RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

June 1963

U.D.C. 547.972:547.973:547.977

THE NATURAL PIGMENTS

N.S. Vul'fson

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1. INTRODUCTION

The natural pigments are complex organic compounds produced by living organisms and by colouring various animal and plant cells and tissues they determine the entire diversity of colour of animate nature.

Even from most ancient times, in the early stages of civilisation, man began to use the natural pigments for the satisfaction of his aesthetic needs. In the second half of the XIXth century many natural dyestuffs were used for colouring textiles, hides, paper, perfumes, food products, etc. With the development of the organic chemical industry, and especially of the aniline dyestuffs industry, the natural pigments were unable to compete with the synthetic dyes and in the great majority of cases lost their former practical value. However, the value of the natural pigments is not exhausted by their practical use for the purpose of dyeing. Most of them play an essential role in the life of those organisms by which they are produced. Many natural pigments exhibit marked physiological and antibiotic activity and are often used as medicines.

The pigments are extremely widely distributed in nature and are extremely diverse chemically[1]. Their classification is possible according to various features, for example, by their origin and occurrence in nature (animal dyestuffs, plant pigments, butterfly wing pigments, flower and fruit pigments, and so forth). However, in many cases the same pigment (or pigments of similar structure) is encountered in different natural sources, and therefore the most desirable classification, used in this paper, is the usual classification of organic compounds by their functional features[2].

2. PIGMENTS OF THE ALIPHATIC AND ALICYCLIC SERIES

This class consists mainly of the so-called polyene pigments or carotenoids[3-5]. These are compounds containing long chains of carbon atoms with a system of conjugated double bonds which is responsible for their colour. The colour deepens as the length of the conjugated system is increased. The pigments of this group include hydrocarbons (some with alicyclic rings at the end of the carbon chain), alcohols (sometimes encountered in the form of esters), ketones, keto-alcohols, aldehydes, acids, esters, epoxides, and compounds with a furan ring[6] (Table 1).

The carotenoids are encountered in both the plant and the animal kingdoms. Many of them (such as carotene) exhibit a high physiological activity (provitamin A). The polyenes of unestablished structure include several antibiotics (capacidin, pentamycin, filipin, mediocydin, trichomycin, etc.) produced by various species of *Streptomyces*[7].

Most of the carotenoids have a completely *trans* configuration, but partly isomerised *trans*–*cis*-isomers[8] are encountered (most frequently isomerised at the central double bond).

TABLE 1. The carotenoids:

R–C(CH$_3$)=CHCH=CHC(CH$_3$)=CHCH=CHCH=C(CH$_3$)CH=CHCH=C(CH$_3$)–R′*.

R	R′	Name	Colour	M.p., °C	Occurrence in nature
Hydrocarbons					
1	1	neurosporene	orange-yellow	124	in the fungus *Neurospora crassa*; in mutants of the red yeast *Rhodotorula rubra*
2	2	lycopene	red	173	in fruits of *Solanum lycopersicum* and many others
3	3	β-carotene	violet	181–184	widely distributed in the vegetable kingdom, microorganisms, fungi, algae, egg-yolk, milk, etc.
3	4	α-carotene	violet	187–188	accompanies β-carotene
2	3	γ-carotene	violet	176.5–178	accompanies β-carotene
Alcohols					
2	5	lycoxanthin	violet-red	168	in fruits of *Solanum dulcamara*, etc.
2	6	rubixanthin	red	160	in fruits of *Rosa rubiginosa*, etc.
2	22	celaxanthin	dark red	204–210	in berries of *Celastrus scandens L.*
3	6	cryptoxanthin	red	169	widely distributed in the plant world (berries, fruit, flowers, lichens, fungi, microorganisms)
6	6	zeaxanthin	yellow-red	204–206	ditto
					in feathers of birds *Chrysoena victor, Rupicola peruviana*
6	7	xanthophyll	red	192–193	as for zeaxanthin; in feathers of birds *Emberiza citrinella, E. icterica, Oriolus oriolus*
5	5	lycophyll	violet-red	179	in fruits of *Solanum dulcamara*
7	7	eschscholtzxanthin	violet	185–190	in petals of *Eschscholtzia californica*
Ketones and keto-alcohols					
3	8	myxoxanthin	violet	168–169	in the algae *Rivularia nitida*, etc.
9	9	rhodoxanthin	blue-black	219	in leaves of *Cryptomeria japonica, Cupressus naitnocki*, etc. in feathers of birds *Phoenicircus nigricollis, Megalopreria magnifica*
10	10	xanthoxanthin		213	in the fungus *Cantharellus cinnabarinus*; in the orange mutants of *Corynebacterium michiganense*
11	11	astacene	violet	240–243	in the shell of the lobster *Astacus gamarus L.*; in feathers of birds *Laniarius atrococineus, L. barbarus, L. erythrogaster*, etc.
12	12	astaxanthin	red	215–216	in lower plants and feathers of birds *Laniarius atrococcineus, L. erythrogaster*, etc.
6	8	capsanthin	red	175–176	in fruit of *Capsicum annum L.*; in flowers of *Tecoma radicans*, etc.
14	14	capsorubin	violet-red	201	in the skin of fruits of *Capsicum annum L.*
15	15	fucoxanthin	brownish red	166–168	in various algae
Aldehydes, acids, esters					
6	21	β-citraurin		147	in the rind of oranges
16	17	bixin	violet-red	198	in the skin of seeds of *Bixa orellana L.*
3	18	torularhodin	red	201–203	in the yeast *Torula rubra*
19	19	crocetin	red	275–276	in fruits of *Gardenia grandiflora*, etc.
20	20	crocin	brownish red	186 (decompn.)	in *Crocus sativus L.*
Epoxides					
3	23	β-carotene epoxide	orange	≈160	in the rind of oranges
4	23	α-carotene epoxide	orange	175	in flowers of *Tragopogon pratensis* and *Raminculus acer*
4	24	trollixanthin		155–156	in flowers of *Trollius europaeus*
24	6	antheraxanthin		205–207	in fruit and flowers of *Capsicum annuum*, etc.
24	24	violaxanthin	brownish yellow	200	in flowers of *Viola tricolor*
Furanoxides					
3	26	citroxanthin	yellow-orange	163–164	in the rind of oranges
4	26	flavochrome	yellow	176–178	in flowers of *Ranunculus acer*
2	26	rubichrome	reddish violet	154	in flowers of *Tagetes patula*
7	26	flavoxanthin	yellow		in flowers of *Ranunculus acer, Ulex europaeus*, etc.
27	27	auroxanthin	yellow	203	in flowers of *Viola tricolor*

* For the significance of R and R′ see Appendix 1 on p. 289.

