yields mostly vanillin and syringaldehyde *63* but also a little *p*-hydroxy-benzaldehyde whilst monocotyledonous lignin yied all three aldehydes (Figure 2.7). Nitrobenzene oxidation yields aromatic aldehydes from benzenoid nuclei with a hydroxyl group para to an aliphatic side chain when the α-carbon atom of the side chain bears a hydroxyl or sulphonic acid group, or is involved in the formation of a carbonyl group or a double bond. This indicates that vanillin, *p*-hydroxy-benzaldehyde and syringaldehyde arise from phenylpropane building units *58* , *59* and *60* respectively.

3.4 Aspects of some Naturally Occuring Aromatic Aldehydes

(Kirk and Othmer, 1948; Guenther, 1957; Bedoukian, 1967; Poucjer, 1974: Windholz, 1989) .

a. Anisaldehyde (aubepine or *p*-methoxy benzaldehyde or anisic aldehyde)

Anisaldehyde is a colorless to yellowish oil, possessing a strong odor characteristic of blooming hawthorn. It's properties are miscible with alcohol or ether, volatile with steam, soluble in 7-8 volume of 50 % alcohol and soluble in 300 volume of water with slight opalescence. On exposure to air, anisaldehyde is oxidized to *p*-anisic acid (m.p. 184.2°C). In combination with sodium bisulfite it is sold as crystallized aubepine. It is also very useful in general perfume work and for the scenting of soaps, particularly in lilac, heliotrope, hawthorn, acacia, mimosa, new mown hay, and sweet pea compositions.

b. Asaronaldehyde (2,4,5-Trimethoxybenzadehyde)

Asaronaldehyde is sparingly soluble in cold water but easily soluble in ether, benzene, or ligroine.

c. Benzaldehyde

Benzaldehyde is one of the first aromatic compounds to be isolated and identified. It is a strongly refractive, colorless liquid possessing a characteristic aromatic odor resembling that of bitter almonds. Benzaldehyde is volatile with steam and is 0.3% soluble in water at room temperature. It is miscible in all proportions with alcohol and ether at 25°C.

Benzaldehyde probably does not occur as such in plants but in the form of glucosides-for instance, amygdalin. Under the influence of enzymes this glucoside is split into benzaldehyde, glucose, and hydrocyanic acid. On exposure to air, benzaldehyde readily oxidizes to benzoic acid. An addition of 10% alcohol prevents oxidation by air, whereas an addition of less alcohol might accelerate the oxidation.

Benzaldehyde is widely used in industry. The N.F. grade serves the beverage and food industry as a flavoring agent and as an odorant. In pharmaceuticals, it is used as an ingredient in compounding and dispensing, as well as a flavoring agent. The technical grade is largely used as an intermediate in the synthesis of other chemicals such as cinnamaldehyde, amylcinnamaldelyde. During World War II it found wide applications in the South Pacific area as an insecticide against mites. Technical benzaldehyde can also be used for masking unpleasant odors in soaps and in sulfonated cutting oils.

d. Cinnamaldehyde

Cinnamaldehyde has long been known to be the main constituent of cinnamon oil. In 1833, Blanchet noticed that on the steam distilltion of Ceylon cinnamon, an oil was obtained, part of which was heavier than water. This heavy oil was subjected to an investigation by Dumas and Peligot who found the main constituent to have the empirical formula C_9H_8O (M.W. 132.16). Cinnamaldehyde is a yellow liquid possessing a powerful odor and flavor characteristic of cinnamon, volatile with steam. It is sparingly soluble in water, soluble in alcohol or ether, insoluble in petroleum ether. Its structure can exist in two isomeric forms. The natural product is the *trans* form, as is the commercial product. Because of its powerful odor, typical of cassia and cinnamon, cinnamaldehyde serves as a valuable ingredient in flavors and in perfumes for the imparting of spicy notes. It is also used widely for the scenting of soaps.

e. *o*-Methoxy cinnamaldehyde

A crystalline substance having an odor recalling cassia. Bertram and Kursten reported its properties: b.p. 295°C (with part decompositon), m.p. 45-46°C. *o*-Methoxy-cinnamaldehyde is very unstable and readily decomposes even without exposure to air and light. It imparts an intensely yellow color to the skin.

f. Cumaldehyde (Cuminic aldehyde, *p*-Isopropylbenzaldehyde, Cuminal)

