CHAPTER II

HISTORICAL

1. The Occurrence of Chemical Compounds in Cassia:

1.1 *Cassia absus* Linn.

Plant part	Chemical compound	Reference
seed	Absin, an abrin-like toxic principle	18
	Chaksine	19
	Fixed oil, 2.15%	18
	Oil from seed has fatty acids consists of hydroxy acid, 0.75%; linoleic, 47.32%; linolenic, 0.41%; oleic, 16.32%; palmitic acids, 0.82%; glycerol, 10.4%.	20
	Galactomannan	21,22
	Isochaksine	19
	Mucilage	23
	Nonsaponified matter, 8.4%	18
	β-Sitosterol	24
	Sitosterol-β-D-glucoside	25

1.2 Cassia acutifolia Delile

(C. alexandrina Thell.; C. senna Linn.)

Plant part	Chemical compound	Reference
leaf	Aloe-emodin	26
	Aloe-emodin anthrone diglucoside	
	Aloe-emodin-8-glucoside	
	Isorhamnetin and its glycoside	27
	Kaempferol and its glycoside	
	Myricyl alcohol	
	Phytosterolin	
	Rhein	26
	Rhein anthrone-8-glucoside	
	Rhein-8-diglucoside	
	Rhein-8-glucoside	
	Rhein-1-monoglucoside	28
	Sennosides A and B, 2-3%	26
	Sennosides C and D	
leaf and glume	Aloe-emodin	29
	Emodin	
	Rhein	
	Sennidins	
	Traces of chrysophanol and some of anthracene derivatives	

Cassia acutifolia Delile (cont.)

Plant part	Chemical compound	Reference
glume	Emodin glycoside	29
	Glucoaloe-emodin	
	Glucorhein	
pod	Aloe-emodin anthrone diglucoside	26
	Aloe-emodin-8-glucoside	
	Rhein anthrone-8-glucoside	
	Rhein-8-diglucoside	
	Rhein-8-glucoside	
	Sennosides A and B, 2.5-4.5%	

1.3 Cassia alata Linn.

Plant part	Chemical compound	Reference
fruit	Oxymethylanthraquinone	18
leaf	Chrysophanol	30
	Kaempferol	31
	Reduced rhein	30
	Rhein	31
	β-Sitosterol	
	Unknown alkaloids	32

Cassia alata Linn. (cont.)

Plant part	Chemical compound	Reference
root	1,5-Dihydroxy-8-methoxy-2-methylanthraquinone-3-O-β-D-glucopyranoside	33
	β-Sitosterol	
	1,3,8-Trihydroxy-2-methylanthraquinone	
seed	Chrysophanol	33
	Galactomannan	34
	Hydroxyanthraquinone	33
	β-Sitosterol	
	Xanthones	
whole plant	Aloe-emodin	35
	Chrysophanol	
	Emodin	
	Hydrocyanic acid	18
	Rhein	35

1.4 Cassia angustifolia Vahl

Plant part	Chemical compound	Reference
leaf	Aloe-emodin	27
	Aloe-emodin glycoside	

<u>Cassia angustifolia</u> Vahl (cont.)

Plant part	Chemical compound	Reference
leaf(cont.)	Essential oil, small amount	27
	Fatty acids :- palmitic and stearic	
	Isorhamnetin	27,36
	Kaempferol	
	Mannitol	20
	Mucilage, 7%	37
	Myricyl alcohol	28
	Phytosterolin	
	Rhein	
	Rhein carboxylic derivatives, 3.54%	38
	Rhein glycoside	28
	Salicylic acid	20
	Sugars :- fructose, glucose, pinitol, and sucrose.	37
	Total sennosides, 4.23%	38
	Calcium, magnesium and potassium salts of organic acids	20
	Calcium salt, 9.6%	36
	Co, Fe, K, Mg, Mn, Na, Phosphate, Sulphate, Carbonate, Chloride, Silicate. (SiO_2, 2.7%; MgO, 7.2%; CaO, 31.6%; P_2O_5, 3.6%.)	
	Sodium and potassium tartrate.	20
	Boron, 32.2 ppm.	39

Cassia angustifolia Vahl (cont.)

Plant part	Chemical compound	Reference
pod	Chrysophanic acid glycoside	40
	Rhein glycoside	
	Sennosides A and B, 1.2-2.5%	30,40
	Traces of aloe-emodin or aloe-emodin glycoside.	40
	Calcium oxalate	20
seed	β-Sitosterol	41

1.5 Cassia auriculata Linn.

Plant part	Chemical compound	Reference
bark	1-Auriculacidin	42
	Oxymethylanthraquinone, 1.9%	18
	Soluble non-tans, 10%	20
	Tannins, 18%	
flower	Auricassidine	43
	Kaempferol	3
	β-Sitosterol	

<u>Cassia auriculata</u> Linn. (cont.)

Plant part	Chemical compound	Reference
leaf	Emodin	44
	Goratensidine	45
	Oxymethylanthraquinone, 0.7%	18
	Rhein carboxylic derivatives, 0.17%	38
	Saturated higher fatty alcohols : compound A($C_{46}H_{92}O_2$), m.p. 83°-84°C compound B($C_{42}H_{98}O_2$), m.p. 80°C compound C($C_{50}H_{100}O_2$), m.p. 88°C	44
	β-Sitosterol	
	Total Sennosides, 0.15%	38
seed	Saponin	46
	β-Sitosterol	41
whole plant	Sennapicrin, cardiac glycoside	18

1.6 <u>Cassia bacillaris</u> Linn.