3. PIGMENTS OF THE AROMATIC SERIES

These pigments are based on hydroxy- and alkoxy--substituted unsaturated ketones, derivatives of a diaroylmethane: 4,4′-dihydroxydicinnamoylmethane, yellow, m.p. 224°; 4-hydroxycinnamoylferuloylmethane, orange, m.p. 168°; and diferuloylmethane (curcumin), red, m.p. 181°–183°, encountered in the roots of *Curcuma longa, C. tinctoria*, etc.; chalcones[9] (I) (Table 2), quinones[10,11], benzoquinones (II) (Table 3), naphthaquinones[12] (III) (Table 4), anthraquinones[13,14] (IV) (Table 5), and anthrones: chrysarobin (1,8-dihydroxy-3-methylanthran-9-one), m.p. 203.5°–204°, the yellow dye of *Andira araroba* wood and emodinanthrone (1,6,8-trihydroxy-3-methylanthran-9-one), m.p. 250°–258°, the yellow dye of *Rhamnus dahurica* wood. Many of these dyestuffs are encountered in nature as glycosides (only the aglycone is shown in all the tables). The structurally similar anthraquinones hypericin (V) (R = CH_3) and pseudohypericin (V) (R = $CHOH.CH_3$), the dark violet and dark red pigments of *Hypericum perforatum* flowers, exhibit photodynamic properties[15], as do other bianthraquinones[16].

The natural pigments of the aromatic series also include compounds displaying physiological and antibiotic acitivity (for example, vitamin K, curcumin, many quinones, etc.). The partly hydrogenated aromatic natural pigments include the antibiotics of the tetracycline group, which are yellow.

The yellow pigment aristolochine† (8-methoxy-3,4--methylene-10-nitro-dihydroxyphenanthrene-1-carboxylic acid), m.p. 281°–286°, isolated from *Aristolochia clematitis* roots is somewhat different from the compounds considered above.

TABLE 2. Chalcones (I)*.

Substituents**	Name	Colour	M.p., °C	Occurrence in nature
$R_1' = R_3' = R_3 = OH$	isoquiritigenin	yellow	200–204	in roots of *Glycyrrhiza glabra*
$R_1' = R_3 = OH$; $R_3' = OCH_3$	2,4′-dihydroxy-4-methoxychalcone	yellow	172–176	in resin from *Xanthorroea australis*
$R_1' = R_3' = R_2 = R_3 = OH$	butein	yellow	214–215	in flowers of *Butea frondosa*, etc.
$R_1' = R_2' = OH$; $R_3' = R_4' = R_5' = OCH_3$	pedicin	orange-red	143–145	in leaves of *Didymocarpus pedicellata*
$R_1' = R_2' = R_3' = R_2 = R_3 = OH$	okanin	orange	235–240	in heartwood of *Cyclicodiscus gabunensis* Harms.; in flowers of *Coreopsis maritima, C. gigantea*
$R_1' = R_3' = R_4' = R_2 = R_3 = OH$	neoplathymenin	orange	232	in heartwood of *Plathymenia reticulata* Benth.
$R_2' + R_3' = OCH_2O$; $R_1 = R_3 = R_5 = OH$	gissopin	orange	265–270	in the fungus *Capsella bursa-pastoris*
$R_1' = R_2' = R_3' = R_5' = R_3 = OH$	carthamin	yellow	–	in pollen from flowers of *Carthamus tinctorius*

* For the formulae of the compounds in all tables and text see Appendix 2, p. 289.

** In all tables unspecified R = H.

† Or aristolochic acid (Ed. of Translation).

TABLE 3. Benzoquinones (II).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_4 = OCH_3$	2,6-dimethoxybenzoquinone	yellow	250–251	in stalks of *Adonis vernalis L.*
$R_1 = R_3 = OH$; $R_4 = n\text{-}C_{11}H_{23}$	embelin	orange-yellow	142–144	in the berries of *Embelia ribes* Burm., etc.
$R_1 = R_3 = OH$; $R_4 = n\text{-}C_{13}H_{27}$	rapanone	orange	141–142	in the root and wood of *Rapanea maximowiszii* Koidz.
$R_1 = R_3 = OH$; $R_2 = CH_3$; $R_4 = C_{10}H_{37}$	maesaquinone	orange-red	122	in fruits of *Maesa japonica* Moritz
$R_1 = R_3 = OH$; $R_2 = R_4 = C_6H_5$	polyporic acid	brown-violet	305	in the fungi *Polyporus rutilans*, etc.
$R_1 = R_3 = OH$; $R_2 = R_4 = p\text{-}C_6H_4OH$	atromentin	brown		in the fungi *Agaricus atrotomentosus*, etc.
$R_1 = OH$; $R_2 = R_4 = o\text{-}C_6H_4COOH$; $R_3 = CH = CHCH = CHCOOH$	muscarufin	orange-red	275.5	in the fungus *Amanita muscaria L.*

TABLE 4. Naphthoquinones (III).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = OH$	lawsone	light yellow	192–195	in leaves of *Lawsonia inermis L.*
$R_3 = OH$	juglone	brown-red	153–154	in the shells of the Grecian walnut *Juglans regia*
$R_1 = OCH_3$	2-methoxy-naphthoquin-1,4-one	yellow	183.5	in leaves of *Impatiens balsamina L.*
$R_1 = CH_3$; $R_2 = OH$	phthiocol	yellow	173–175	pigment of tuberculosis bacterium
$R_1 = CH_3$; $R_3 = OH$	plumbagin	golden yellow	76–78	in roots of *Plumbago europaea L.*, etc.
$R_1 = CH_3$; $R_2 = R_3 = OH$	droserone	yellow	178–181	in roots of *Drosera peltata*
$R_1 = CH_3$; $R_2 = R_3 = R_4 = OH$	hydroxydroserone	red	192–193	in the tubers of *Drosera whittakerii*
$R_1 = OH$; $R_2 = CH_2CH = C(CH_3)_2$	lapachol	yellow	139–142	in the heartwood of *Avicennia tomentosa*
$R_1 = CH(OH)CH_2CH = C(CH_3)_2$; $R_3 = R_4 = OH$	alkannin	brownish red	147–149	in roots of *Anchusa tinctoria*, etc.
$R_1 = OH$; $R_2 = CH_2CH = C(CH_3)CH_2OH$	lomatiol	yellow	127–128	in seeds of *Lomatia ilicifolia*, etc.
$R_1 = CH_3$; R_2 = phytyl	vitamin K	yellow	oil	in *Alfalfa* and other green plants

