CHAPTER II

HISTORICAL

Occurrence of Chemical Compounds in Species of *Albizia*

1. *Albizia adianthifolia* W.F. Wight.

Plant Part	Chemical Compound	Reference
Root	Acacic acid and Polysaccharide : glucose, arabinose, xylose and rhamnose in ratio 1:1:1:1	Comean, 1974
	Glucuronic acid and Polysaccharide : rhamnose and arabinose	Varshney, 1973
	4′,5,7 -trihydroxyflavanone (Naringenin)	Nogueira, 1962
	4′,5,7 -trihydroxyflavanone-7-rhamnoglucoside (Naringin)	Nogueira, 1962
	β- Phenethylamine	Nogueira, 1962
Wood	3-3′-4′-7-8-pentahydroxyflavanone	Candy, 1978
	Melanoxetin	Candy, 1978
	Okanin	Candy, 1978
Trunkbark	Histamine	Mazzani *et al.*, 1983
	N-acetylhistamine	Mazzani *et al.*, 1983
	Imidazole acetic acid	Mazzani *et al.*, 1983

2. *Albizia amara* Boiv.

Plant Part	Chemical Compound	Reference
Seed	Echinocystic acid	Varshney, 1973
	Neutral genin	Varshney, 1973
	(-)-2,3-*cis*-3,4-*cis*-3-O-methylmelacacidin and its methyl ether	Deshpande and Shastri, 1977
	3′-O-methylmelanoxetin	Deshpande and Shastri, 1977
	Arachidic acid	Chandra,Sud and Handa, 1956
	Behenic acid	Chandra,Sud and Handa, 1956
	Budmunchiamine A,B,C	Pezzuto, 1991
	Budmunchiamine D,E,F,G,H,I	Pezzuto, 1992
	Lignoceric acid	Chandra,Sud and Handa, 1956
	Linoleic acid	Chandra,Sud and Handa, 1956
	Myristic acid	Chandra,Sud and Handa, 1956
	Oleic acid	Chandra,Sud and Handa, 1956
	Palmitic acid	Chandra,Sud and Handa, 1956

2. *Albizia amara* Boiv. (cont.)

Plant Part	Chemical Compound	Reference
Seed	β-Sitosterol	Chandra,Sud and Handa, 1956
	Stearic acid	Chandra,Sud and Handa, 1956
	Albizziin	Krauss, 1970
	S-(β-carboxy-ethyl)-L-cysteine	Krauss, 1970
Leaves	S-(β-carboxy-isopropyl)-L-cysteine	Krauss, 1970
	Pipecolic aicd	Krauss, 1970
Wood	A mixture of oleanolic and echinocystic acid with glucose, arabinose and rhamnose	Reddy, 1967
	4′-O-methylquercetin-3-rutinoside	Reddy, 1967
	Oleanolic acid	Reddy, 1967

3. *Albizia anthelmintica* Brongn.

Plant Part	Chemical Compound	Reference
Seed	4-Hydroxypipecolic acid	Krauss, 1970
	Albizziin	Krauss, 1970
	S-(β-carboxy-ethyl)-L-cysteine	Krauss, 1970
	S-(β-carboxy-isopropyl)-L-cysteine	Krauss, 1970
Root Bark	Musenin	Kariyone *et al*, 1972 ;Tschesche, 1957
	Deglucomusenin	Kariyone *et al*, 1972

3. *Albizia anthelmintica* Brongn. (cont.)

Plant Part	Chemical Compound	Reference
Root Bark	Echinocystic acid :	
	3-O-[α-L-arabinosyl-(1-2)]- [α-L-arabinosyl-(1-6)]-2-acetamino-2-deoxy-β-D-glucosyl	Carpani, 1989
	3-O-[α-L-arabinosyl-(1-6)]-2-acetamino-2-deoxy-β-D-glucosyl	Carpani, 1989
	3-O-[β-D-glucosyl-(1-3)]- [α-L-arabinosyl-(1-2)]-[α-L-arabinosyl-(1-6)]-2-acetamino-2-deoxy-β-D-glucosyl	Carpani, 1989
	Histamine	Mazzani *et al.*, 1983

4. *Albizia baromensis* Benth.

Plant Part	Chemical Compound	Reference
Root	Acacic acid and Polysaccharide; glucose, arabinose, xylose, and rhamnose in ratio 1:1:1:1	Comean, 1974

5. *Albizia distachya* Benth.

Plant Part	Chemical Compound	Reference
Rootnodule	Asparagine	Le,Goas and Larher, 1982
	α-Alanine	Le,Goas and Larher, 1982

6. *Albizia falcata* Backer.

Plant Part	Chemical Compound	Reference
Seed	Albizziin	Krauss, 1970
	S-(β-carboxy-ethyl)-L-cysteine	Krauss, 1970
	S-(β-carboxy-isopropyl)-L-cysteine	Krauss, 1970
	Djenkolic acid	Krauss, 1970
	4-Hydroxylpipecolic acid	Krauss, 1970
Wood	α-Spinasterol	Yatagai *et al*, 1978
	Quercetin	Yatagai *et al*, 1978
	(±) - taxifolin	Yatagai *et al*, 1978
	(±) - fustin	Yatagai *et al*, 1978

7. *Albizia ferruginea* Benth.

Plant Part	Chemical Compound	Reference
Root	16β,21β-dihydroxyolean-21-en-28-oic acid	
	Acacic acid and Polysaccharide : glucose, arabinose, xylose and rhamnose in ratio 1:1:1:1	Comean, 1974

8. *Albizia glaberima* Benth.

Plant Part	Chemical Compound	Reference
Gum	Aldobiouronic acid	Anderson, 1966
Root	Acacic acid and Polysaccharide : glucose, arabinose, xylose and rhamnose in ratio 1:1:1:1	Comean, 1974

9. *Albizia gummifera* Benth.

Plant Part	Chemical Compound	Reference
Bark	Albitocin	Varshney, 1973; Lipton, 1963
Gum	Galactose and Arabinose	Adriaens, 1943

10. *Albizia julibrissin* Durazz.

Plant Part	Chemical Compound	Reference
Seed	Albizziin (α-amino-β-ureido-propionic acid)	Gmelin, 1959; Krauss, 1970
	S-(β-carboxy-isopropyl)-L-cysteine	Krauss, 1970
	S-(2-carboxyethyl)-L-cysteine	Gmelin, 1959
	L-2-amino-3-ureido-propionic acid	Kariyone, 1972
	Albizia julibrissin proteinase inhibitor A-II, A-III, B-I, B-II	Odani *et al*, 1979
	Albizide	Sergienko, Mogilevtseva and Chirva, 1977
	Lauric acid	Badami and Daulatabad, 1969
	Lignoceric acid	Badami and Daulatabad, 1969
	Linoleic acid	Badami and Daulatabad, 1969
	Myristic acid	Badami and Daulatabad, 1969

10. *Albizia julibrissin* Durazz. (cont.)

Plant Part	Chemical Compound	Reference
Seed	Oleic acid	Badami and Daulatabad, 1969
	Palmitic acid	Badami and Daulatabad, 1969
	Stearic acid	Badami and Daulatabad, 1969
	Arachidic acid	Badami and Daulatabad, 1969
	Behenic acid	Badami and Daulatabad, 1969
Seedling	Isowillardine synthase	Murakoshi *et al*, 1978
	Willardine synthase	Murakoshi *et al*, 1978
Heartwood	4,6-Dimethoxyphthalide	Nakano and Takashima, 1975
	(±)-pinitol	Nakano and Takashima, 1975
	α -Spinasterol	Nakano and Takashima, 1975
	α -Spinasterone	Nakano and Takashima, 1975
Plant tissue	Serotonin and norepinephrine	Apple, 1973 You *et al*, 1982 ;

10. *Albizia julibrissin* Durazz. (cont.)

Plant Part	Chemical Compound	Reference
Stembark	Machaerinic acid methyl ester	Kong and Woo, 1983
	Acacic acid lactone	You *et al*, 1982 ; Woo, 1985
	3′,4′,7′-Trihydroxyflavone	Chamsuksai,Choi and woo, 1981
	α -Spinasteryl-D-glucoside	Tovivich, Woo and Chamsuksai, 1982 ; Chamsuksai and Woo, 1984
	Acacigenin B	Kong and Woo, 1983
	21-[4-(ethylidine)-2-tetrahydrofuran-methacryloy] machaerinic acid	Woo and Kong, 1984
	Carbohydrate : Alju A, Alju B	Moon *et al*, 1985
	7,3′,4′-Trihydroxyflavone	Chamsuksai and Woo, 1984
	Eleutheroside D	Kinjo, 1991
Plant tissue	Glaberide I :	
Stembark	4-0-β-D-apiofuranosyl-β-D-glucopyranoside	Kinjo, 1991
	4-O-β-D-glucopyranoside	Kinjo, 1991
	Icariside E-5	Higuchi *et al*, 1992
		Higuchi,Kinjo and Nohara, 1992
	Julibrine I, II	
	Julibroside I, II, III	Ikeda *et al*, 1995
	Julibrotriterpenoidal lactone A	Kang and Chen, 1992

10. *Albizia julibrissin* Durazz. (cont.)

Plant Part	Chemical Compound	Reference
Plant tissue Stembark	4′-O-β-D-apiofuranosyl-β-D-Glucopyranoside-5-5′-dimethoxy-7-oxo-lariciresinol	Kinjo, 1991
	4-O-β-D-apiofuranosyl-β-D-Glucopyranoside-5-5′-dimethoxy-lariciresinol	Kinjo, 1991
	Liriodendrin	Higuchi,Kinjo and Nohara, 1992
	Lyoniresinol-4,9′-*bis*-O-β-glucopyranoside	Higuchi *et al*, 1992
	Lyoniresinol-9′-O-β-D-glucopyranosyl-β-D-glucopyranoside	Higuchi *et al*, 1992
	1-O-β-D-apiofuranosyl(1-2)-β-D-glucopyranoside-3-4-5-trimethoxyphenol	Higuchi,Kinjo and Nohara, 1992
	3-O-β-D-Glucoside-3-hydroxy-5-hydroxy-methyl-4-methoxy-methyl-2-methylpyridine	Higuchi,Kinjo and Nohara, 1992
	α -Spinasterol	Nakano, 1975
	α -Spinasterol-3-O-β-D-Glucoside	Chamsuksai, 1982
	α -Spinasterol-β-D-Glucoside	Chamsuksai, 1981
	α -Spinasterol-glucoside	Tovivich, 1981
	Stigmast-7-en-3-β-ol	Chamsuksai, 1981
	Syringaresinol tetraglucoside	Kinjo, 1991
	Syringaresinol triglucoside	Kinjo, 1991

10. *Albizia julibrissin* Durazz. (cont.)

Plant Part	Chemical Compound	Reference
Plant tissue Stembark	(-)-Syringaresinol-4-4′- *bis*-O-β-D-apiofuranosyl(1-2)-β-D-glucopyranoside	Kinjo *et al*, 1991
	(-)-Syringaresinol-4-4′- *bis*-O-β-D-glucopyranoside	Kinjo *et al*, 1991
	(-)-Syringaresinol-4-O-β-D- apiofuranosyl(1-2)-β-D-glucopyranoside	Kinjo *et al*, 1991
	(-)-Syringaresinol-4-O-β-D-apiofuranosyl(1-2)-β-D-glucopyranosyl-4′-O-β-D-glucopyranoside	Kinjo, 1991
	Syringaresinol-4-O-β-D-apiofuranosyl(1-2)-β-D-glucopyranoside	Kinjo, 1991
	Syringaresinol-4-O-β-D-glucopyranoside	Kinjo, 1991
	(-)-Syringaresinol-4-O-β-D-glucopyranoside	Kinjo *et al*, 1991
	Syringic acid methyl ester -4-O-β-D-apiofuranosyl-β-D-glucopyranoside	Kinjo, 1991
	Vomifoliol-3′-O-β-D-apiofuranosyl-β-D-glucopyranoside	Higuchi *et al*, 1992
Flower	Cyanidin-3-glucoside	Ishikura, Ito and Shibata, 1978
	Quercetin	Kaneta *et al*, 1980
	Apigenin	Kaneta *et al*, 1980
	Isorhamnetin	Kaneta *et al*, 1980
	Luteolin	Kaneta *et al*, 1980
	Acacetin	Kaneta *et al*, 1980
	Kaemferol	Kaneta *et al*, 1980

10. *Albizia julibrissin* Durazz. (cont.)

