and 0.045 g of zone 1 and 0.093 g of zone 2 of the trienoic compounds. Part of the fragments isolated was methylated with diazomethane and analyzed by GLC, and another part was converted by treatment with NH_4OH into the ammonium soaps and subjected to TLC on cellulose.

SUMMARY

A set of known but rarely encountered acids — the 20:0, Δ^{11}-20:1, $\Delta^{11,14}$-20:2, and $\Delta^{11,14,17}$-20:3 acids — has been found in the lipids of the seeds of *Helleborus abchasicus*, family *Ranunculaceae*.

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CIRCULAR DICHROISM OF QUINOID PIGMENTS FROM FAR EASTERN REPRESENTATIVES OF THE FAMILY BORAGINACEAE

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The electronic absorption and circular dichroism (CD) spectra of ten natural and modified quinoid pigments are described. An assignment has been made of the dichroic absorption in the 250-600 nm region of the CD spectra of the pigments investigated. It has been shown that in the solution of stereochemical questions for such compounds the most informative region of the CD spectrum is the 250-350 nm interval.

It is known that the naphthoquinones found in plants of the family Boraginaceae possess a high physiological activity. From nine Far Eastern representatives of the family we have isolated and identified eleven quinoid pigments forming derivatives of shikonin [1]. In the present paper we describe the electronic absorption and circular dichroism (CD) spectra of ten natural and modified quinoid pigments.

The parameters of the electronic absorption spectra of the pigments investigated are given in Table 1. Assignment of the bands in the 250-600 nm range of the absorption spectra is known for compounds having a naphthazarin system in their structure [2]. Small bands due to electronic transitions of the quinoid and benzenoid chromophores appear in this region (Fig. 1a). An intense broad band in the visible region of the spectrum (400-600 nm), which is responsible for the color of the naphthoquinone pigments, is due to the excitation of the p—π* transitions of the unbound electrons of the 5,8-hydroxyls of the benzenoid chromophore. The position of the maximum of this band depends on the nature of the substituent of the side chain. Thus, the replacement of the hydrogen at C-11 by a hydroxy, a chlorine atom, or an acetoxy group shifts the maximum by 2, 6 and 9 nm, respectively, into the red region (Table 1, compounds I, II, VII, and III). The passage of the 5,8-hydroxyls into the anionic form

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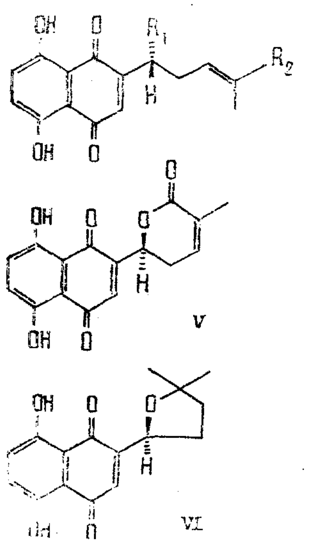
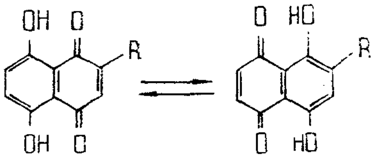


	R_1	R_2
I	H	CH_3
II	OH	CH_3
III	OAc	CH_3
IV	$O-\overset{O}{\overset{\|}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OH$	CH_3
VII	Cl	CH_3
VIII	OH	CH_2OH
IX	OH	COH
X	OH	COOH

Structure of the quinoid pigments investigated

in an alkaline medium shifts this band far into the red region, which leads to a change in the color of a solution of the pigments from red to blue [3]. The following strong band with with a maximum at 275 nm is due to a combination of the p—π* transitions of the benzenoid and the quinoid chromophores. In constrast to the 1,4-naphthoquinones and juglones which have two bands in this region (benzenoid and quinoid), the majority of the naphthazarins each gives a single band, which is connected with the tautomeric nature of the naphthazarin system:

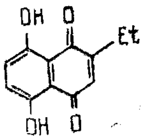


The position of this band and its intensity are practically constant for all the pigments investigated. A weak band in the absorption spectra in the 330-340 nm region is due to the excitation of electronic transitions of the quinoid chromophore. This band strongly overlaps with the band at 275 nm, which makes an accurate determination of its maximum difficult.