TABLE 5. Anthraquinones (IV).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_2 = OH$	2-hydroxyanthraquinone	yellow	302–306	in roots of *Oldenlandia umbellata L.*
$R_1 = R_2 = OH$	alizarin	orange-red	289–290	in roots of *Rubia tinctorum*
$R_1 = OCH_3$; $R_2 = OH$	α-methyl ester of alizarin	orange	178–179	in roots of *Oldenlandia umbellata L.*
$R_2 = OCH_3$; $R_3 = OH$	monomethyl ether of hystazarin	yellow-orange	232–235	ditto
$R_1 = R_3 = OH$	purpuroxanthin (xanthopurpurin)	yellow	268–270	in roots of *Rubia tinctorum, R. sikkimensis*
$R_1 = R_2 = R_3 = OH$	anthragallol	orange	310–314	in bark of *Coprosma lucida*
$R_1 = R_3 = OH$; $R_2 = OCH_3$	2-methyl ether of anthragallol	yellow	218–220	in bark of *Coprosma lucida*
$R_1 = R_2 = OCH_3$; $R_3 = OH$	1,2-dimethyl ether of anthragallol	yellow	230–232	in bark of *Coprosma lucida, Oldenlandia umbellata L.*
$R_1 = R_3 = OCH_3$; $R_2 = OH$	1,3-dimethyl ether of anthragallol	yellow	209	in bark of *Oldenlandia umbellata L.*
$R_1 = R_2 = R_4 = OH$	purpurin	orange-yellow	253–259	in bark of *Rubia tinctorum*
$R_2 = CH_3$	tectoquinone	light yellow	175–177	in wood of *Tectona grandis*
$R_2 = CH_3$; $R_3 = OH$	3-hydroxy-2-methyl-anthraquinone	yellow	302	in bark of *Coprosma lucida*

TABLE 5 (contd.)

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_3 = OH$; $R_2 = CH_3$	rubiadin	yellow	297	in roots of *Rubia tinctorum*, in bark of *Coprosma lucida*
$R_1 = OCH_3$; $R_2 = CH_3$; $R_3 = OH$	1-methyl ether of rubiadin	golden yellow	290–291	in roots of *Morinda longiflora*
$R_1 = OCH_3$; $R_2 = OH$; $R_3 = CH_3$	digitolutein	yellow	222	in leaves of *Digitalis lutea, D. purpurea*
$R_1 = R_3 = OH$; $R_2 = CH_3$	chrysophanic acid	golden yellow	193–196	in roots of *Rumex patientia, R. obtusifolius*
$R_1 = R_6 = OH$; $R_2 = CH_3$	soranjidiol	orange-yellow	287–289	in bark of rhizomes of *Morinda umbellata, M. citrifolia*
$R_1 = R_4 = R_5 = OH$; $R_2 = CH_3$	1,4,5-trihydroxy-2-methyl-anthraquinone	dark red	218	in mycelia of *Penicillium islandicum* Sopp.
$R_1 = R_5 = R_6 = OH$; $R_2 = CH_3$	morindone	orange-red	281–284	in bark of rhizomes of *Morinda umbellata*
$R_3 = R_5 = R_6 = OH$; $R_2 = CH_3$	chrysarone	golden yellow	165–166	in roots of *Rheum rhaponticum L.*
$R_3 = R_5 = R_8 = OH$; $R_2 = CH_3$	rhabarberone	orange-yellow	212	in roots of *Rheum palmatum, R. officinale*
$R_4 = R_5 = R_7 = OH$; $R_2 = CH_3$	emodin	orange-red	254–256	in bark of *Rhamnus purshiana*; in roots of *Rheum palmatum*
$R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = CH_3$	physcion	orange-yellow	203–207	in lichens *Parmelia parietina*
$R_4 = R_5 = R_8 = OH$; $R_2 = CH_3$	helminthosporin	reddish brown	226–227	in mycelia of *Helminthosporium graminneum* Rabenhorst
$R_1 = R_4 = R_5 = OH$; $R_2 = CH_3$	islandicin	red	218	in mycelia of various moulds of *Penicillium islandicum* Sopp.
$R_1 = R_4 = R_5 = R_7 = OH$; $R_2 = CH_3$	catenarin	red	246	in mycelia of *Helminthosporium graminneum* Rabenhorst
$R_1 = R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = CH_3$	erythroglaucin	red	205–206	in mycelia of *Penicillium glaucum*
$R_1 = R_4 = R_5 = R_8 = OH$; $R_2 = CH_3$	cynodontin	reddish brown	260	in mycelia of *Helminthosporium cynodontis* Marignoni
$R_1 = R_5 = R_6 = R_7 = OH$; $R_2 = CH_3$	copareolatin	dark red	298	in bark of *Coprosma areolata*
$R_1 = R_8 = OH$; $R_3 = CH_2OH$	aloe-emodin (rottlerin)	orange-yellow	223–225	in bark of *Rhamnus purshiana*
$R_1 = R_3 = OH$; $R_2 = CH_2OH$	lucidin	yellow	> 330	in bark of *Coprosma lucida, C. acerosa*
$R_4 = R_5 = R_7 = OH$; $R_2 = CH_2OH$	citreorosein	dark orange	288	in mycelia of *Penicillium cyclopium*
$R_5 = R_7 = OH$; $R_4 = OCH_3$; $R_1 = CH_2OH$	carviolin	yellow	280 (decompn.)	in mycelia of *Penicillium carminoviolaceum*
$R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = CH_2OH$	fallacin	yellow-brown	245–248	in lichens *Xanthoria fallax* Arc.
$R_3 = R_4 = R_5 = R_6 = R_7 = OH$; $R_2 = CH_2OH$	asperthecin	orange-red	–	in mycelia of *Aspergillus quadrillineatus*
$R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = C_3H_6OH$	nalgiovensin	orange	199–200	in mycelia of *Penicillium nalgiovensis* Laxa
$R_1 = Cl$; $R_4 = R_5 = OH$; $R_7 = OCH_3$; $R_2 = C_3H_6OH$	nalgiolaxin	yellow	248–248.5	ditto
$R_1 = OCH_3$; $R_2 = CHO$; $R_3 = OH$	damnacanthal	orange-yellow	208	in roots of *Damnacanthus major, D. indicum*
$R_4 = R_5 = OH$; $R_2 = COOH$	rhein	orange	321	in roots of *Rheum palmatum*
$R_1 = R_3 = OH$; $R_2 = COOH$	munjistin	orange-yellow	231	in roots of *Ribia munjista*
$R_1 = R_2 = R_4 = OH$; $R_3 = COOH$	pseudopurpurin	red	220–224 (decompn.)	in roots of *Rubra cordifolia*
$R_4 = R_5 = R_7 = OH$; $R_2 = COOH$	emodic acid	orange-yellow	363–365 (decompn.)	in mycelia of *Penicillium cyclopium* Westling
$R_1 = R_6 = R_8 = OH$; $R_2 = COOH$; $R_3 = CH_3$	endocrocin	orange	318 (decompn.)	in the lichen *Nephromopsis endocrocea* Asachina
$R_1 = R_3 = R_6 = OH$; $R_2 = COOCH_3$; $R_7 = CH_2OH$	rhodocladonic acid	ruby red		in fruits of the *Cladonia* series
$R_1 = R_3 = R_4 = R_6 = OH$; $R_8 = CH_3$; $R_5 = COOH$; $R_2 = CO(CHOH)_4CH_2$	carminic acid	red		colouring substance of cochineal
$R_1 = R_3 = R_4 = R_6 = OH$; $R_8 = CH_3$; $R_5 = COOH$; $R_2 = COCH_3$	kermesic acid	red		ditto