Plant Part	Chemical Compound	Reference
Flower	Linalool	Li *et al*, 1988
	α-Ocimene	Li *et al*, 1988
	Isopentan-1-ol	Li *et al*, 1988
Leaf	Quercetin	Kariyone, 1972
	Calcium oxalate	Borchert, 1985
	Acetylcholine	Farooq, Varshney and Hasan, 1958
	3-O-(3,4-dihydroxy-*trans*-cinnamoyl)-4-O-malonyl quinic acid	Schaller and Schidknecht, 1992
	3-O-(4-hydroxy-*trans*-cinnamoyl) quinic acid	Schaller and Schidknecht, 1992
	Riboflavin	Schaller and Schidknecht, 1992
	5-Hydroxytryptamine	Smith, 1977
Entire Plant	Hyperoside	Kaneta *et al*, 1980

11. *Albizia lebbeck* Benth.

Plant Part	Chemical Compound	Reference
Seed	Lebbekanin A	Varshney *et al*, 1973
	Albigenin	Varshney, 1973
	Echinocystic acid	Varshney, 1973
	Oleanolic acid	Varshney, 1973
	Albigenic acid	Varshney, 1973

11. *Albizia lebbeck* Benth. (cont.)

Plant Part	Chemical Compound	Reference
Seed	Arachidic acid	Farooq and Varshney, 1954
	Behenic acid	Rudrappa and Revadi, 1991
	Heneicos-*cis*-7-enyl-24-hydroxy-tetracosa-*cis*-10-enoate	Agrawal and Singh, 1991
	Linoleic acid	Farooq and Varshney, 1954
	Linolenic acid	Rudrappa and Revadi, 1991
	Myristic acid	Kafuku and Hata, 1934
	Oleanolic acid	Agrawal and Singh, 1991
	Oleic acid	Farooq and Varshney, 1954
	Palmitic acid	Farooq and Varshney, 1954
	Stearic acid	Farooq and Varshney, 1954
Pods	Lebbekanin C	Varshney, 1973
Bark	Acacic acid	Varshney, 1973
	Friedelan-3-one	Tripathi, 1974

11. *Albizia lebbeck* Benth. (cont.)

Plant Part	Chemical Compound	Reference
Bark	Campesterol	Tripathi, 1974
	β-Sitosterol	Tripathi, 1974
	(+)-Leucocyanidin	Rayudu, 1965
	D-Catechin tannin	Rayudu, 1965
	Stigmasterol	Tripathi, 1974
	α-Amyrin ; β-Amyrin	Jain and Mishra, 1963
	Crocetin	Jain and Mishra, 1963
	Friedelin	Chandler and Hooper, 1979
	Hexenol Acetate	Jain and Mishra, 1963
	Lupeol	Jain and Mishra, 1963
Wood	Lebbekanin E	Varshney, Pal and Vyas, 1976
	Lebbekanin B	Varshney, Pal and Vyas, 1976
Heartwood	(-)-Melacacidin	Rayudu and Rajadurai, 1966
	Lebbecacidin	Rayudu and Rajadurai, 1966

11. *Albizia lebbeck* Benth. (cont.)

Plant Part	Chemical Compound	Reference
Heartwood	3′-O-Methylmelanoxetin	Deshpande and Shastri, 1977
	(-)-2,3-*cis*-3,4-*cis*-3-O-methylmelacacidin	Deshpande and Shastri, 1977
	(+)-Pinitol	Gupta, Malik and Seshadri, 1966
	3,3′,4′,7,8-pentahydroxyflavone	Gupta, Malik and Seshadri, 1966
	(-)-Leucopelargonidin	Gupta, Malik and Seshadri, 1966
	Melanoxetin	Deshpande and Shastri, 1977
	3′-O-methylmelanoxetin	Deshpande and Shastri, 1977
	Okanin	Gupta, Malik and Seshadri, 1966
Leaves	Vincinin II	Morita at el, 1978
	Reynantrin	Morita at el, 1978
	Rutin	Morita at el, 1978
	Robinin	Morita at el, 1978
	Aspartic acid	Gaulier, 1968
	Aspartic acid amide	Mukherjee, 1977
	Glutamic acid	Gaulier, 1968
	Glutaric acid; α -Keto; Glycyl serine	Mukherjee, 1977

11. *Albizia lebbeck* Benth. (cont.)

Plant Part	Chemical Compound	Reference
Leaves	Leucyl phenylalanine	Mukherjee, 1977
	Methionine	Gaulier, 1968
	Oxaloacetic acid	Mukherjee, 1977
	Phosphoenol glyoxalate; Phosphoenol pyruvate	Mukherjee, 1977
Flower	Lebbekanin F,G	Varshney and Jain, 1978
	Lebbekanin D,H	Morita at el, 1978
	β -Sitosterol	Varshney and Jain, 1978
	Quercetin glycoside	Varshney, 1973

12. *Albizia lebbeckoides* Benth.

Plant Part	Chemical Compound	Reference
Pericarp of fruit	Albizziagenin	Forroq and Varshney, 1953

13. *Albizia lophantha* Benth.

Plant Part	Chemical Compound	Reference
Seed	Albizziine (2-amino-3-ureido-propionic acid)	Reinbothe, 1962
	Djenkolic acid	Watt and Breyer, 1962
Root	Alanine	Krauss,1970
	Arginine	Krauss,1970

13. *Albizia lophantha* Benth.(cont.)

Plant Part	Chemical Compound	Reference
Root	Aspartic acid	Krauss,1970
	Glutamic acid	Krauss,1970
	Glycine	Krauss,1970
	C-S-lyase	Gregor and Gmelin, 1979
	Serine	Krauss,1970
Leaf	L-Djenkolic acid	Krauss,1970
	L-Glutamine	Krauss,1970
Leaf	β -Phenethylamine	Willaman and Schubert, 1961
	Pipecolic acid	Krauss,1970
	4-Hydroxy pipecolic acid	Krauss,1970
	Proline	Krauss,1970
Fruit	Allantoin	Hofmann, Schlee and Reinbothe, 1969
	Histidine	Hofmann, Schlee and Reinbothe, 1969
Entire plant	Purine	Hofmann, Schlee and Reinbothe, 1969
	4-Hydroxy-piperidine-2-carboxylic acid	Virtanen and Kari, 1955

14. *Albizia lucida* Benth.

Plant Part	Chemical Compound	Reference
Seed	Echinocystic acid	Varshney, 1973
	Oleanolic acid	Varshney, 1973
	A neutral sapogenin	Varshney, 1973
	3-O-[α-L-arabinosyl-(1-6)]- [β-D-glucopyanosyl-(1-2)]-β-D-glucopyranosyl echinocystic acid	Orsini, Pelizzoni and Verotta, 1991
	3-O-[β-D-xylopyanosyl-(1-2)]- α-L-arabinosyl-(1-6)-(β-D-glucopyanosyl-(1-2)]-β-D-glucopyranosyl echinocystic acid	Orsini, Pelizzoni and Verotta, 1991
	3-O-[β-D-xylopyanosyl-(1-2)]- β-D-fucopyranosyl-(1-6)-2-acetamido-2-Deoxy-β-D-glucopyanosyl echinocystic acid	Orsini, Pelizzoni and Verotta, 1991
	3-O-β-D-glucoside-3-hydroxy-5-hydroxy-methyl-4-methoxy-methyl-2-methyl pyridine	Orsini, Pelizzoni and Verotta, 1991
	3-O-β-D-glucoside-5-(hydroxy-methyl)-4-(methoxy-methyl)-2-methyl pyridine	Orsini at el, 1989
Bark	β -Sitosterol	Varshney and Sharma, 1969
Entire plant	α -Spinasterol	Banerjee and Mahato, 1965

15. *Albizia myriophylla* Benth.

Plant Part	Chemical Compound	Reference
Wood	Catechin tannin	Sasorith, 1969
Bark	Albizzine A	Ito at el, 1994
	Albizzioside A, B, C	Ito at el, 1994
	(-)-Syringaresinol-4-O-β-D- apiofuranosyl(1-2) -β-D-glucopyranoside	Ito at el, 1994

16. *Albizia odoratissima* Benth.

Plant Part	Chemical Compound	Reference
Heartwood	(+)-Penta-O-methyldihydromelanoxetin	Ramachandra and Reddy, 1963
Seed	Odoratissimin	Varshney, 1973
	Machaerinic acid	Varshney, 1973
	Acacic acid	Varshney, 1973
	Saponin	Varshney and Khan, 1961
	Albizziin	Krauss,1970
	Arachidic acid	Ahmad and Akhtar, 1991
	Behenic acid	Ahmad and Akhtar, 1991
	Capric acid	Ahmad and Akhtar, 1991
	S-(2-carboxyethyl)-L-cysteine	Krauss,1970
	S-(β-carboxyisopropyl)-L-cysteine	Krauss,1970

16. *Albizia odoratissima* Benth. (cont.)

Plant Part	Chemical Compound	Reference
Seed	L-Djenkolic acid	Krauss,1970
	Echinocystic acid	Varshney and Khan, 1962
	Lauric acid	Ahmad and Akhtar, 1991
	Lignoceric acid	Ahmad and Akhtar, 1991
	Linoleic acid	Rudrappa and Revadi, 1991
	Linolenic acid	Rudrappa and Revadi, 1991
	Myristic acid	Ahmad and Akhtar, 1991
	Odoratissimin	Varshney and Khan, 1962
	Oleic acid	Rudrappa and Revadi, 1991
	Palmitic acid	Rudrappa and Revadi, 1991
	4-Hydroxy-pipecolic acid	Krauss, 1970
	Stearic acid	Ahmad and Akhtar, 1991

17. *Albizia procera* Benth.

Plant Part	Chemical Compound	Reference
Seed	Proceranin	Varshney at el, 1973
	Proceric acid	Varshney, 1973
	Prosapogenin A (Lactone)	Varshney, 1973
	Prosapogenin B (Lactone)	Varshney, 1973
	Proceranin A	Varshney, 1973
	Albizziin	Gmelin, 1958
	Arachidic acid	Farooq at el, 1959
	Echinocystic acid	Varshney and Badhwar, 1972
	Fixed Oil	Varshney, Vyas and Beg, 1980
	Linoleic acid	Farooq at el, 1959
	Machaerinic acid	Roy,1967
	3-Dihydroxy-olean-12(13)enoic acid	Farooq,Varshney and Hasan, 1959
	Ethyl-3- -21-dihydroxy-olean-12-en-28-oate	Ray, 1963
	Oleic acid	Farooq at el, 1959
	Palmitic acid	Farooq at el, 1959
	Stearic acid	Farooq at el, 1959
Root	α -Spinasterol	Benerji, Misra and Nigam, 1979
	Oleanolic acid	Benerji, Misra and Nigam, 1979

17. *Albizia procera* Benth. (cont.)

Plant Part	Chemical Compound	Reference
Heartwood (Heartwood and Bark)	Pterocarpan	Deshpande and Shastri, 1977
	Biochanin A	Deshpande and Shastri, 1977
	Formononetin	Deshpande and Shastri, 1977
Gum	Genistein	Deshpande and Shastri, 1977
	Daidzein	Deshpande and Shastri, 1977
	β -Sitosterol	Varshney, Bhatnagar and Logani, 1965
	Aldobiuronic acid and its D-galactose, L-arabinose and L-rhamnose in ratio 3:2:0.7	Farooqis and Koul, 1965
Leaf	N-Hentriacontane	Banerji, Misra and Nigam, 1979
	Hexacosan-1-ol	Banerji, Misra and Nigam, 1979

18. *Albizia stipulata* Boiv.

Plant Part	Chemical Compound	Reference
Root	Acacic acid and Polysaccharide : glucose, arabinose, xylose and rhamnose in ratio 1:1:1:1	Comean,1974
Bark	Oleanolic acid	Narayanan *et al*, 1977
	Hydroxyoleanolic acid	Narayanan *et al*, 1977
Leaf	Protein	Sharma, Chander and Negi, 1969

19. *Albizia sericocephala* Benth.

Plant Part	Chemical Compound	Reference
Gum	Aldobiouronic acid	Anderson, 1966

20. *Albizia zygia* Macbride.

Plant Part	Chemical Compound	Reference
Seed	Albizziin	Krauss,1970
	S-(β-carboxyethyl)-L-cysteine	Krauss,1970
	L-Djenkolic acid	Krauss,1970
Root	Acacic acid and Polysaccharide : glucose, arabinose, xylose and rhamnose in ratio 1:1:1:1	Comean,1974
Root	Albizziaprenal	Pachaly, Redeker and Schoppa, 1983

20. *Albizia zygia* Macbride.(cont.)

