SUMMARY

The complex mixture of glycerides of a seed oil containing oxidized acyl radicals in the triglycerides (10 groups of glycerides) has been separated for the first time. New groups of monohydroxyacyl triglycerides (oxoacyl, ∿0.1% of the oil, and hydroperoxyacyl, ∿0.1%) and di(oxyacyl)triglycerides (epoxacyl-hydroxyacyl, ∿0.36%) have been detected and isolated.

A new α-oxodienoic acid has been found for which the following structural formula is proposed as the most probable: 11-oxooctadeca-cis-9,cis-12-dienoic acid.

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THE STEREOCHEMISTRY OF TERPENOID COUMARINS

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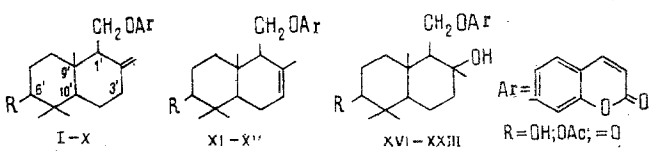
UDC 547.9:582.89

From plants of the genera *Ferula* and *Coladonia* have been isolated a number of terpenoid coumarins with an exocyclic methylene group at C_2' (farnesiferol A series) (I-X) [1-10], with an endocyclic double bond at C_2'-C_3' (conferol series) (XI-XV) [11-16], and with a hydroxy group C_2' (samarcandin series) (XVI-XXIII) [17-24] in the bicyclofarnesyl residue, and their relative configurations have been demonstrated.



Absolute configurations have been put forward for representatives of the coumarins of the farnesiferol A series — farnesiferol A (I) and gummosin (II) [7-9]. On the basis of the results of a study of spectra using paramagnetic shift reagents (PSRs) the trans linkage of

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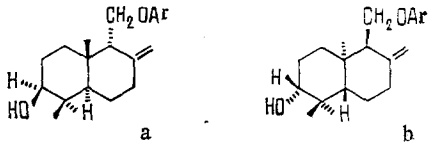
the decalin rings has been suggested for all coumarins. However, two types of trans linkage are still possible — steroid (a) and nonsteroid (b) — and no attention has been devoted to this.



a b

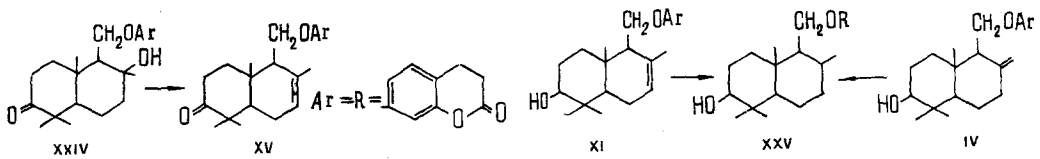
The PMR method with PSRs does not give an unambiguous result in the determination of the type of linkage. Consequently, in establishing the relative configurations of badrakemin and coladonin Perel'son et al. [7] predicted that the given stereochemistry might correspond to their mirror isomers.

Recently, the same relative configuration has been proposed for deacetylkellerin [24] as for mogoltavidin [21] and the same for ferucrin [24] as for nevskin [25]. We performed the following investigations in order to refine the stereochemistry of the known terpenoid coumarins and to determine the interconnection between the three series of coumarins.

In a study of the stereochemistry of natural compounds, especially the aporphine alkaloids, it has been shown that the sign of the specific rotation of a criterion of the absolute configuration [26-28]. On this basis, we also directed our attention to the change in the sign of rotation as a function of the stereochemistry of the terpenoid coumarins.

It is known that the molecules of the coumarins of the samarcandin series have five asymmetric centers (C_1', C_2', C_6', C_9', C_{10}') and in the coumarins of the farnesiferol A and conferol series there are four (C_1', C_6', C_9', C_{10}'). A comparison of the signs of the specific rotations of the coumarins of the farnesiferol A and conferol series (Table 1) shows that a change in the orientations of the substituents at C_1' and C_6' does not affect the sign.

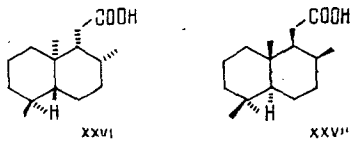
Among the coumarins of the samarcandin series there are substances with both d and l rotation. As mentioned above, the latter differ from the coumarins of the farnesiferol and conferol series by an additional asymmetric center, C_2'. It is probably just this center that makes a contribution to the change in the sign of the specific rotations in this series of coumarins. To confirm this hypothesis we dehydrated samarcandone (XXIV) with sulfuric acid in ethanol. This led to anhydrosamarcandone with l rotation, which proved to be identical with conferone (XV) [11]. Then hydrogenation of conferol (XI) and badrakemin (IV) in ethanol led to the same tetrahydro derivative (XXV), also with l rotation.



XXIV XV XI XXV IV

Thus, we have effected a transition between the three series of coumarins — the samarcandin, the conferol, and the farnesiferol A series.