Many natural pigments of the aromatic series were earlier widely used for dyeing silk; for example, alizarin (the principal dyestuff of madder, which also contains purpurin, xanthopurpurin, munjistin, and rubiadin), carthamin, curcumin (also used today as an indicator in acidometry), cochineal, etc.

4. PIGMENTS OF THE HETEROCYCLIC SERIES

a. Oxygen-Containing Heterocyclics

In this class are the yellow pigment pongamol (4-methoxy--5-acetylbenzoylbenzofuran), m.p. 128°–129°, isolated from *Tephrosia lanceolata* roots and usnic acid (3,8-diacetyl-7,8--dihydroxy-2-keto-4a,6-dimethyl-2,4a-dihydrobenzofuran), m.p. 203°, a yellow pigment encountered in many lichens, for example, in *Usnea barbata*. The dihydrofuran derivatives include the lactone of pulvinic acid (VI, R = H), m.p. 221°–222°, the pale yellow colouring matter of the lichen *Sticta coronata* and others, salicin (VI, R = OH), m.p. 244°–245°, the orange-red pigment of the lichen *Calycium chrysocephalum* and others, dihydrofuranones (VII) (Table 6), and also the coumaranones[9], five-membered cyclic isomers of chalcones and flavones (VIII) (Table 7).

TABLE 6. Dihydro-α-furanones (VII).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
R_1 = OH	pulvinic acid	yellow	215–217	in the lichens *Sticta coronata*
R_1 = NHCH(COOCH$_3$).CH_3 – $CH(CH_3)_2$	epanorin	yellow	135–136	in the lichens *Lecanora epanora* Acl
R_1 = NHCH(COOCH$_3$).CH_2 – C_6H_5	rhizocarpic acid	lemon yellow	177–179	in the lichens *Rhizocarpon geographicum*
R_1 = OCH_3	vulpinic acid	yellow	146–148	in the lichens *Cetraria vulpina*
R_1 = OC_2H_5	callopisminic acid	lemon yellow	127–128	in the lichens *Callopisma vitellinum* Ehrchardt
R_1 = R_3 = OCH_3	pinastric acid	golden yellow	203–205	in the lichens *Cetraria pinastri*
R_1 = R_2 = OCH_3	lepraric acid	golden yellow	159–160	in the lichens *Lepraria citrina*

TABLE 7. Coumaranones (VIII).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
R_2 = R_1' = R_2' = OH	sulphurein	yellow	280–285	in flowers of *Cosmos sulphureus*
R_2 = R_3 = R_1' = R_2' = OH	aureusidin	yellow	270–275	aglucone of the pigment of flowers of *Oxalis cernua*, etc.
R_1 = R_2 = R_1' = R_2' = OH	maritimein	yellow	–	in flowers of *Coreopsis maritima*
R_2 = R_1' = R_2' = OH R_1 = OCH_3	leptosin	orange--yellow	252–254	in the petals of *Coreopsis grandiflora*

The pigments which are most widely represented in nature are chroman derivatives[17], for example, flavonoids[18–25], flavones[26] (IX, X = H) (Table 8), flavonols (IX, X = OH, OCH_3, OSO_3K) (Table 9), flavanones (X, X = H) (Table 10), and flavananols (X, X = OH) (Table 10), anthocyanins[27–29] (XI) (Table 11), and isoflavones[30,31] (XII) (Table 12). The group of isoflavones also includes the yellow pigments: osajin (XIII, R = H), m.p. 189°, and pomiferin (XIII, R = OH), m.p. 200.5°, contained in the fruit of *Maclura pomifera* Raf. Other compounds which contain chroman rings are the dark red pigments dracorhodin (XIV, R = CH_3, R′ = H), m.p. 168°–169° (with decomposition), present in the resin of *Deamonorops draco*, and carajurin (XIV, R = OH, R′ = OCH_3), m.p. 205°–207°, found in the leaves of *Bignonia chika*; the red dye dracorubin (XV), m.p. 315°, also present in the resin of *Deamonorops draco*, and the other biflavanoid pigments[32,33]; the yellow pigment rottlerin (XVI), m.p. 200°–207°, and isorottlerin (XVII), m.p. 182°, present in the fruits of *Rottlera tinctoria* Roxb[34], dehydrodeguelin (XVIII, R = H), m.p. 232°–233°, present in the seeds of *Tephrosia vogelii* and dehydrotoxicarol (XVIII, R = CH_3), m.p. 234°, found in the roots of plants of the Derris family.

