Review Jour. Chem. Soc. Pak. Vol. 12, No.2, 1990.

Naturally Occurring Xanthones in Higher Plants and Ferns

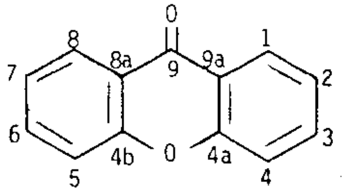
H.M.G. Al-Hazimi* and G.A. Miana**
*Department of Chemistry, College of Science, King Saud University, P.O.Box. 2455, Riyadh-11451, Saudi Arabia.
**Department of Chemistry, Gomal University, D.I. Khan, Pakistan.

(Received 25th October, 1989, revised 8th January, 1990)

Summary: Naturally occurring xanthones appearing in the literature during the period 1979-to date have been reviewed.

Introduction

Xanthones are, perhaps one of the most abundant group of secondary metabolites in nature. These compounds possess the parent xanthone molcule which has not been previously found as a natural product. More than 340 natural xanthones are known [1] and their occurrence in higher plants is restricted to limited number of plant families. However, most of the natural xanthones have been isolated from the species belonging to the families: *Guttiferae* and *Gentianaceae*. Work on xanthones isolated from the members of the latter two families has been reviewed in 1980 by Sultanbawa [2]. In 1977, Hostettmann and Wagner [3] have reviewed xanthone glycosides. More recently, a review in the field of xanthones by Russian [4] has appeared in the literature, but it was not informative as that one by Sultanbawa [2]. The number of natural xanthones has increased considerably in the recent years. Thus the purpose of the present review is dealing with the tabulation and phytochemical aspects of natural xanthones (simple, prenylated and glycosides) isolated from plants in the period 1979-present.



Xanthone nucleus
(xanthen(9)one)

Isolation techniques

Xanthones are found in nature either in the free state or as C- or O- glycosides. There is no one method of extraction which can be adopted as a standard technique for the isolation of xanthones from natural sources. However, continuous solvent is still the usual method of extraction. The least polar, as well as xanthones of intermediate polarities can be obtained with chloroform whereas the strongly polar xanthones require alcohol (EtOH or MeOH) or alcohol-water for extraction. The dried parts of the plant are extracted with hot alcohol [4-7] particularly for those plants which accumulate xanthone glycosides. The organic extracts are chroma- tographed over silica gel or polyamide columns using different solvent systems. Polyamide columns are frequently applied for the separation of xanthone glycosides [3]. Further purification of xanthones obtained from the columns may be carried out on preparative TLC or over Sephadex LH 20 columns. Frequently used solvents in TLC have been already summarized [3]. HPLC analysis was used recently for the separation of naturally occurring xanthones [5-8]. DCCC technqiue was also used for the isolation of xanthones [9,10].

Plant Distribution

As previously mentioned, natural xanthones encountered in the present review are only those isolated in the last decade. A list of genera and their corresponding plant families is given in Table-1. Thus the xanthones were isolated from species belonging to 30 genera. Species of the family *Guttiferae* and *Gentianaceae* still constitute the major sources of this class of natural compounds.

Xanthones are common in woody parts (such as barks and stems) and roots. They are also abundant in other parts of the plants such as flowers, leaves and pollens.

Table-1

Genus	Plant family
Calophyllum	*Guttiferae*
Caraipa	"
Garcinia	"
Haploclathra	"
Hypericum	"
Mammea	"
Mesua	"
Psorospermum	"
Rheedia	"
Tovomita	"
Vismia	"
Canscora	*Gentianacea*
Centaurium	"
Frasera	"
Gentiana	"
Gentianopsis	"
Hoppea	"
Ixanthus	"
Swertia	"
Tripterospermum	"
Chrozophora	*Euphorbiaceae*
Cudrania	*Moraceae*
Delbergia	*Leguminosae*
Halenia	*Asteraceae*
Iris	*Iridaceae*
Mangifera	*Anacardiaceae*
Polygala	*Polygalaceae*
Asplenium	*Aspleniaceae*
Hymenophyllum	*Hymenophyllaceae*
Trichomanes	*Hymenophyl*laceae
Veratrilla	

Simple Xanthones

Table-2 contains about 80 free and prenylated xanthones isolated from higher plants during the period 1979-present, and they have been arranged in accordance with their oxygenation pattern. The vast majority of xanthones encountered in Table-2 have been isolated from the plant species belonging to *Guttiferae* and *Gentianaceae*. All the listed free xanthones in the latter Tables are structurally systematic with the exception of compound 21 (2,5-dihydroxy-1,6-dimethoxyxanthone) which has been recently isolated from *Garcinia thwaitesh* [33]. Till to date, this compound is still the single example in nature of 1,2,5,6- oxygenation pattern of xanthones.

Of the three dioxygenated xanthones included in Table 2, two were isolated from species of *Guttiferae* while the third occurred in a species belonging to *Leguminosae*. 2-Hydroxy-3-methoxyxanthone (compound No. 3) was already listed in Sultanbawa review [2] and it has been mentioned herein due to the recent appearance of its full data [13]. Six partially methylated trioxygenated compounds as well as one completely methylated xanthone have been isolated from 4 genera as in Table-2.

About 20 tetraoxygenated xanthones have been isolated from 13 genera; seven belong to the family *Guttiferae* while four belong to *Gentianaceae*. Most of the tetraoxygenated xanthones in Table-2 have three substituents on one ring (commonly as 1,2,3- and 1,3,4-) while the fourth on the other ring. Among the tetraoxygenated xanthone encountered in Table-2, only one has the four substituents on one ring. Compound 21 is the only representative natural xanthone known having 1,2,5,6-substitution pattern.

Thirteen pentaoxygenated xanthones hagve been reported from various genera as in Table 2. All these xanthones have been isolated from plant species of the family *Gentianaceae* except compound 36 which has been isolated from *Helenia elliptica* (*Asteraceae*). Interestingly, the latter xanthone is the only pentaoxygenated xanthone having free hydroxyl at position 5. Three partially methoxylated xanthones, 1,3,5,6,7,8 and 1,2,3,4,5,7 have been isolated from two genera (Table-2).

Prenylated Xanthones

The recently isolated prenylated xanthones (compounds 45-76) and the plants from which they have been isolated are given in Table-2. As it could be noticed from the latter Table, the occurrence of these compounds is restricted to the plant species of *Guttiferae* with the exclusion of cudraxanthones A,B and C (59, 62, 67) which have been isolated from a plant species belongings to the family *Moraceae*.

