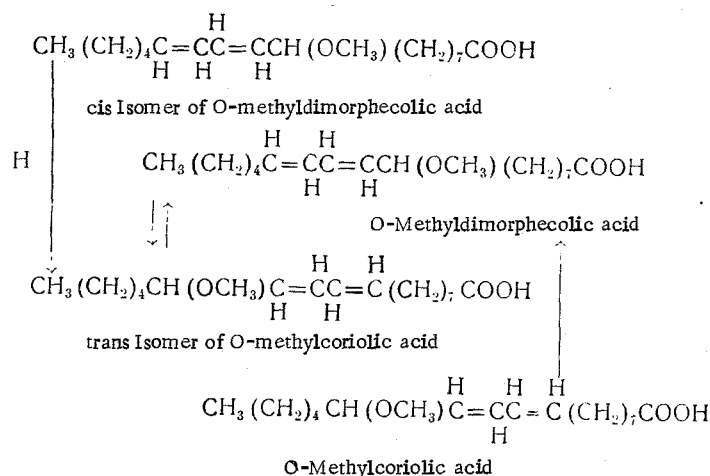# TAUTOMERISM OF THE α-HYDROXYDIENIC ACIDS OF THE
SEED OIL OF Artemisia absinthium

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In an investigation of the fatty acids of the seed oil of Dimorphotheca ecklonis, a rearrangement (Scheme 1) of the dimorphecolic acid into the trans isomer of coriolic acid was observed [1]. Simultaneously [2], the hypothesis was put forward and was later confirmed [3] of an "allyl" rearrangement of α-hydroxydienic systems with conjugated ethylenic bonds in the study of the seed oil of Tragopogon porrifolius. On methylation of the hydroxyl in these systems with 0.1 N methanolic sulfuric acid [3], the formation not only of position isomers but also of geometric isomers was observed (Scheme 1):

$$CH_3(CH_2)_4 \overset{H}{\underset{H}{C}} = \overset{}{\underset{H}{C}} C = \overset{}{\underset{H}{C}} CH(OCH_3)(CH_2)_7COOH$$

cis Isomer of O-methyldimorphecolic acid

$$CH_3(CH_2)_4 \overset{H}{\underset{H}{C}} = \overset{H}{\underset{}{C}} C = \overset{H}{\underset{H}{C}} CH(OCH_3)(CH_2)_7COOH$$

O-Methyldimorphecolic acid

$$CH_3(CH_2)_4 CH(OCH_3) \overset{}{\underset{H}{C}} = \overset{H}{\underset{}{C}} C = \overset{H}{\underset{}{C}} (CH_2)_7 COOH$$

trans Isomer of O-methylcoriolic acid

$$CH_3(CH_2)_4 CH(OCH_3) \overset{H}{\underset{}{C}} = \overset{H}{\underset{H}{C}} C = \overset{H}{\underset{}{C}} (CH_2)_7 COOH$$

O-Methylcoriolic acid

Scheme 1

On studying the α-hydroxydienic acids of the seed oil of Artemisia absinthium [4] we observed the same rearrangements, but in an α-hydroxydienic system with no O-methyl group and with a static, and not dynamic (as a result of chemical action), conjugation effect (Scheme 2).
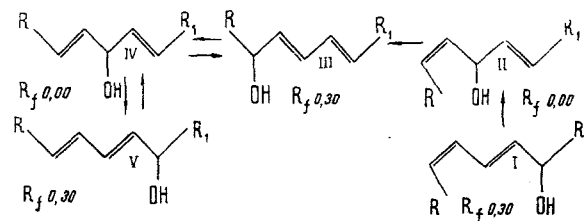
Scheme 2

We obtained a mixture of methyl esters of the fatty acids by transesterification of the triglycerides in methanol in the presence of sodium methoxide. From this mixture by ascending column chromatography we isolated two zones of methyl esters of α-hydroxydienic acids which in a thin layer had R_f values of 0.30 and 0.00.