The coumarin derivatives include the yellow pigments: daphnetin (7,8-dihydroxycumarin), m.p. 255°–256°, aglucone of the glucoside daphnin, present in the bark of *Daphne alpina*; ellagic acid (XIX, R = OH), widely distributed in the wood of many species, for example, in *Quebracho colorado*, its dimethyl ether (XIX, R = OCH_3), m.p. 337°–338°, encountered in the roots of *Euphorbia formosana* Hay; luteic acid (XX), m.p. 338°–342° (with decomposition), the red dye of the fruits of *Terminalia chebula*, etc. Xanthones (XXI) also belong to this group (XXI) (Table 13). The oxygen--containing heterocyclic compounds also include thelephoric

TABLE 8. Flavones (IX, X = H).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
R_2 = R_4 = OH	primetin	yellow	230–231	in leaves of *Primula modesta*
R_1 = R_3 = OH	chrysin	yellow	275	in heartwood of *Pinus strobus*, etc.
R_1 = OH; R_3 = OCH_3	tectochrysin	yellow	163	in heartwood of *Pinus strobus*, etc.
R_1 = R_2 = R_3 = OH	baicalein	yellowish brown	264–265	in roots of *Oroxylum indicum* Vent.
R_1 = R_3 = OH; R_2 = OCH_3	oroxylin-A	yellow	231–232	ditto
R_1 = R_3 = OH; R_4 = OCH_3	wogonin	yellow	199–201	in roots of *Scutellaria baicalensis*
R_1 = R_3 = OH; R_2 = R_3' = OCH_3	pectolinarigenin	yellow	215–219	aglycone of flower pigment of *Linaria vulgaris* L.
R_1 = R_3 = R_2' = R_3' = OH	luteolin	yellow	328–330	in flowers of *Reseda luteola* L., etc.
R_1 = R_3 = R_3' = OH; R_2' = OCH_3	chrysoeriol	yellow	330–331	in haulm of *Eriodictyon glutinosum* Benth.
R_1 = R_3 = R_2' = R_3' = OH; R_2 = *n*-HOC$_6$H$_4$CH–CHCO (O)	fukugetin	yellow	288–290	in bark of *Garcinia spicata*
R_1 = R_2 = R_3 = R_4 = R_2' = = R_3' = OCH_3	nobiletin	yellow	134–137	in rind of *Citrus nobilis* Lour.
R_1 = R_3 = R_1' = R_3' = OH	lotoflavin	yellow	–	aglycone of pigment from *Lotus arabicus* L.
R_1 = R_3 = R_2' = R_3' = R_4' = = OH; R_4 = OCH_3	acrammerin	brown	335–340	in pods of *Gleditschia triacanthos*
R_1 = R_3 = R_3' = OH; R_2' = R_4' = OCH_3	tricin	yellow	191–192	in leaves of *Triticum dicoccum*

TABLE 9. Flavonols (IX).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
X = OH				
$R_1 = R_3 = OH$	galangin	yellow	216–221	in roots of *Alpinia officinarum* Hance
$R_1 = OH$; $R_3 = OCH_3$	izalpinin	yellow	195	in seeds of *Alpinia chinensis* Rosc.
$R_1 = R_3 = R_1' = OH$	datiscetin	yellow	268–273	aglycone of dye from wood of *Datisca cannabina L.*
$R_1 = R_3 = R_3' = OH$	kaempferol	yellow	275–277	in leaves of *Delphinium consolida*, etc.
$R_1 = R_3' = OH$; $R_3 = OCH_3$	rhamnocitrin	yellow	221–222	in berries of *Rhamnus cathartica*
$R_1 = R_3 = OH$; $R_3' = OCH_3$	kaempferide	yellow	225–229	in roots of *Alpinia officinarum* Hance
$R_1 = R_4 = R_3' = OH$	pratoletin	yellow	285	in flowers of *Trifolium pratense*
$R_1 = R_3 = R_4 = R_3' = OH$	herbacetin	yellow	280–283	in flowers of *Gossypium indicum*
$R_1 = R_3 = R_3' = OH$; $R_4 = OCH_3$	tambuletin	yellow	269–271	in seeds of *Xanthoxylum acanthopodium*
$R_1 = OH$; $R_3 = R_4 = R_3' = OCH_3$	tambulin	yellow	205	in fruit of *Xanthoxylum acanthopodium*
$R_3 = R_2' = R_3' = OH$	fisetin	yellow	330 (decompn.)	in wood of *Rhus cotinus L.*, etc.
$R_1 = R_3 = R_2' = R_3' = OH$	quercetin	yellow	312–316 (decompn.)	in stems of *Erica vulgaris* and many others
$R_2 = R_3 = R_3' = OH$; $R_1 = OCH_3$	azaleatin	yellow	~ 320	in flowers of *Rhododendron mucronatum*
$R_1 = R_2 = R_3' = OH$; $R_3 = OCH_3$	rhamnetin	yellow	220–295	in berries of *Rhamnus tinctoria*, etc.
$R_1 = R_3 = R_3' = OH$; $R_2' = OCH_3$	isorhamnetin	yellow	~ 305 (decompn.)	in petals of *Cheiranthus cheiri*, etc.
$R_1 = R_3' = OH$; $R_3 = R_2' = OCH_3$	rhamnazin	yellow	214–218	aglycone of dye from *Rhamnus* berries
$R_1 = R_2' = OH$; $R_3 = R_3' = OCH_3$	ombuin	yellowish brown	229–230	aglycone of pigment from leaves of *Phytolacca dioica L.*
$R_1 = R_2 = R_3 = R_2' = R_3' = OH$	quercetagenin	yellow	316–320	in flowers of *Tagetes patula*, etc.
$R_1 = R_3 = R_2' = R_3' = OH$; $R_1' = OCH_3$	patuletin	yellow	262–264	in flowers of *Tagetes patula*
$R_1 = R_3' = OH$; $R_2 = R_3 = OCH_3$	chrysosplenetin	yellow	158–159	aglycone of pigment from stems of *Chrysosplenium japonicum*
$R_1 = R_3 = R_4 = R_2' = R_3' = OH$	gossypetin	yellow	311–313	in flowers of *Hibiscus sabdariffa*, etc.; aglycone of flower pigment of *Gossypium* family
$R_1 = R_3 = R_1' = R_3' = OH$	morin	light yellow	286–290	in wood of *Morus tinctoria L.*
$R_3 = R_2' = R_3' = R_4' = OH$	robinetin	yellow	324–334	in wood of *Robinia pseudacacia*
$R_1 = R_3 = R_2' = R_3' = R_4' = OH$	myricetin	yellow	350–357	in bark of *Myrica nagi*, etc.
$R_1 = R_3 = R_4 = R_2' = R_3' = R_4' = OH$	hibiscetin	yellow	340–350	in flowers of *Hibiscus sabdariffa*
$X = OCH_3$				
$R_2 = R_3' = OH$; $R_1 = R_2 = R_4 = OCH_3$	calycopterin	yellow	224	in leaves of *Digitalis thapsi*
$R_1 = R_2' = OH$; $R_3 = R_3' = OCH_3$	ayanin	orange-yellow	172–173	in heartwood of *Distemonanthus benthamianus*
$R_1 = R_2 = R_2' = OH$; $R_3 = R_3' = OCH_3$	hydroxyayanin-B	yellow	208–209	ditto
$R_1 = OH$; $R_3 = R_2' = R_3' = OCH_3$	artemisetin	yellow	261–264	in *Artemisia absinthium*
$R_1 = R_3' = OH$; $R_3 = R_4 = R_2' = OCH_3$	ternatin	yellow	210–210.5	in bark of *Melicope ternata, M. simplex*
$R_1 = R_3 = OH$; $R_2 = R_4 = R_2' = R_3' = OCH_3$	eriantin	yellow	161	in *Blumea eriantha*
$R_1 = R_2' = R_3' = OH$; $R_3 + R_4 = OCH_2O$	wharangin	yellow	277–278	in bark of *Melicope ternata*
$R_1 = OH$; $R_2 = R_3 = OCH_3$; $R_2' + R_3' = OCH_2O$	melisimplin	yellow	234–236	in bark of *Melicope simplex*
$R_1 = R_2' = R_3' = OH$; $R_3 = R_3' = OCH_3$	hydroxyayanin-A	yellow	229–230	in heartwood of *Distemonanthus benthamianus*
$R_1 = OH$; $R_2 = R_4 = R_2' = R_3' = R_4' = OCH_3$	gardenin	yellow	163–164	in resinous exudation from *Gardenia lucida* Roxb.