Plant Part	Chemical Compound	Reference
Root	Phytol	Pachaly, Redeker and Schoppa, 1983
Leaves,Bark	Lupen-20(30)-en-3β-ol	Schoppa and Pachaly, 1981
	Stigmast-5-en-2β-ol	Schoppa and Pachaly, 1981
	5 α-Stigmasta-7,22-dien-3β-ol	Schoppa and Pachaly, 1981
	Lupeol	Pachaly, Redeker and Schoppa, 1983
Gum	L-arabinose	Kariyone *et al*, 1972
	D-mannose	Kariyone *et al*,1972
	D-galactose	Kariyone *et al*,1972
	L-rhamnose	Kariyone *et al*,1972
	D-glucuronic acid	Kariyone *et al*,1972
	4-O-methyl-D-glucuronic acid	Kariyone *et al*,1972
	3-O-β-galactopyranosyl-D-arabinose	Kariyone *et al*,1972
	3-O-β-D-galactopyranosyl-D-galactose	Kariyone *et al*,1972
	6-O-β-D-galactopyranosyl-D-galactose	Kariyone *et al*,1972
	4-O-α-(4-O-methyl-D-glucopyranuronosyl)-D-galactose	Kariyone *et al*,1972
	4-O-β-D-glucopyranuronosyl-D-mannose	Kariyone *et al*,1972

I. Spermidine and Related Alkaloids

Chemical Nature of Spermidine and Related Alkaloids

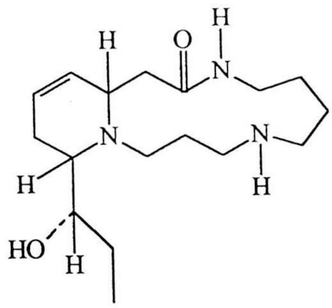
The two polyamines, spermidine and spermine are analogues of the diamine putrescine, which is produced by reductive decarboxylation of lysine. They may be regarded therefore as being derived from a core unit of putrescine, which is then substituted on N either once or twice by propylamine residues(Cordell, 1981).

The structures of some polyamine are shown in below(Smith, 1972) :

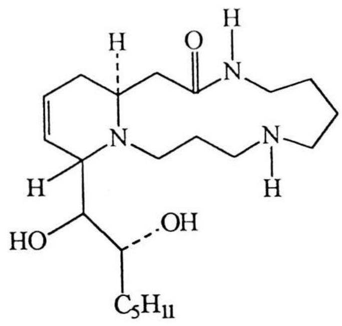
$NH_2(CH_2)_3NH_2$	1,3 -Diaminopropane
$NH_2(CH_2)_4NH_2$	Putrescine
$NH_2(CH_2)_5NH_2$	Cadaverine
$NH_2(CH_2)_4NH\text{-}\underset{\underset{NH}{\|}}{C}\text{-}NH_2$	Agmatine
$NH_2(CH_2)_3NH(CH_2)_3NH_2$	3,3′ - Diaminodipropylamine
$NH_2(CH_2)_3NH(CH_2)_4NH_2$	Spermidine
$NH_2(CH_2)_4NH(CH_2)_4NH_2$	Homospermidine
$NH_2(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$	Spermine
$NH_2\underset{\underset{NH}{\|}}{C}\text{-}NH_2(CH_2)_4NH\text{-}\underset{\underset{NH}{\|}}{C}NH_2$	Arcain
$NH_2\underset{\underset{NH}{\|}}{C}NH(CH_2)_3NH(CH_2)_4NH\underset{\underset{NH}{\|}}{C}NH_2$	Hirudonine

The polyamines, spermidine and spermine, are nonprotein nitrogenous base that are widely distributed in natural materials. They occur in almost all animals and microorganisms and possibly most higher plants. The highest concentration of spermidine and spermine in animal tisssue are found in pancreas, prostate, and human semen (Tabor and Tabor, 1964). The polyamines of human semen are formed primarily in the prostate gland, an organ the size of a chestnut located to the base of the bladder. They may be present for their bacteriostatic effects or for stabilization of DNA. Spermidine and spermine also occur (12:1 ratio) in high concentration in human semen (0.5-3.5 ml)(Cordell, 1981) .Detection and isolation from higher plants used as food stuffs include cabbage leaves, tomato juice, apple and spinach as well as the leaves of wheat, maize, pea, black current and tobacco. The crystals of spermine phosphate were first detected by Leeuwenhoek in 1678. The name was given by Ladenburg some 210 year later, although the structure of this simple amine was not deduced until 1926. Shortly thereafter, spermine was isolated from ox pancreas, and the postulated structure was also confirmed by synthesis(Tabor and Tabor, 1964 ; Smith, 1972).

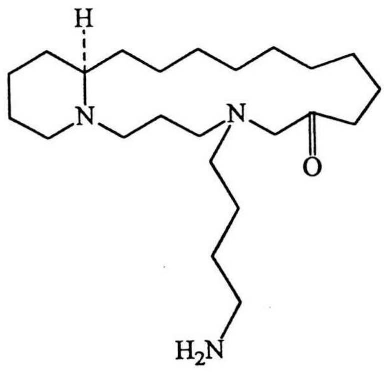
Structurally, the most interesting alkaloids containing spermidine and spermine are those containing a macrocyclic ring. Typically these compounds are produced by the condensation of one nitrogen molecule with a carboxylic acid molecule, and the nucleophilic attach of a second nitrogen molecule on an electrophilic center within the unit containing carboxylic acid. Several alkaloids contain spermidine joined with two cinnamic acid units in any of several ways (e.g. lunarine, codonocarpine and pleurostyline). This can clearly result in quite a substantial number of structure types, and some representative examples are shown in Figure 1(Cordell, 1981).



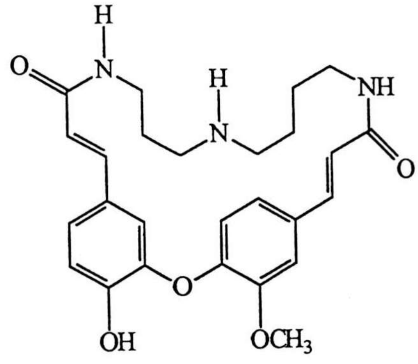
Palustrine



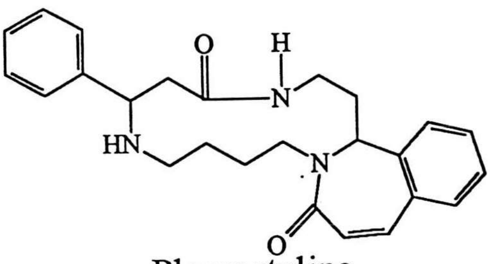
Cannabissativine



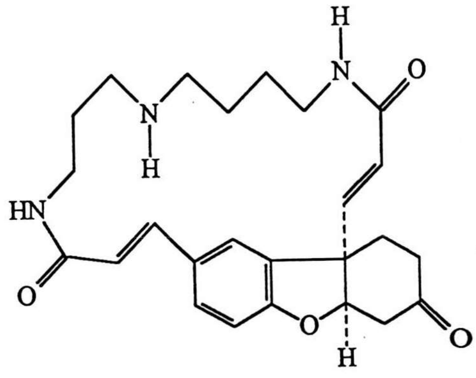
Oncinotine



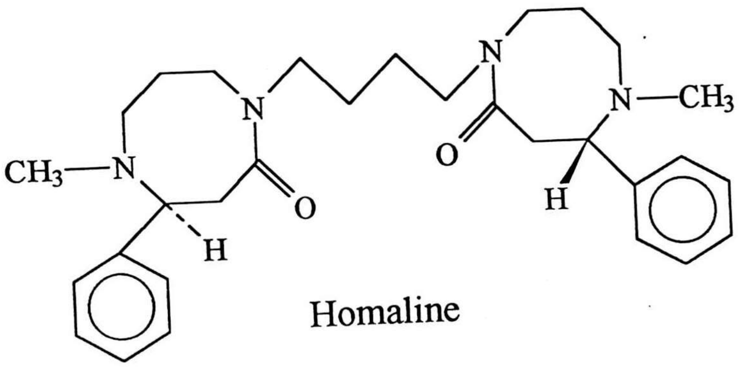
Codonocarpine



Pleurostyline



Lunarine



Homaline

Figure 1 Related alkaloids of spermidine

Biosynthesis

1. Biosynthesis of Spermidine and Spermine in Microorganisms

The biosynthesis of spermidine and spermine were carried out with growing cultures of *Escherichia coli* and *Aspergillus nidulans*, using either C^{14}-labeled ornithine or C^{14} - N^{15} -labeled 1,4-diaminobutane (Tabor and Tabor, 1964) and with 2-C^{14}- methionine in *Neurospora crassa* indicated that 1,4-diaminobutane and methionine were precursors of spermidine and spermine in the organisms (Figure 2) (Tabor, Rosenthal and Tabor, 1961) In *E. coli* , putrescine (1,4 -diaminobutane) may be derived either from ornithine by direct decarboxylation , or from agmatine, the decarboxylation product of arginine, with the formation of urea. (Smith, 1972) In the mean while, three enzymes were purified from the cell free extracts of *E. coli* that carried out the three reaction shown in Figure 2. Reaction 1 represents the formation of S-adenosylmethionine from ATP and methionine. The methionine-activating enzyme was purified from liver and yeast. In reaction 2, the enzyme from *E. coli* extracts catalyzes the decarboxylation reaction. It requires Mg++ and its inhibited by cyanide. The product of the reaction is decarboxylated S-adenosylmethionine. In reaction 3, this propylamine residue derived from decarboxylated S-adenosylmethionine is then donated to an amino group on putrescine to give spermidine and methylthioadenosine. No synthesis of spermine can be found under the test condition. (Pachaly, Redeker and Schoppa, 1983; Tabor and Tabor, 1964 ; Tabor, Rosenthal and Tabor, 1961)

2. Biosynthesis of Spermidine and Spermine in Animals

In the rat ventral prostate gland, the pathway of biosynthesis is similar to that found in *E. coli*, but putrescine is formed from ornithine by decarboxylation, and arginine decarboxylase appears to be absent(Smith, 1972). The presence of polyamines in animal tissues dose not indicate biosynthesis , since it is possible that

animals derive their polyamines either from the diet or from the intestinal flora. Polyamines were present in
germ-free animals which had been on regular diet, but no polyamine analyses have been carried out germ-free animals that have been on a purified diet. The presence of polyamines has been determined with conventional animals on a purified diet (Tabor and Tabor, 1964).

The formation of spermidine and spermine from C^{14} -1,4 -diaminobutane and from C^{14} -methionine has been demonstrated in developing chick embryos(Tabor and Tabor, 1964). In the presence of limiting concentrations of S-adenosylmethionine the only product of putrescine is spermidine, and no spermine was detected. The amounts of spermidine and spermine formed depend on the ratio of putrescine:spermidine(Smith, 1972).

3. Biosynthesis of Spermidine and Spermine in Plants

Richards and Coleman in 1952, used a classic experiment, showed that potassium deficient barley plants accumulated putrescine, and this has been confirmed in many other plants(Cordell, 1981). Ornithine was subsequently found to be only poorly incorporated, and the discovery of agmatine suggested arginine decarboxylation as an early step in putrescine biosynthesis in barley (Figure 2). The agmatine losses ammonia to give N-carbamylputrescine, which is further hydrolysed to putrescine. The enzyme converting arginine to agmatine (arginine decarboxylase) and the enzyme converting N-carbamylputrescine to putrescine (N-carbamylputrescine amidohydrolase) were found to be significantly more active in the extracts of the potassium-deficient barley leaves on the basis of fresh weight, dry weight, total nitrogen and protein nitrogen(Tabor and Tabor, 1964).

In higher plants agmatine is therefore hydrolysed to putrescine in two steps with the formation of ammonia and carbon dioxide. Very little is known about the conversion of putrescine to spermidine in higher plants. But it is commonly regarded that decarboxylated S-adenosylmethionine also provides the propylamine group in this case (Smith, 1972).

Alkaloid Biosynthesis

1,4-diaminobutane or 1,5-diaminopentane is incorporated into various alkaloids that contain piperidine or pyrrolidine rings which are found during the enzymatic oxidation of 1,4-diaminobutane and 1,5-diaminopentane by hog kidney diamine oxidase. There is no definitive proof that oxidation by diamine oxidase is the first step in this incorporation. The results, in general , are consistent with this possibility. Various possible formulations however, have been suggested for the later step in the biosynthesis of the alkaloids, but direct evidence concerning their validity is not available. Most of the incorporation experiments have been carried out with intact plants or with isolated shoots, leaves or roots(Tabor and Tabor, 1964).