Plant part	Chemical compound	Reference
leaf and stem	Unknown alkaloids	47

1.7 Cassia bakeriana Craib

Plant part	Chemical compound	Reference
leaf	Anthraquinones	48

1.8 Cassia bicapsularis Linn.

Plant part	Chemical compound	Reference
fruit and leaf	Unknown alkaloids	32

1.9 Cassia brasiliensis Niederl

Plant part	Chemical compound	Reference
flower and leaf	Unknown alkaloids	32

1.10 Cassia carnaval Speg.

Plant part	Chemical compound	Reference
leaf	Carnavaline	49
	Cassine	
	Prosopinone	50

1.11 <u>Cassia chrysocarpa</u> Desw.

Plant part	Chemical compound	Reference
epicarp	Hydroxyanthracene derivatives	51

1.12 <u>Cassia corymbosa</u> Larrañaga

Plant part	Chemical compound	Reference
leaf	Anthraquinones, 0.40% Ash, 5.21% Water, 38.1%	52

1.13 <u>Cassia didymobotrya</u> Fres.

Plant part	Chemical compound	Reference
bark	Tannins	18
leaf	Anthraquinones	18
pod	Casseine	18
root	Anthraquinones	18
seed	Choline Raffinose	18

1.14 Cassia emarginata Linn.

Plant part	Chemical compound	Reference
leaf	Unknown alkaloids	32

1.15 Cassia excelsa Shrad.

Plant part	Chemical compound	Reference
bark	Cassilysidine	53
leaf	Casselsine	7
	Cassilysine	53
	Cassine	7

1.16 Cassia fistula Linn.

Plant part	Chemical compound	Reference
bark	Fistucacidin	54,55
	Hexacosanol	56
	Leucopelargonidin trimer with no free glycol unit.	57
	Lupeol	56
	Non-tans, 12-14%	20
	Oxymethylanthraquinone, 1.2%	18
	Rhein glycoside	57
	β-Sitosterol	56
	Tannins, 10-12%	20

<u>Cassia fistula</u> Linn. (cont.)

Plant part	Chemical compound	Reference
flower	Ceryl alcohol	58
	Fistulin rhamnoside	
	Kaempferol	57,58
	Leucopelargonidin with a free glycol unit	57
	Methyleugenol	59
	Rhein	58
	Rhein glycoside	57
	Unsaturated hydrocarbon wax, 2.27%	18
fruit pulp	Aloin	60
	Barbaloin	
	Citric acid	61
	Mucilage, pectin	20
	Oxymethylanthraquinone, 1.05%	18
	Rhein	62
	Sennosides A and B	63
	Sucrose, fructose, glucose	61
	Tannin-like substance	
	Unsaturated hydrocarbon wax	60
heartwood	Barbaloin	54
	Fistucacidin	
	Rhein	
leaf	Free and combined rhein	64
	Rhein carboxylic derivatives, 1.23%	36
	Sennidins	61
	Sennosides A and B	
	Total sennosides, 1.80%	36

Cassia fistula Linn. (cont.)

Plant part	Chemical compound	Reference
pod	Fistulic acid	63
	Oxymethylanthraquinone, 0.95%	18
	Sucrose	65
	Wax consisted of 57.2% n-triacontyl lignocerate and 42.8% delignocerate of n-triacontane-1,30-diol.	
sapwood	Fistucacidin	66
seed	Fixed oil, 2.04%	18
	Galactomannan	67
	Gum	68
	β-Sitosterol	41
	Traces of anthraquinones	18
	Water soluble gum more than 23%	69

1.17 Cassia frondosa Ait.

Plant part	Chemical compound	Reference
whole plant	Chrysophanol	70
	Emodin	
	Rhein	

1.18 Cassia garrettiana Craib

Plant part	Chemical compound	Reference
heartwood	Cassialoin	71
	Chrysophanol	
	Chrysophanol dianthrone	
	l-11-Desoxyaloin	
leaf	Aloe-emodin	72

1.19 Cassia glauca Lamk.

Plant part	Chemical compound	Reference
flower	Quercetin	73
leaf	Anthraquinones	48
seed	Ash, 4.07%; crude protein, 27.75%; fat, 7.78%; total soluble carbohydrate (as glucose), 13.80%.	74

1.20 Cassia goratensis Fresen (C. singueana Delile)

Plant part	Chemical compound	Reference
leaf	Goratensidine	45
	Tannins	75

Cassia goratensis Fresen (cont.)

Plant part	Chemical compound	Reference
root	Chrysophanol	76
	Physcion	
seed	Chrysophanol	77
	5-Hydroxyanthraquinone	78
	Physcion	77

1.21 Cassia grardis Linn.

Plant part	Chemical compound	Reference
leaf	Aloe-emodin	177
	Tannins	79

1.22 Cassia hoffmanseggii Mart. ex Benth.

Plant part	Chemical compound	Reference
leaflet	Hydroxyanthracene derivatives	51

1.23 <u>Cassia jaegeri</u> Keay

Plant part	Chemical compound	Reference
leaf	Apigenin flavonoids Brown pigment Leucoanthocyanin Heterosides of chrysophanol, emodol, and physcion Polyhydroxyflavan	75

1.24 <u>Cassia jahnii</u> Britton et Rose

Plant part	Chemical compound	Reference
flower	Carnaubyl alcohol Ceryl alcohol Docosyl alcohol 1-Octacosanol β-Sitosterol	80
leaf	Anthraquinones Cassine Dihydrocassine β-Sitosterol	80

1.25 Cassia javanica Linn.

Plant part	Chemical compound	Reference
bark	Octacosanol β-Sitosterol	81
flower	Dihydrorhamnetin-3-O-β-D-glucopyranoside Kaempferol-3-rhamnoglucoside Leucocyanidin-4′-O-methyl ether-3-O-β-D-galactopyranoside. Quercetin Quercetin-3′,4′,7-trimethyl ether-3-O-β-D-rhamnopyranoside. β-Sitosterol	5
heartwood	Cerotic acid Hentriacontane β-Sitosterol β-Sitosterol-D-glucoside	81
leaf	Ceryl alcohol Hentriacontane Hentriacontanol Heptacosane Octacosane Octacosanol Total sennosides, 0.20%	81 36

1.26 <u>Cassia laevigata</u> Willd.