Xanthonolignoids

Xanthonolignoids are rare group of naturally occurring products; so far only five compounds are known. The first representative was Kielcorin [80] isolated early in 1977's from *Kielmeyera* species [70]

Table-2

No.	Structure (trivial name)	M.P.	Botanical Sources	(Part Used)*	Ref.	Identification** (methods used)
Di-and Trioxygenated xanthones						
1	2,5-OH	216-218°	Hypericum canariensis L	(F, L, S)	11,12	(1a, 1b, 2, 3^{+}, 5)
2.	2,6-OH	310°	Mammea acuminata	(T)	13	(1a, 1b, 2, 3^{+}, 5, 8)
3	2OH; 3-OMe	186.5-187.5°	Dalbergia latifolia Roxb.	(W)	14	(1a, 1b, 7)
		174.0-175°	Hypericum mysorense	(T)	15	(2,3,5)
4.	1,3-OH; 2-OMe	176-178°	Visimia guaramirangae	(R)	16	(1a, 1b, 3, 5, 7, 8)
5.	3,5-OH; 1-OMe	354-155°	Canscora decussata	(Ae)	17	(1a, 2,3^{+}, 5,7)
6.	1,7-OH; 4-OMe	239.5-240.5°	Visima guaramirangae	(R)	16	(1a, 1b, 3^{+}, 5, 7,8)
7	4,8-OH; 1-OMe	230-231°	Vismia guaramirangae	(R)	16	(1a, 1b, 3, 5, 7)
8	2,7-OH; 3-OMe	299-300°	Dalbergia latifolia Roxb.	(H)	14	(1a, 1b, 3^{+}, 8, 9)
9	2-OH, 3,4-OMe	186-189°	Hypericum sampsonii Hance	(Wh)	19	(1a, 1b, $3^{\#}$, 5)
10	2,3,4-OMe	149-150°	Hypericum ericoides	(F,L,S)	20,	(1a, 2, 3, 5)
					20a	(9)
Tetraoxygenated xanthones						
11	1,2,3-OH, 5-OMe	256-258°	Centaurium erythraea Rafn	(Wh)	21	(1a, 1b, 3 (C_5D_5N), 5,8)
12	1,3,8-OH, 2-OMe	262-264°	Centaurium linarifolium		22	(1a, 1b, 2, $3^{\#}$, 5)
or	1,3,8-OH, 4-OMe		(Lamark) G. Beck			
13	1,5-OH, 2,3-OMe	254-255°	Calophyllum walkeri Wight		23	(1a, 1b, 2, 3^{+}, 5,8)
			Halenia elliptica D. Don		24	(1a, 1b, 2, 3, 5, 7)
14	1,3-OH, 2,7-OMe		Veratrilla baillonii Franch	(R)	25	(1a, 2, 3, 5)
			Gentiana lutea L.		26	
15	1,7-OH, 2,3-OMe	225-228°	Frasera speciosa (R)	27	(3)	
			Halenia elliptica D. Don		24	(1a, 2, 5)
16	1,6-OH, 5,7-OMe	231-233°	Hypericum canariensis	(S,L,F)	2	(1a, 1b, 2, 3, 5)
			Caraipa densiflora		28	
17	1,5-OH, 6,7-OMe		Tovomita brasiliensis		29	
			Caraipa densiflora		30	(1a, 2, 3)
18	3,8-OH, 1,4-OMe or	170-172°	Centaurium linarifolium		22	(1a, 1b, 2, 3^{+}, 5)
	3,8-OH, 1,2-OM		(Lamark) G. Beck			
19	14-OH, 3,5-OMe		Centaurium erythrea		31	
20	1,7-OH, 3,4-OMe	285-288°	Veratrilla baillonii Franch	(R)	32	(1a, 2, 3, 4, 5)
	(Veratrilogenin)					
21	2,5-OH, 1,6-OMe	207-208°	Garcinia thwaitesii	(B,T)	33	(1a, 1b, 2, $3^{\#}$, 5, 7)
22	1,3-OH, 5,6-OMe	205-207°	Haploclathra liantha	(TW)	34	(1a, 1b, 2,3^{+}, 5, 10)
	(Leiaxanthone)		Centaurium linarifolium		35	
			(Lamark) G. Beck			
23	5,6-OH; 1,3-OMe	294-295°	Mesua ferrea L. (B, H)	36	(1a, 1b, 2, 3^{+}, 5, 7, 8)	
	(Ferrxanthone)					
24	1,7-OH; 3,8-OMe	193.5-194°	Gentiana barbata		37	(1a, 2, 7, 8)
	(Gentiacaulein)		Gentiana detonsa	38		

Table-2: continued.

No.	Structure (trivial name)	M.P.	Botanical Sources	(Part Used)*	Ref.	Identification** (methods used)
			Gentianopsis paludosa		39,40	
			Haploclathra paniculata	(TW)	51	
			Swertia connata	42		
			Swertia petiolata Royle		44	
24a	1,3,7-OH; 8-OMe		Haploclathra leiantha		38	(1a, 1b, 2, 3, 5)
	(Haploxanthone)		Haploclathra paniculata			
25	3,7-OH; 1,8-OMe	282-284°	Haploclathra paniculata	(TW)	41	(1a, 1b, 2, 3^+, 5,8)
			(Mart) Benth			
26	1-OH; 2,3,4-OMe	206°	Hypericum ericoides	(F, L, S)	20	(1a, 1b, 2, 3^+, 5)
27	1-OH; 3,5,6-OMe	179-181°	Canscora decussata Schult	(R)	43	
		185-187°	Centaurium erythrea Rafn	(R)	45	(1a, 2, 3, 5)
28	8-OH; 1,3,5-OMe	210°	Swertia mussottii Franch		46	(1a, 1b, 2, 3)
			Swertia bimaculata	(Wh)	47	
29	7-OH; 1,3,8-OMe		Haploclathra leiantha	(TW)	48	(1a, 1b, 2, 3^+, 5)
	(Anthaxanthone)					
Penta- and Hexaoxygenated Xanthones						
30	12,3-OH; 7,8-OMe	231-234°	Swertia iberica (R)	49	(1a,1b, 3(TFA)	
	(Swertiaiberin)					
31.	1,4,8-OH; 3,7-OMe	233-234°	Triterospermum lanceolatum	(Wh)	50	(1a, 1b, 2, 3 and 4^+)
	(Lanceolin)					
32	1,2-OH; 3,4,5-OMe	208-2°	Halenia eliptica D.Don		24	(1a, 2, 3^+, 5, 7, 8)
33	1,3-OH; 4,7,8-OMe	218-220°	Tripterospermum lanceolatum	(Wh)	50	(1a, 1b, 2, 3 and 4^+, 5)
	(Methyllanceolin)					
34	1,3,8-OH;2,6-OMe	231-233°	Ixanthus viscosus	(Ae)	18	(3,4^+)
34a	1,8-OH; 2,3,6-OMe	177-178°	Ixanthus viscosus	(Ae)	18	(3,4)
35	1,4-OH; 2,3,7-OMe	160-61°	Swertia bimaculata	(Wh)	47	(1a, 3, 5, 10)
			Veratrilla baillonii		25	
36	1,5-OH; 2,3,7-OMe	258°	Halenia elliptica D. Don		24	(1a, 1b, 2, 3, 5, 7,8)
37	1,7-OH; 2,3,4-OMe	164-68°	Frasera speciosa	(R)	27	(1a, 1b, 3)
38	1,7-OH; 3,4,8-OMe	217.5°	Swertia mussotii F.		46	(1a, 1b, 2,3^+, 8)
39	1,8-OH; 3,4,5-OMe	231°	Gentiana corymbifera	(F,L,R,S)	51	(1a, 1b, $3^{\#}$, 5)
	(3-methylcorymbiferin)					
40	1,8-OH; 3,4,6,-OMe	225-227°	Centaurium linarifolium		22	(1a, 1b, 2,3)
			(Lamark G Beck)			
		236-37°	Centaurium erythraea	(Wh)	52	
41	3,6-OH; 1,5,7-OMe	196-98°	Canscora decussata S.		53	(1a, 1B, 5, 7)
42	1,6,8-OH; 3,5,7-OMe	213-15°	Centaurium erythraea Rafn.		54	(1a, 1b, 3, 3^+, 5)
		215-17°	Centaurium linarifolium		22	
			(Lamark) G. Beck			

Table-2: continued.