Immediately after their elution from the chromatographic column (i.e., when they were fresh), the methyl esters with R_f 0.30 showed equal intensities of the absorption of ethanolic bonds in the infrared region of the spectrum at 980 and 947 cm^{-1}. This means that the native dienic systems had the trans,cis configuration (see Scheme 2, system 1). The same systems showed absorption in the ultraviolet at 233 nm.

The methyl esters with R_f 0.00, also in the fresh state, showed no conjugation of the ethylenic bonds, since they were transparent in the ultraviolet at 230-233 nm, and in the IR spectrum we found the absorption only of isolated trans- and cis-ethylenic bonds (955 cm^{-1} and 3050 cm^{-1}, respectively) (see Scheme 2, system II).

In the infrared and ultraviolet regions of the spectrum, the α-hydroxydienic acids obtained by methods of countercurrent distribution or preparative thin-layer chromatography or simply when subjected to any operation to determine their structure [4] showed only trans,trans-dienic conjugation (980 cm^{-1} and 231 nm) in the case of the methyl esters with R_f 0.30 and isolated trans ethylenic bonds (955 cm^{-1}) in the methyl esters with R_f 0.00. When the methods mentioned were used, geometric isomerization of the α-hydroxy-trans,cis-dienic systems I into the more thermodynamically stable systems III, IV, and V took place.

System II proved to be even more unstable. It was very difficult to detect the presence of cis-isolated bonds in the methyl esters with R_f 0.00, requiring a considerable degree of care in the preparation of the corresponding substances for recording their IR spectra. Furthermore, continuous monitoring by thin-layer chromatography (TLC) in various stages of the investigation showed that the methyl esters with R_f 0.30 form methyl esters with migration characteristics corresponding to R_f 0.00 (see Scheme 2). Thus, geometric and position isomerization take place simultaneously.

Methyl esters having trans-isolated ethylenic bonds (with system IV) are stable compounds in the presence of the static conjugation effect. After their isolation by preparative TLC, we investigated them in the way described below.
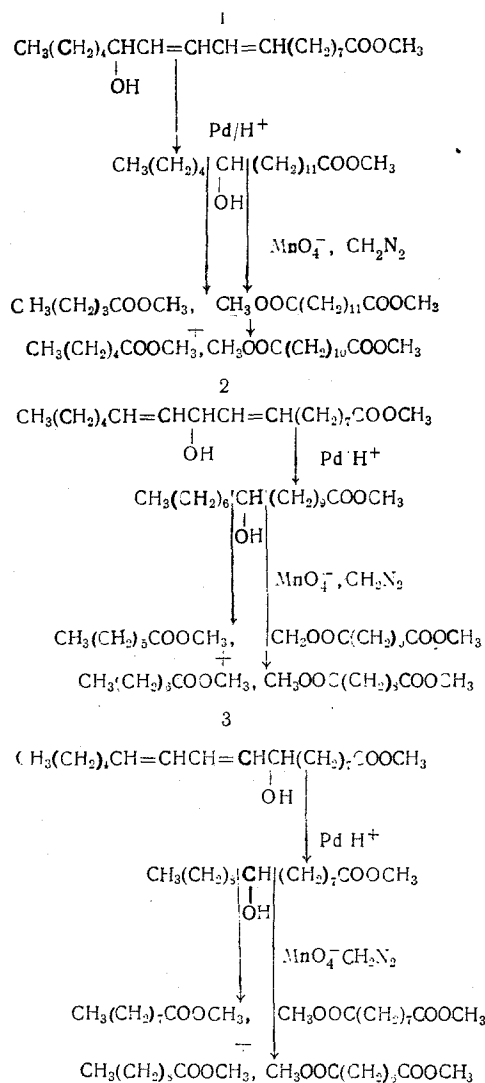
In an attempt to determine the position of the hydroxy group in the methyl esters having R_f 0.00, we hydrogenated the ethylenic bond and destructively oxidized the saturated derivatives (Scheme 3). Degradation fragments shown in the scheme were detected in the form of monomethyl esters of the monocarboxylic acids and dimethyl esters of the dicarboxylic acids by gas-liquid chromatography at 120 and 200°C.

