ADVANCES IN THE CHEMISTRY OF NATURAL ISOFLAVONOIDS

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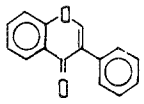
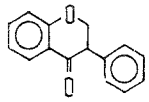
UDC 547.972

The majority of known isoflavonoids are considered as diphenylpropane derivatives [1]. They include isoflavones, isoflavanones, isoflavanes, isoflavenes, coumestans, pterocarpans, and some others (I-XI). In 1970 [1], the number of known natural structures was more than 100, of which the aglycones of the isoflavones were represented by 58. In recent years, the number of isoflavonoid structures described has risen sharply. This is due to the fact that a large number of plants have been subjected to study of the purposes of chemotaxonomy and that NMR and mass spectroscopy are widely used for determining their structures.

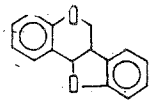
Isoflavonoid Rings



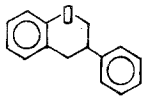
I. Isoflavone



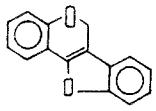
II. Isoflavanone



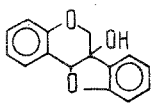
III. Pterocarpan



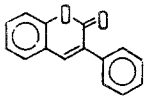
IV. Isoflavan



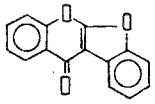
V. 6a,11a-dehydropterocarpan



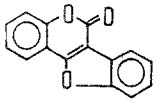
VI. 6a-hydroxypterocarpan



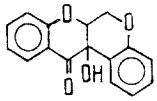
VII. 3-Arylcoumarin



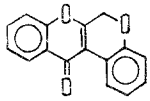
VIII. Coumaronochromone



IX. Coumestan



X. 12a-Hydroxyrotenoid



XI. 6a,12a-Dehydrorotenoid

In addition to the determination of structures, great attention is being devoted to elucidating the pathways of the biogenesis of isoflavonoids in higher plants and to determining their biological action on animal organisms.

It has been established that a number of isoflavonoid compounds possesses blood-vessel strengthening, estrogenic, antisclerotic, antimicrobial, and antifungal actions [2, 3, 5].

Isoflavonoids are found in the families Fabaceae, Iridaceae, Rosaceae, Moraceae, Amaranthaceae, and Podocarpaceae [1, 2, 4, 7]. Reports have appeared of their isolation from bacteria [8, 9], but one of the reports was subsequently refuted [10].

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 669-689, November-December, 1978. Original article submitted December 25, 1978.

0009-3130/78/1406-0569$07.50

TABLE 1. Structures, Physicochemical Properties, and Distribution of Simple Isoflavones

Name	Structure	mp, °C	UV spectrum, λ_{max}, nm	Source of isolation (genus)
Daidzein	4',7-Dihydroxy	320	250, 260 sh, 302	Baptisia [11], Cyclolobium [12], Chamaecytisus [12], Cytisus [12], Dalbergia [13], Glycine [1], Genista [12], Medicago [13], Pueraria [2], Teline [13], Trifolium [2], Ulex [12].
Formononetin	7-Hydroxy-4'-methoxy-	255–265	250, 300 sh	Baptisia [11], Cladrastis [15], Cicer [2], Cytisus [12], Dalbergia [13], Genista [12], Machaerium [16], Ononis [13], Pterocarpus [17], Sophora [13], Termopsis [18, 19], Tipuana [20], Trifolium [4]
Isoformononetin	4'-Hydroxy-7-methoxy	—	—	Machaerium [16]
Kakkatin	4',6-Dihydroxy-7-methoxy	290	322, 263	Pueraria [60]
—	4',7-Dihydroxy-6-methoxy	311–312	—	Mildbraedeodendron [39]
Cabreuvin	3',4',7-Trimethoxy	164–165	—	Myroxylon [21], Myrocarpus [2]
Podospicatin	2',5,7-Trihydroxy-5',6-dimethoxy	—	263 302	Podocarpus [2]
Cladrin	7-Hydroxy-3', 4'-dimethoxy	257–258	—	Cladrastis [22]
Pseudobaptigenin	7-Hydroxy-3', 4'-methylenedioxy	295–298	241 sh, 249, 260 sh, 296	Baptisia [11], Cladrastis [23]
Teralin	4',7-Dihydroxy-2'-methoxy	274–275	251, 302	Termopsis [24]
Genistein	4',5,7-Trihydroxy	290–293	263, 325 sh	Calycotome [13], Chamaespartium [12], Chronanthus [13], Cytisus [12], Genista [12], Glycine [4], Lupinus [4, 25], Stauracanthus [12], Teline [13], Termopsis [18]
Biochanin A	5,7-Dihydroxy-4'-methoxy	212–216	261–263, 326 sh	Andira [13], Baptisia [11], Cicer [13], Cotoneaster [13], Dalbergia [54], Ferreirea [39], Medicago [13], Trifolium [39]
Irilone	4',5-Dihydroxy-6,7-methylenedioxy	231	—	Iris [46]
—	5,7-Dihydroxy-3',4'-methylenedioxy	245	336, 294, 265	Sophora [66]
Calycosin	3',7-Dihydroxy-4'-methoxy		288, 259, 247 sh, 217	Baptisia [37], Pterocarpus [37], Termopsis [18]
Prunetin	5',4-Dihydroxy-7-methoxy	237–241	262, 5, 325 sh	Prunus [6], Dalbergia [2], Pterocarpus [2]
Retusine	7,8-Dihydroxy-4'-methoxy	249	261, 308 sh	Dalbergia [41], Dipteryx [40]
8-Methylretusine	7-Hydroxy-4',8-dimethoxy	220–221	256, 270 sh	Dipteryx [40]
3'-Hydroxy-8-methyl retusine	3',7-Dihydroxy-4',8-dimethoxy	208–212	254, 289, 306	Dipteryx [40], Xantoceras [42]
5-Methylgenistein	4',7-Dihydroxy-5-methoxy	290–312	257, 282	Adenocarpus [12], Calycotome [12], Cytisus [26], Chronanthus [13], Erinacea [12], Genista [28], Laburnum [12, 27], Lupinus [25], Lygos [12], Ormosia [29], Stauracanthus [13], Teline [12], Ulex [12]