Since all the pigments, with the exception of deoxyshikonin (I), have an asymmetric center at C-11, they should posses chiroptic properties. Optically active compounds are usually characterized by the value of the specific rotation for the D-line of sodium, $[\alpha]_D$. The CD and optical rotatory dispersion (ORD) spectra give many times more information on their structure. There are practically no results of chiroptic methods for such systems in the scientific literature: The ORD spectrum of the naphthoquinone pigment alkannin has been given in only one paper [4], and the CD spectra of such compounds have not been studied previously.

Figure 1b gives the CD spectrum of the pigment shikonin (II), which has, as established previously [5], the R configuration of the asymmetric center. A broad positive band in the visible region of the CD spectrum of shikonin corresponds in form to the benzenoid band in the same region of the absorption spectrum (Fig. 1a). The strong positive CD band following it is due to electronic transitions of the quinoid chromophore, and to it corresponds a weak band in the 330-340 nm region of the absorption spectrum. A strong band at 275 nm in the absorption spectrum due to a combination of transitions of the benzenoid and quinoid chromophores corresponds to two bands of different signs in the CD spectrum in this region. Consequently, asymmetry at the C-11 atom leads to the separation of the transitions of these chromophores in the CD spectrum of shikonin. Since it is known that the benzenoid transition for 1,4-naphthoquinones lies in a shorter-wave region than the quinoid transition [2], the positive Cotton effect (CE) in this region of the CD spectrum is assigned to the benzenoid

TABLE 1. Electronic Absorption Spectra of the Quinoid Pigments (methanol)

Compound*	Positions and intensities of the bands		
	benzenoid	quinoid	combination
I	547(3,57),511(3,82),483(3,80)	330 (2,97)	275 (3.94)
II	551(3,60),513(3,82),484(3,78)	330 (3,05)	276 (3,88)
III	560(3,67),520(3,90),488(3,85)	330 (3,02)	276 (3,95)
IV	556(3,58),517(3,77),487(3,75)	330 (3.05)	276 (3,86)
V	557(3,23),514(3,46),487(3,44)	330 (2,74)	275 (3 59)
VI	551(3,51),513(3,74),487(3,40)	330 (2.94)	275 (3.81)
VII	556(3,50),517(3,75),489(3,73)	330 (2,96)	274 (3,93)
VIII	552(3,58),514(3,81),484(3,78)	330 (2,97)	276 (3,88)
IX	555(3,59),517(3,81),486(3,78)	330 (3,02)	278 (3,91)
X	553(3,58),514(3,80),486(3,70)	330 (3,00)	276 (3.85)
	542(3,48),508(3,71),481(3,68)	333 (2.82)	275 (3,85)

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*The absorption spectrum of 2-ethyl-5,8-dihydroxy-1,4-naphthoquinone (in methanol) [2] is given for comparison.

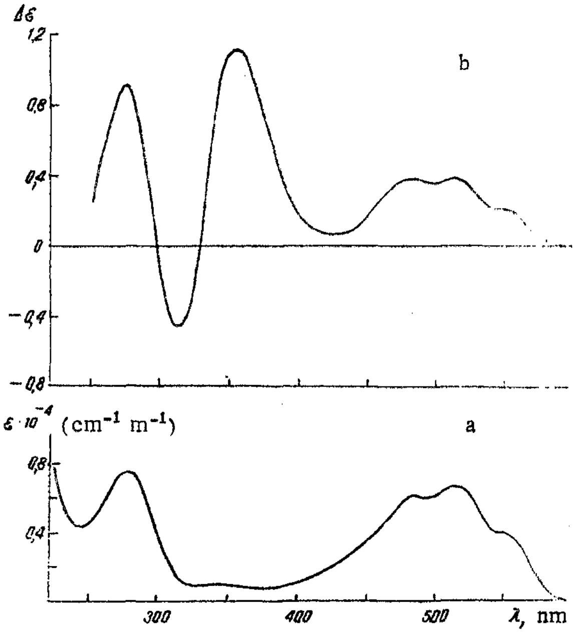

Fig. 1. Electronic absorption spectrum (a) and CD spectrum (b) of 5,8-dihydroxy-2-(1'-hydroxy-4'-methylpent-3'-enyl)naphthoquinone (shikonin) (II).

chromophore and the negative one to the quinoid chromophore. The positions and intensities of these two bands, and also of the second quinoid band of the CD spectra of the pigments investigated are given in Table 2.