No.	Structure (trivial name)	M.P.	Botanical Sources	(Part Used)*	Ref.	Identification** (methods used)
43	1,6-OH; 3,5,7,8-OMe	178-79°	Centaurium linarifolium (Lamark) G Beck		55	(1a, 1b, 2, $3^{\#}$, 5)
44	1,7-OH; 2,3,4,5-OMe	245°	Halenia elliptica D. Don		24	(1a, 1b, 2,3,5,7,8)
			Prenylated xanthones			
45		242-44°	Garcinia mangostana L.	(Fr)	56	(1a, 2,3, 5,7,8)
45a		above 240°	Garcinia manogostana	(L)	107	(5,7)
46		220-22°	Garcinia mangostana L.	(Fr)	56	(1a, 2,3^{+}, 5,7,8)
47	(Hypericanarin)	240°	Hypericum canariensis L.	(Ae)	12	(1a, 1b, 2, 3^{+}, 5)
47a		193-95°	Garcinia mangostana	(L)	107	(1a, 2, 3^{+}, 5)
48	(Hyperxanthone)	285°	Hypericum sampsonii Hance	(Wh)	19	(1a, 1b, $3^{\#}$, 5)
49	(Rheediachromenoxanthone)	223-24°	Rheedia gardneriana Pl. & Tr Rheedia brasilliensis Pl. & Tr.	(R (R)	) 57 58	(1a, 1b, 2, $3^{\#}$, 5, 7, 8)
50	(Garcinone A)	224-25°	Garcinia mangostanta	(Fr)	59	(1a, 1b, 2, 5, 7)
51	(6-Deoxy-mangostin)	171-74°	Calophyllum thwaitesii		60	(1a, 2, 3, 5)
52		168-69°	Garcinia quadrifaria	(S)	61	(1a, 1b, 2, $3^{\#}$, 5, 7)
53	(Calocalabaxanthone)	164-66°	Calophyllum calaba **var.calaba**	(B)	60,62	(1a, 2, $3^{\#}$, 5, 7)
54	(Calothwaitesixanthone)	169-172°	Calophyllum thwaitesii		60	(1a, 2, 3, 4, 5)
55	(Demethylcalabaxanthone)	85°	Calophyllum walkeri	(S)	63	(1a, 1b, 2, 3, 5)
56	(Calozeyloxanthone)	236°	Calophyllum zeylanicum Kosterm	(B)	64	(1a, 1b, 2, 3 and $4^{\#}$, 5, 7,8)
57	Yellow amorphous solid		Calophyllum walkeri	(S)	63	(1a, 1b, 3, 5,7)
58	(Thwaitesixanthonol)	176°	Calophyllum walkeri	(S)	63	(1a, 1b, 2, 3, 5,7)
59	(Cudraxanthone A)	212-216°	Cudrania tricuspidata (Carr.) Bur.	(R)	65	(1a, 1b, 2, 3,4,5)
60		173-174°	Rheedia brasiliensis Pl. & Tr	(R)	58	(1a, 1b, $3^{\#}$, 5)
61.	(Garcinone C)	216-218	Garcinia mangostana L.	(Fr)	59	(1a, 2, 3 and 4^{+}–, 5,7)
62	(Cudraxanthone C)	yellow powder	Cudrania tricuspidata (Carr.) Bur.	(R)	65	(1a, 1b, 2, 3,4,5)
63	(Isorheediaxanthone B)	212-213° 218°	Rheedia gardneriana Pl. & Tr Rheedia brasiliensis Pl. & Tr.	(R) (R)	57 58	(1a, 1b, 2,$3^{\#}$, 5)
64	(Rheediaxanthone B)	208-211°	Rheedia benthamiana Pl. & Tr. Rheedia gardeneriana Pl. & Tr.	(R) (R)	67 57	(1a, 1b, 2, $3^{\#}$(C_5D_5N), 4^{+} ,5,7,11,12)
65		188-189°	Rheedia brasiliensis Pl. & Tr.	(R)	58	(1a, 1b, 3, 5,7,12)
66	(7-Prenyljacareubin)	218-220°	Rheedia gardneriana Pl. & Tr.	(R)	68	(1a, 1b, 2, $3^{\#}$, 5)
67	(Cudraxanthone B)	163-167°	Cudrania tricuspidata (Carr.) Bur.	(R)	65	(1a, 1b, 2, 3,4,5)
68.	(Garcinone B)	190-192°	Garcinia mangostana L.	(Fr)	59	(1a, 1b, 2, 3 and 4^{+}, 4)
69		156-157°	Garcinia mangostana L.		69	(3,4,5,9)
70		194-195°	Rheedia brasilliensis Pl. & Tr.	(R)	58	(1a, 1b, 3, 5,7,11)
71	(Pyranojacareubin)	259.5-260.5°	Rheedia gardeneriana Pl. & Tr.	(R)	68	(1a, 1b, 2, 3,5)

Table-2: continued.

No.	Structure (trivial name)	M.P.	Botanical Sources	(Part Used)*	Ref.	Identification** (methods used)
72	(Rheediaxanthone A)	259-261°	Rheedia bethamiana Pl. & Tr.	(R)	67	(1a, 1b, 2,$3^{\#}$ (C_5D_5N), 4^{+}, 5,7)
		245-247°	Garcinia staudtii Engl.	(S)	61	
			Rheedia gardneriana Pl. & Tr.	(R)	57	
			Rheedia brasiliensis Pl. & Tr.	(R)	58	
73	(Rheediaxanthone C)	260-262°	Rheedia benthamiana Pl. & Tr.	(R)	67	(1a, 1b, 2, $3^{\#}$ (C_5D_5N), 4^{+}, 5, 11)
			Rheedia gardneriana Pl. & Tr.	(R)	57	
			Rheedia brasiliensis Pl. & Tr.	(R)	58	
74	(Nvervosanthone)	amorphous	Garcinia nervosa	(S)	66	(1a, 2,$3^{\#}$, 5,7)
75	(Isocowanin)	160°	Garcinia pyrifera	(S)	66	(1a, 2,3, and $4^{\#}$, 5)
76	(Isocowanol)	amorphous	Garcinia pyrifera	(S)	66	(1a, 2,$3^{\#}$, 5,8)
77	(Cadensin D)	243-245°	Hypericum canariensis L	(Ae)	12	(1a, 16, s, 3^{+}
78	(Diacetylacadensin C)	242-246°	Vismia guaramirangae Huber	(R)	16	(1a, 1b, 3,5)
79	(Triacetylcadensin C)	210-214	Vismia guaramirangae Huber	(R)	16	(1a, 3, 5)

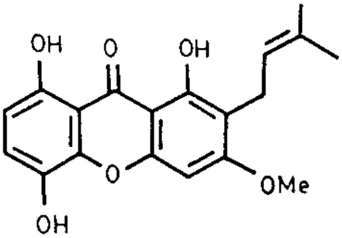
---

[*] Ae : aerial part; B: bark; F: flowers ; Fr: fruits; H:heartwood; L: leaves; R: roots; S: stems; T: timber ; Wh: whole plant; W: Wood; TW: trunk wood.

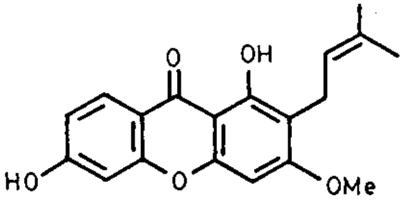
[**] UV in MeOH(1a); UV with shift reagent (1b); IR (2): ^{1}H NMR (3): ^{13}C NMR (4) ; MS (5); X-ray (6); acetate deriv. (7); methyl ether (8); synthesis (9); C,H analysis (10); Optical rotation (II); action of acids (12).