TABLE 1. (Continued)

Name	Structure	mp, °C	UV spectrum, λ_{max}, nm	Source of isolation (genus)
Glycyteine	4',7-Dihydroxy-6-methoxy	311–313	256, 319	Derris [30], Glycyne [2]
Dipteryxin	7,8-Dihydroxy-4',6-dimethoxy	250–254	266, 325	Dipteryx [40]
Fujikinetin	7-Hydroxy-6-methoxy-3',4'-methylenedioxy	279–281		Cladrastis [43]
—	2',7,8-Trimethoxy-4',5'-methylenedioxy	204–206	246, 251, 302	Pterodon [44]
Texasin	6',7-Dihydroxy-4'-methoxy	285–287	227 sh , 254, 324	Baptisia [35]. Platymiscium [12]
Afrormosin	7-Hydroxy-4',6-dimethoxy	229	226, 254, 326	Afrormosia [2], Amphimas [2], Baptisia [11], Cladrastis [33], Dalbergia [13], Myrocarpus [33], Myroxylon [33], Pterodon [2].
5-Methoxyafrormosin	7-Hydroxy-4',5,6-trimethoxy	235–236	—	Cladrastis [34]
Milldurone	2',6,7-Trimethoxy-4',5'-methylenedioxy	233–234	232, 256, 312	Cordyla [2], Mildbraedeodendron [39], Milletia [2], Pterodon [2]
Orobol	3',4',5,7-Tetrahydroxy	270	287	Baptisia [11], Lathyrus [13], Tipuana [36]
3'-O-Methylorobol	4',5,7-Trihydroxy-3'-methoxy	—	262, 288 sh	Dalbergia [31], Termopsis [18]
Santal	3',4',5-Trihydroxy-7-methoxy	223	283, 287, 5 sh	Baptisia [2], Pterocarpus [2]
Pratensein	3',5,7-Trihydroxy-4'-methoxy	272–273		Trifolium [32], Termopsis [18]
Cladrastin	7-Hydroxy-3',4',6-trimethoxy	206–207	206, 220, 262, 320	Cladrastis [34]
Tectorigenin	4',5,7-Trihydroxy-6-methoxy	227–230	268, 320 sh	Baptisia [11], Dalbergia [2]
Isotectorigenin	4',5,7-Trihydroxy-8-methoxy	238-240	—	Dalbergia [2]
7-Methyltectorigenin	4',5-Dihydroxy-6,7-dimethoxy	235–236	268	Dalbergia [2], Pterocarpus [2]
4',7-Dimethyltectorigenin	5-Hydroxy-4',6,7-trimethoxy	184	267, 325 sh	Dalbergia [2]
Muningin	4',6-Dihydroxy-5,7-dimethoxy	285	—	Pterocarpus [2]

TABLE 1 (Continued)

Name	Structure	mp, °C	UV spectrum, λ_{max}, nm	Source of isolation (genus)
Irisolone	4'-Hydroxy-5-methoxy-6,7-methylenedioxy	271	—	Iris [45]
—	2',7,8-Trimethoxy-4',5'-methylenedioxy	204—206	246, 251, 302	Pterodon [44]
Iristectorigenin	4',5,7-Trihydroxy-3',6-dimethoxy	153—155	267, 292, 346	Iris [98]
—	2',6,7-Trimethoxy-4',5'-methylenedioxy	233—234	—	Pterodon [48]
Irigenin	5,5',7-Trihydroxy-2',6-dimethoxy	185	269, 335	Iris [45]
		—	263, 302	Podocarpus [2]
Irisflorentin	3',4',5,5'-Tetramethoxy-6,7-methylenedioxy	175	—	Iris [45]
—	2',3',4',6,7-Pentamethoxy	170—172	—	Pterodon [48]
Irisolidone	5,7-Dihydroxy-4',6-dimethoxy	189—191	340, 271	Iris [2], Sophora [66]