TABLE 9 (contd.)

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$X = OSO_3K$				
$R_1 = R_3 = R_3' = OH$; $R_2' = OCH_3$	persicarin	yellow	280 (decompn.)	in leaves of *Polygonum hydropiper L.*
$R_1 = R_3' = OH$; $R_3 = R_2' = OCH_3$	7-methyl ether of persicarin	yellow	212–213	in leaves of *Polygonum hydropiper L.*

TABLE 10. Flavanols (X, X = H).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_2 = R_3 = R_2' = OH$	carthamidin	yellow	218	aglycone of flower pigment of *Carthamus tinctorius*
$R_1 = R_2 = R_1' = R_2' = OH$	homoeriodictyol	yellow	223–225	in stems of *Eriodictyon glutinosum* Benth.
$R_2 = R_1' = R_2' = OH$; $R_3 = OCH_3$	methoxybutin	yellow	195–197	in petals of *Coreopsis grandiflora* Nutt.
$R_1 = R_2 = R_1' = OH$; $R_2' = OCH_3$	hesperetin	yellow	224–225	aglycone of citrus pigment
Flavanonol, (X, X = OH)				
$R_1 = R_2 = OH$	pinobanksin	yellow	177–178	in heartwood of *Pinus strobus*, etc.

TABLE 11. Anthocyanins (XI).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_2 = R_3 = R_2' = OH$	apigenidin chloride	red	> 300	aglycone of petal pigment of *Gesneria fulgens*
$R_1 = R_2 = R_3 = R_2' = OH$	pelargonidin chloride	reddish brown	> 300	aglycone of petal pigment of *Pelargonium zonale*, etc.
$R_1 = R_2 = R_3 = R_4 = R_2' = OH$	cyanidin chloride	reddish brown	> 300	aglycone of flower pigment of *Chrisanthemum indicum L., Aster chinensis L., Centaurea cyanus L.*, etc.
$R_1 = R_2 = R_3 = R_2' = OH$; $R_1' = OCH_3$	peonidin chloride	brown	> 300	aglycone of flower pigment of *Viola tricolor*; berries of *Oxycocos macrocaprus* Pers., etc.
$R_1 = R_2 = R_3 = R_1' = R_2' = R_3' = OH$	delphinidin chloride	dark violet	> 300	aglycone of flower pigment of *Viola tricolor, Salvia patens*; berries of *Empetrium nigrum*, etc.
$R_1 = R_2 = R_3 = R_1' = R_2' = OH$; $R_3' = OCH_3$	petunidin chloride	sulphur brown	> 300	aglycone of flower pigment of *Petunia hybrida*, etc.
$R_1 = R_2 = R_3 = R_2' = R_3' = OH$; $R_1' = OCH_3$	malvidin chloride	dark brown	> 300	aglycone of flower pigment of *Cyclamen persicum* Mill., *Primula polyantha, Iris ensata*, etc.
$R_1 = R_2 = R_2' = OH$; $R_1' = R_3' = OCH_3$	hirsutidin chloride	violet	> 300	aglycone of flower pigment of *Primula hirsuta*.

TABLE 12. Isoflavones (XII).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_3 = R_2' = OH$	daidzein	light yellow	315–323 (decompn)	aglucone of pigment from *Soja hispida*
$R_1 = R_3 = OH$; $R_2' = OCH_3$	biochanin-A	light yellow	212–216	in *Cicer arietinum*
$R_1 = R_3 = R_2' = OH$; $R_2 = OCH_3$	tectorigenin	light yellow	227–230	aglucone of pigment from *Iris tectorum*
$R_1 = R_3 = R_1' = R_2' = OH$	orobol (santol)	light yellow	270.5	aglucone of pigment from *Orobus tuberosus L.*
$R_1 = R_1' = R_2' = OH$; $R_2' = OCH_3$	santal	yellow	223	in wood of *Pterocarpus santalinus L.*
$R_1 = R_3 = R_1' = OH$; $R_2 = R_2' = R_3' = OCH_3$	irigenin	yellow	185	aglycone of pigment from *Iris florentina*

TABLE 13. Xanthones (XXI).