Cumaldehyde is an oil possesing a disagreeable odor characteristic of cumin seed, volatile with steam. On oxidation with alkaline potassium permanganate, cumaldehyde yields cumic acid. Cumaldehyde is used for the compounding of synthetic cumin oil which serves for the flavoring of curry sauces and of exotic dishes in general. Because of its powerful odor, this aldehyde must be used sparingly.

g. Hydrocinnamaldehyde (β-phenylpropionaldehyde, Benzylacetaldehyde)

Hydrocinnamaldehyde is a colorless liquid with a powerful floral fragrance of hyacinth type and not unlike phenylacetic aldehyde. On exposure to air, hydrocinnamaldehyde oxidizes to hydrocinnamic acid. It is used widely but sparingly in all kinds of floral perfume compositions, especially lilac, jasmine, rose, and sweet pea.

h. Phenylacetaldehyde (α–Tolualdehyde, Phenylacetic aldehyde)

Phenylacetaldehyde is a viscous and highly odorous liquid widely used as the base of hyacinth oils. It is used quite widely in perfumes and in cosmetics. It serves in the compounding of hyacinth, narcissus, jonquil, jasmine, lilac, lily, certain rose types, and of general floral scents to which it imparts a refreshing top note, characteristic of hyacinth.

i. Piperonal (3,4-Methylenedioxy benzaldehyde, Heliotropin)

Piperonal consists of colorless, shiny crystals. It possesses a sweet, flower-like odor, characteristic of heliotrope. It is readily volatile with steam. The boiling point at 760 mm. is 263°C. It is soluble in the usual organic solvents, sparingly soluble in cold water, more readily in hot water from which it can be recrystallized in the form of large crystals. The solubility in water is 2:1000 at 12°C. Five parts of piperonal are soluble in 100 parts of 70% alcohol at 10°C. On exposure to light and air, piperonal turns yellow and finally decompose, being very slowly oxidized to piperonylic acid. Piperonal is used widely in perfumery and for the scenting of cosmetics and soaps. Due to its distinct heliotrope odor it serves in lilac, carnation, sweet pea, and in fancy bouquets of all types. It blends well with coumarin and vanillin and imparts a lasting sweetness wherever used.

j. Salicylaldehyde (*o*-Hydroxybenzaldehyde)

Salicylaldehyde is an aromatic liquid with an odor recalling that of meadow-sweet. It is volatile with steam, sparingly soluble in water, miscible with alcohol and ether. Oxidation of salicylaldehyde yields salicylic acid. Small quantities of salicylaldehyde are used in flavor work, also in the compounding of synthetic flower oils. The principal use, however, is a starting material for the synthesis of coumarin.

k. Vanillin (4-Hydroxy-3-methoxybenzaldehyde, Protocatechualdehyde-3-methyl ether)

This important aromatic aldehyde is widely distributed in nature, although it occurs in essential oils, gums, and balsams only in small quantities. Most likely plants do not contain vanillin as such but in the form of glucosides which by enzyme action release vanillin. The most important source of natural vanillin is the vanilla bean (fruit). The vanilla beans are collected while they are still unripe and just when they begin to turn yellow at the ends. When picked they are odorless. The curing process is responsible for the aroma of vanilla and after sorting the pods into long, short, and broken grades. Vanilla contains about 2% of vanillin together with anisaldehyde, anisyl alcohol, and free anisic acid. Vanillin crystallizes from hot water in the form of colorless needles. It possesses a strong and intensely sweet odor characteristic of vanilla. On careful heating, vanillin can be sublimated without decomposition; by prolonged heating at 105°C vanillin decomposes with formation of nonvolatile products. It is readily soluble in alcohol, ether, chloroform, soluble in hot water,

relatively insoluble in cold water, for which reason vanillin can be recrystallized from water. At 75-80°C, 1 part of vanillin dissolved in 20 parts of water, at 14°C in 90-100 parts of water. At 7-8°C the greater part of vanillin will gradually crystallize from water. Vanillin is the main ingredient in artificial vanilla flavors. It is used most extensively for the flavoring of confectionery, baked goods, candies, chocolates, ice creams, etc. It serves widely also in perfumes and cosmetics for imparting sweet and lasting notes. It blends well with heliotropin and coumarin. Vanillin can serve as a starting material for the synthesis of other compouds and for the manufacture of a range of pharmaceuticals. Vanillin derivative, ethyl vanillin; which has not been found in nature, has a truer vanilla bean flavor than vanillin and is generally considered to be the of four times stronger in flavor.