TABLE 2. Glycosidic Structures of Natural Isoflavones

Name	Structure	mp, °C	UV spectrum, λ_{max}, nm	Source of isolation
	I. Isoflavone C-Glycosides			
Prunetin 8-C-glycoside	8-C-Glucosyl-4', 5-dihydroxy-7-methoxy	286—287	287 sh 216	Dalbergia [52]
Puerarin	8-C-Glucosyl-4', 7-dihydroxy	187	—	Pueraria [63]
Di-O-acetylpuerarin	8-C-Glucosyl-7-hydroxy-4',6"-di-O-acetyl	250—251	—	Pueraria [62]
Paniculatin	6,8-Di-C-glucosyl-5,7-dihydroxy	225-227	265	Dalbergia [74]
Dalpanitin	8-C-Glucosyl-4', 5,7-trihydroxy-3'-methoxy	213—214	—	Dalbergia [53]
Volubilinin	8-C-Glucosyl-5, 7-dihydroxy-4',6-dimethoxy	159—161	340, 263	Dalbergia [54]
Volubilin	8-C-Rhamnopyranosyl-3',5-dihydroxy-4',7-dimethoxy	>300	336, 268	Dalbergia [57]
	II. Isoflavone O-glycosides			
Daidzin	7-Glycosyloxy-4'-hydroxy	215—217	310, 258	Piptanthus [50], Psoralea [59], Pueraria [61], Termopsis [68]
Ononin	7-Glucosyloxy-4'-methoxy	210—212	300, 261, 250, 230 sh,	Dalbergia [56], Ononis [58], Piptanthus [50], Termopsis [68], Trifolium [70]
Genistin	7-Glucosyloxy-4',5-dihydroxy	254—256	330, 262	Adenocarpus [28], Genista [12], Sarothamnus [64], Termopsis [67], Ulmus [12].
Genistein 7-rhamnoglucoside	4',5-Dihydroxy-7-rhamnoglucosyloxy	—	—	Baptisia [11]
Genistein 4',7-diglucoside	4',7-Diglucosyloxy-5-hydroxy	—	320, 259	Termopsis [68], Piptanthus [13]
Sophoricoside	4'-β-Glucosyloxy-5,7-dihydroxy	297,5	330 sh, 262	Piptanthus [73], Sophora [4]
Sophorabioside	5,7-Dihydroxy-4', β-neohesperidosyloxy	247, 248	—	Sophora [4]
Wistin	7-Glucosyloxy-4', 6-dimethoxy	206—210	322, 261	Cladrastis [15], Wistaria [49, 78]
Spherobioside	7-Rutinosyloxy-4',5-dihydroxy	204	350 sh 305	Baptisia [51]
Pseudobaptisin	3'4'-Methylenedioxy-7-rutinosyloxy	150—151 (hydrate) 247—250	295, 268, 248 sh 220	Baptisia [79], Maackia [79]
Texasin 7-glucoside	7-Glucosyloxy-6-hydroxy-4'methoxy	—	325, 258, 225 sh	Baptisia [35]
—	7-Glucosyloxy-5-hydroxy-4'-methoxy	207—209	336/263	Termopsis [68], Trifolium [70]
Trifoside (prunetrin)	4'-Glucosyloxy-5-hydroxy-7-methoxy	183—194	325, 264	Prunus [6], Trifolium [72]
Sissotrin	7-Glucosyloxy-5-hydroxy-4'-methoxy	205—206. 282 (anhydr.)	325 sh , 262	Dalbergia [55, 56]
Calycosin 7-glucoside	7-Glucosyloxy-3'-hydroxy-4'-methoxy	—	—	Baptista [11], Termopsis [18]
Biochanin A 7-glucoside	7-Glucosyloxy-5-hydroxy-4'-methoxy	208—210	323, 262	Termopsis [68], Trifolium [70]

TABLE 2 (Continued)

Name	Structure	mp, °C	UV spectrum, λ_{max}, nm	Source of isolation
Biochanin A diglucoside	7-[O-β-Glucosyl-(1→6)-β-D-glucosyloxy]-5'-hydroxy-4'-methoxy	224—226	324, 262	Sophora [65]
Biochanin A xylogluco-side	5-Hydroxy-4'-methoxy-7-0-[xylosyl-(1→6)-β-glucosyloxy]	228—230	324, 263	Sophora [65]
—	7-Glucosyloxy-5-malonyloxy-4'-methoxy	214—216	335, 263	Trifolium [69]
Lanceolarin	7-O-Apiosylgluco-syloxy-5-hydroxy-4'-methoxy	—	325 sh, 262	Dalbergia [2]
Tectoridin	7-Glucosyloxy-4', 5-dihydroxy-6-methoxy	258	331, 266	Baptista [11], Dalbergia [2], Iris [2]
Orobol 7-glucoside	7-Glucosyloxy-3', 4',5-trihydroxy	185	322, 262	Orobus [78]
Orobol 7-rhamnogluco-side	3',4',5-Trihydroxy-7-rhamnogluco-syloxy	—	330, 286, 259, 219	Baptista [11], Termopsis [68]
3'-O-Methylorobol 7-glucoside	7-Glucosyloxy-4', 5-dihydroxy-3'-methoxy	—	288, 260 sh.	Termopsis [68]
Fujikinin	7-β-Glucosyloxy-6-methoxy-3', 4'-methylenedi-oxy	231 - 232,5	—	Cladrastis [80]
Irisolone 4'-bioside	4'-Biosyloxy-5-methoxy-6,7-methylenedioxy	173—175	—	Iris [75]
Dalpatin	7-Glucosyloxy-2', 6-dimethoxy-4', 5'-methylenedi-oxy	261—263	—	Dalbergia [53]
Iridin	7-Glucosyloxy-3', 5-dihydroxy-4', 5',6-trimethoxy	213—217	325 sh, 268	Iris [76]
Iristectorin A	7-β-D-Glucosyl-oxy-3',5,7-dihy-droxy-4',6-di-methoxy	—	—	Iris [77]

The most studied group is that of the simple isoflavones [1], the structure of which are given in Table 1. In contrast to the composite isoflavones they have no additional rings and isoprenyl radicals. Table 2 shows the structures of their glycosides.

The majority of isoflavones accumulate in plants of the family Fabaceae, and more rarely in the Iridaceae and Rosaceae. The hydroxy and methoxy groups in them may be present not only at C_5 and C_7 in ring A and 3' and 4' in the lateral phenyl radical but also in positions 6 and 8 (afrormosin, texasin, 8-methylretusine, and at C' in the lateral phenyl radical (cavuinin, tlatlancuayin). Some of them have a methylenedioxy grouping in the lateral phenyl radical, or in ring A (tlatlancuayin, maxima substance A, milldurone) (see Table 1). In the glycosides, of the carbohydrate components we find most frequently glucose in the form of the β-pyranose and bioses — rutinose and neohesperidose (see Table 2). Acylated glycosides have been reported [62, 69, 71]. At the present time, the structures of a number of the glycosides have been confirmed by their synthesis [78, 79, 81-83].

Complex isoflavones contain isoprenoid chains and additional furano or pyrano rings (Table 3). These compounds are also the most characteristic for the family Leguminosae (Derris, Piscidia, Milletia, Mundulea, Neurautanenia, etc.). Wide use is made of NMR spectroscopy to establish the structures of isoflavones and their glycosides [2, 91-97, 106].

Table 4 gives details of the NMR spectroscopy of some complex isoflavones [106].

In contrast to the isoflavones, the isoflavonone group has few representatives. At the present time, only 13 isoflavanones are known; their structures are shown in Table 5. Almost all of them have been isolated from plants of the family Fabaceae. The UV spectra of these compounds each have two absorption maxima (270 and 310 nm) by means of which it is easy to distinguish them from the isoflavones.