Substituent	Name	Colour	M.p., °C	Occurrence in nature
$R_1 = R_7 = OH$	euxanthone	yellow	236–240	in heartwood of *Platonia insignis* Mart.
$R_1 = R_7 = OH$; $R_3 = OCH_3$	gentisin	yellow	267–274	in root of *Gentiana lutea*
$R_1 = R_3 = OH$; $R_7 = OCH_3$	isogentisin	yellow	241	ditto
$R_1 = R_3 = R_8 = OH$; $R_6 = OCH_3$	swertianol	yellow	263–267	in *Swertia japonica*
$R_1 = R_8 = OH$; $R_3 = R_6 = OCH_3$	swertirin	yellow	185–186	in stalks of *Swertia chirata*
$R_1 = R_2 = OH$; $R_6 = R_8 = OCH_3$	swertinin	yellow	217	in stalks of *Swertia decussata*
$R_1 = OH$; $R_2 = R_6 = R_8 = OCH_3$	decussatin	yellow	149–150	in flowers and roots of *Swertia decussata*
$R_1 = R_4 = R_8 = OH$; $R_3 = CH_3$	ravenelin	yellow	267–268	in mycelia of *Helminthosporium ravenelli* Curtus
$R_2 = R_8 = OH$; $R_1 = OCH_3$; $R_7 = CH_3$ or $R_2 = R_3 = OH$; $R_8 = OCH_3$; $R_7 = CH_3$	rubrofusarin	orange-red	210–211	in mycelia of *Fusarium culmorum* Saco
$R_1 = OH$; $R_2 = R_8 = OCH_3$; $R_7 = CH_3$ or $R_2 = OH$; $R_1 = R_8 = OCH_3$; $R_7 = CH_3$ or $R_8 = OH$; $R_1 = R_2 = OCH_3$; $R_7 = CH_3$	asperxanthone	yellowish red	203	in mycelia of various moulds *Aspergillus niger*

acid (XXII), the black-violet dye of many types of Thelephora, to which the structure of a phenanthrene derivative was earlier ascribed. Brasilein (XXIII, R = H) and haematoxilin (XXIII, R = OH), isolated from the wood of the mahogany (Leguminosae family) and the logwood (*Haematoxylon campechianum*) stand somewhat apart. This last substance, although itself colourless, was widely used for mordant dyeing cotton (bluish red and violet).

Many dyes of the groups considered above are encountered as glycosides (there are some exceptions)[31,35]. The most frequent carbohydrate is glucose, but rhamnose, galactose, arabinose, and others are also found.

b. Nitrogen-Containing Heterocyclics

Indole derivatives. Among the oldest natural dyestuffs used by man in dyeing are indigo[36] and purple of the ancients (antique purple). Indigo was extracted from the leaves of the tropical plant *Indigofera tinctoria*, and also *Isatis tinctoria* and *Polygonum tinctorium*, growing in Western Europe and in the south of the USSR. The plants contain not indigo itself, but the glucoside of indoxyl, indican, which is decomposed on hydrolysis into glucose and indoxyl, and is oxidised by atmospheric oxygen into indigo. Indican is accompanied by an isomer, indirubin (also formed from indoxyl), and other dyestuffs (including kaempferol). The purple of the ancients, present in the molluscs *Murex bandaris*, is 6,6'-dibromoindigo. The indole derivatives also include the high-molecular-weight pigments, the melamines[37].

Pyrrole derivatives. Three important groups of natural pigments belong to this class; the blood pigments, chlorophyll, and the bile pigments. They all contain a skeleton consisting of four pyrrole nuclei linked by methine bridges, only in the first two is the system closed to give the so-called porphyrin ring and in the last the ring is not closed. Haemoglobin of the blood is an iron-containing complex of protoporphyrin IX and a protein, globin[38]. The prosthetic group of haemoglobin — haem — which contains iron(II), is readily oxidised to haematin, which with acids gives salts, such as haemin. Porphyrins (XXIV) which are encountered in nature[39] are shown in Table 14. Chlorocruoroporphyrin is near in structure to protoporphyrin (a formyl group replaces one vinyl group) and is the prosthetic group of the pigment chlorocruorin from Spirographis.

As well as carotene and xanthophyll, the chloroplasts of the green parts of plants contain two pigments in 3 : 1 ratio, close in structure to the blood pigments, the blue-green chlorophyll-a (XXV, R = CH_3) and the yellow-green chlorophyll-b (XXV, R = CHO), which play an important role in plant photosynthesis. In addition, plants contain protochlorophyll-a (XXV, R = C_2H_5) in which ring A is dehydrogenated[40].

Vitamin B_{12}, which is widely distributed in nature and contains coordinated cobalt, belongs to this group of natural pigments.

TABLE 14. Porphyrins (XXIV).

Substituent	Name	Occurrence in nature
$R_1 = R_5 = CH_3$; $R_2 = CH = CH_2$; $R_3 = R_4 = CH_2CH_2COOH$	protoporphyrin IX	prosthetic group of haemoglobin and cytochrome (another protein), in faeces, in yeasts, in lettuce, spinach, potatoes, etc., in bird feathers. In the form of the Mg complex in mutants of *Chlorella vulgaris*
$R_1 = R_5 = CH_3$; $R_2 = C_2H_5$; $R_3 = R_4 = CH_2CH_2COOH$	mesoporphyrin IX	in faeces, in amber
$R_1 = R_5 = CH_3$; $R_2 = H$; $R_3 = R_4 = CH_2CH_2COOH$	deuteroporphyrin IX	in faeces
$R_1 = R_5 = CH_3$; $R_2 = CH(OH)CH_3$; $R_3 = R_4 = CH_2CH_2COOH$	haematoporphyrin IX	in mutants of *Chlorella vulgaris*
$R_1 = R_4 = CH_3$; $R_2 = R_3 = R_5 = CH_2CH_2COOH$	coproporphyrin I	in faeces, urine, yeasts, bird feathers
$R_1 = R_5 = CH_3$; $R_2 = R_3 = R_4 = CH_2CH_2COOH$	coproporphyrin III	ditto
$R_1 = R_4 = CH_2COOH$; $R_2 = R_3 = R_5 = CH_2CH_2COOH$	uroporphyrin I	»
$R_1 = R_5 = CH_2COOH$; $R_2 = R_3 = R_4 = CH_2CH_2COOH$	uroporphyrin III	»

TABLE 15. Pterins (XXVIII).