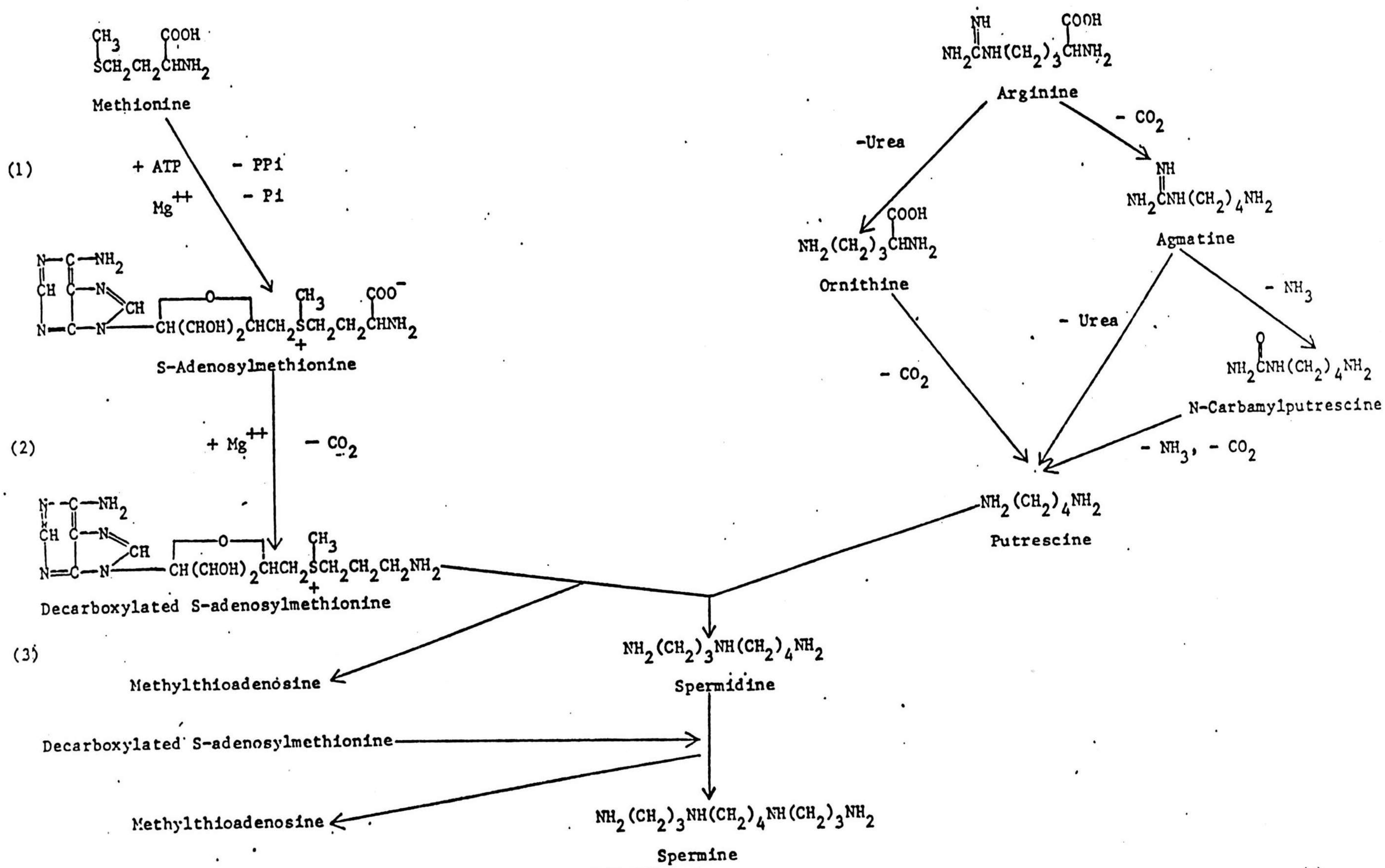


Figure 2 Biosynthesis pathway of polyamines, spermidine and spermine

Biological Effects

In 1948, Hebst and Snell found that putrescine was an essential growth factor for the bacterium *Hemophilus parainfluenzae*; yeast extract, corn steep liquor, and pea seeds were good sources. Subsequently, spermine and spermidine were also found to possess growth-promoting activity for several types of bacteria, and for *Escherichia coli*, spermidine has effect of synchonizing cell division. Spermine acts to stimulate the growth of Chinese hamster cells and also tuber explants of *Helianthus tuberosus* L.

Spermidine induces phenylalanine-ammonia lyase activity in excised pea pods, indicating that the poly amines possibly act as triggering devices for several other plant mechanisms. In this respect the consistently high concentrations of these amines in seeds of several plants is worth mentioning. At higher concentration ($\sim 5 \times 10^{-4}$ M) spermine acts as an antibacterial against *Staphylococcus aureus*, and several other examples of antibacterial activity of the polyamines are well established. At 0.075 m mol/kg spermine produces renal failure within a week in several animal species, and at 0.33 m mol/kg in humans, vomiting , albuminuria, hematuria, and hyperglycemic are observed(Cordell, 1981).

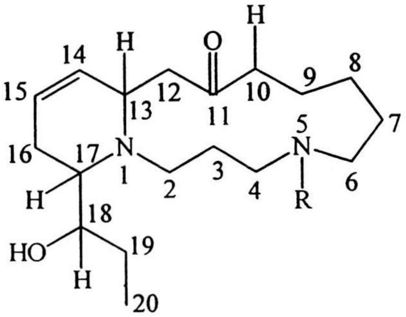
Rosenthal *et al*, showed that spermine has a marked renal toxicity in mouse, rat, guinea pig, rabbit and dog. Spermidine is much less toxic than spermine and 1,4-diaminobutane is not toxic at comparable doses. Spermine has two different effects on blood coagulation : (a) like protomine, spermine (but not spermidine or 1,4-diaminobutane) decrease the clotting time of heparinized blood; (b) spermine in high concentration prolongs the coagulation time of unheparinized blood. The ability of spermine, spermidine or several related synthetic polyamines can antagonize the antibacterial action of quinacrine and quinine(Tabor and Tabor, 1964).

Sevage and Drabble have reported that the addition of spermine or spermidine to the growth medium prevents the emergence of resistant cells of *Staphylococcus aureus* and of *Aerobacter aerogenes*, when sensitive strains of these organisms are treated with streptomycin, penicillin , or several other antibiotics(Tabor and Tabor, 1964).

Palustrine

1. Introduction

The horsetail alkaloid, palustrine, is a toxic principle of *Equisetum palustre* L. which is a harmful plant in moist meadows in Europe. It effects domestic animals, especially cows, causing loss of appetite, decreased weight, decreased milk secretion, intestinal disturbances and a tendency to abnormal birth(Tabor and Tabor, 1964). The horsetail alkaloid, palustrine, was partially characterized by Glet, Gutschmidt and P. Glet in 1936. Its total synthesis and an investigation of its structure were definitively established by Natsume in 1984, who showed that palustrine has a carbon atom corresponding to the numbering given in the structure below.



Palustrine

Palustrine is a macrocyclic spermidine alkaloid, starting from the piperidine derivative. The palustrine content of the dried plants is usuallly about 0.03-0.06 % , though the occurrence of various subspecies have made it difficult to determine the reasons of these fluctuations: however, in general it appears that the palustrine level increases from May to September. Temperature is also important, since frost cause a marked reduction in the alkaloid content(Smith, 1971).

2. The Chemistry of Palustrine

The first investigation of palustrine began in 1950 by Wöhlbier and Beckman under the name equisetin, and an empirical formula was established by Eugster, Griot and Karrer in 1953(Smith, 1971). As previously mentioned, it contains a lactam ring, and yields spermidine on alkalifusion. Catalytic hydrogenation follows Eschweiler-Clark methylation and first gives N-methyl-dihydropalustrine. This bis-tertiary base then reacts with methyl iodide and the quaternary product submits to Hofmann degradation. The des-base mitxure obtained was reduced catalytically and the product boiled for several hours with strong hydrochloric acid.

Along with other cleavage products, dihydropalustraminic acid was isolated and identified by derivative and spectroscopic data. Dihydropalustrine can be broken down further to the des-base, and evidence for 3,4-dihydropalustrine is given by the formula for dihydropalustrine(Badawi *et al*, 1973). N-formylated palustrine is present in *Equisetum palustre* L. as the minor alkaloid, palustridine (Figure 3).

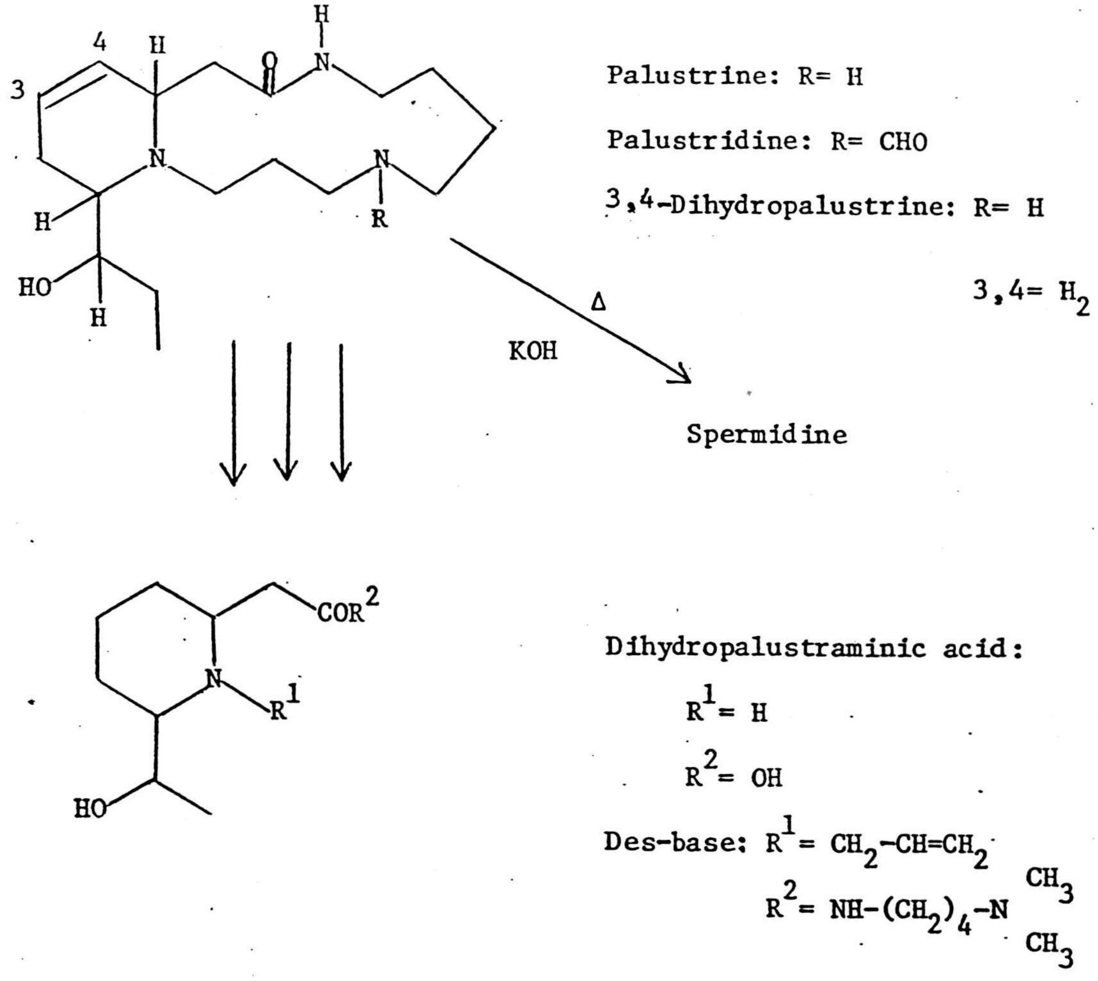
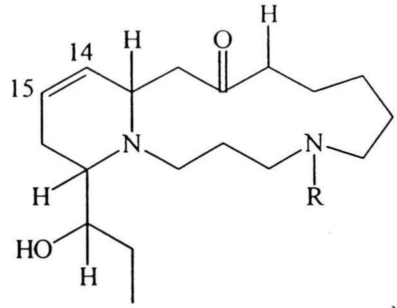


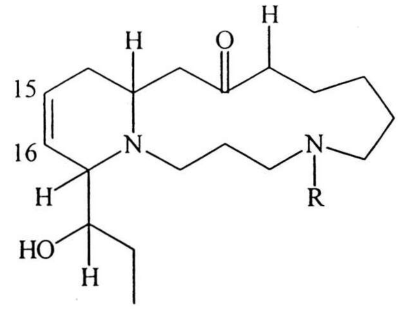
Figure 3 Derivative of Palustrine

3. <u>Chemical Synthesis of Palustrine</u>

Previously the proposed structure for the horsetail alkaloid, palustrine, was reported to be a synthesis of the compound (2),starting from the piperidine derivative (3) obtained by on oxygenative nucleophile introduction reaction. However, this synthesis material (2), whose structure was verified by an x-ray analysis, was found to be different from the natural product which was isolated by Eugster. The recent report of Natsume (1984) shows that the total synthesis of (±) - palustrine,as shown in Figure 4, is the same as the natural product. He established that the correct structure of palustrine should be expressed as a compound (1).