$^{+1}$HNMR taken in DMSO-d_6

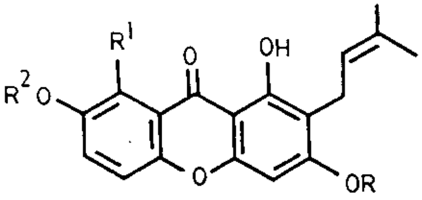
$^{\#1}$H NMR taken in Me_2CO-d_6



47a



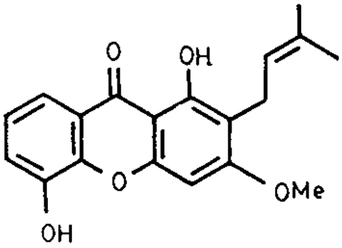
45a



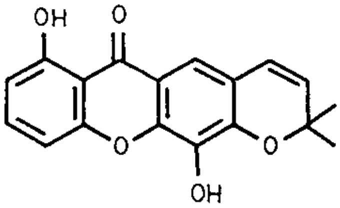
46. R = Me ; $R^1 = R^2$ = H

51. R = R^2 = H ; R^1 = 3,3-dimethylallyl

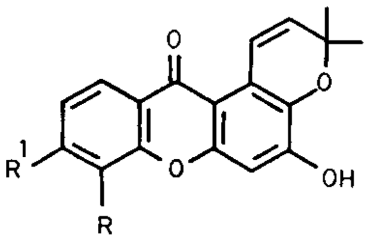
53. R = H ; R^2 = Me, R^1 = 3,3-dimethylallyl