Substituent	Name	Colour	Occurrence in nature
$R_2 = OH$	xanthopterin	yellow	in wings of the lemon butterfly *Gonopteryx rhamni*; in the shell of the crab *Cancer pagurus*; in the astsidiae *Microcosmus polymorphus*
$R_1 = R_2 = OH$	leucopterin	white	in wings of the cabbage butterfly *Pieris brassica*
$R_1 = CH_3$; $R_2 = OH$	chrysopterin	yellow	in wings of the butterfly *Gonopteryx rhamni*
$R_1 = C(OH) = C(OH)CH_2OH$; $R_2 = OH$	erytropterin	red	in wings of the butterfly *Gonopteryx rhamni*
$R_2 = CH(OH)CH(OH)CH_3$	biopterin	yellow	in beer yeasts

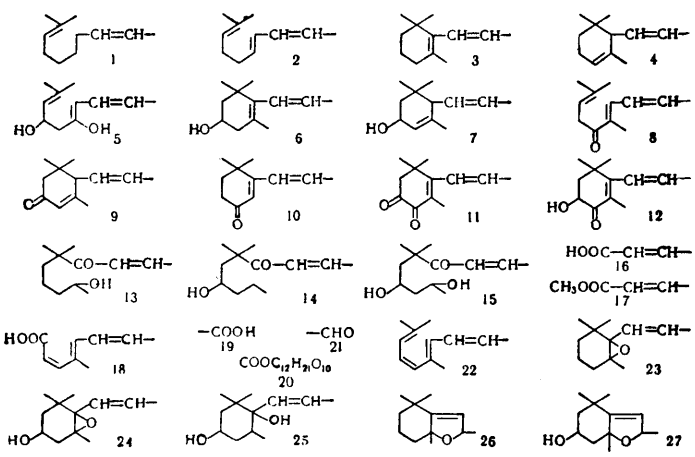
The group of bile pigments includes bilirubin (XXVI, R = $CH=CH_2$), mesobilirubin (XXVI, R = C_2H_5), and urobilin, distinguished from the last by the A, B, and C rings being hydrogenated[41]. Also among the pyrrole derivatives is prodigiosin, the red pigment of the bacterium *Serratia marinorubra* (XXVII), m.p. 151°–152°.

Phenazine derivatives. Hemipyocyanine, 1-hydroxyphenazine, m.p. 158°; phenazinecarbonic acid, m.p. 242°, and pyocyanine, 1-hydroxy-9-methylphenazine, m.p. 242°, which is dark blue and is found in *Pseudomonas pyocyanea* and *P. aureofaciens* all belong to this class. Vitamin B_2 (lactoflavin, riboflavin), 6,7-dimethyl-9-ribityl-isoalloxazine, which is also widely distributed in nature is similar to this group of pigments.

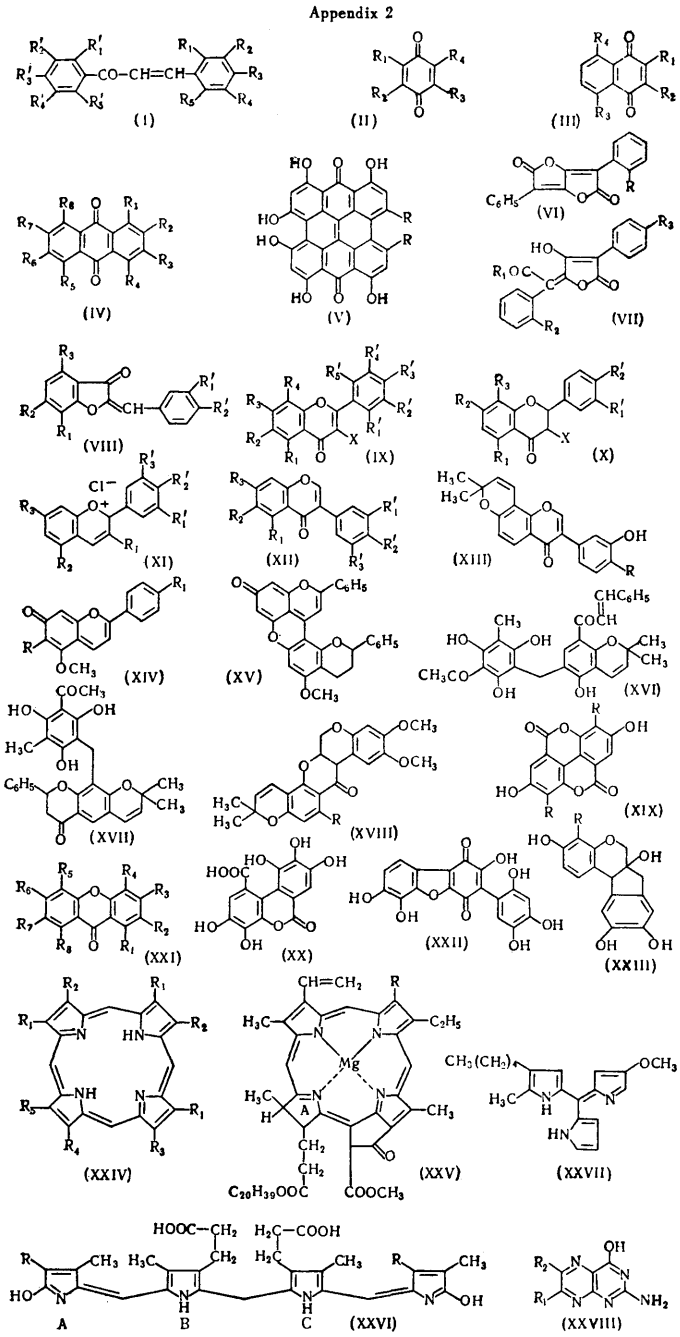
The pigments of the group of ommochromes[44] belong to the oxazine derivatives.

Another rather widely distributed group of natural pigments is the derivatives of pteridine[45–47] (XXVIII) first isolated from the dust of butterfly wings. Some of them are physiologically active and are also structurally close to folic acid.

Appendix 1 (to Table 1)



Appendix 2



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Institute of the Chemistry of
Natural Compounds,
Academy of Sciences of the USSR

U.D.C. 547.86:547.867

CHEMISTRY OF ALLOXAZINES AND ISOALLOXAZINES

V. M. Berezovskii and T. V. Eremenko

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