TABLE 3. Complex Isoflavones

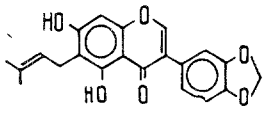
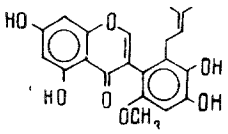
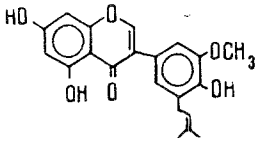
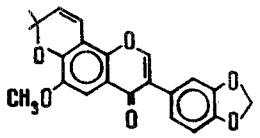
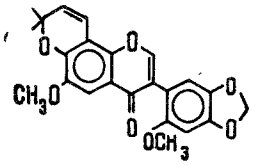
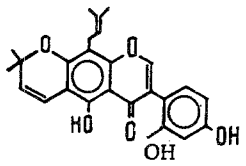
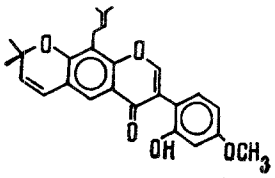
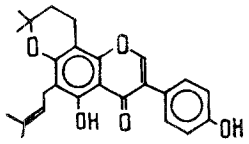
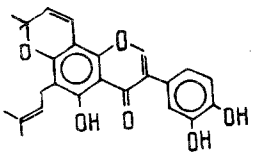
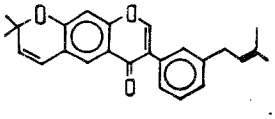
Formula	Name	Sources of isolation
	Derrubone	Derris [84]
	Piscidone	Piscidia [2]
	Piscerythrone	Piscidia [2]
	Durmillone	Milletia [2]
	Ichthynone	Piscidia [2]
	Auriculatin	Milletia [85]
	Auriculin	Milletia [2]
	Osajin	Maclura [86] Moraceae
	Pomiferin	Maclura [86]
	Chandalone	Derris [88]

TABLE 3 (Continued)

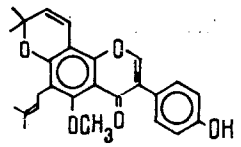
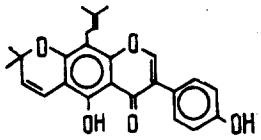
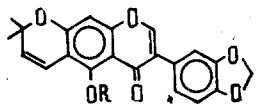
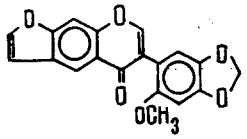
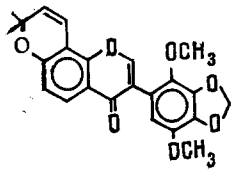
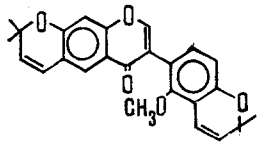
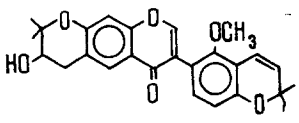
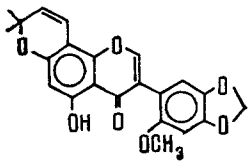
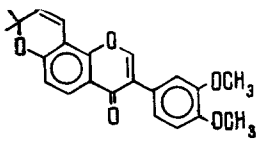
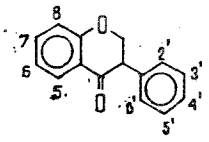
Formula	Name	Source of isolation
	Scandinone	Derris [2]
	Scandenone	Derris [2]
	R=H— Robustone R=CH_3– Robustone methyl ether	Derris [84]
	Dehydroneotenone	Neorautanenia, Pachyrrhisus [2]
	Ferrugone	Milletia [2]
	Munetone	Mundulea [2]
	Mundulone	Mundulea [2]
	Jamaicin	Piscidia [2]
	Toxicarol isoflavone	Derris [2]

TABLE 4. Chemical Shifts (δ Scale) of the Protons of Some Complex Isoflavones [106]

Compound	Solvent	Chemical shifts of the following protons										
		H-2	H-5	H-6	H-2	H-3'	H-5'	H-6'	2''-C(CH$_3$)$_2$	H-3''	H-4''	O-CH$_2$-O
Durmillone	$CDCl_3$	7,93	7,56		7,12 7,18		6,85 (J=8 Hz)	6,97	1,55	5,72	6,80	5,97
Ichthynone	$(CH_3)_2SO$	8,36	7,43				7,0 (J=8 Hz)	7,10		5,95 (J=10 Hz)	6,80	6,10
Ferrugone	$CDCl_3$	7,89	7,53			6,61		6,80	1,56	5,71	6,79	5,93
	$CDCl_3$	7,92	8,06 (J=8,5 Hz)	6,84				5,54	1,50	5,72 (J=10 Hz)	6,83	6,03
Jamaicin	$CDCl_3$	7,92	8,03	6,85		6,62		6,85	1,49	5,79	6,80	5,95

TABLE 5. Isoflavanones



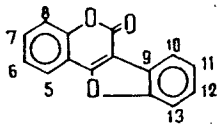
Name	Structure	Source of isolation
Padmakastein	4',5-Dihydroxy-7-methoxy	Cerasus [6]
Ferreirin	2',5,7-Trihydroxy-4'-methoxy	Ferreirea [4]
Homoferreirin	5,7-Dihydroxy-2',4'-dimethoxy	Ferreirea [4], Ougeinia [89], Cicer [90]
Sophorol	2',7-Dihydroxy-4',5'-methylenedioxy	Maackia [2], Sophora [4]
Dalbergioidin	2',4',5,7-Tetrahydroxy	Dalbergia [2], Ougeinia [2]
Ougenin	2',4',5-Trihydroxy-3',7-dimethoxy-6-methyl	Ougeinia [89]
Neotenone	2'-Methoxy-4',5'-methylenedioxy-6:7-furano	Neorautanenia [2], Pachyrrhizus [2]
Violanone	3',7-Dihydroxy-2',4'-dimethoxy	Dalbergia [2]
Parvisoflavonone	4',5,7-Trihydroxy-2',3'-dimethoxy	Poecilanthe [2]
—	5,7-Dihydroxy-4'-methoxy	Andira [118]
—	6,7-Dimethoxy-3',4'-methylenedioxy	Cordyla [2]
Kievetone	2',4',5,7-Tetrahydroxy-8-(3-methylbut-2-enyl)	Phaseolus [125]
Nepseudin	2,'3',4'-Trimethoxy-6:7-furano	
Onogenin	7-Hydroxy-6-methoxy-3',4'-methylenedioxy	Ononis [115]