Plant part	Chemical compound	Reference
fruit	Oxymethylanthraquinone, 0.1%	18
leaf	Unknown alkaloids	32
seed	β-Sitosterol, 0.014%	18

1.27 <u>Cassia leptophylla</u> Vog.

Plant part	Chemical compound	Reference
leaf	Anthraquinone derivatives	82

1.28 <u>Cassia marginata</u> Roxb.

Plant part	Chemical compound	Reference
bark	l-Leucopelargonidin	6
	Tannins	83
flower	Margicassidin	84
heartwood	3,4,3',5'-Tetrahydroxystilbene	84
leaf	Butein-4'-glycoside	83
	d-Catechin	
	Kaempferol glycoside	86
	d-Leucofisetinidin	83

1.29 Cassia marylandica Linn.

Plant part	Chemical compound	Reference
leaf	Diosmetin	87,88
	N-Methyl-β-phenethylamine alkaloid	89
	Saponoside	
	Traces of chrysophanol, physcion and their β-glycosides.	87
	Two 7-glycosides of diosmetin	87,88
	Two heterosides of emodol of the glucofrangulin type (one α and the other β)	87

1.30 Cassia mimosoides Linn.

Plant part	Chemical compound	Reference
fruit	Oxymethylanthraquinone, 0.1%	18
leaf	Emodin	90
	Emodin glycoside	
	Luteolin-7-glycoside	
	Tannins	
root	Physcion	91

Cassia mimosoides Linn. (cont.)

Plant part	Chemical compound	Reference
seed	Emodic acid Emodin Physcion Luteolin Luteolin-7-glycoside	91

1.31 Cassia multijuga Linn.

Plant part	Chemical compound	Reference
whole plant	Anthraquinone glycosides	79

1.32 Cassia nodosa Buch. Ham. ex Roxb.

Plant part	Chemical compound	Reference
flower	Azralidoside	92
	Ceryl alcohol	93
	Fatty acids:- arachidic, behenic, lignoceric, linoleic, linolenic, oleic, palmitic, and stearic.	
	Nodolidate	

Cassia nodosa Buch. Ham. ex Roxb. (cont.)

Plant part	Chemical compound	Reference
flower (cont.)	Nodososide	94
	Phytosterolin	95
	γ-Sitosterol	
leaf	Kaempferol glycoside	86
seed	Fixed oil	93
	Galactomannan	

1.33 Cassia obovata Collad

Plant part	Chemical compound	Reference
leaf and pod	Aloe-emodin	1
	Reduced aloe-emodin	
	Rhein	
	Sennidins	
	Sennosides A and B	
	Small amount of chrysophanol	

1.34 Cassia obtusa Roxb.

Plant part	Chemical compound	Reference
leaf	Aloe-emodin	4
	Chrysophanol	
	Dulcitol	
	Emodin	
	Emodin rhamnoside	
	Isorhamnetin	
	Kaempferol	
	Kaempferol glucoside	
	Kaempferol-3-rhamnoside	
	Kaempferol-3,7-dirhamnoside	
	Lupenone	
	Lupeol	
	Physcion	
	Physcion glucosylrhamnoside	
	β-Sitosterol	
	β-Sitosterol-β-D-glucoside	

1.35 Cassia occidentalis Linn.

Plant part	Chemical compound	Reference
flower	Emodin	96
	Physcion	
	Physcion-1-β-D-glucopyranoside	
	β-Sitosterol	

Cassia occidentalis Linn. (cont.)

Plant part	Chemical compound	Reference
fruit	Oxymethylanthraquinone, 0.25%	18
leaf	Chrysophanol	97
	Dianthronic heteroside	98
	C-Flavonoside of apigenin	
	4,5,4′,5′-Tetrahydroxy-2,2′-dimethylbianthraquinone.	97
root	A similar substance to rhein	99
	Cassiollin	100
	Chrysophanol	98,100
	Emodin	
	Free anthraquinones, 1.9%	99
	Helminthosporin	101
	Heterodianthrone consisted of chrysophanol and physcion.	98
	Islandicin	101
	Oxymethylanthraquinone, 0.3%	18
	Physcion	102
	Phytosterol	
	Quercetin	99
	Reduced or oxidised physcion	98
	Stigmasterol	100,101
	Total anthraquinones, 4.5%	99
	Xanthorin	101

Cassia occidentalis Linn. (cont.)

Plant part	Chemical compound	Reference
seed	Achrosine	18
	Aloe-emodin	2
	Amino acids:- alanine, arginine, aspartic acid, cystein-cystine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, proline, serine, threonine, and unidentified amino acid.	103
	Chrysarobin	18
	Chrysophanol	2
	Emodin	18
	Fatty oil:- linoleic acid, 31.4%; linolenic acid, 6.3%; oleic acid, 30.7%; saturated fatty acids, 19.7%; volatile constituents, 0.7%; unsaponified matter, 7.4%.	20
	Galactomannan	104
	N-Methylmorpholine alkaloid	105
	Physcion	106
	Physcion-1-glycoside	107
	Physcion homodianthrone	98
	Rhein	2
	Rhein-like and nonrhein-like glycosides	
	Total soluble carbohydrate, 5.52% as glucose, lactose, maltose, raffinose and sucrose.	108
	Toxic albumin	18

1.36 <u>Cassia ovata</u> Mérat. et Lens. ex Geiger.

Plant part	Chemical compound	Reference
leaf	Hydroxymethylanthraquinone, 0.8%	109

1.37 <u>Cassia patellaria</u> DC.

Plant part	Chemical compound	Reference
seed	Unknown alkaloids	32

1.38 <u>Cassia petersiana</u> Bolle

Plant part	Chemical compound	Reference
leaf	Anthraquinones	18

1.39 <u>Cassia podocarpa</u> Guill and Perr.