The degradation fragments of group 2 showed that the methyl esters with system I gave the saturated derivative methyl 11-hydroxyoctadecanoate. In addition to this, the degradation fragments of groups 1 and 3 showed that the products of the hydrogenation of the methyl α-hydroxyoctadecadienoate with system IV included methyl 13-hydroxyoctadecanoate and methyl 9-hydroxyoctadecanoate. Consequently, the hydrogenation process in the presence of a dynamic conjugation effect is preceded by the formation of two isomers with conjugated ethylenic bonds, namely the methyl α-hydroxyoctadecadienoates of groups 1 and 3 (see Scheme 3).

We obtained the same degradation fragments from the oxidation of the saturated derivatives of the methyl α-hydroxyoctadecadienoates having R_f 0.30. (See scheme 3 on following page).

Similar fragments were obtained in the oxidative degradation of the products of the hydrogenation of coriolic acid and the cis isomer of dimorphecolic acid (see Scheme 1) isolated from the oil of Tragopogon porrifolius [5]. Here, no formation of the fragments of group 2 was detected. However, it is not difficult to notice that the 1 → 2 transition (see Scheme 3) is an allyl rearrangement [6, 7] which, as is well known, takes place so readily that it is possible to speak of true tautomerism. The reverse process 2 → 1 is just as likely as the rearrangements 2 → 3 and 3 → 2. As can be seen, the allyl rearrangements take place with the formation of three α-hydroxydienic position isomers of groups 1, 2, and 3 after the isolation of even one of them from the natural raw material. This takes place particularly readily on chemical action.

On subjecting the methyl esters of the α-hydroxydienic acids to dehydration, we likewise [8] did not achieve the complete conversion of the hydroxydienic system into a conjugated trienic system. The degradation products absorbed in the ultraviolet at 231, 261, 271, and 282 nm. Consequently, in addition to the appearance of the conjugation of three ethylenic bonds (261, 271, and 282 nm) as a result of 1,2-elimination, part of the undehydrated system IV (see Scheme 2) was retained, then being a source for the formation of systems

1

$CH_3(CH_2)_4CHCH=CHCH=CH(CH_2)_7COOCH_3$
|
OH

| Pd/H$^+$

$CH_3(CH_2)_4CH(CH_2)_{11}COOCH_3$
|
OH

| MnO$_4^-$, CH$_2$N$_2$

$CH_3(CH_2)_3COOCH_3$, $CH_3OOC(CH_2)_{11}COOCH_3$
$CH_3(CH_2)_4COOCH_3$, $CH_3OOC(CH_2)_{10}COOCH_3$

2

$CH_3(CH_2)_4CH=CHCHCH=CH(CH_2)_7COOCH_3$
|
OH | Pd H$^+$

$CH_3(CH_2)_6CH(CH_2)_9COOCH_3$
|
OH

| MnO$_4^-$, CH$_2$N$_2$

$CH_3(CH_2)_5COOCH_3$, $CH_2OOC(CH_2)_9COOCH_3$
$CH_3(CH_2)_3COOCH_3$, $CH_3OOC(CH_2)_9COOCH_3$

3

$CH_3(CH_2)_4CH=CHCH=CHCH(CH_2)_7COOCH_3$
|
OH |

| Pd H$^+$

$CH_3(CH_2)_5CH(CH_2)_7COOCH_3$
|
OH

| MnO$_4^-$ CH$_2$N$_2$

$CH_3(CH_2)_7COOCH_3$, $CH_3OOC(CH_2)_7COOCH_3$
$CH_3(CH_2)_5COOCH_3$, $CH_3OOC(CH_2)_5COOCH_3$

Scheme 3

III and V (231 nm). In actual fact, among the dehydration products we detected methyl esters of octadecatri-
enoic acids (paper chromatography, Rf 0.72; TLC, Rf 0.98) and methyl esters of α-hydroxydienic acids (paper
chromatography, Rf 0.93; TLC, Rf 0.00 and 0.30). This shows that the mixture of isomers includes an isomer
with nonconjugated ethylenic bonds.