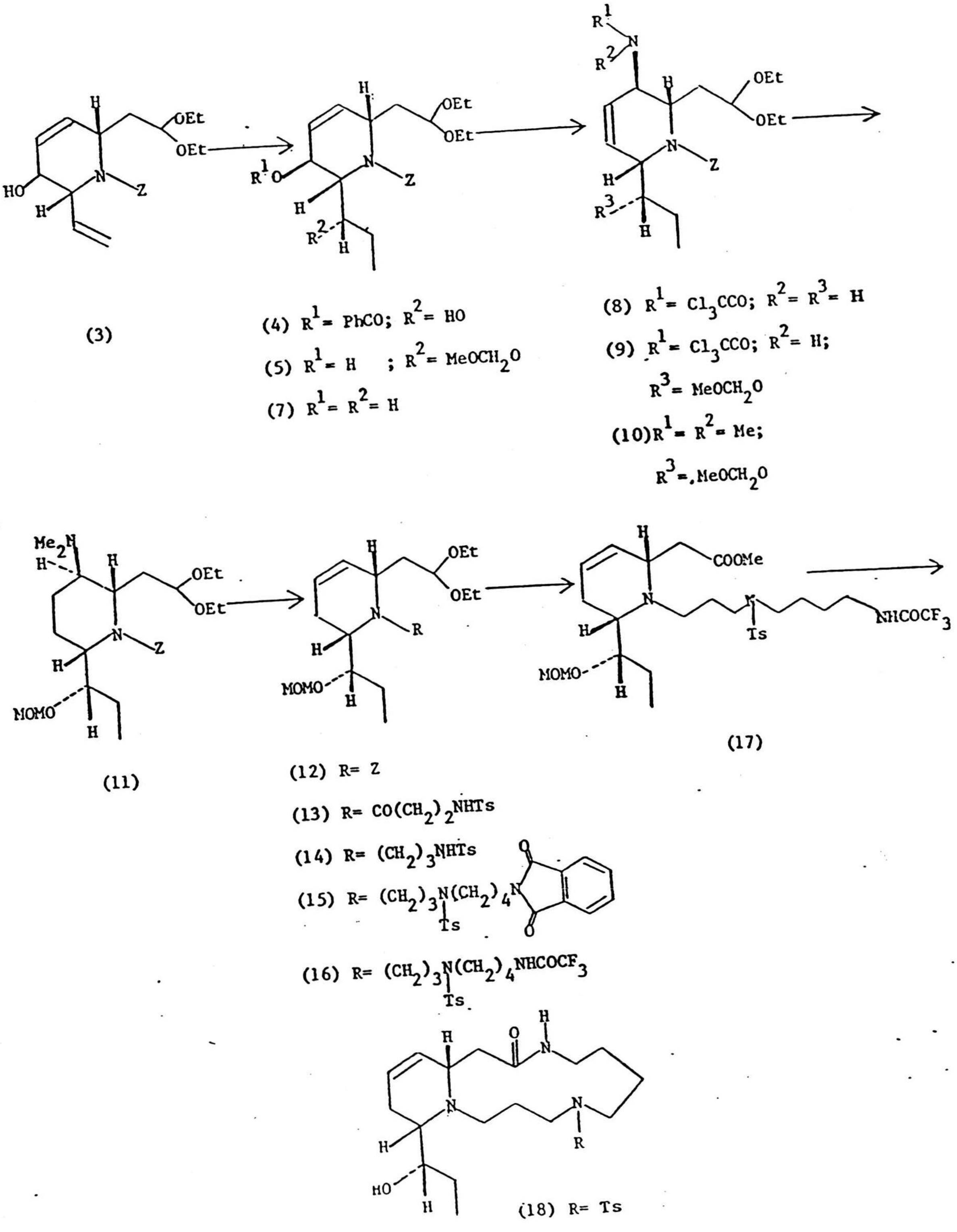
(1)



(2)

Using the piperidine derivative (3) , direct and indirect routes can be envisaged for the introduction of the double bond at the desired location. The compound (3) was converted to (4) by stereospecific preparation, and (4) was transformed into a methoxymethyl (MOM) ether (5) by treatment with $MeOCH_2Cl$ and diisopropylethylamine, followed by hydrolysis of the benzoate with K_2CO_3 in MeOH. Compound (5) was condensed with Cl_3CCN in dry xylene to afford the rearranged compound (9). Alkaline hydrolysis of (9) followed by N-methylation gave a dimethylamino derivative (10). The double bond was hydrogenated catalytically and the Hofmann degradation of (11) formed the expected compound (12). The N-protecting group of (12) was eliminated with Na in

NH_3-THF, and amine was treated with 3-tosylaminopropionyl chloride in the presence of K_2CO_3 in a mixture of PhMe-PhH-H_2O (1:3:3) to produce (13). The compound (13) was reduced with $LiAlH_4$ to produce (14). The resulting compound (14) was condensed with N-(4-bromo-1-butyl)-phthalimide in order to form the spermidine side chain, as in (15). The terminal nitrogen function of (15) was changed to the trifluoroacetamide moiety to produce (16). Immediate oxidation of the aldehyde with Jones reagent and treatment with CH_2N_2 produced the methyl carboxylate (17). The compound (17) was hydrolyzed with $Ba(OH)_2$ and the acid chloride. The MOM group was eliminated during the operation and the desired compound (18), mp. 163-165 ^{o} C (Me_2CO-Et_2O) was formed. Cleavage of the N-Ts group formed the final compound [(±) - (1)] mp. 180-182 ^{o} C (Me_2CO-Et_2O), and identity with freshly isolated palustrine was confirmed by comparison of TLC (Al_2O_3, CH_2Cl_2-MeOH (15:1)), MS, IR($CHCl_3$), ^{1}H NMR (400 Mhz, CD_3OD), and ^{13}C NMR (C_6D_6, 60 ^{o} C) spectra(Natsume and Ogawa, 1984).



(3)

(4) R^1= PhCO; R^2= HO

(5) R^1= H ; R^2= $MeOCH_2O$

(7) R^1= R^2= H

(8) R^1= Cl_3CCO; R^2= R^3= H

(9) R^1= Cl_3CCO; R^2= H; R^3= $MeOCH_2O$

(10) R^1= R^2= Me; R^3= $MeOCH_2O$

(11)

(12) R= Z

(13) R= $CO(CH_2)_2NHTs$

(14) R= $(CH_2)_3NHTs$

(15) R= $(CH_2)_3N(Ts)(CH_2)_4N$-phthalimide

(16) R= $(CH_2)_3N(Ts)(CH_2)_4NHCOCF_3$

(17)

(18) R= Ts

(1) R= H

Figure 4 Chemical synthesis of palustrine.

Occurrence of the Polyamines in Natural Materials

1. The Polyamines in Microorganisms

Polyamine	Source	Reference
Spermine	*Aspergillus nidulans*	Tabor, 1964
	Saccharomyces cerevisiae	Tabor, 1964
Acetylated derivatives	*Escherichia coli*	Rosenthal, 1961
of Spermine	*Staphylococcus aureus*	Rosenthal, 1961
Spermidine	*Ustilago maydis*	Smith, 1971
Spermidine, Putrescine	*Chlorella ellipsoidea*	Smith, 1971

2. The Polyamines in Animal Tissue

Polyamine	Source	Reference
1,3-Diaminopropane	Steer	Tabor, 1964
	Rat	Tabor, 1964
	Guinea pig liver	Tabor, 1964
	Human semen	Tabor, 1964
1,4-Diaminobutane (Putrescine)	Pancreas of several species Liver of several species	Tabor, 1964
	Ox lung	Tabor, 1964
	Bovine	Tabor, 1964
	Pig brain	Tabor, 1964
	Human semen	Tabor, 1964
	Pupae and caterpillars of the silkworm	Tabor, 1964

2. The Polyamines in Animal Tissue (cont.)

Polyamine	Source	Reference
1,5-Diaminopentane (Cadaverine)	Liver	Tabor, 1964
Spermidine and Spermine	Pancreas of mouse, rat, guinea pig and dog	Tabor, 1964
	Prostate gland of rat, and dog	Tabor, 1964
	Liver of mouse, rat and guinea pig	Tabor, 1964
	Kidney of mouse and guinea pig	Tabor, 1964
	Testis of rat	Tabor, 1964
	Brain of rat	Tabor, 1964
	Muscle of mouse	Tabor, 1964
Mammamine (Spermidine)	Lactating mammary gland of rat	Tabor, 1964
Diamidinospermidine (Hirudonine)	Leech	Tabor, 1964

3. The Polyamines in Plants

Polyamine	Source	Reference
Agmatine	*Ricinus sp.*	Smith, 1971
(1-guanidino-4-aminobutane)	*Saccharum officinarum* L.	Smith, 1971
Arcain	*Prunus tigiunus* Fr.	Smith, 1971
(1,4-diguanidinobutane)	*Luffa cylindrica* Roem.	Smith, 1971
Cadaverine	*Hordeum vulgare* L.	Smith, 1971

3. The Polyamines in Plants (cont.)

Polyamine	Source	Reference
Cadaverine	*Avena sativa* L.	Smith, 1971
	Zea mays L.	Smith, 1971
	Sorghum vulgare Pers.	Smith, 1971
Cannabisativine	*Cannabis sativa* L.	Cordell, 1981
Chaenorrhine	*Chaenorrhinum origanifolium* (L.) Milk et Lge.	Cordell, 1981
Codonocarpine	*Codonocarpus australis* L.	Tabor, 1964
1,4-Diaminobutane (Putrescine)	*Datura stramonium* L.	Tabor, 1964
	Atropa belladonna L.	Tabor, 1964
	Citrus sp.	Tabor, 1964
	Hordeum vulgare L.	Tabor, 1964
	Brassica pekinensis Rupr.	Tabor, 1964
	Oryza sativa L.	Smith, 1971
	Avena sativa L.	Smith, 1971
	Zea mays L.	Smith, 1971
	Sorghum vulgare Pers.	Smith, 1971
Galegin (3-methylbut-2-enyl-guanidine)	*Galega officinalis* L.	Smith, 1971
Homaline	*Homalium pronyense* Guillanm.	Cordell, 1981
Inandenines	*Oncinotis inandensis* Wood et Evans	Badawi *et al*, 1973
Lunarine	*Lunaria biennis* Moench.	Cordell, 1981
	L. rediviva L.	Cordell, 1981
Oncinotine	*Oncinotis nitida* Benth.	Cordell, 1981

3. The Polyamines in Plants (cont.)

Polyamine	Source	Reference
Palustrine	*Equisetum palustre* L.	Eugster, 1970
	E. arvense L.	Eugster, 1970
	E. limosum L.	Eugster, 1970
	E. silvaticum L.	Eugster, 1970
Palustridine	*E. palustre L.*	Eugster, 1970
	E. limosum L.	Tabor, 1964
Pancine	*Penthaclethra macrophylla* Benth.	Badawi *et al*, 1973
Pithecolobine	*Samanea saman* Merr.	Badawi *et al*, 1973
Pleurostyline	*Pleurostylia africana* Loes.	Cordell, 1981
Putrescine amides	*Kniphofia flavovirens* Goetzei.	Badawi *et al*, 1973
	K. foliosa Hochst.	Badawi *et al*, 1973
	K. tuckii Baker.	Badawi *et al*, 1973
Solapalmitine and Solapalmitenine	*Solanum tripartitum* Dinal.	Badawi *et al*, 1973
Spermine and Spermidin	*Triticum aestivum* L.	Smith,1970
	Fragaria chinensis Duchesne.,var. *ananassa*	Smith,1970
	Malus sylvestris Mill.	Smith,1970