Plant part	Chemical compound	Reference
leaf	Anthraquinone derivatives(as emodin), 0.2%	110

1.40 Cassia renigera Wall.

Plant part	Chemical compound	Reference
stem-bark	1-Hydroxy-3,8-dimethoxy-2-methylanthraquinone	111
	5-Hydroxy-4′-methoxy flavanone-7-pyranoside	

1.41 Cassia reticulata Willd.

Plant part	Chemical compound	Reference
leaf	Cassiaxanthone	112
	Chrysophanol	113
	Emodin	
	Rhein	114,115

1.42 Cassia siamea Lamk.

Plant part	Chemical compound	Reference
bark	Betulic acid	116
	Betulin	
	Betulinic acid	117
	Cassiamins A, B, and C.	118,119
	Cassianin	116,120
	Chrysophanol	118
	Chrysophanol-9-anthrone	121
	Lupenone	122
	Lupeol	118
	Siameanin	116,120
	Tannins, nearly 9%	11

Cassia siamea Lamk. (cont.)

Plant part	Chemical compound	Reference
flower	5-Acetonyl-7-hydroxy-2-methylchromone	123
	Flavone glucoside, m.p. 212°-214°C	124
	Fructose, glucose, sucrose	
	Lupeol	
	Oligosaccharides A and B	
	d-Pinitol	
	β-Sitosterol	
	Two phenolic compounds, m.p. 205°-206°C and 207°-208°C	
heartwood	Cassiamin	125
	Chrysophanhydranthrone	20
	Chrysophanol	125
	2,3,2′,3′-Tetrahydroxystilbene	
leaf	5-Acetonyl-7-hydroxy-2-methylchromone	126,127
	Cassiamin A	127
	Chrysophanol	
	p-Coumaric acid	
	Hydrocyanic acid	18
	Physcion	127
	Rhein carboxylic derivatives, 0.05%	36
	β-Sitosterol	127

Cassia siamea Lamk. (cont.)

Plant part	Chemical compound	Reference
leaf(cont.)	Tannins, 7%	11
	Thalictiin	127
	Total sennosides, 0.07%	36
	Toxic alkaloid	128
pod	Tannins, 6%	11
	Toxic alkaloid	128
root	Hydrocyanic acid	18
seed	Fixed oil, 44.7%	18
	Siamin, an isoquinoline alkaloid	129
	β-Sitosterol	39
stem	Hydrocyanic acid	18
wood	Ash, 0.3%; alcohol-benzene extractives, 18.2%; cellulose, 33.8%; lignan, 37.3%; mannan, 0.17%; moisture, 11.2%; pentosans, 15.6%.	130

1.43 Cassia sieberiana DC.

Plant part	Chemical compound	Reference
leaf	Aloe-emodin Chrysophanol Emodin Isoquercetin Pelargonidin or Peonin Physcion Quercetin Rhein Rhein-8-glycoside Small quantities of catechol tannins	131
root	Anthraquinone derivatives, 0.15-0.20% Condensed catecholic tannins l-Epicatechol gallate Leucopelargonidin Tannins Traces of caffeic, chlorogenic, gallic acids and gallocatechol	132
whole plant	Hydrocyanic acid	18

1.44 Cassia sophera Linn. (C. torosa Cav.)

Plant part	Chemical compound	Reference
flower	Chrysophanol	133
	Rhamnetin-3-O-β-D-glucoside	
fruit	Unknown alkaloids	32
leaf	Rhein carboxylic derivatives, 0.05%	36
	Total sennoside, 0.07%	
	Unknown alkaloids	32
seed	Dehydroascorbic acid, 93.1 mg%	134
	Emodin anthrone	135
	Physcion	
	β-Sitosterol	41
	Total ascorbic acid, 107.3 mg%	134
seedling	Chrysophanol	136
	Emodin	
	Germichrysone	
	Physcion	
	Torochrysone	

1.45 Cassia speciosa Shrad.

Plant part	Chemical compound	Reference
leaf	Anthraquinone derivatives	82

1.46 Cassia spectabilis DC.

Plant part	Chemical compound	Reference
flower and fruit	Unknown alkaloids	32
leaf	Iso-6-cassine Spectaline	15
leaf and stem	Cassine Cassinicine Physcion β-Sitosterol Stigmasterol 1,3,8-Trihydroxy-2-methylanthraquinone	16
seed	Iso-6-cassine Iso-6-carnavaline Spectaline Spectalinine Small amount of cassine	137

1.47 Cassia splendida Vog.

Plant part	Chemical compound	Reference
fruit	Hydroxyanthracene derivatives	51

1.48 Cassia timoriensis DC.

Plant part	Chemical compound	Reference
leaf	Barakol	177

1.49 Cassia tomentella Domin.

Plant part	Chemical compound	Reference
fruit	Unknown alkaloids	32

1.50 Cassia tora Linn. (C. obtusifolia Linn.)

Plant part	Chemical compound	Reference
flower	Kaempferol glycoside	138
leaf	Kaempferol-3-diglucoside Rhein carboxylic derivatives, 0.11% Total sennosides, 0.14%	139 36
leaf and stem	Fatty acids:- linoleic, 13.1%; linolenic, 26.0%; oleic, 5.7%; palmitic, 20.8%; stearic, 6.4% and fatty acid of C up to C_{34}	140

Cassia tora Linn. (cont.)