In order to establish their structure, they were subjected to the dehydrogenation and the isoflavones formed were identified by the usual methods [2]. With the exception of sophorol, all known isoflavanones were optically inactive. Characteristic for the majority of isoflavanones is the presence of a hydroxy group in position 2'. Among them is known one C-glycoside — dalpanin, isolated from *Dalbergia paniculata* [2].

An interesting group of isoflavonoids is the coumestan derivatives, which are known under the names of coumestans, coumaronocoumarins, and coumestones [101].

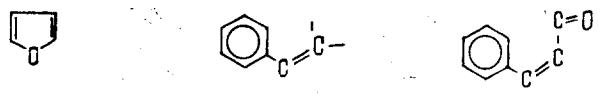
The first natural representative of this group — wedelolactone — was described in 1957 [2]. At the present time, 19 compounds are known. Their physicochemical properties are given in Table 6. Only one of them is a glycoside. The majority of the compounds have been isolated from species of the family Fabaceae. Wedelolactone, a demethylwedelolactone glycoside, and norwedelolactone have been isolated from two genera of the family Compositae (Eclipta, Wedelia).

TABLE 6. Coumestans



Name	Structure	mp, °C	UV spectrum, λ_{max} nm	Source of isolation
Coumestrol	7,12-Dihydroxy	385	244, 304, 344	Medicago [101], Trifolium [100]
Erosnin	11,12-Dihydroxyfurano [2',3' : 6,7]	300	240, 285, 290, 350, 365	Pachyrrhizus [101]
12-Methoxycoumestrol	7-Hydroxy-12-methoxy	331—332	242, 302, 342	Medicago [99], Trifolium [100]
11-Methoxycoumestrol	7,12-Dihydroxy-11-methoxy	329	248, 308, 351	Medicago [99]
	7-Hydroxy-11,12-dimethoxy	305	246, 280, 305 350	Medicago [102]
Flemichapparin C	7-Methoxy-11,12-methylenedioxy	272	246, 296, 308 345	Flemingia [103]
Wedelolactone	5,11,12-Trihydroxy-7-methoxy	327—300	211, 250, 303 350	Eclipta [101], Wedelia [101]
Norwedelolactone	5,7,11,12-Tetrahydroxy	360	—	Eclipta [101], Wedelia [101]
Psoralidin	7,12-Dihydroxy-6-isopentenyl	315	208, 244, 305 347	Psoralea [101]
Trifoliol	7,10-Dihydroxy-12-methoxy	332	268, 309, 348	Trifolium [100]
Medicagol	7-Hydroxy-11,12-methylenedioxy	325	245, 309, 347	Medicago [104]
Lucernol	6,7,12-Trihydroxy	350	232, 310, 355 372	Medicago [101]
Glycyrol	5,12-Dihydroxy-6-isopentenyl-7-methoxy	—	—	Glycyrrhiza [101]
5-O-Methylglycyrol	12-Hydroxy-6-isopentenyl-5,7-dimethoxy	—	—	Glycyrrhiza [101]
Isoglycyrol	12-Hydroxy-7-methoxy-2,2'-dimethylpyrano [2',3' : 5,6]	—	—	Glycyrrhiza [101]
Sojagol	7-Hydroxy-6',6'-dimethyl-(12 : 13; 2', 3')-chromano	284—286	—	Glycine [105], Phaseolus [124]
Repensol	7,10,12-Trihydroxy	—	—	Trifolium [100]
Sativol	8,12-Dihydroxy-7-methoxy	303	241, 305, 342	Medicago [101]
Wedelolactone glycoside	7-Glucosyloxy-5,11,12-trihydroxy	—	—	Eclipta [101]

Their UV spectra each show three absorption maxima which correspond to the three chromophoric groups



(240± 10 nm) (295± 10 nm) (345± 10 nm)

The presence of a free hydroxy group at C_7 can easily be established from the bathochromic shift of the long-wave maximum in the presence of sodium acetate, and the presence of an ortho-dihydroxy grouping from the bathochromism in the presence of boric acid and sodium acetate [101].

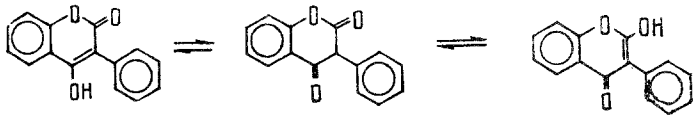
In the IR spectra of the coumestans it is easy to detect the lactone carbonyl group from a band at 1700-1730 cm^{-1}, the band of hydroxy groups at 3700-3500 cm^{-1}, and the bands of a furanocoumarin system at 1280, 1270, 1170-1160, and 1080-1070 cm^{-1}. The NMR spectra have been well studied. The positions of the protons have been determined by comparing the

TABLE 7. Results of the NMR Spectroscopy of Natural Coumestans

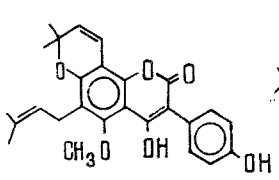
Coumestan	Chemical shifts of the following protons, ppm (δ scale)					
	H-5	H-6	H-8	H-10	H-11	H-13
Coumestrol	7,95	7,20	7,00	—	7,20	7,00
Coumestrol acetate	7,90	7,18	7,26	8,03	7,13	7,48
Trifoliol	7,83	7,03	6,97	—	6,42	6,80
Trifoliol diacetate	7,88	7,13	7,21	—	7,03	6,73
Sativol diacetate	7,83	7,03	—	8,06	7,18	7,50
Lucernol triacetate	7,82	—	7,40	8,06	7,20	7,49
7,11,12-Trimethoxycoumestan	7,85	6,95	6,97	7,52	—	7,18
7,11,12-Triacetoxycoumestan	7,98	7,18	7,31	7,89	—	7,59
11-Methoxycoumestan	7,82	—	—	7,39	—	—

NMR spectra of the coumestans with the spectra of the corresponding benzofurans. The chemical shifts of the protons are given in Table 7. The mass spectra of individual coumestans have also been described [101].