3. The Polyamines in Plants (cont.)

Polyamine	Source	Reference
Spermine and Spermidine	*Pyracantha coccinea* Roem.	Smith,1970
	Lycopersicon esculentum Mill.	Smith,1970
	Cucurbita pepo L. *var. medullosa* Alef.	Smith,1970
	Spinacea oleracea L.	Smith,1970
	Salix babylonica L.	Smith,1970
	Pisum sativum L.	Smith,1970
	Zea mays L.	Smith,1970
	Raphanus sativus L.	Smith,1970
	Ribes nigrum L.	Smith,1970
	Nicotiana tabacum L.	Smith,1970
	Petunia hybrida Vilm.	Smith,1970
	Helianthus tuberosus L.	Smith,1970
	Hordeum vulgare L.	Smith, 1971
	Oryza sativa L.	Smith, 1971
	Avena sativa L.	Smith, 1971
	Sorghum vulgare Pers.	Smith, 1971
Spermine	*Phaseolus vulgaris* L.	Smith, 1971
Spermidine	*Cucumis melo* L.	Smith, 1971
	Brassica pekinensis Rupr.	Smith, 1971
	Lycopersicon esculentum Mill.	Smith, 1971
Sphaerophysin (4-[3-methylbut-2-enyl-amino-(I)]-butyl-1-guanidine)	*Sphaerophysa salsula* Pall.	Smith, 1971

3. The Polyamines in Plants (cont.)

Polyamine	Source	Reference
Subaphylline	*Salsola subaphylla* L.	Badawi *et al*, 1973
Tetramethyl,4-diaminobutane	*Citrus* sp.	Badawi *et al*, 1973
	Hyoscyamus sp.	Tabor, 1964

II. Triterpenoids

1 Chemistry of triterpenoids

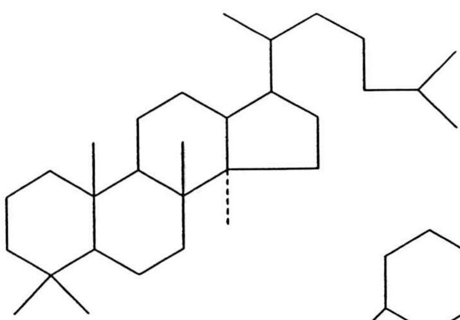
Triterpenes are C_{30} compounds, produced from two molecules of farnyesyl pyrophosphate (FPP) condensed head-to-head to squalene. The majority of natural triterpenes are pentacyclic compounds. The next largest group is the tetracyclic triterpene. There is also a small number of triterpenes with various other cyclic structures. The only important acyclic triterpene is squalene (and its 2,3-oxide as a metabolic intermediate). Most triterpenoids are alcohols (3-OH), they are found free and as glycosides (saponins) or esters. Free triterpenoids are often components of resins, latex, or cuticle. Saponins are powerful surface active agents and can cause lysis of red blood cells. Some of them have been used as fish poisons. There are probably upward of 500 naturally occuring triterpenes of known structure, new compounds and new structural types are still being discovered(Stumpf and Conn, 1980).

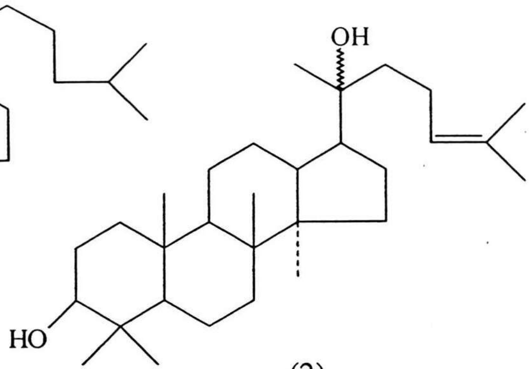
2 Classification of triterpenoids

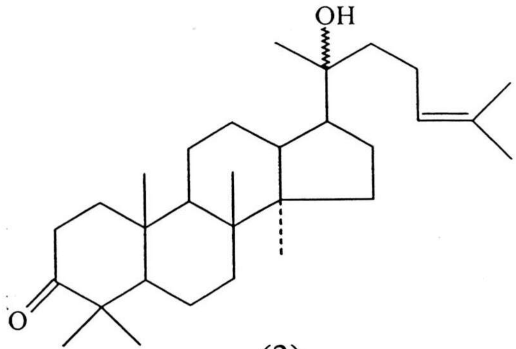
The triterpenes consist of two large groups, either tetracyclic or pentacyclic in form and miscellaneous groups.

2.1 Tetracyclic Triterpenes (Porter and Spurgeon, 1981; Devon and Scott, 1972)

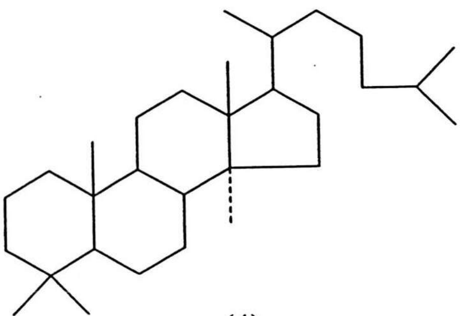
a) Damarane type 1: - dammarenediol 2 , dipterocarpol 3

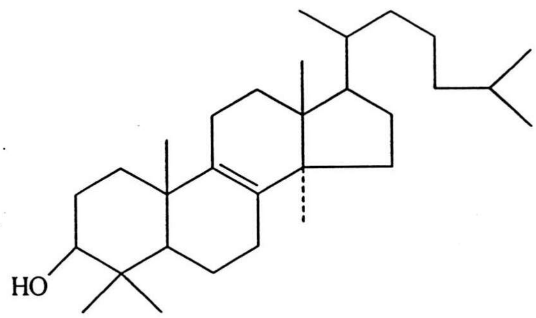

(1)


(2)

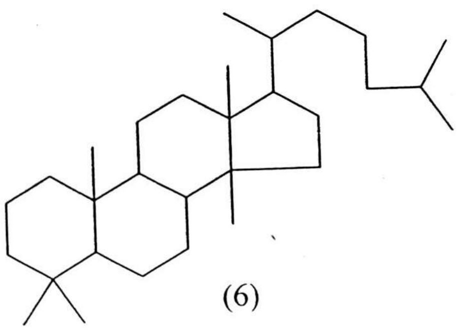

(3)

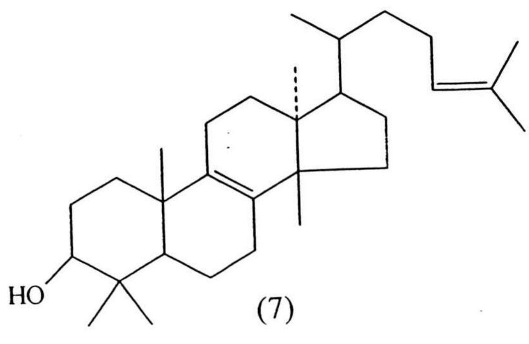
b) Lanostane type 4 : - Lanorterol 5


(4)

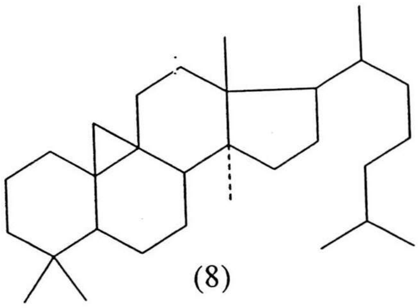

(5)

c) Euphane type 6 : - Euphol 7

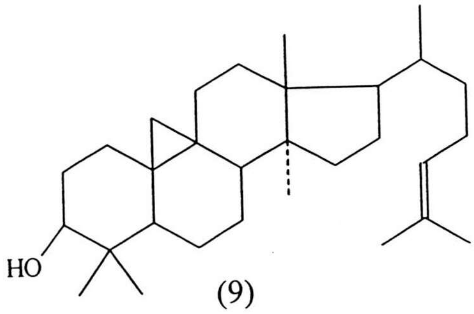

(6)


(7)

d) cycloartane 8 : - cycloartenol 9

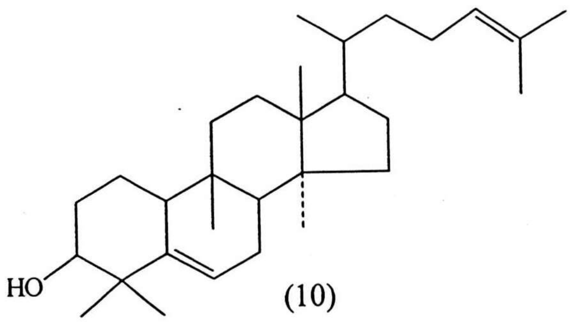


(8)



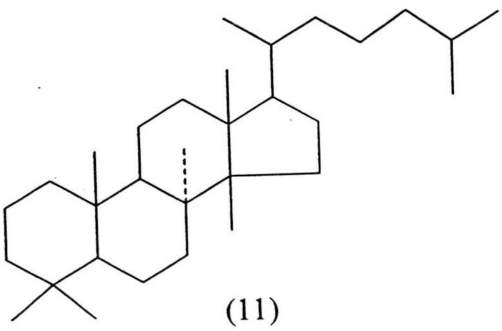
(9)

e) Cucubitacin 10

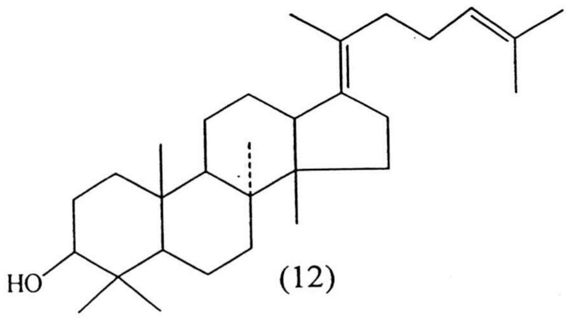


(10)

f) Protostane type 11 : - Protosterol 12



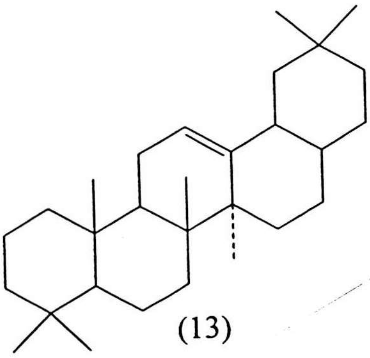
(11)



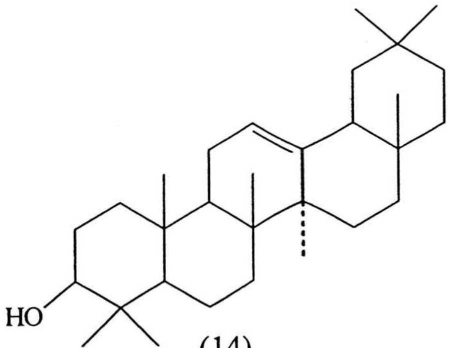
(12)

2.2 Pentacyclic triterpenes (Porter and Spurgeon, 1981; Devon and Scott, 1972)

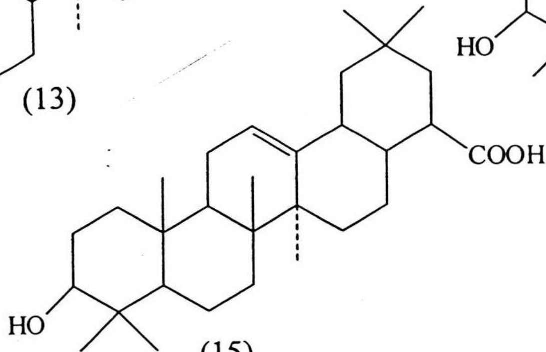
a) Oleanene tyupe 13 : - β- amyrin 14 , oleanolic acid 15



(13)

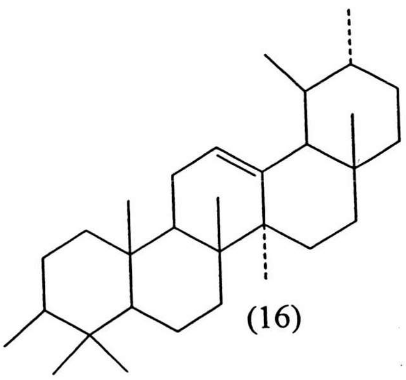


(14)