Relative configurations have been proposed previously for samarcandin [24], conferol [4], and badrakemin [7-9] in which the substituents at C_1' ($-CH_2OAr$) and at C_9' ($-CH_3$) were in the cis position to one another, i.e., with the C_1' $-CH_2OAr$ group assuming the equatorial orientation. But at the same time the steroid trans linkage of rings A/B was proposed for samarcandin and conferol and the nonsteroid trans linkage for badrakemin. Consequently, the choice of one of the two types of linkages to establish the absolute configurations of the three series of coumarins is of theoretical interest. In a study of the absolute configuration of zonarol — a hydroquinone with an iresane residue — a sesquiterpene acid (XXVI) with levorotation was obtained which was compared with the dextrorotatory acid (XXVII) from ambrein and manool, and on the basis of this comparison an absolute configuration with the nonsteroid trans linkage was proposed for zonarol [29].



XXVI XXVII

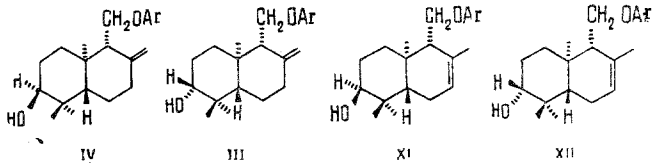
On the other hand, the same type of linkage was established on the basis of physical methods [7-9] for a coumarin derivative with an iresane residue — gummosin, the isomer of

TABLE 1. Specific Rotations of Coumarins

Farnesiferol A series		Conferol series		Samarcandin series	
Compound	$[\alpha]_D$, deg	Compound	$[\alpha]_D$, deg	Compound	$[\alpha]_D$, deg
I. Farnesiferol A	−55	XI. Conferol	−84.2	XVI. Samarcandin	+30
II. Gummosin	−54	XII. Moschatol	−77.4	XVII. Isosamarcandin	+26.75
III. Coladonin	−50	XIII. Conferol acetate	−101	XVIII. Ferucrin	+32
IV. Badrakemin	−64	XIV. Feselol acetate	−119.1	XIX. Kellerin	+66.4
V. Polanthin	−50	XV. Conferone	−51	XX. Samarcandin acetate	+32.8
VI. Polanthinin	−32			XXI. Isosamarcandin acetate	+20.5
VII. Coladin	−65			XXII. Nevskin	−79
VIII. Badrakemin acetate	−37.8			XXIII. Coladocin	−4.58
IX. Mogoltadone	−41.7				
X. Badrakemone	−42				

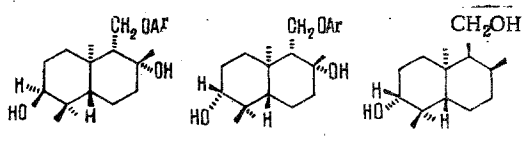
badrakemin at C_1', a substance with levorotation. Tetrahydrobadrakemin (tetrahydroconferol) and the acid from zonarol have levorotation. Consequently, in badrakemin the decalin ring in the iresane moiety has the nonsteroid trans linkage, as in zonarol. Bearing in mind the transition from samarcandin to badrakemin via conferol that we have performed, it may be concluded that they also possess this type of linkage.

On the basis of the facts given above, we propose to consider the relative configurations of badrakemin (IV) and coladonin (III) [7-9] as absolute and to adopt for conferol (XI) and moschatol (feselol) (XII) the absolute configurations with the nonsteroid trans linkage.



IV III XI XII

To determine the orientation of the methyl group at C_2' in coumarins of the samarcandin series, we compared the signs of the specific rotations of samarcandin (XVI), the saturated diol from farnesiferol A (XXVIII), and tetrahydrobadrakemin (XXV). It has been reported previously [3] that the hydrogenation of farnesiferol A forms a diol with an equatorial methyl group at C_2', although in other similar cases hydrogenation leads predominantly to the formation of substances with an axial methyl group. The anomalous dextrorotation of the diol from farnesiferol A, although it has the nonsteroid trans linkage, is explained by the equatorial orientation of the methyl group at C_2' in the saturated diol (XXVIII). Thus, it may be concluded that in the coumarins of the samarcandin series with tetrarotation the methyl group at C_2' has the equatorial orientation and the absolute configurations of samarcandin (XVI) and of isosamarcandin (XVII) are as follows:



XVI XVII XXVIII

It follows from this that the coumarins of the samarcandin series with levorotation have the axial orientation of the C_2' methyl group.

A comparison of the peaks of the ions in the mass spectra of isosamarcandin acetate and coladocin, substances with levorotation [23], showed that they differ by the relative intensities of the peaks of the $(M - 18)^+$ ions, and on this basis the authors concerned proposed a C_2' stereochemistry in coladocin. The latter differs from isosamarcandin acetate by

the axial orientation of the methyl group at C_2', which is also in harmony with our conclusion based on the differences of the signs of the specific rotations of the coumarins.

A comparison of the signs of the rotations of known coumarins shows that oxo and acetoxy substituents at C_6' do not affect the sign of the rotation, and coumarins of the conferol and farnesiferol series always have levorotation, regardless of the nature and orientation of a substituent at C_6'.