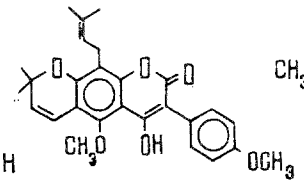
The isoflavonoids also include a group of 3-aryl-4-hydroxycoumarins, which are tautomeric with the 2-hydroxyisoflavones:



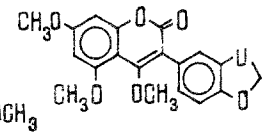
Representatives of this group are scandenin, lonchocarpin, derrusin, robustin, robustic acid, and their methyl derivatives, which have been isolated from plants of the genus *Derris* (XII-XVI) [88, 112, 113].



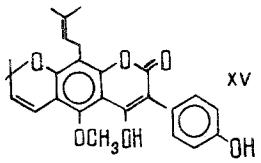
Scandenin XII



Lonchocarpin XIII

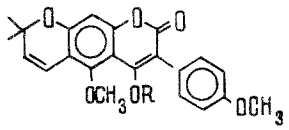


Derrusnin XIV



Lonchocarpic Acid

XVI



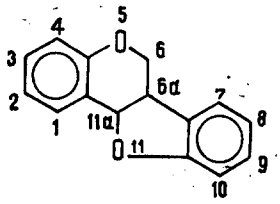
R=H – Robustic Acid

R=CH_3 – Methyl Robustate

The wood of a series of tropical plants, the Caesalpiniaceae and Fabaceae, contains derivatives of pterocarpan (coumaranochroman). They have been isolated from the genera *Andira, Baphia, Maackia, Dalbergia, Machaerium, Neorautanenia, Swartzia*, etc. (Table 8). Some of them — for example, neodulin, pisatin — are formed in the plants when they are attacked by a fungal infection [2]. They possess a well pronounced antifungal action. Some pterocarpans have a hydroxy group in the 6a position (pisatin, 6a-hydroxyphaseollin, variablin), and 6a,11*a*-dehydropterocarpans are occasionally found [134] (Table 8). The IR spectra of the pterocarpans each have two absorption maxima: a well-defined one at 285-310 nm and a weakly defined one in the 280-287 nm region.

The majority of these compounds are optically active and have a negative value of $[\alpha]_D$ [2]. It has been established by the investigations of a number of authors [2, 127] that the absolute configuration for the (–)-pterocarpans is 6aR,11aR, and for the (+)-enantiomers 6aS,11aS. The protons at 6a and 11a are in the cis position:

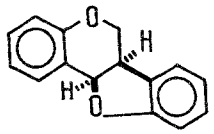
TABLE 8. Pterocarpans



Name	Structure	Source of isolation
(−)-Medicarpin	3-Hydroxy-9-methoxy	Aldina [118], Dalbergia [120], Medicago [121], Trifolium [2], Swartzia [2]
(+)-Medicarpin	3-Hydroxy-9-methoxy	Dalbergia [2]
(±)-Medicarpin	"	Aldina [118], Dalbergia [120], Machaerium [2], Platymiscium [119]
(−)-Homopterocarpin	3,9-Dimethoxy	Baphia [4, 122], Pericopsis [2], Pterocarpus [2], Swartzia [2]
(+)-Homopterocarpin	"	Machaerium [2]
(−)-Maackiain	3-Hydroxy-8,9-methylenedioxy	Andira [2], Dalbergia [120], Diplotropis [118], Maackia [4], Sophora [129], Swartzia [2]
(+)-Maackiain	"	Aldina [118]
(±)-Maackiain	"	Aldina [118], Dalbergia [120], Pterocarpus [2], Sophora [2]
(−)-Pterocarpin	3-Methoxy-8,9-methylenedioxy	Baphia [122], Lonchocarpus [114], Pterocarpus [1], Sophora [2]
—	(−)-3-Hydroxy-4,9-dimethoxy	Swartzia [2]
—	(−)-4-Hydroxy-3-methoxy-8,9-methylenedioxy	Dalbergia [2]
—	(−)-3,4-Dihydroxy-8,9-methylenedioxy	Dalbergia [2]
—	(−)-3,4-Dimethoxy-8,9-methylenedioxy	Swartzia [2]
(−)-Phylenopteran	3,9-Dihydroxy-7,10-dimethoxy	Lonchocarpus [114]
(−)-9-Methylphylenopteran	3-Hydroxy-7,9,10-trimethoxy	Lonchocarpus [114]
(−)-2-Hydroxypterocarpin	2-Hydroxy-3-methoxy-8,9-methylenedioxy	Neorautanenia [109], Swartzia [123]
(−)-2-Methoxypterocarpin	2,3-Dimethoxy-8,9-methylenedioxy	Neorautanenia [111]
Neodulin	8,9-Methylenedioxyfurano[2,3]	Neorautanenia [2]
Ficinin	8,9-Methylenedioxyfurano[2, 3]	Neorautanenia [2]
(+)-Leiocarpin	8,9-Methylenedioxy-3,4-dimethylpyrano	Apuleia [2]
(−)-Phaseollin	3-Hydroxy-9,10-dimethylpyrano	Phaseolus [2]
(−)-Phaseollidin	3,9-Dimethoxy-10-isopentenyl	Phaseolus [125]
(−)-Neorautane	8,9-Methylenedioxy-2,3-dimethylpyrano	Neorautanenia [2]
	(−)-3-Hydroxy-2-isopentenyl-8,9-methylenedioxy	Neorautanenia [2]
(−)-Ficifolinol	3,9-Dihydroxy-2,8-diisopentenyl	Neorautanenia [110]
(−)-Folitenol	3-Hydroxy-2-isopentenyl-2,2-dimethylpyrano [2',3' : 9,10]	Neorautanenia [110]
(−)-Folinin	2,2,9,9-Tetramethyl (dipyrano[3',2' : 2,3] [2", 3" : 9,10]	Neorautanenia [110]