45

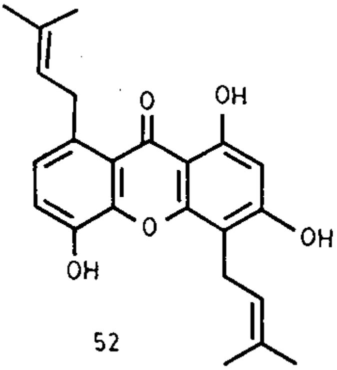


49

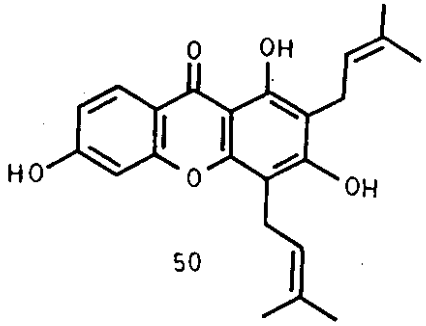


47. R = OH ; R^1 = H

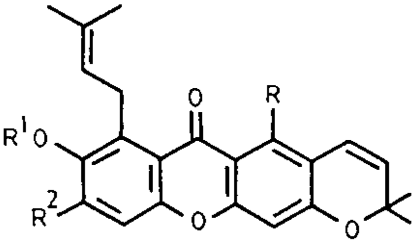
48. R = H ; R^1 = OH



52

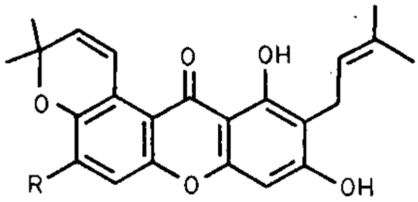


50



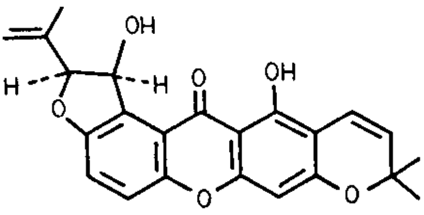
55. R = R^1 = R^1 = R^2 H

69. R = R^2 = OH; R^1 = Me

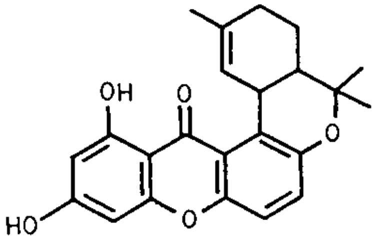


54. R = H

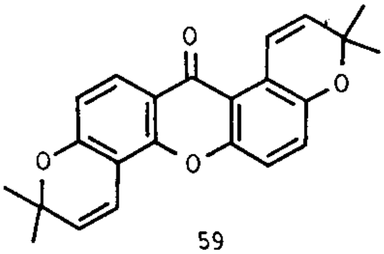
55. R = OH



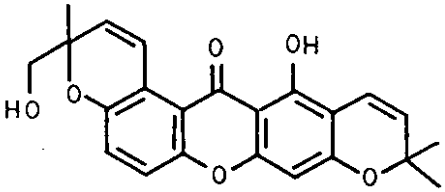
57



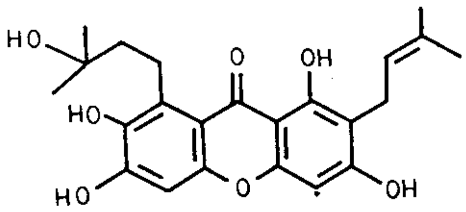
56



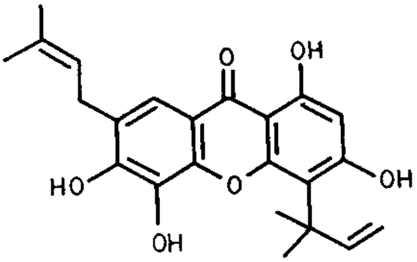
59



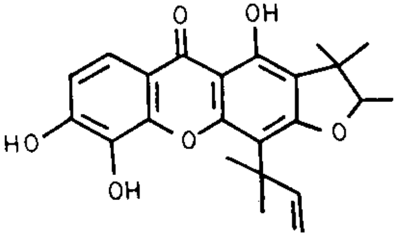
58



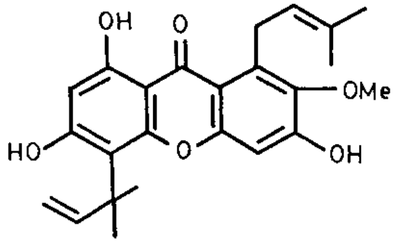
61



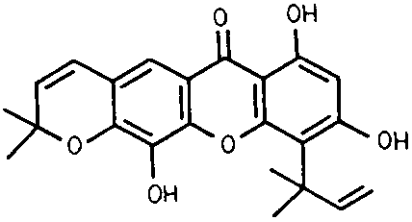
60



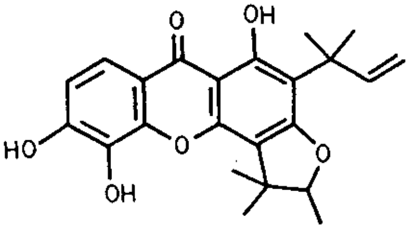
63



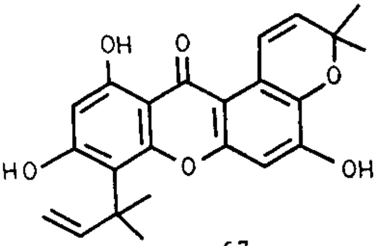
62



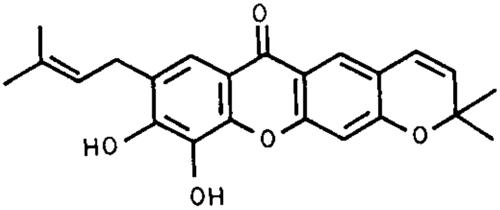
65



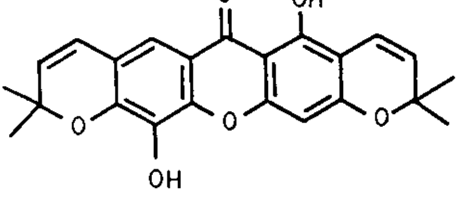
64



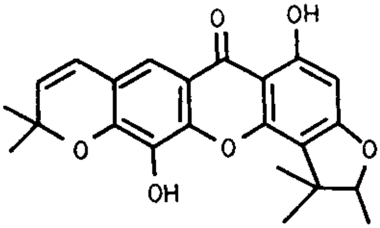
67



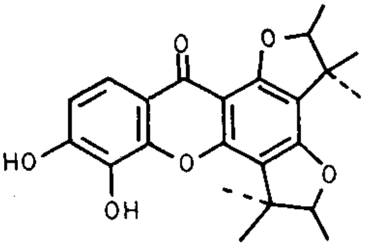
66



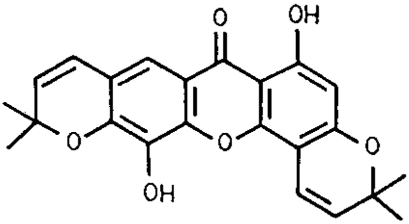
71



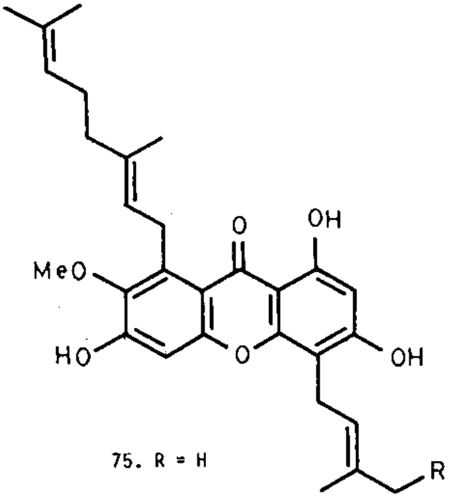
70



73

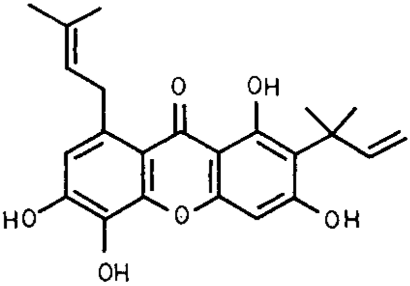


72

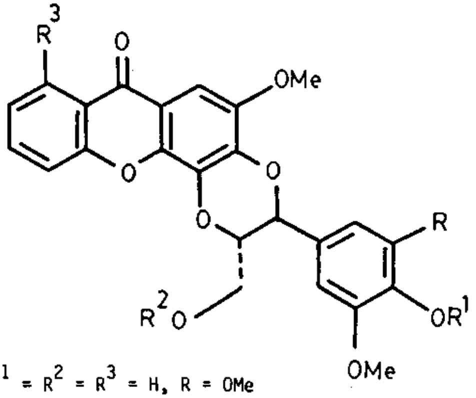


75. R = H

76. R = OH



74



77. $R^1 = R^2 = R^3 = H$, R = OMe

78. $R^3 = H$; $R^1 = R^2 = Ac$; R = OMe

79. $R^1 = R^2 = Ac$; R^3 - OAc; R = OMe

80. $R = R^1 = R^2 = R^3 = H$

Table-3. Naturally occurring O-glycosides

Glycoside (trivial name)	Oxidation* pattern								Natural source	Ref.
	1	2	3	4	5	6	7	8		
81	O-glu	O-CH2-O	-	-	-	-	-		Polygala triphylla	72
82	O-glu	OH	OMe	--	-	-	-		Polygala triphylla	72
83	O-glu	-	OH	-	OMe	-	-	-	Canscora decussata (Wh)	53,75
84	O-ste	-	OMe	OMe	OMe	-	-	-	Swertia hookeri (Wh)	74
85	OH	-	OMe	-	-	-	O-prim	-	Gentiana lutea (R)	77
86	O-prim	-	OMe	-	-	-	OH	-	Gentiana lutea (R)	77
87 (Tripteroside)	OH	-	OH	-	-	O-glu	OH	-	Tripterospermum taiwanense	
88	O-glu	-	OMe	-	-	-	OH	OH	Swertia paniculata Wall.	83
89	O-glu	-	OMe	-	-	-	OMe	OH	Swertia paniculata Wall.	83
90	O-glu	-	OMe	-	OMe	-	-	OMe	Chrozophora prostrate (R)	108
91	O-glu	-	OMe	-	-	-	OMe	OMe	Swertia paniculata Wall.	83
92	O-glu	-	OMe	-	-	-	OH	OMe	Gentiana bartata	81
93 (Lanceroside)	O-glu	-	OMe	-	-	-	OMe	O-glu	Tripterospermum lanceolatum	75
94	O-lam	-	OH	-	-	OH	OH		Asplenium adiantum nigrum	6
95 (Isoswertianolin)	OH	-	OMe	-	O-glu	-	-	OH	Swertia japonica M.	78
									Swertia hookeri (Wh)	74
									Swertia angustifolia	79
									Swertia connata	42
96	OH	-	OH	-	OMe	-	-	O-glu	Swertia hookeri (Wh)	74
97	OH	-	OMe	-	OMe	-	-	O-glu	Swertia speciosa (Ae)	80
98 (Veratriloside)	OH	-	OMe	OMe	-	-	O-glu	-	Veratrilla baillonii (F)	32
99	OH	-	OMe	-	O-glu	OH	OMe	-	Canscora decussata	53
100	OH	-	OMe	-	OH	OH	O-glu	-	Hoppea dichotoma (Wh)	82
101	OH	-	OMe	-	OMe	OH	O-glu		Canscora decussata (Wh)	73
102	O-rut	-	OMe	-	OMe	OMe	OMe		Chrozophora prostrata (R)	108

by Gottlieb and co-workers. The same authors were able to isolate other two xanthonolignoids named cadensins A and B from *Caraipa densiflora* [70]. Kielcorin was also obtained from different species of *Hypericum* [71]. Recently, Kielcorin was isolated from two natural sources, *Vismia guaramirangae* [16] and *Hypericum canariensis* [12]. In further work cadensin C (isolated as acetyl derivatives 78 and 79; see Table-2) and cadensin D (77) have been obtained from the latter two species, respectively.

Xanthone Glycosides

Naturally occurring xanthone glycosides were reviewed by Hostettman and Wagner in 1977 [3]. Three years later, these natural compounds were also encountered in Sultanbawa review [2]. Xanthone glycosides are of two types, C-glycosides (resistant to acidic and enzymatic hydrolysis) and O-glycosides which have typical glycosidic binding. Within the last ten years more than thirty xanthone glycosides have been described as tabulated in Tables-3 and 4.