The orientation of the C_2' methyl group effects the sign of the rotation of the coumarins of the samarcandin series with a nonsteroid trans linkage, and nevskin is the first representative of the coumarins of this series with levorotation.

In view of what has been said above, it may be assumed that coladonin (III), badrakemin (IV), conferol (XI), moschatol (XV), samarcandin (XVI), and isosamarcandin (XVII) have the following absolute configurations.

Substance	Configuration	Substance	Configuration
I. Farnesiferol A	1'S,6'R,9'S,10'R	XI. Conferol	1'R,6'S,9'S,10'R
II. Gummosin	1'S,6'S,9'S,10'R	XII. Moschatol	1'R,6'R,9'S,10'R
III. Coladonin	1'R,6'R,6'S,10'R	XVI. Samarcandin	1'S,2'R,6'S,9'S,10'R
IV. Badrakemin	1'R,6'S,9'S,10'R	XVII. Isosamarcandin	1'S,2'R,6'R,9'S,10'R

Previously [21], a configuration has been proposed for mogoltavidin as an isomer of samarcandin with an axial $-CH_2OAr$ substitutent at C_1'. However, this is not in harmony with our conclusions based on the signs of the rotations.

In fact, careful measurement of the specific rotation of mogoltavidin in various solvents at various concentrations has shown that it, like samarcandin, rotates to the right. A mixture of mogoltavidin with samarcandin showed no depression of the melting point, and their PMR and IR spectra are identical. Consequently, mogoltavidin is identical with samarcandin, and mogoltavin (anhydromogoltavidin) [12] and mogoltavicin (mogoltavidin acetate) are identical with anhydrosamarcandin (conferol) and samarcandin acetate [17].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer (tablets with KBr), and the PMR spectra on a JNM-4H-100 MHz spectrometer. The R_f values are given in the chloroform–ethyl acetate (3:1) system on "Silufol-R" plates. The spots were revealed with the Kutácek reagent.

Isolation of Samarcandin. The comminuted roots of *Ferula samarcandica* collected in 1973 in the Tashkent oblast were extracted with ethanol (4 × 3 liters). The extract was concentrated, diluted with water (1:2), and treated with diethyl ether. The ethereal extract was washed successively with 5% sodium carbonate and 1% caustic soda solutions. The mother ethereal solution was washed with water, dried over Na_2SO_4, and distilled, giving 47 g of residue. Of the combined neutral substances, 22 g was deposited on a column (3 × 90 cm) containing KSK silica gel (160 nm, 1:25) and elution was performed with chloroform and chloroform–ethyl acetate (25:1). Fractions 19-26 yielded 2.4 g of samarcandin with mp 176-177°C (from ether), R_f 0.08.

Oxidation of Samarcandin. Samarcandin (0.5 g) was oxidized in acetone solution with 0.5 g of chromium trioxide. After working up, 0.37 g of the keto derivative was isolated, and it was purified on a column (1 × 25 cm) of silica gel, being eluted with chloroform. This gave 0.29 g of samarcandone with mp 216-217°C, R_f 0.21.

Dehydration of Samarcandone. A solution of 0.3 g of samarcondone in 30 ml of 10% sulfuric acid in ethanol was heated at 80°C for an hour. Then it was diluted with water and was treated with ether (3 × 100 ml). The ethereal extract was washed with 5% caustic soda solution and with water. Elimination of the solvent yielded 0.22 g of the anhydro compound. It was purified on a column of silica gel, being eluted with hexane–ethyl acetate (3:1); $C_{24}H_{28}O_4$, mp 142-143°C (from ether), R_f 0.73, $[\alpha]_D^{20}$ −50° (c 1.0; chloroform). A mixture with an authentic sample of conferone isolated from *Ferula korshinskyi* gave no depression of the melting point.

Hydrogenation of Conferol and Badrakemin. Conferol and badrakemin (100 mg each) were hydrogenated in the presence of Adams platinum oxide in ethanol. Each absorbed 2 moles of hydrogen. After the usual working up, tetrahydroconferol, $C_{24}H_{34}O_4$ with mp 194-195°C (from

ether), and tetrahydrobadrakemin, $C_{24}H_{34}O_4$ with mp 195-196°C (from ether), $[\alpha]_D^{20}$ −68° (c 1.0; chloroform), were isolated. A mixture of the tetrahydroderivatives gave no depression of the melting point.

Proof of the Identity of Mogoltavidin and Samarcandin. Mogoltavidin, $C_{24}H_{32}O_5$, mp 161-163°C [21], gave no depression of the melting point in admixture with samarcandin, $[\alpha]_D^{20}$ +24° (c 1,2; chloroform); $[\alpha]_D^{20}$ +26° (c 1.5; ethanol).

SUMMARY

A transition has been effected between three series of terpenoid coumarins. A method has been proposed for establishing the type of linkage of the rings of coumarins with the bicyclofarnesyl residue according to the sign of the rotation of the compound concerned.

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