1. 4-methoxysalicylaldehyde (2-Hydroxy-4-methoxybenzaldehyde)

4-Methoxysalicylaldehyde, $C_8H_8O_3$ (M.W. 152.14), has been found in the order Gentianales which might prove of real interest. It has been reported from several genera of Asclepiadaceae and Apocynaceae. Friedlaender and Schuloff reported its properties: m.p. 41°C, characteristic aromatic odor, suggestive of vanillin.

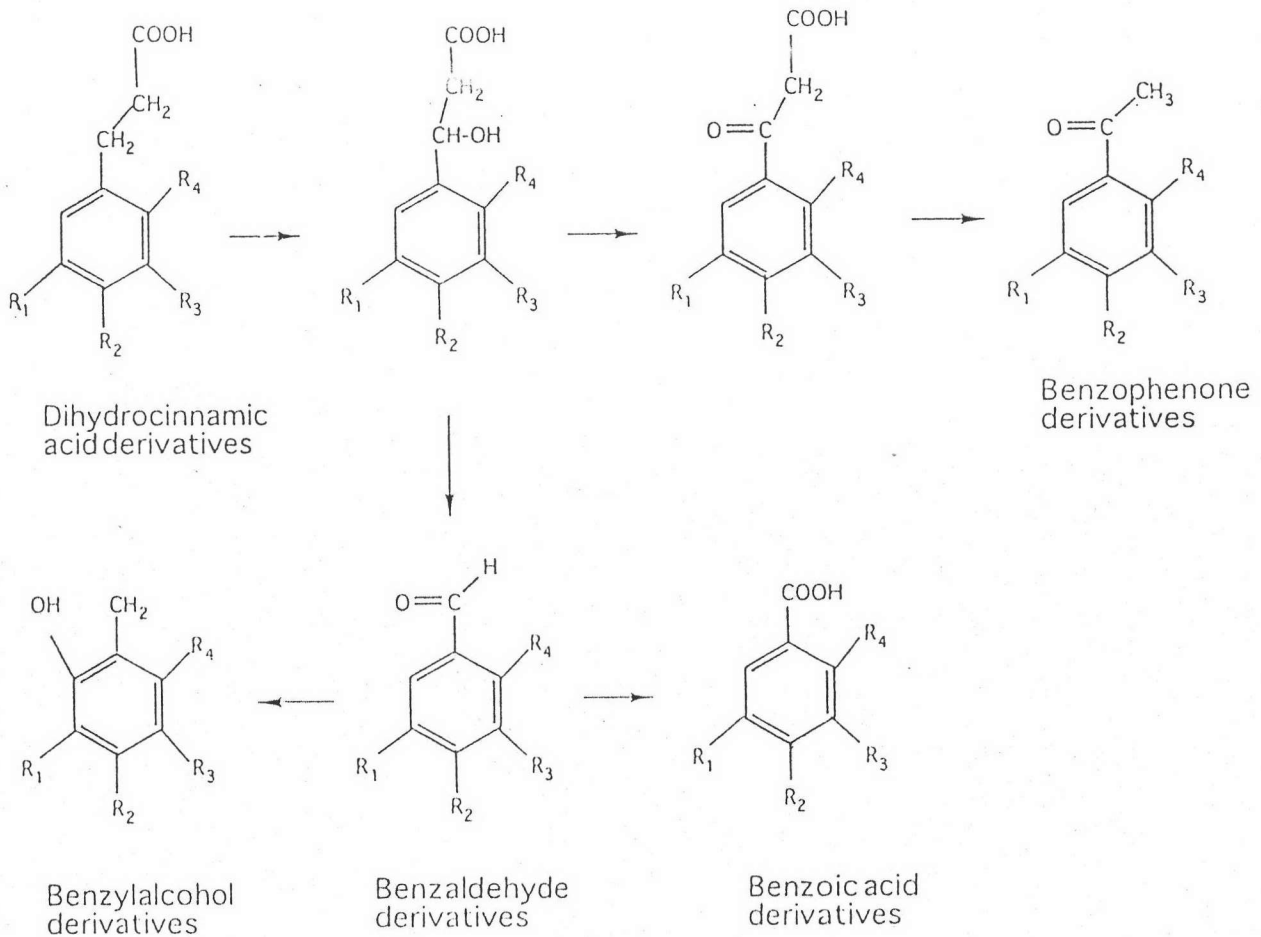


Figure 2.6 Biosynthesis of benzaldehyde derivatives

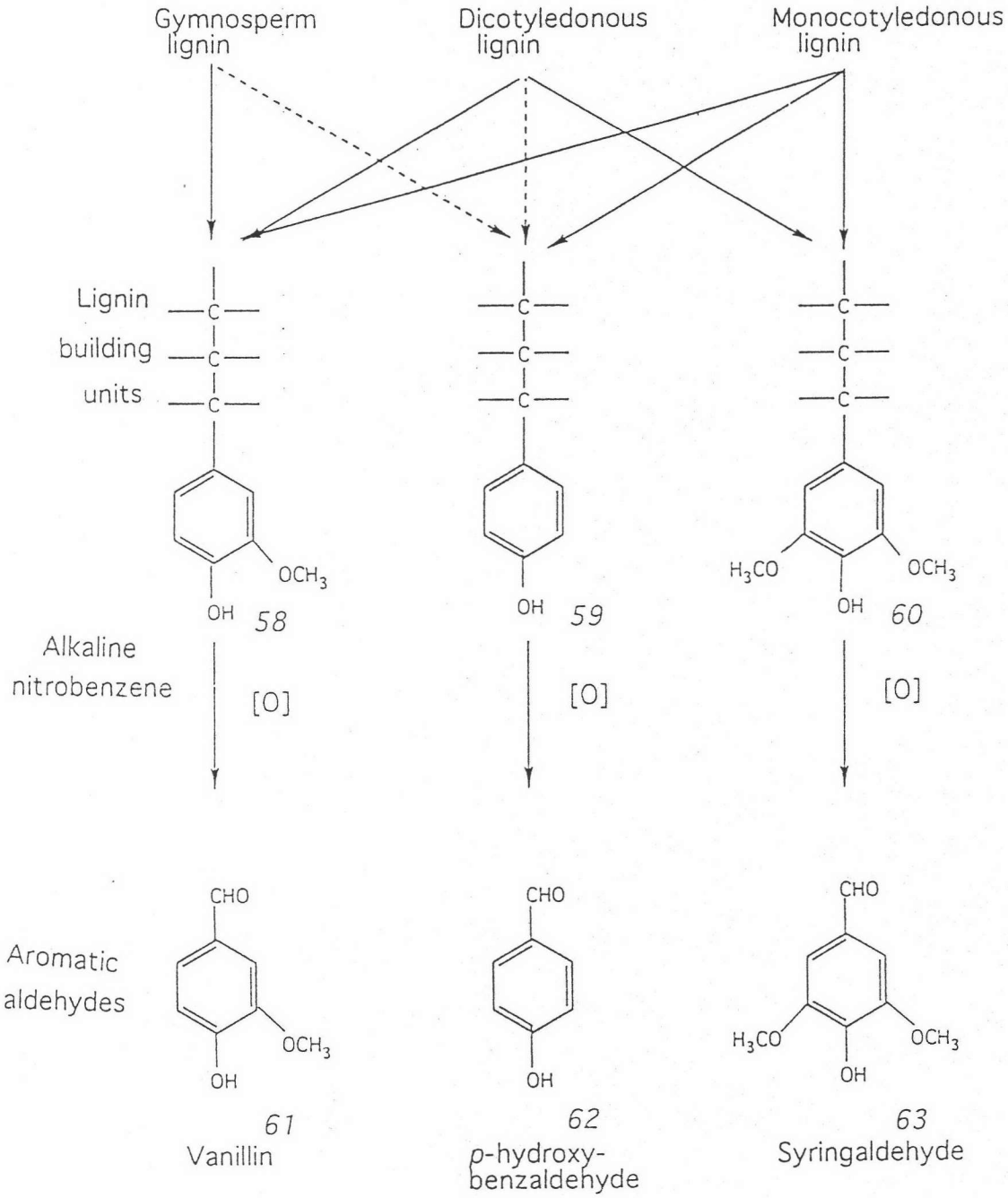


Figure 2.7 Aromatic aldehydes released from lignin by mild oxidation with Alkaline Nitrobenzene