O-Glycosides

From about 15 plant species, in the last decade, more than 20 xanthone-O-glycosides have been isolated. As indicated in Table-3 their natural occurrence is restricted to the family *Gentianaceae* except compounds 81 and 82 which have been isolated from a member belonging to *Polygalaceae* [72] and compounds 90, 102 which have been isolated from a species belonging to the family *Euphorbiaceae* [108]. Furthermore, compound 94 has been isolated from a fern *Asplenium adiantum-nigrum (Asplen-iaceae)*. Sor far *O*-monosides and *O*-biosides are known, *β-D*-glucose is the only monosaccharide to be identified in xanthone *O*-glycosides whereas three disaccharides have been discovered to date. The disaccharides are primeverose (6-*O*-(*β*-*D*-xylopyranosyl)-*β*-*D*-glucopyranose, rutinose (6-*O*-(*α*-*L*-rhamnopyranosyl)-*β*-*D*-glucopyranose and laminaribiose (3-*O*-*β*-glycosyl-*D*-glucose). The former disaccharide is the more common while the second has been found only twice in a trioxygenated xanthone isolated from *Canscora decussata* [17] and in a tetraoxygenated xanthone of *Gentiana bavarica* L. [97]. On the other hand, laminaribose occured once in a tetraoxy genated xanthone (3,7,8- trihydro-xyxanthone-1-*O*-*β*-laminaribioside, see Table-3) isolated recently from a fern species [6]. This xanthone is the only xanthone-*O*-glycoside isolated so far from a fern. As it could be noted from Table-3, aglycones usually are tri-, tetra- or pentaoxygenated. The 1,3-oxygenation pattern is found in each compound. Substitution never occurs at position 2 of those xanthone-O-glycosides isolated from plant species belong to the *Gentianaceae* (see Table-3). In the previous review [3] in *O*-glycosides of *Gentianaceae,* substitution never occurs in position 6. This is also the case for the *O*-glycosides of the latter plant family as in Table-3, except for the pentaoxygenated xanthones isolated from *Canscora decussata* [53,73] and *Hoppea dichotoma* [82]. Only, two trioxygenated glycosides were known at the time of the last review on xanthone published in 1980 [2]. The latter pattern of glycosides now seems to be more common. These glycosides are represented by a total of 8 compounds their natural occurrence has been restricted to the members of the family *Gentiandceae;* only two of them (81 and 82) isolated from a species of the family *Polygalaceae.* Compounds 85 and 86 have been isolated in 1983 from *Gentiana lutea* [77]. Recently, in 1988, Hayashi and Yamagishi [109] have isolated the latter two xanthones from the same natural sources, but they claimed that these xanthones have been reported for the first time in nature.

C-Glycosides

Xanthone *C*-glycosides are not widespread in nature as the corresponding *O*-glycosides. Thus, *C*-glycosylxanthones are rare natural products, and

Table-4: Naturally occurring xanthone-C-glycosides

Glycoside (trivial name)		Oxidation pattern*								Natural sources	Ref.
		1	2	3	4	5	6	7	8		
103	(Lancerin)	OH	-	OH	glu	-	-	OH	-	Tripterospermum lanceolatum	
104		OH	glu	OH	-	OH	OH	-	-	Tris florentina L.	
										Canscora decussata Schult	
105	(Irisxanthone)	OH	glu	OH	-	OMe	OH	-	-	Iris florentina	
106	(Mangiferin)	OH	glu	OH	-	-	OH	OH	-	**	
107	(Homomangiferin)	OH	glu	OMe	-	-	OH	OH	-	Mangifera indica L.	
108	(Mangiferin-6-O-β-D-glycoside)	OH	glu	OH		-	-	O-glu	OH	Gentiana aslepiadea	
109	(Maniferin-7-O-β-D-glucose)	OH	glu	OH	--	OH	O-glu	-		Gentiana aslepiadea	
110	(Isomangiferin)	OH	-	OH	glu	-	OH	OH	-	**	
111	(7-O-Methylisomangiferin)	OH	-	OH	glu	-	OH	OMe	-	Iris florentina L.	
112	(7-O-Methylmangiferin)	OH	glu	OH	-	-	OH	OMe	-	Iris florentina L.	84,88
113	(Dilatatin)		OH	All	OH	-	-	OH	OH	Hymenophyllum diliatum	90,91
114	(6'-O-Acetylmangiferin)	OH	Ac-	glu	OH	-	-	OH	OH	Trichomanses reniforme	90
115	(2'-O-Benzoylmangiferin)	OH	2 Bz-glu		OH	-	-	OH	OH	Hymenophyllum recurvum	90
116	(4'-O-Benzoylmangiferin)	OH	4 Bz-glu		OH	--	OH	OH	-	Hymenophyllum recurvum	90
117	(6'-O-Benzoylmangiferin)	OH	6 Bz-glu		OH	--	OH	OH	-	Hymenophyllum recurvum	90
118		OH	glu	OMe	OMe		OMe	-	-	Hopppea dichotoma	82
119		OH	glu	OMe			OMe	OMe	OMe	Iris florentina L.	84
										Hoppea dichotoma	82

*glu = glucose ; All = allose

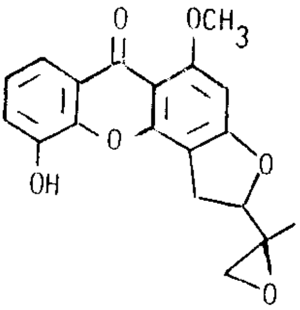
**Mangiferin and Isomangiferin have been isolated from several plant species.

only seven *C*-glycosides (compounds 104-110) were mentioned in Sultanbawa review [2] in 1980. Mangiferin (106) and isomangiferin (110) are the most common *C*-glycosides. Two *O*-glucosides of mangiferin have been isolated from *Gentiana aslepiadea* [89]. Such compounds were earlier identified in ferns [95,96], although the position of the *O*-sugar could not be determined at that time. Recently, mangiferin and isomangiferin were detected in a large number of fern species [6,90-92]. Furthermore, novel acetylated and benzoylated *C*-glycosylxanthones were reported in ferns for the first time in 1980 by Markham and Wallace [90]. The latter compounds as well as the previously unreviewed *C*-glycosylxanthones are presented in Table-4. The sugar moiety in all known xanthone *C*-glycosides is glucose except for dilatatin (113) which has allose in its structure. Allose is a rarely occuring sugar in nature. Only very recently, this sugar has been identified in glycoside combination with naturally occurring phenols [93,94].

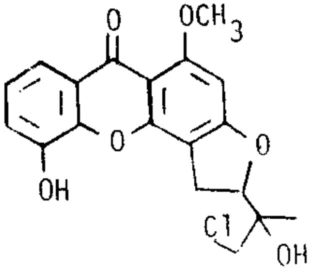
Activities of Plant Species/Xanthones

Plants of the families *Gentianaceae* and *Guttiferae* represent the principal sources of xanthones. In the past, several authors have suggested that these compounds may become useful taxonomic markers, and the data accumulated so far seems to support these suggestions. The growing interest in xanthones could be easily explained in terms of their pharmacological activity. The extracts of most *Swertia* species showed mutageneic activities [98,99] and the xanthone glycosides and their aglycones as well as stearyl derivatives have produced varying responses to central nervous and cardiovascular systems [39,80,100-102]. *Swertia japonica* M. is a well known Japanese folk medicine [78] and *Swertia paniculata* is used in the indian system of medicine as a bitter tonic and in the treatment in some mental disorders [83]. Similarly, *Canscora decussata* has a therapeutic use in mental disorders [3]. The extract of *Swertia hookeri* is used for a variety of therapeutic purposes, e.g. in the treatment of microbial infections and as a mood elevator [74]. Two new xanthone glycosides obtained from *Tripterospermum lanceolatum* [75] showed remarkable biological activities [103,104].

Recently, psorospermin (120) and the structurally related xanthone (121) have been isolated from the root extracts of *Psorospermum febrifugum* Sprach [105,106] a species belongs to the family *Guttiferae*. *Psorospermin* (120) showed a significant antitumor activity against P-388 leukemia in vivo system and cytotoxicity against KB in vitro system [105].