In the CD spectra of pigments (III) and (IV) (Fig. 2), each containing an acyl substituent at C-11, two additional bands appear in the 400-440 nm region. These CD bands correspond with respect to their position in the spectrum to the n–π* transitions of quinoid chromophores of 1,4-naphthoquinones [6]. The presence of the acyl carbonyl in the immediate vicinity of the quinoid chromophore probably leads to a perturbation of this transition which is insignificant in the CD spectrum of shikonin (II).

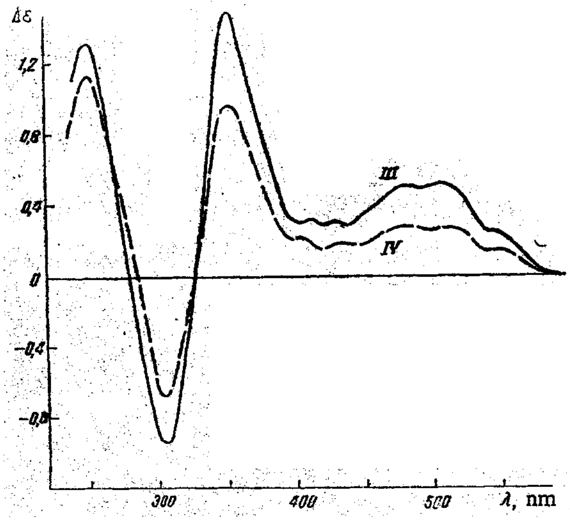

Fig. 2. CD Spectra of 2-(1'-acetoxy-4'-methylpent-3'-enyl)-5,8-dihydroxy-1,4-naphthoquinone (acetylshikonin) (III) and of 5,8-dihydroxy-2-[1'-(3"-hydroxy-3"-methylbutanoyloxy)-4'-methylpent-3'-enyl]-1,4-naphthoquinone (IV).

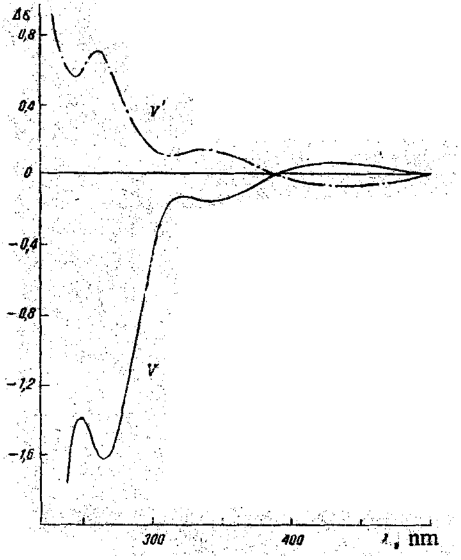

Fig. 3. CD spectra of the δ-lactone of 5-(5',8'-dihydroxy-1',4'-naphthoquinon-2'-yl)-2-enoic acid (V) and its synthetic analog (V').

The configuration of the asymmetric center of pigment (V), which was first isolated by ourselves [7], has remained unknown. To solve this problem we have synthesized from shikonin a compound corresponding to the structure of pigment (V) and having the R configuration of the asymmetric center [8]. The CD spectrum of the natural pigment (V) (Fig. 3), differing considerably from the CD spectra of the shikonin derivatives described above,* has a negative benzenoid band at 266 nm, and the quinoid band adjacent to it appears in the form of a negative minimum at 310 nm (see Table 2). The second quinoid band also a negative sign. In the visible

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*The electronic transitions of the unsaturated lactone ring of pigment (V) appear in the 200-250 nm region and, apparently, make no appreciable contribution to the region of the CD spectra under investigations (250-600 nm).