Plant part	Chemical compound	Reference
root	Leucopelargonidin-3-O-α-L-rhamnopyranoside	138
	Myricyl alcohol	80
	β-Sitosterol	139
	1,3,5-Trihydroxy-6,7-dimethoxy-2-methyl-anthraquinone.	
seed	Aloe-emodin	141,142
	Aloe-emodin monoglucoside	
	Amino acids:- alanine, aspartic acid, glutamic acid, glycine, isoleucine, leucine, methionine, phenylalanine, proline, and serine.	103
	Auratio-obtusin	143
	Chryso-obtusin	
	Chrysophanic acid-9-anthrone	144
	Chrysophanol	141,142
	Chrysophanol anthrone	
	Chrysophanol diglucoside and triglucoside	
	Emodin	
	Fixed oil:- linoleic, lignoceric, oleic, and palmitic acids.	145
	Glucoaurantio-obtusin	146
	Gluco-obtusifolin	

Cassia tora Linn. (cont.)

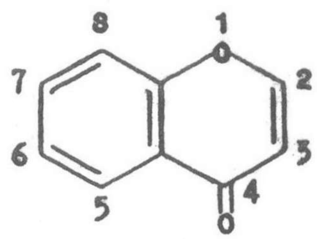
Plant part	Chemical compound	Reference
seed(cont.)	8-Hydroxy-3-methylanthraquinone-1-β-gentiobioside.	147
	Norrubrofusarin	148,149
	Obtusifolin	141
	Obtusin	143
	Oxytocic substance	150
	Physcion	141,142
	Physcion diglucoside	
	Polysaccharides consisted of D-glucose, D-galactose, D-mannose and D-xylose in molar ratio of 2 : 2 : 7 : 1.	151
	Protein, 23.2%	152
	Rhein	141,142
	Rhein-like and nonrhein-like glycosides	2
	Rubrofusarin	148,149
	Rubrofusarin-6-β-gentiobioside	153
	β-Sitosterol	39,145
	Torachrysone	154
	Toralactone	155
	Total soluble carbohydrates, 5.56% as arabinose, glucose, lactose, maltose, raffinose, rhamnose and sucrose.	108,142
	Crude fiber, 13.16%; ether extract, 7.75%; N-free extract, 51.34%; total ash, 6.63%; CaO, 1.22%; P_2O_5, 1.62%.	20

Cassia tora Linn. (cont.)

Plant part	Chemical compound	Reference
whole plant	Glycosides D-Glucose D-Mannitol Myricyl alcohol β-Sitosterol Tannins Sodium chloride Sodium sulphate Total ash, 10.5% :- calcium, iron, magnesium. potassium, sodium, phosphate, and sulphate.	156

2. Chromone

Benzo-γ-pyrone or chromone, the name given by Von Kostanecki, is the parent compound of important vegetable colouring matters, which are derived from flavone (2-phenylchromone), flavonol (3-hydroxyflvone), flavanone (2,3-dihydroflavone), and isoflavone (3-phenylchromone). In consequence these phenylchromone have been more systematically studied than the simple chromones, although a number of 2-methylchromones have been obtained from natural sources[157]. The chromone nucleus with its numbering system is as follows:



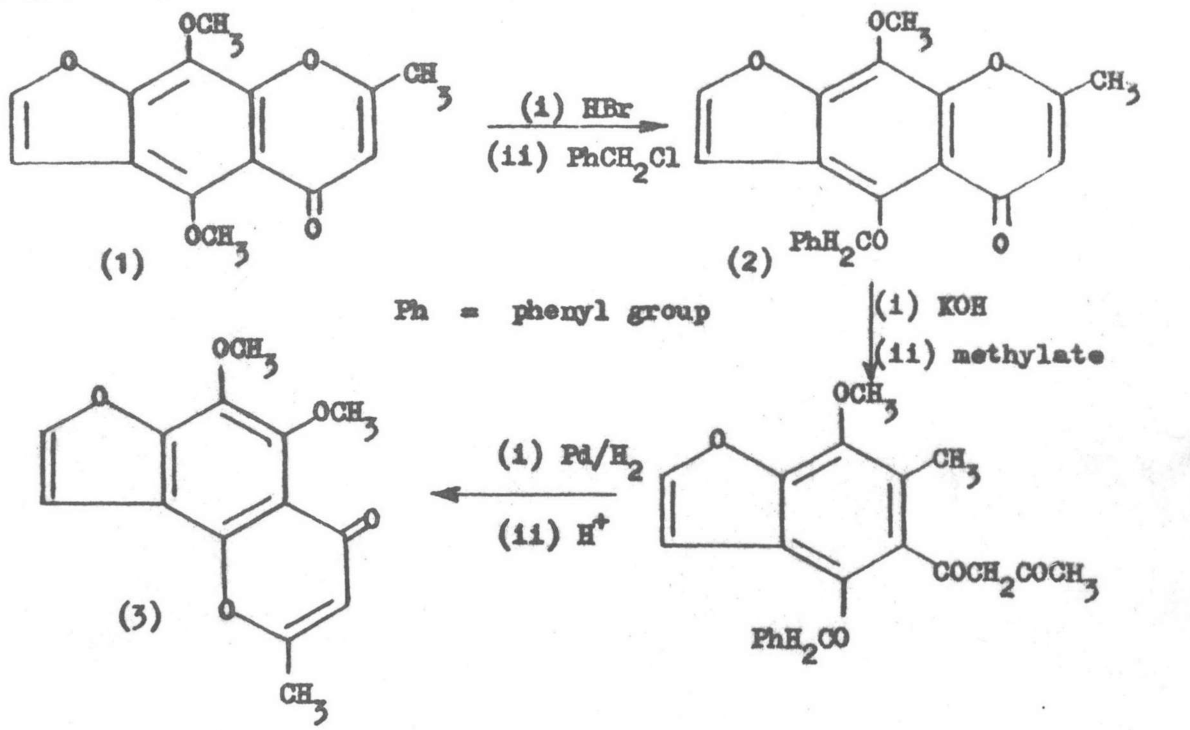
Numbering system in the chromone nucleus.

Naturally occurring chromones generally have a methyl group at C-2 and are oxygenated at C-5 and C-7. Thus despite their overall resemblance to the carbon skeleton of the coumarins, they may be regarded as derived from the condensation of five molecules of acetic acid.