120



121

References

1. H.M.G. Al-Hazimi and G.A. Miana, Book on Naturally Occuring Xanthones, in progress.
2. M.U.S. Sultanbawa, *Tetrahedron,* **36**, 1465 (1980).
3. K. Hostettman and H. Wagner, *Phytochemistry*, **16**, 821 (1977).
4. D.O.A. Denisova and V.I.Glyzin, *Usp.Khim.*, 51(10), 1753 (1982), CA, 98:2710d.
5. I.Sakamato, K.Morimoto, O.Tanaka and H.Inouye, *Chem.Pharm.Bull.,* **31**, 25 (1983)
6. F.Imperato, *Phytochemistry,* **19**, 2030 (1980).
7. G.A. Miana and H.M.G.Al-Hazimi, *Phytochemistry,* **23**, 1637 (1984).
8. M.Hostettmann, K.Hostettmann and O. Sticher, *Phytochemistry*, **20**, 443 (1981).
9. M.Hostettmann, K.Hostettmann and O.Sticher, *Phytochemistry,* **20**, 443 (1981).
10. K. Hostettman, M. Hostettman-Kaldas and O. Sticher, *Helv. Chim. Acta.*, **62**, 2079 (1979).
11. M.L. Cardona, J.R. Pedro, E. Seonae and R Vidal, *J. Nat. Prod.*, **48**, 467 (1985).

12. M.L. Cardona, M.I. Fernandez, J.R. Pedro, E. Seoane and R. Vidal, *J. Nat. Prod.*, **49**, 95 (1986).

13. W.M. Bandaranayake, S. Karunanayake, S. Sotheeswaran and M.U.S. Sultanbawa, *Indian J. Chem.*, **19B**, 463 (1980).

14. D.M.X. Donnelly, T.O. Criodain and M.O'-Sullivan, *Proc. R. Ir. Acad., Sect. B* **83B**, 1-16 (1983).

15. A.A.L.Gunatilaka, A.M.Y. Jasmin De Silva and S. Sotheeswaran, *Phytochemistry,* **21**, 1751 (1982).

16. F.D. Monache, M.M.Mac-Quhae, G.D. Monache, G.M.B. Bettolo and R.A. De Lima, *Phytochemistry,* **22**, 227 (1983).

17. S. Ghosal, P.S. Chauhan, K. Biswas and R.K. Chaudhuri, *Phytochemistry,* **15**, 1041 (1976).

18. E.P. Ortega, R.E.Lopez-G, R.M. Rabanal, V Darias and S. Valverde, *Phytochemistry*, **27**, 1912 (1988).

19. M. Chen and C. Chen, *Heterocycles*, **23**, 2543 (1985).

20. M.L. Cardona and E. Seoane, *J. Nat. Prod.*, **45**, 134 (1982).

20a. O.R. Gottlieb, M. T. Magtalhaes, M. Camey, A.A. Mesquita and D.B. Correa, *Tetrahedron*, **22**, 1777 (1966).

21. N.M.Neshta, V.I.Glyzin, A.A. Savina and A.V. Patudin, *Khim. Prir. Soedin*., 787 (1983).

22. M. Parra, E. Seoane and A. Tortajada, *J. Nat. Prod.*, **47**, 868 (1984).

23. M. Dahanayak, I. Kitagawa, R. Somanathan and M.U.S.Sultanbawa, *J.Chem.Soc., Perkin I*, 2510 (1974).

24. Sun Hongfa, Hu Beling, Fan Shufen and *J. Ding, Zhiwa Xuebao,* **25**, 460 (1983).

25. Yang Yan-Bin and Zhou Jun, *Yan-nan Chih Wu Chiu*, **2**(4), 468 (1980) CA: 85 12639q.

26. M.R. Ramos, *An. Fac. Farm. Porto,* **26**, 5 (1966).

27. D.L. Dreyer and J.H. Bourell, *Phytochemistry*, 20, 493 (1981).

28. R. Alves de Lima, O.R. Gottlieb and A.A. Mesquita, *An. Acad. Brasil Cienc.*, **42**, 133 (1970).

29. Raimundo, B.F., C.A.S. Miranda and O.R. Gottlieb, *Acta.Amazonica*, **12**, 801 (1982).

30. R. Alves de Lima, O.R. Gottlieb and A.A. Mesquita, *Phytochemistry*, **11**, 2307 (1972).

31. N.M. Neshta, V.I. Glyzin and A.V. Patudin, *Khim. Prir. Soedin*, 110 (1984).

32. Yang Han-Bin and J. Zhou, *Yao Hsueh Hsueh Pao,* **15**, 625, (1980), CA: 94 117779t.

33. A.A.L. Gunatilaka, H.T.B. Sriyani, S. Sotheeswaran and E.S Waight, *Phytochemistry,* **22**, 233 (1983).

34. T.J. Nagem and J.C. De Silveira, *Phytochemistry,* **25**, 503 (1986).

35. M. Parra, M.T. Picher, E. Seoane and A. Tortajada, *J. Nat. Prod.*, 48, 998 (1985).

35a. E.D. Burling, A. Jefferson and F. Scheinmann, *Tetrahedron*, **21**, 2653 (1965).