TABLE 2. Circular Dichroism Spectra of the Quinoid Pigments (in methanol)

Compound	Positions (nm) and intensities (Δε) of the CD bands		
	quinoid	quinoid	benzenoid
II	357 (+1,12)	312 (−0,46)	277 (+0,94)
III	353 (+1,48)	303 (−0,96)	250 (+1,32)
IV	354 (+0,97)	305 (−0,67)	250 (+1,08)
V	340 (−0,15)	310 (−0,13)*	266 (−1,64)
VI	345 (+0,72)	304 (+0,99)	268 (−0,92)
VII	360 (+0,22)	312 (−0,76)	268 (+0,90)
VIII	353 (+1,97)	305 (−1,08)	275 (+1,42)
IX	345 (+1,24)	295 (−1,00)	250 (+1,18)
X	348 (+1,49)	298 (−0,76)	257 (+0,86)

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*For pigment (V), a negative minimum is observed in the region of the second quinoid transition (310 nm).

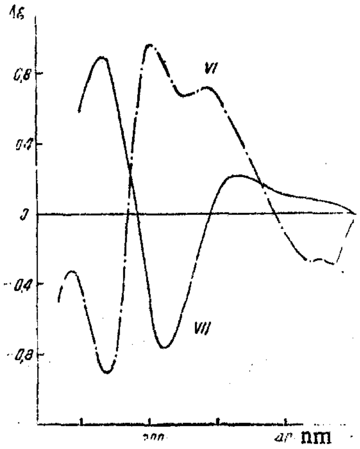

Fig. 4. CD spectra of 2-(2',2'-dimethyltetrahydrofuran-5'-yl)-5,8-dihydroxy-1,4-naphthoquinone (cycloshikonin) (VI) and of 2-(1'-chloro-4'-methylpent-3'-enyl)-5,8-dihydroxy-1,4-naphthoquinone (chloroshikonin) (VII).

region where the broad band of the benzenoid chromophore appears in the absorption spectrum (see Table 1), pigment V has no dichroic absorption. The CD spectrum of the synthetic analog (Fig. 3) is the mirror counterpart of the CD spectrum of the natural pigment. This has permitted the conclusion that the pigment under investigation (V) has the S configuration of the asymmetric center at C-11.

In the 250-350 nm region, the CD spectrum of chloroshikonin (VII) (Fig. 4) corresponds completely to the CD spectra of pigments (II)-(IV) that have been described. At the same time, the long-wave CD bands are considerably distorted, the quinoid band at 360 nm decreases sharply in amplitude and the broad band in the visible region that is characteristic for the CD spectrum of shikonin is absent. Thus, in the solution of similar sterochemical problems the most informative region of the CD spectrum is the 250-350 nm interval. Figure 4 shows the CD spectrum of cycloshikonin (VI), for which the configuration of the asymmetric center is unknown. In the 250-350 nm region it is completely opposite to the CD spectrum of shikonin (Fig. 1b) and has the same sign of the benzenoid band at ≈260 nm as the pigment (V) (see Table 2), for which we have established the S configuration at C_{11}. This feature in the CD spectra of cycloshikonin (VI) has permitted us to make the assumption of the S configuration at C_{11} of this pigment, although cyclization and hydrogenation may lead to a deviation from the interconnection of the sign of the band at 260 nm and the configuration of the asymmetric center of the pigment at C_{11} that has been found.

EXPERIMENTAL

The isolation of pigments (I)-(V) from hexane extracts of the roots and the preparation of the modified derivatives (VI)-(X) has been described previously [1, 7, 8]. The absorption spectra were recorded on a Beckman Acta MVI spectrophotometer. The CD spectra were recorded on a Jobin Yvon Dichrographe III at a concentration of the pigments of 0.5 mg/ml (methanol) in quartz cells 0.1 cm thick.

SUMMARY

1. The electronic absorption spectra of ten quinoid pigments from Far Eastern representatives of the family Boraginaceae have been described.

2. The CD spectra of natural pigments have a naphthazarin system have been investigated for the first time.

3. It has been shown that in the solution of stereochemical problems for such compounds the most informative region of the CD spectrum is the 250-350 nm interval.

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