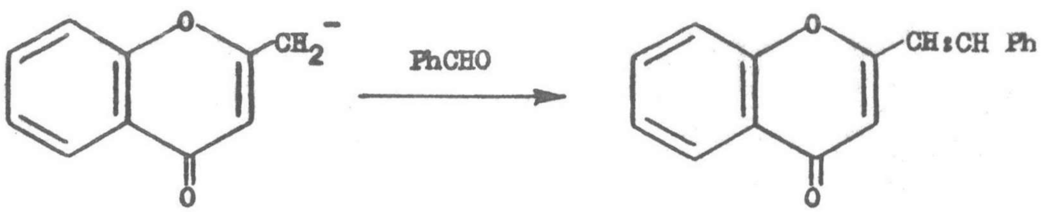
2.1 The Chemical Nature of Chromone

The general properties of chromones follow from those of the monocyclic γ-pyrones. Though their ability to form salts with acids is known, it has never been exploited but it could be useful, as chromones are generally much more soluble than coumarins in hydrochloric acid. Like other γ-pyrones, chromones do not behave as ketones except towards reagents of the bifunctional type, hydrazine and hydroxylamine opening the ring and generating pyrazoles and isoxazoles derived from the related β-diketones(158).

Careful hydrolysis sometimes converts chromones to the related β-diketones themselves, but the only example to be mentioned here occurs as a step in conversion of khellin(1) into isokhellin(3) as shown below(158).



More vigorous alkaline hydrolysis induces fission of the β-diketone at both sensitive links, giving acetic acid, acetone, a salicylic acid and an o-hydroxyacetophenone. The exact composition of the mixture depends on the concentration of the base and also, to a large extent, on the type of substitution in the benzene ring, as this determines which of the carbonyl groups will add the nucleophilic hydroxide ion more readily; some chromones have been mistaken for coumarins because they yield acetic acid but no acetone. In anhydrous basic media, the methyl group at the 2-position is often active enough to form yellow styryl derivatives(4) with aromatic aldehydes, but similarly placed ethyl groups are not so active. Again, 2-methylchromones give a red colour when warmed with sodium hydroxide in ethoxyethanol, provided that no free phenolic hydroxy group is present[158].



(4)

In 5-hydroxychromones there is strong hydrogen bonding. Such compounds usually give intense blue or violet ferric reactions, are not easily soluble in aqueous alkali and can not readily be methylated. Like 5-hydroxyflavones, they form with uranyl acetate brightly coloured complexes, useful as a means of differentiation from ordinary o-hydroxyketones which give only yellow complexes. Unlike 5-hydroxyflavones, however, 5-hydroxychromones do not respond to the boric acid-citric acid or the boric acid-oxalic acid tests. 5,7-Dihydroxychromones are easily detected by the blue unstable colour produced by alkaline hydrogen peroxide[158].

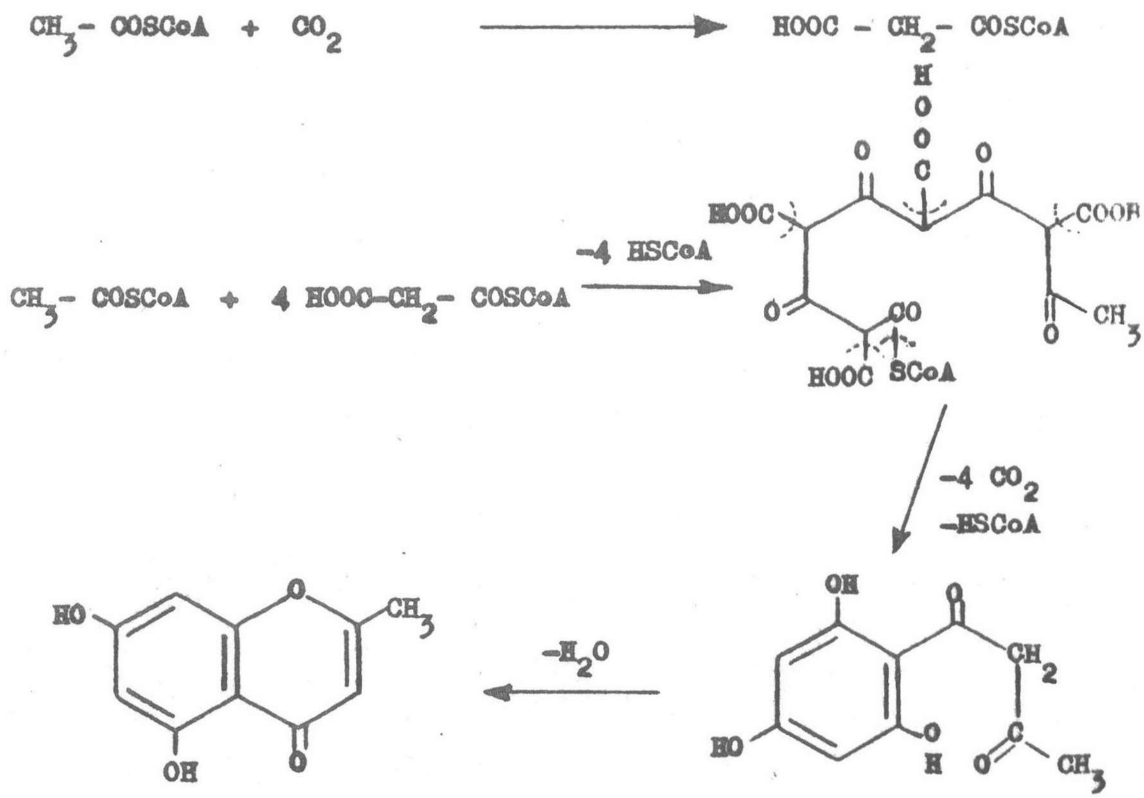
In general, chromones absorb ultraviolet light near 250 and 290 nm ($\log\epsilon$, $\sim$4). There is usually an inflection at about 310 nm and in some chromones, this resolves itself into a new peak at 330 nm. Minor differences in spectra being dependent on the substituents present, they often have diagnostic value, and some chromones exhibit a characteristic fluorescence in ultraviolet light[158].