36. S. Walia and S.K. Mukerjee, *Phytochemistry,* **23**, 1816 (1984).

37. G.G. Nikolaeva, V.L. Glyzin, D. A. Fesenko and A.V. Patudin, *Khim. Prir. Soedin.*, (2), 255 (1980).

38. T.J. Nagem and J.C. Da Silveira, *Phytochemistry*, **28**, 2211 (1989).

39. Y.Zong and Xu Chengyu, *Yaoxue Tongbao,* **17**, 206 (1982).

40. B. Zang, J. Chang and S.H. Ho, *TS'aO Yao,* **11**, 149 (1980).

41. T.J. Nagem and J.C.D. Silveira, *Phytochemistry,* **25**, 2681 (1986).

42. E.V. Solov'eva, O.A Denisova, V.I. Glyzin and A.V. Patudin, *Khim. Prir. Soedin* **6**, 840 (1980).

43. S. Ghosal, R.K. Chaudhuri and A. Nath, *J.Pharm.Sci*., **62**, 137 (1973).

44. S. Bhan, A.K. Kalla, *Res.J., Fac.Sci., Khashmir University,* **1**(1- 2), 10 (1982).

45. M. Kaouadji, I. Vaillant and A.M. Mariotte, *J. Nat. Prod.,* **49**, 359 (1986).

46. Sun Hongfa and Ding Jingye, *Zhiwu Xuebao,* **23**, 464 (1981).

47. S. Ghosal, P.V. Sharma and R.K. Chaudhuri, *Phytochemistry*, **14**, 2671 (1975).

48. T.J. Nagem and J.C.D.Silveira, *Phytochemistry*, **27**, 646 (1988).

49. O.A. Denisova, V.I.Glyzin, A.V. Patudin and D.A. Fesenko, *Khim. Prir. Soedin.,* **16**(2), 145 (1980).

50. C.Lin, M. Chung, K. Gan and J. Chiang, *Phytochemistry,* **26**, 2381 (1987).

51. M. Massias, J. Carbonnier and D. Molho, *Phytochemistry,* **20**, 1577 (1981).

52. S. Takagi and M. Yamaki, *Yakugaku Zasshi,* **102**, 546 (1982).

53. S. Ghosal and K. Biswas, *Phytopchemistry*, *18*, 1029 (1979).

54. N.M. Neshta, G.G. Nikolaeva, V.I. Sheichenko and A.V. Patudin, *Khim. Prir. Soedin.*, 258 (1982).

55. M. Parra, M.T. Picher, E. Seoane and A. Tortajada, *J. Nat. Prod.,* **47**, 123 (1984).

56. A.K. Sen, K.K. Sarakar, P.C. Majumder and N. Benerji, *Phytochemistry*, **20**, 183 (1981).
57. G.D. Monache, F.D. Monache, G.B. Bettolo and R.A. Lima, *J. Nat. Prod.*, **46**, 655 (1983).
58. G.D. Monache, B. Botta, J.F. De Mello, J.S. Coelho and F. Menichini, *J. Nat. Prod.*, **47**, 620 (1984).
59. A.K. Sen, K.K.Sarkar, P.C. Majumder, N.B.R. Uusvuori and T.A Hase, *Phytochemistry*, **21**, 1747 (1982).
60. H.R.W. Dharmaratne, S. Sotheeswaran, S. Balasubramaniam and J. Reisch, *Phytochemistry*, **25**, 1957 (1986).
61. P.G. Waterman and R.A. Hussain, *Phytochemistry*, **21**, 2099 (1982).
62. V. Kumar, S. Sotheeswaran, S. Surendrakumar and S. Balasubramaniam, *Phytochemistry*, **21**, 807 (1982).
63. S.A. Ampofo and P.G. Waterman, *Phytochemistry*, **25**, 2617 (1986).
64. S.P. Gunasekera, S. Sotheeswaran and M.U.S. Sultanbawa, *J. Chem. Soc., Perkin I*, 1831 (1981).
65. T. Nomura, Y. Hano and T. Fujimoto, *Heterocycles*, **20**, 213 (1983).
66. S.A.Ampofo and P.G. Waterman, *Phytochemistry*, **25**, 2351 (1986).
67. F.D. Monache, B. Botta, M. Nicoletti, J.S. Coelho and F.D. Lyra, *J. Chem. Soc., Perkin I*, 484 (1981).
68. G.D. Monache, F.D. Monache, P.G. Waterman, E.G. Crichton and R.A.Lima, *Phytochemistry*, **23**, 1757 (1984).
69. A.K. Sen, K.K. Sarkar, P.C. Majumder, N. Banerji, R. Uusvuori and T.A. Hase, *Phytochemistry*, **19**, 2223 (1980).
70. J.F.Castelao, O.R. Gottlieb, R.A. Lima, A.A. Mesquita, H.E. Gottlieb and E. Wenkert, *Phytochemistry*, **16**, 735 (1977).
71. H. Nielsen and P. Arends, *Phytochemistry*, 17, 2040 (1978).
72. S. Ghosal, P.C. Basumatri and S. Banerjee, *Phytochemistry*, **20**, 249 (1981).
73. S. Ghosal, K. Biswas and R.K. Chaudhuri, *J. Chem. Soc., Perkin I*, 1597 (1977).
74. S. Ghosal, K. Biswas and D.K. Jaiswal, *Phytochemistry*, **19**, 123 (1980).
75. Lin Chun-Nan, C.H. Chang, M. Arisawa, M. Shimizu and N. Morita, *Phytochemistry*, **21**, 205 (1982).
76. Lin Chun-Nan, C.H. Chang, M. Rrisawa, M. Shimizu and N. Morita, *Phytochemistry*, 21, 948 (1982).
77. G.G Nikolaeva, V.I. Glyzin, M.S. Maidentseva, V.I. Sheichenko and A.V. Patudin, *Khim. Prir. Soedin*, 1, 107 (1983).
78. I. Sakamoto, T. Tanaka, O. Tanaka and T. Tomimori, *Chem. Pharm. Bull.*, **30**, 4088 (1982).
79. S. P. Dhoubhadel, P.P. Wagley and S. Devi, Indian *J. Chem., Sect. B,* 19B (10) 929 (1980).
80. K.S. Khetwal and R.S. Bisht, *Phytochemistry*, 27, 1910 (1988).
81. G.G. Nikolava, V.I. Glyzin, A.V. Patudin and D.A. Fesenko, *Khim. Prir. Soedin.*, **3**, 392 (1981).
82. S. Ghosal, D.K. Jaiswal and K. Biswas, Phytochemistry, **17**, 2119 (1978).
83. A. Prakash, P.C. Basumatry, S. Ghosal and S.S. Handa, *Planta Medica*, **45**, 61 (1982).
84. M. Fujita and T. Inoue, *Chem. Pharm. Bull.*, **30**, 2342 (1982).
85. M. Fujita and T. Inoue, *Yakugaku Zasshi*, **101**, 1118 (1981).
86. S. Ghosal and R.K. Chaudhuri, *Phytochemistry*, **12**, 2025 (1973).
87. M. Arisawa, N. Morita, Y. Kondo and T. Takemoto, *Chem. Pharm. Bull.*, **21**, 2562 (1973).
88. M. Aritomi and T. Kawasaki, *Chem. Pharm. Bull.*, **18**, 2224 (1970).
89. M. Goetz and J. Guillarmod, *Helv. Chim. Acta.*, **66**, 2104 (1977).
90. K.R. Markham and W. Wallace, *Phytochemistry*, **19**, 415 (1980).
91. K.R. Markhan and A.D. Woolhouse, *Phytochemistry*, **22**, 2827 (1983).
92. P.M.Richardson, *Phytochemistry*, **22**, 309 (1983).
93. T. Okuyama, K. Hosoyama, Y. Hiraga, G. Kurono and T. Takemoto, *Chem. Pharm. Bull.*, **26**, 3071 (1978).
94. V.M. Chari, R. Grayer, J.B. Harborne and B.G. Osterdahl, *Phytochemistry*, **20**, 1977 (1981).
95. D.M.Smith and J.B. Harborne, *Phytochemistry*, **10**, 2117 (1971).
96. V.I. Glyzin, A.I. Ban'Kiwski, M.G. Pimenov and K.I. Borydev, *Khim. Prir. Soedin.*, **9**, 434 (1973).
97. K. Hostettmann, R. Tabacchi and A. Jacot-Guillarmod, *Helv. Chim. Acta.*, **57**, 294 (1974); K. Hostettman, A Jacot-Guillarmod and V.M. Chari, *Helv. Chim. Acta.*, **59**, 2592 (1976).
98. H. Kanamori, I. Sakamoto, M. Mizuta, K.

Hashimoto and O. Tanaka, *Chem. Pharm. Bull.*, **32**(, 2290 (1984).

99. I. Morimoto, F. Watanabe, T. Osawa and T. Okatsuo, *Mutat. Res.*, **97**, 81 (1982).
100. D. L. Verma and K.S. Khetwal, *Sci. Cult.*, **51**, 305 (1985).
101. S. Ghosal and R.K. Chaudhuri, *J. Pharm. Sci.*, **64**, 888 (1975).
102. S. Ghosal, K. Biswas and R.K. Chudhuri, *J. Pharm. Sci.*, **17**, 721 (1978).
103. C-N Lin, C-H Chung, M. Arisawa, M. Shimizu and N. Morita, *Shoyakugaku Zasshi*, **38**, 80 (1984).
104. H. Hikino, T. Ohsawa, Y. Kiso and Y. Oshima, *Planta Med.*, **50**, 353, (1984).
105. S.M. Kupchan, D.R. Streelman and A.T. Sneden, *J. Nat. Prod.*, **43**, 296 (1980).
106. J.M. Cassady, P. Cong, T.G. McCloud and C-J. Chang, *J. Nat. Prod.*, **49**, 412 (1986).
107. M. Parveen and N.U. Khan, *Phytochemistry*, **27**, 3694 (1988).
108. A. Agrawal and H. Singh, *Phytochemistry*, 27, 3692 (1988).
109. T. Hayashi and T. Yamagishi, *Phytochemistry*, **27**, 3696 (1988).