TABLE 8 (Continued)

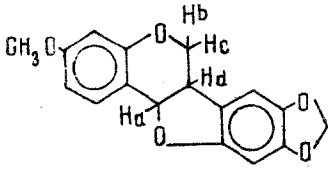
Name	Structure	Source of isolation
(−)-Gangetin	9-Hydroxy-10-isopentenyl-1-methoxy-2,3-dimethylpyrano	Desmodium [2]
Edulan	1,9-Dimethoxy-2,2-dimethylchromano[2',3' 5,6]	Neorautanenia [107]
Edudiol	3,9-Dihydroxy-2-isopentenyl-1-methoxy	Neorautanenia [107]
Neoraucarpene	2-Isopentenyl-3,4-dimethoxy-8,9-methylenedioxy	Neorautanenia [107]
Neorautanin	9-Dimethoxy-8,9-methylenedioxy	Neorautanenia [107]
Edulenol	3-Hydroxy-2-isopentenyl-1,9-dimethoxy	Neorautanenia [107]
3-De-O-methylneoraucarpene	3-Hydroxy-2-isopentenyl-4-methoxy-8,9-methylenedioxy	Neorautanenia [107]
—	3,10-Dihydroxy-9- methoxy	Platymiscium [119]
Neobanol	8,9-Methylenedioxyfurano[2,3]	Neorautanenia [108]
—	3-Hydroxy-2,9-dimethoxy	Pisum [126]
—	2,3,9-Trimethoxy	Pisum [126]
—	4-Hydroxy-2,3,9-trimethoxy	Pisum [126]
Pisatin	6a-Hydroxy-3-methoxy-8,9-methylenedioxy	Pisum [126]
Variablin	6a-Hydroxy-3,9-dimethoxy	Dalbergia [2]
6a-Hydroxyphaseollin	3,6a-Dihydroxypyrano[9, 10]	Phaseolus [1]
Dehydropterocarpin	3-Methoxy-8,9- methylenedioxy	Swartzia [2]
Trifolirhizin	3-Glucopyranosyloxy-8,9-methylenedioxy	Ononis [117], Trifolium [116]
Sophora japonicin	3-β-D-Glucosyloxy-8,9-methylenedioxy	Sophora [131]
Trifolirhizin 6'-monoacetate	6'-O-Monoacetyl-3-glucosyloxy-8,9-methylenedioxy	Sophora [129]



XVII

6aR, 11aR-(−)-Pterocarpan

In the NMR spectra of the pterocarpans it is easy to distinguish the protons of the heterocycle [2] (XVIII).



XVIII

Pterocarpin

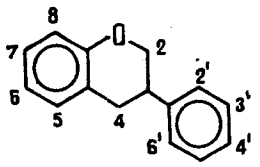
δ scale

Ha—5.45 ppm
Hd—4.19 ppm
Hc—3.63 ppm
Hd—3.43 ppm

J_{bc}=10.8 Hz
J_{cd}=10.5 Hz
J_{bd}=5.1 Hz
J_{ad}=6.9 Hz
J_{ac}=0.8 Hz
J_{ab}=0.6 Hz

In the biogenetic aspect, the isoflavans are close to the pterocarpans [2]. They have also been isolated from plants in the form of optically active isomers. (+)-Vestitol, (−)-duratin, and (−)-mucronulatone have the 2S configuration and have been isolated from Brazil-

TABLE 9. Isoflavans



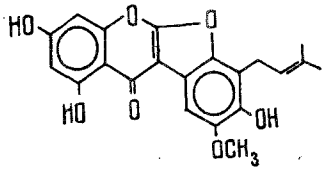
Name	Structure	mp, °C	$[\alpha]_D$, deg	Source of isolation
(—)-Duartin	3',7-Dihydroxy-2',4',8-trimethoxy	149	—25	Machaerium [133]
(—)-Mucronulatol	3',7-Dihydroxy-2',4'-dimethoxy	145	—18,5	Machaerium [133]
(+)-Mucronulatol	"	227	—	Dalbergia [133], Glycyrrhiza [132]
(+)-Vestitol	2',7-Dihydroxy-4'-methoxy	156	+21,6	Dalbergia [133], Machaerium [133]
(—)-Vestitol	"	—	—	Cyclolobium [2]
Isovestitol	4',7-Dihydroxy-2'-methoxy	—	—	Anthyllis, Lotus, Tetragonolobus [128]
Demethylvestitol	2',4', 7-Trihydroxy	—	—	"
Sativan	7-Hydroxy-2',4'-dimethoxy	—	—	"
(—)-Mucroquinone	7-Hydroxy-4',8-dimethoxy-2',5'-quinone	192	—15,4	Machaerium [133]
—	(3S)-2'-Hydroxy-4',7-dimethoxy	—	—	Dalbergia [2]
(+)-Laxifloran	4',7-Dihydroxy-2',3'-dimethoxy	63—64 (dimethyl ether)	—	Lonchocarpus [114]
(+)-Lonchocarpan	4',7-Dihydroxy,2',3',6'-trimethoxy	186—187	—	Lonchocarpus [114]
Phaseollin isoflavone	2',7-Dihydroxy-3':4'-pyrano	—	—	Phaseolus [125]
(+)-Licoricidin	2'4'-Dihydroxy-3'6-diisopentyl-7-methoxy	—	—	Glycyrrhiza [2]
(3R)-Claussequinone	7-Hydroxy-4'-methoxy-2',5'-quinone	—	—	Cyclolobium [2]
Unanisoflavone	3',7-Dihydroxy-2',4'-dimethoxy-5'-dimethylpropenyl	184	—73,5	Sophora [130]
—	(2S)-3',6,7-Trihydroxy-2',4'-dimethoxy	188—889	—17,3	Brya [134]

ian species of *Dalbergia* and *Machaerium* [2]. The dimethyl ethers of (+)-laxifloran and (+)-lonchocarpan have the R configuration at C_3 and have been isolated from the African plant *Lonchocarpus laxiflorus* [114] (Table 9). It is also possible to include among the isoflavan derivatives the isoflavan quinones: (2S)-(—)-mucroquinone from *Machaerium mucronulatum* and (3R)-claussequinone from *Cyclolobium claussenii* [33].