The infrared absorption of chromones has been less studied, but it seems that there is usually carbonyl absorption at 1660 cm^{-1} and other absorption at 1620 cm^{-1}, a pattern providing a quick and reliable way of differentiating chromones from coumarins[158].

2.2 Biogenesis of Chromones

A trapping experiment with 5,7-dihydroxy-2-methylchromone indicated that this compound was formed from acetate in plant. Both the benzene and pyrone rings were acetate derived[159].

Many reports have shown that the coupling of acetate unit comes from the reaction of one mole of acetyl co-enzyme A and many moles of malonyl co-enzyme A by the similar pathway as in biological fatty acid synthesis. The intermediate product is a carboxylated poly-β-ketonic acid, then cyclises to aromatic compound and simultaneously decarboxylate. After decarboxylation, the intermediate product is an aromatic 1,3-diketone, loosing water, forming γ-pyrone ring at the same time to give the main skeleton of chromone as 5,7-dihydroxy-2-methylchromone (Fig. III., p. 46)[160].



5,7-Dihydroxy-2-mehtylchromone

Figure III. Biogenesis of chromone nucleus

The methyl group in such compounds are introduced after the formation of the main skeleton(161).

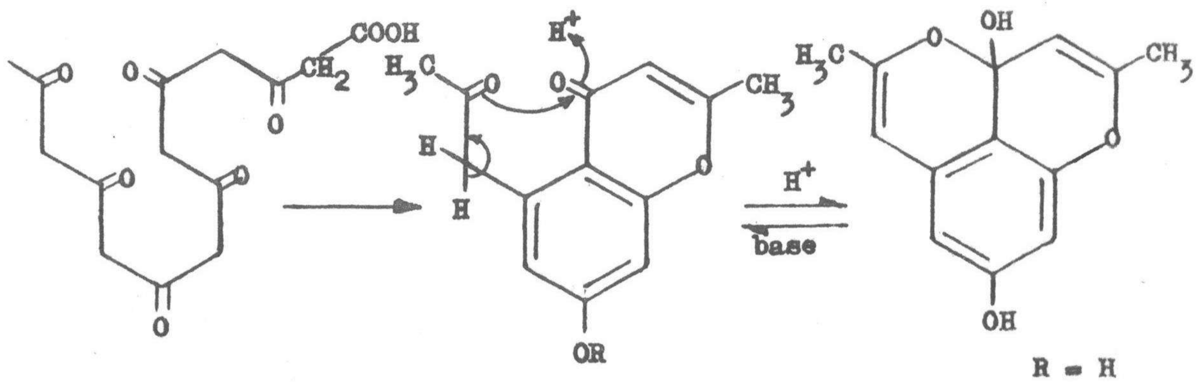
A biosynthetic pathway of furanochromones is proposed :
acetate ⟶ 5,7-dihydroxy-2-methylchromone ⟶ peucenin ⟶ ⟶ visamminol ⟶ ⟶ visnagin and khellin(159).

2.3 The Chemical Nature of Barakol

Barakol($C_{13}H_{12}O_4$) was first isolated in 1969 by Hassanali et al.[126] from the leaves of Cassia siamea Lamk. In 1978, Wagner et al.[127] reported that 5-acetonyl-7-hydroxy-2-methylchromone was found in the leaves of Cassia siamea Lamk. The product of the acid treatment of this chromone was identified as barakol[123]. Barakol can be crystallised from aqueous methyl alcohol or ethyl alcohol as pale yellow needles, m.p. 165°C(decomposed) and is stable in hydroxylic solvents or in moist atmosphere[126]. Chemical dehydration of barakol was readily achieved over phosphorous pentoxide or in vacuum. The resulting dark green amorphous compound, anhydrobarakol($C_{13}H_{10}O_3$) was extremely unstable[175]. Chloroform solution of barakol when slightly warmed, turned to brown and precipitated dark polymeric material. Anhydrobarakol could be reconverted into barakol by dissolution in aqueous methyl alcohol[175]. Barakol is very rapidly degraded by base, but with strong acids it reversibly forms anhydro-salts which may be dried and which do not decompose at room temperature in the solid state[126]. The strong basic character of barakol was demonstrated by the fact that crystalline hydrobromide and hydrochloride derivatives, $C_{13}H_{10}O_3$, HX, salts of the anhydro-base, could be prepared by addition of concentrated hydrobromic or hydrochloric acid to a methanolic solution of barakol. The readily reversible dehydration and salt formation of barakol was reminiscent of anthocyanin chemistry[175]

2.4 Biogenesis of Barakol

Bycroft et al.[175] had proposed the possible biogenesis of barakol from polyketide derived from seven acetate units by forming the intermediate compound (I). The scheme is illustrated below.



(I) (II)

A proposed biogenesis route of barakol[175]

Cyclisation of compound (I) to barakol can be regarded as an interaction of enolate anion with the chromone carbonyl. It seemed reasonable that the reverse reaction of barakol (II) to the intermediate compound (I) might also occur[175].

It is now known that barakol is an artifact compound.

2.5 Chemical Synthesis of Anhydrobarakol

It was reported that the chemical synthesis of anhydrobarakol took place from the derivative of dimethyl hexaketone (III), of which both terminal keto groups had been protected as ketals. Treatment of (III) with diisopropylamine gave 80% of the expected resorcinol (IV). Removal of the ketal groups by treatment with acid, caused concomitant cyclisation to the naturally occurring chromone (V) (87%); further treatment of chromone (V) with sulphuric acid gave the tricyclic metabolite barakol (VI) in 80% yield (Fig. IV, p. 49)[176].