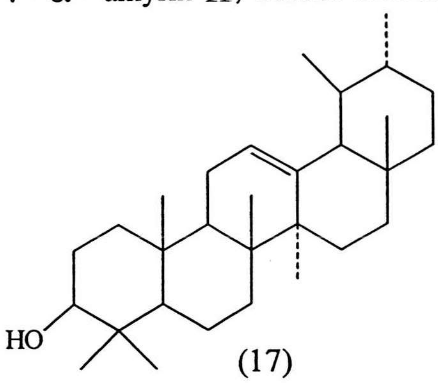


(15)

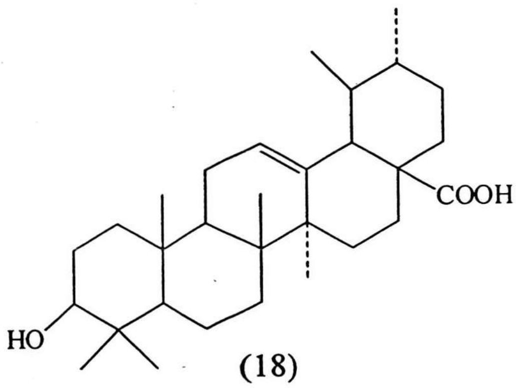
b) Ursene type 16 : - α - amyrin 17, Ursolic acid 18



(16)

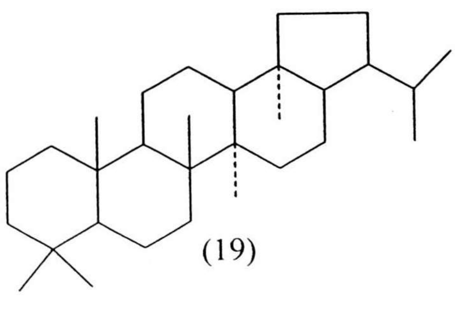


(17)

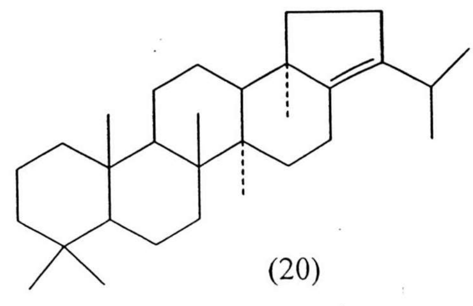


(18)

c) Hopane type 19 : - hopene 20

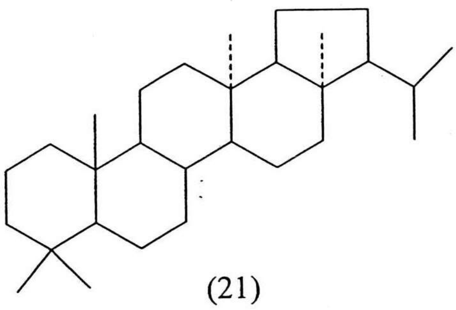


(19)

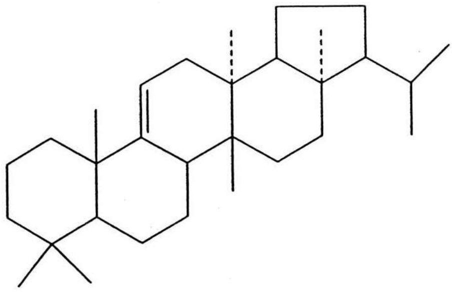


(20)

d) Fernane type 21: - Fernene 22

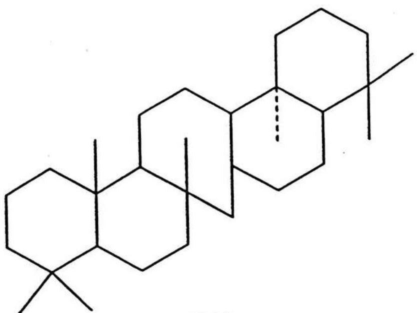


(21)

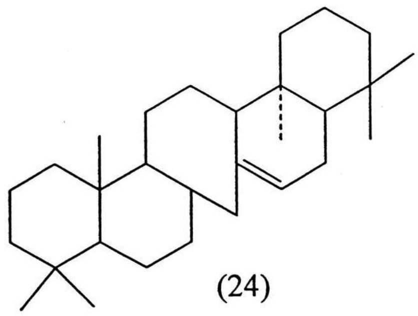


(22)

e) Serratane type 23:- Serratene 24

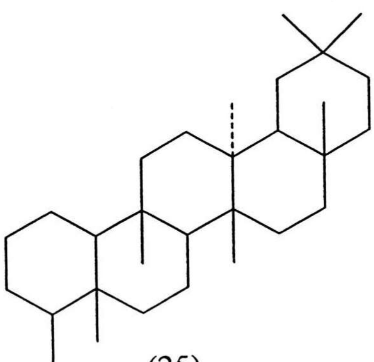


(23)

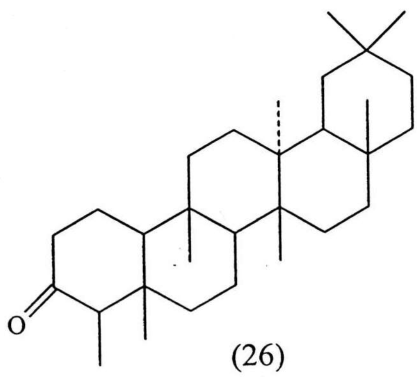


(24)

g) Friedelane type 25 : -Friedelin 26

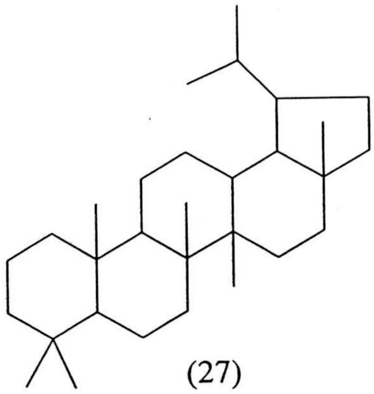


(25)

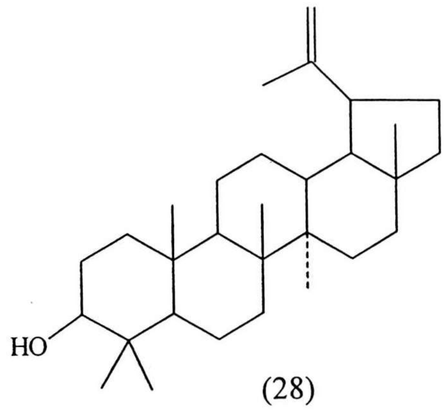


(26)

h) Lupane type 27 :- Lupeol 28

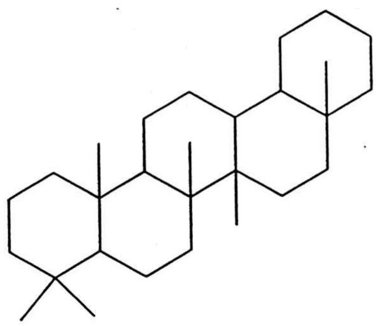


(27)

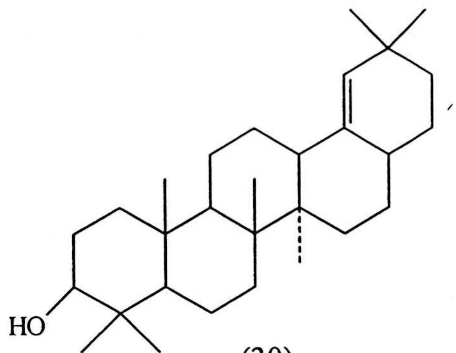


(28)

i) Germanicane type 29 :- germanicol 30

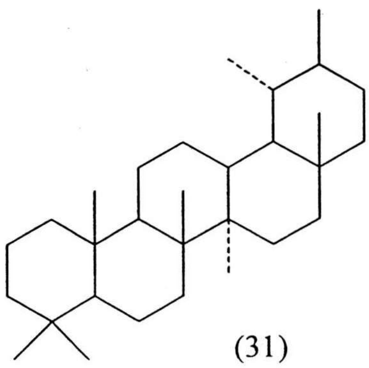


(29)

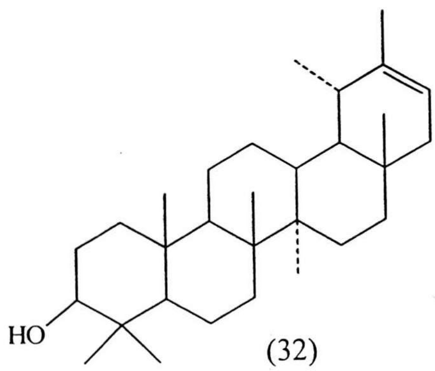


(30)

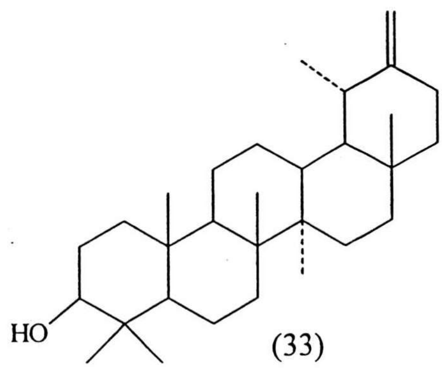
j) Taraxasterane type 31 :- γ- taraxasterol 32 , taraxasterol 33



(31)

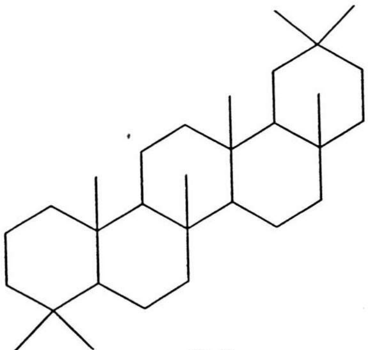


(32)

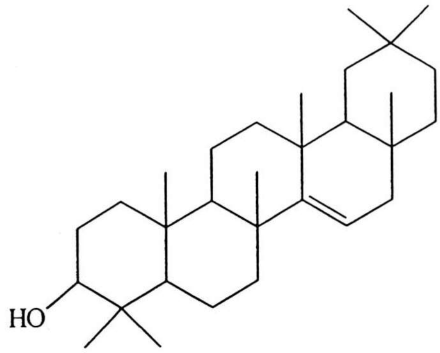


(33)

k) Taraxerane type 34 :- taraxerol 35

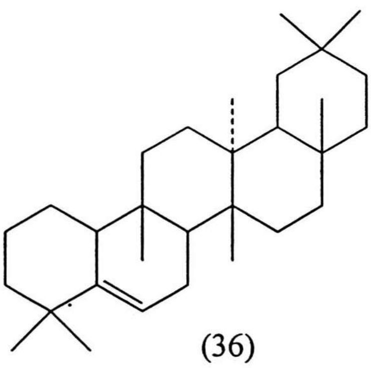


(34)

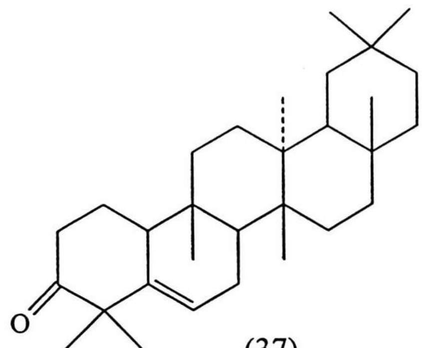


(35)

l) Glutinane type 36 :- Glutinone 37



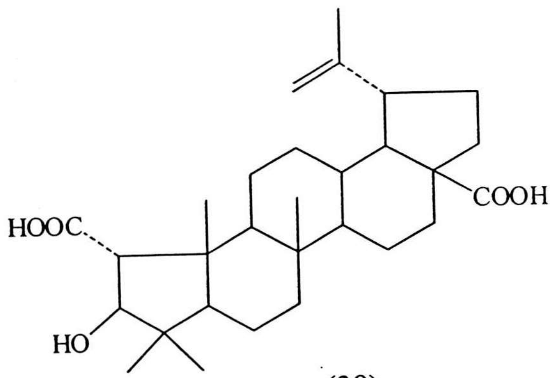
(36)



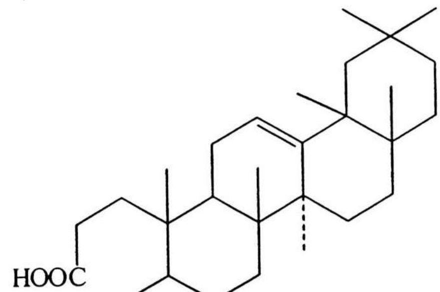
(37)

2.3 Miscellaneous

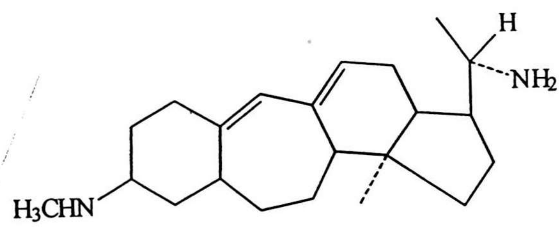
This group is some examples of unusual variations in the major types of triterpenes to be known. Ceanothic acid 38 is a member of the lupane type in which ring A has been contacted to five carbons. Nyctanthic acid 39 is a member of the oleanane group in which ring A has been opened. The seven membered ring of buxenine-G 40 are especially interesting. The limonins (or meliacins) are the bitter principle of *Citrus* species. An example of these is limonin 41 itself. The basic unit from which they are believed to be derived is tetracyclic triterpene euphol. Believed to be related to these by the distribution of methyl groups and general stereochemistry are an additional group known as the quassins. These also are believed to be derived., biogenically, from euphol. A partly cyclized squalene is illustrated by ambrein 42, onocerin 43 and lansic acid 44(Mclean and Ivimey, 1956 ; Rendel, 1953).