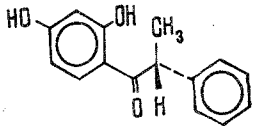
In 1976-1977, derivatives of 3-isoflavene were isolated from *Gliricidia sepium*: 2',3',7-trihydroxy-4'-methoxy-3-isoflavene (sepiol) and 2'-O-methylsepiol [135].

The rotenoids also belong to the isoflavonoid group. A distinction is made between pyranorotenoids (deguelin, tephrosin, toxicarol) pyranomethylenedioxyrotenoids (millettone), pyranorotenoids (rotenone, sumatrol, amorphin, elliptone, and malaccol), and furanomethylenedioxyrotenoids (dolineone, pachyrrhizone, and isomillettone) [136]. They have been isolated from plants of the family Leguminosae (the genera *Derris, Tephrosia, Lonchocarpus, Piscidia, Amorpha, Dalbergia, Neorautanenia, Pachyrrhizus,* and *Milletia*).

More details concerning their structure and distribution and the methods of determining their structures have been given in reviews [1, 2]. Of other isoflavonoid structures we must mention the coumaronochromone lisetin isolated from *Piscidia erythrina* (XIX) and a representative of the α-methyldeoxybenzoins — (—)-angolensin (XX) [2].



XIX



XX

The diisoflavone disain has been isolated from *Maclura aurantica* (family Moraceae) [87].

In a study of the distribution of the isoflavonoids in the family Leguminosae it is possible to establish that in the individual tribes the isoflavones are present together with some definite group of isoflavonoids [136]. For example, isoflavones + coumestans in the tribe Trifoliae, isoflavones + rotenoids in the tribe Galegeae, isoflavones + pterocarpans in the tribe Podalyriae, isoflavones + pterocarpans and isoflavanones in the tribe Sophoreae, isoflavones + pterocarpans, isoflavanones, 3-phenylcoumarins, coumestans, and rotenoids in the tribe Phaseolieae, and isoflavones + pterocarpans, isoflavanones, 3-phenylcoumarins, rotenoids, and isoflavans in the tribe Dalbergioideae. This fact is of definite interest not only for the chemotaxonomy of the family but also for studying the pathways of the biogenesis of these compounds in plants.

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ACID HYDROLYSIS OF THE HYDROXYETHYL DERIVATIVE OF THE AMYLOPECTIN STARCH OF WAXY MAIZE

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UDC 615.545(088.8)

Interest in starches and their chemical modifications has risen as the result of the appearance of reports on their successful use for medical purposes. According to the available literature information, hydroxyethylated starch (HES) is used for preparing a new blood substitute [1, 2], is being studied as a cryoprotector for erythrocytes [3-5] and other blood cells [6, 7], and is being used in leucophereses [8] and the preparation of erythrocytes [9]. To obtain HESs with different molecular weights, degrees of substitution, characteristic viscosities [η], and molecular-weight distribution, together with other methods acid hydrolysis, is used [2, 5], since the ether bonds in HESs are resistant to the action of acids and alkalis and the hydroxyethyl groups are not split off under the conditions of acid hydrolysis [10].

Continuing our investigations [11, 12] on the preparation and study of the physicochemical properties of hydroxyethyl derivatives of the amylopectin starch (HEAPS) of waxy maize [All-Union State Standard (GOST) 7697-66*], we have used acid hydrolysis to obtain a series of HEAPS hydrolysates with different physicochemical properties.

The present work was devoted to obtaining hydrolyzates of HEAPS with molecular weights of 200,000 (±20,000) and 50,000 (±5000) and a degree of substitution of 0.60-0.70, which may be of interest for their subsequent study as cryoprotectors, since there are positive results in the literature on the study as blood substitutes [2, 13, 14] and cryoprotectors [5, 15] of hydroxyethylated starches with molecular weights of 40,000-90,000 and 100,000-200,000 and degrees of substitution of 0.5-0.7. As the initial raw material for obtianing the HEAPS we used partially hydrolyzed amylopectin starch (PHAPS) with different degrees of polymerization [16].

TABLE 1. Results of the Determination of the Relative Viscosities of HEAPS during Hydrolysis

Expt. No.	Relative viscosity									
	Time of hydrolysis, min									
	0	10	20	30	40	50	60	70	80	90
1	5,9	—	2,9							
2	5,9	2,9	2,5							
3	5,8	2,9	2,7							
4	5,9	2,9	2,7							
5	5,9	2,9	2,5	2,3	—	1,9	1,8			
6	5,9	2,7	2,4	2,1	2,1	1,9	1,8			
7	5,7	2,9	2,5	2,1	—	1,9	1,8			
8	5,9	—	—	2,4	2,3	2,2	2,0			
9	5,7	2,9	—	2,3	2,1	1,9	1,9			
10	5,7	2,9	2,6	2,2	2,0	1,9	1,9			
11	11,4	3,5	2,9	2,5	2,3	2,1	2,0	1,9	1,8	1,7

Scientific-Research Institute of Hematology and Blood Transfusion, Ministry of Public Health of the USSR, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 689-692, November-December, 1978. Original article submitted June 27, 1978.

 0009-3130/78/1406-0586$07.50