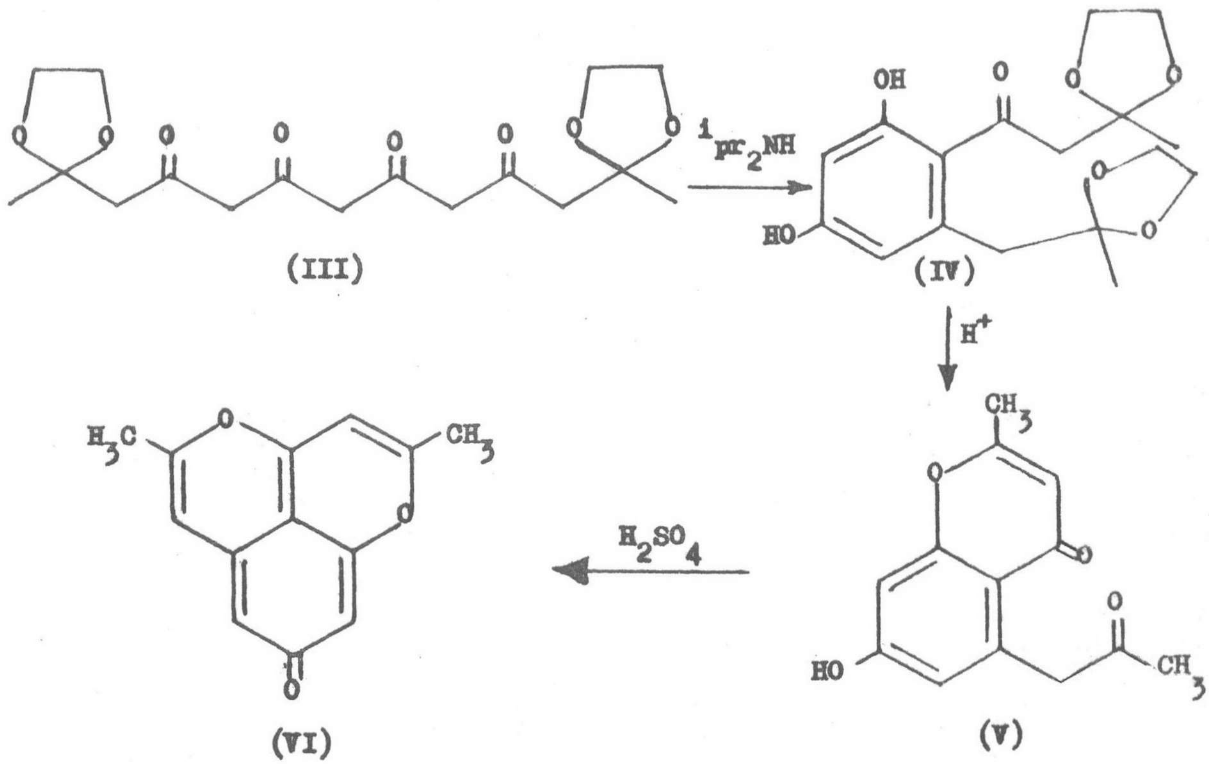


Figure IV. The chemical synthesis of anhydrobarakol

2.6 Chromone Bearing Plants

Botanical origin and plant part	Isolated chromone	Reference
Ammi visnaga Lamk. (fruit) (Umbelliferae)	Ammiol Khellin Khellinol Khellol glucoside Visamminol Visnagin	160
Angelica japonica A. Gray (Umbelliferae) (root)	Hamaudol	162

Botanical origin and plant part	Isolated chromone	Reference
Backhousia angustifolia Benth. (Myrtaceae)	Angustifolionol	160
Cassia siamea Lamk. (flower and leaf) (Caesalpiniaceae)	5-Acetonyl-7-hydroxy-2-methylchromone	123,127
Cedrelopsis grevei Baill. (Meliaceae)	Ptaeroxylin	163
Cneorum pulverulentum Vent. (Cneoraceae) (fruit)	Sorbifolin and its methyl ether	164
C. tricoccum Linn. (leaf) (Cneoraceae)	Cneorum chromone G.	164
(twig)	Sorbifolin and its methyl ether	
Dianella revoluta R. Br. (root) (Liliaceae)	5,7-Dihydroxy-6-methyl--2-nonacosylchromone and with homologues	165,166
Eleutherine bulbosa Urb. (bulb) (Iridaceae)	Eleutherine	160
Eugenia caryophyllata Thunb. (Myrtaceae) (flowering bud)	Eugenin Eugenitin Isoeugenitin Isoeugenitol	160
Leptorumohra miqueliana (aerial part of plant) (Aspidiaceae)	Leptorumol	167

Botanical origin and plant part	Isolated chromone	Reference
Lophomyrtus bullata Burret (Myrtaceae) (essential oil)	2-Isopropylchromone	168
Nauclea orientalis Linn. (wood) (Rubiaceae)	Noreugenin	169
Peucedanum ruthenicum Bieb. (Umbelliferae)	A new chromone $C_{12}H_{12}O_4$, m.p. 119°– 121°C	170
P. ostruthium K. Koch	Peucenin	160
Ptaeroxylon obliquum Radlk. (Ptaeroxylaceae) (wood)	Alloptaeroxylin	171
	Deoxykarenin	172
	Heteropeucenin-7-methyl ether	171
	Karenin	172
	Peucenin	172,173, 174
	Ptaerochromone	173
	Ptaerocyclin	174
	Ptaeroxylin	171
	Umtatin	171,174
Spathelia sorbifolin Linn. (Rutaceae) (root)	Sorbifolin	164
Stypandra grandis C. T. White (Liliaceae) (root)	5,7-Dihydroxy-6-methyl--2-nonacosylchromone and with homologues	165,166