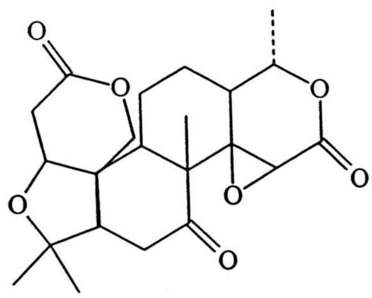
(38)



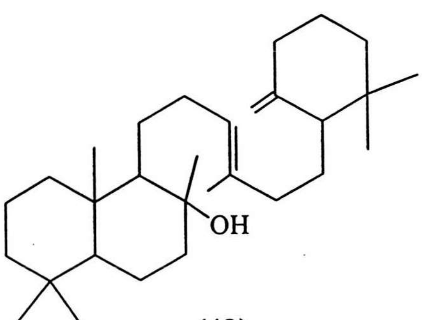
(39)



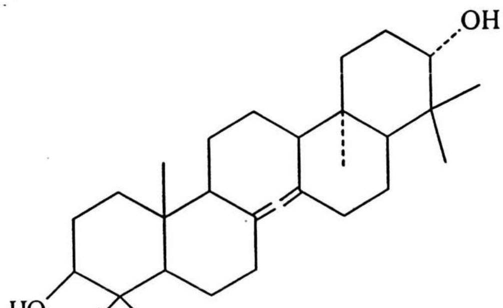
(40)



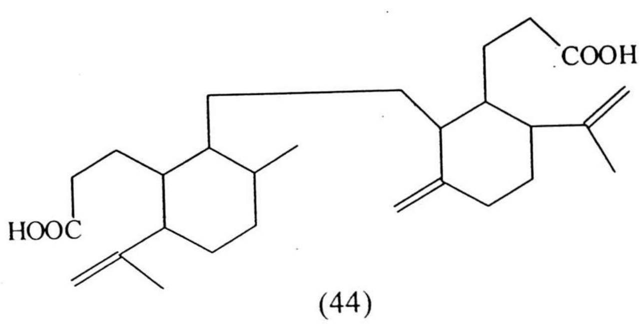
(41)



(42)



(43)



(44)

3 Biosynthesis of Pentacyclic triterpenes (The amyrins) (Bell and Charlwood, 1980; Miller, 1973; Porter and Spurgeon, 1981; Richards and Hendrickson, 1964) (Figure 6)

The amyrins are derived biosynthetically from the acyclic C30 hydrocarbon, squalene. The formation of squalene follows the same pathway as the plant sterol which have been discussed elsewhere in squalene biosynthesis (Figure 5). The evidence is not repeated here.

Cyclization of a squalene 129 chain in the amyrins has squalene-2, 3-oxide 130 as an intermediate between squalene and triterpene, its conversion to lanosterol 131. Lanosterol can rearrange by migration of the C-16 methylene group to the structure 132. The migrations during the pause at the tetracyclic stage result in a rearrangement of the carbon backbone of squalene such that C-16 is now joined to C-18 in pentacyclic triterpenes. The terminal isoprene unit is folded as a boat, its cyclization onto the tetracyclic nucleus already for product intermediate 133. A carbon skeleton rearrangement by C-20 methylene migration from C-21 to C-22 will produce a new intermediate 134. From intermediate 134 can serve as the origin for a variety of 1,2 shifts and proton losses. Migration of hydride and a methyl group gives β-amyrin 135. If the migration of the intermediate 132 is followed by a hydride migration from C-21 to C-22 to yield the intermediate 136 and there then occurs the in dicated series of 1,2-shifts, α-amyrin 137 will arise.

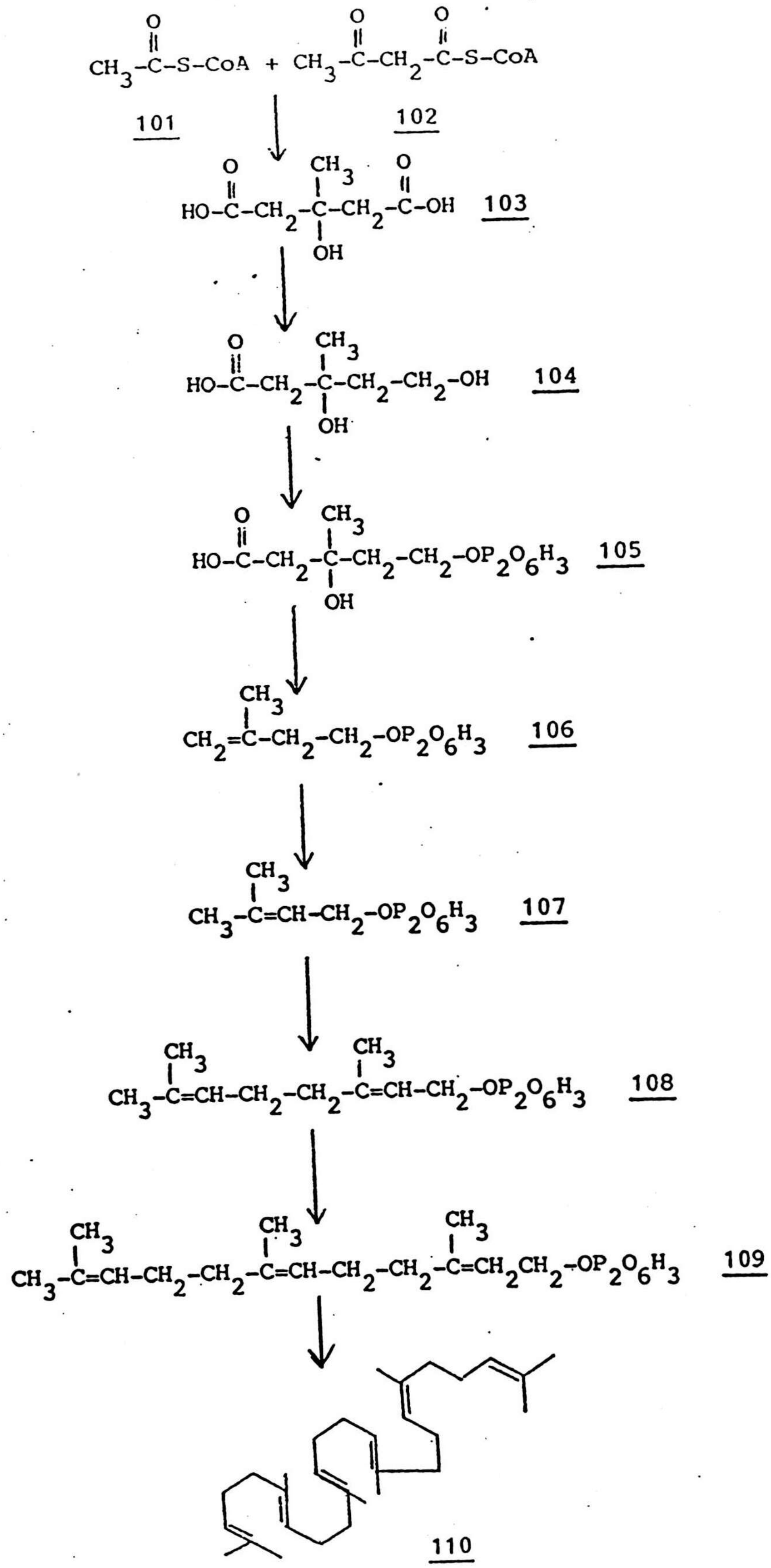


Figure 5 Squalene Biosynthesis

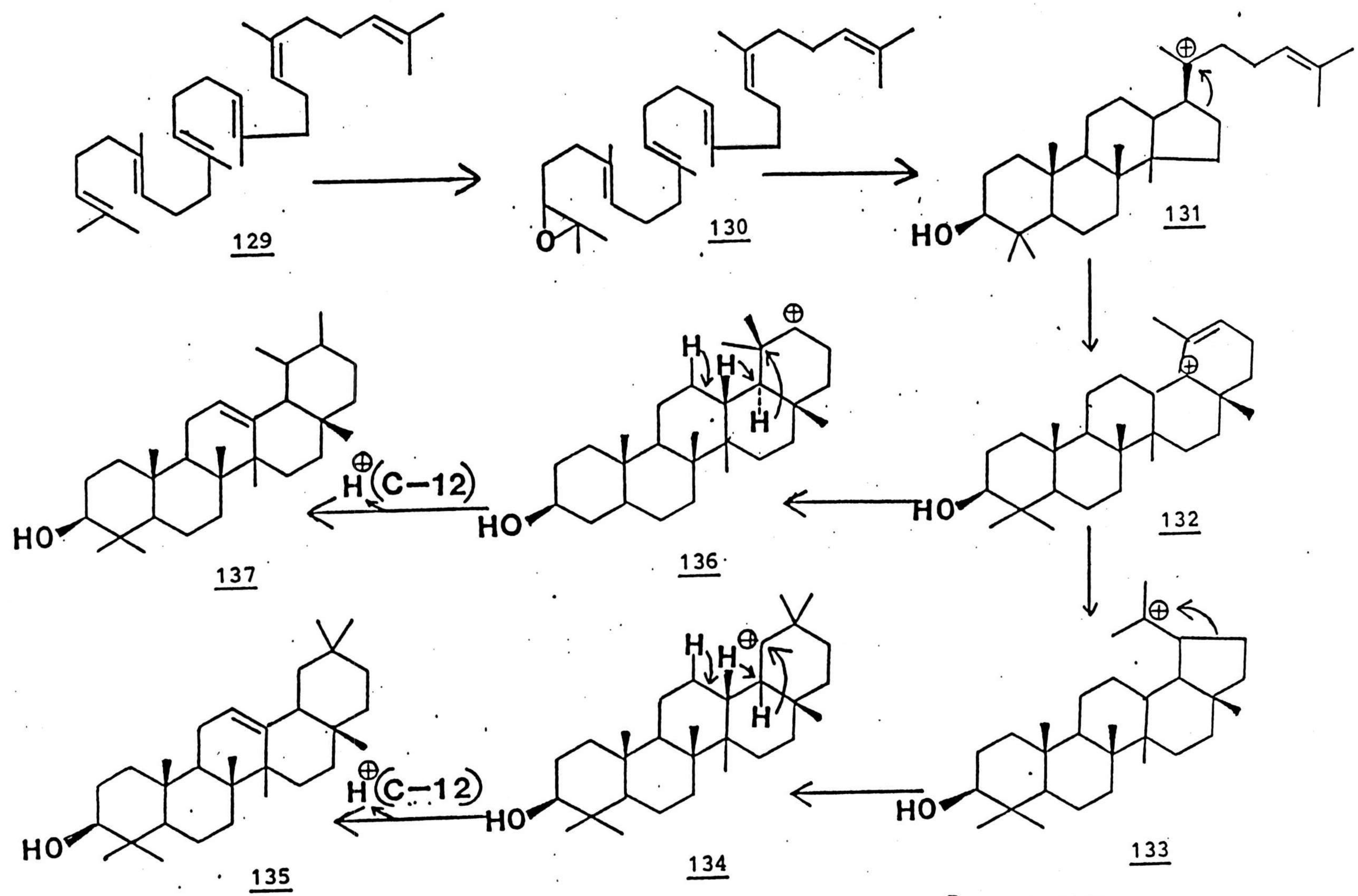


Figure 6 Biosynthesis pathway of the amyrins (α- amyrin 137, β-amyrin 135)