The intensity of the absorption of the methyl esters of the α-hydroxydienic acids in the ultraviolet varied
constantly and did not correspond to 100% of the above-mentioned esters with conjugated ethylenic bonds having
Rf 0.30. The same phenomenon has been observed previously [9] but was not discussed. However, depending
on the interval of time that had passed from the moment of isolation of the esters to the recording of their ul-
traviolet spectrum, as a result of an allyl rearrangement a certain amount of hydroxydienic isomer with noncon-
jugated ethylenic bonds was formed. The fact that no oxidative changes took place in this process is shown by
the retention of the elementary composition and the formation of the same degradation fragments that were ob-
tained in the oxidative cleavage of the α-hydroxydienic acids with conjugated ethylenic bonds: caproic and
azelaic fragments.

The following characteristics were also obtained for the methyl ester of an α-hydroxydienic acid with
nonconjugated ethylenic bonds (Rf 0.00). The elementary composition and the molecular weight of 310 (mass
spectrum) of the methyl ester corresponds to the empirical formula $C_{19}H_{34}O_3$. The fragments from oxidative
degradation – caproic and azelaic acids – show the location of the α-hydroxydienic system between the 13th and
19th carbon atoms. In addition to this, the addition of hydrogen in the presence of Pd/Al with the formation of
methyl esters of monohydroxyoctadecanoic acids of groups 1, 2, and 3 with a molecular weight of 314 (mass

527

spectrum) shows the presence of two ethylenic bonds between the 13th and 9th carbon atoms. IR spectrum (ν_{max}, cm^{-1}): 3600-3000, 1180, 1100 (secondary hydroxyl), 2940, 1410, 1380 (methyl group), 2870, 1460, 725 (methylene group), 1740 (ester group), 1440, 1250, 1135, 1180 (methylene of $-CH_2COO-$) and 1640 and 955 (isolated trans-ethylenic bonds). There is transparency in the ultraviolet in the region of conjugated ethylenic bonds.

The information that we have obtained has permitted some change in ideas on the tautomeric transformations of α-hydroxydienic systems described previously [3] in connection with the observation of the dynamic conjugation effect appearing in the process of methylation at the hydroxy group. Thus, while previously [3] the hypothesis was put forward of the existence of a delocalized pentadienyl carbonium ion as an intermediate in the "allyl" rearrangement of α-hydroxydienic systems with conjugate ethylenic bonds, in the present paper we have shown the actual existence of an intermediate with relative stability in the presence of the static conjugation effect which contains the 11-hydroxy-trans,trans-9,12-dienic systems formed from a 13-hydroxy-cis, trans-9,11- or a 9-hydroxy-trans,cis-10,11-dienic system.

At the same time, we can call the "allyl" rearrangement a double allyl rearrangement, since the observed simultaneous position and geometric isomerization is based on two such rearrangements.

The tautomeric transformations and the conditions of their occurrence are in harmony with information obtained previously [4]. On isolating the methyl esters of the fatty acids by transesterification of the oil, we obtained the native methyl esters of α-hydroxyoctadeca-trans,cis-dienoic acids. On isolating the fatty acids [4] by alkaline hydrolysis (followed by the decomposition of the soaps with 10-15% sulfuric acid), as was to be expected in the case of a dynamic conjugation effect, we obtained α-hydroxy-trans,trans-dienic position and geometric isomers of the native α-hydroxyoctadeca-trans,cis-dienoic acids. It follows from the facts given that the free α-hydroxydienic system behaves in an acid system in the same way as its O-methyl derivative and that the native acids of the oil of the seeds of Artemisia absinthium have the cis,trans configuration.

EXPERIMENTAL

The conditions for isolating the oil, for periodate−permanganate and permanganate degradation, for hydrogenation, dehydration, paper chromatography, gas−liquid chromatography, and spectroscopy have been described previously [4]. Thin-layer and descending column chromatography on KSK silica gel (150 and 100 mesh, respectively) were performed in the hexane−diethyl ether (8:2) system [8].

SUMMARY

On investigating the α-hydroxydienic acids of the oil of the seeds of Artemisia absinthium, we observed tautomeric transformations of the free α-hydroxydienic systems. It has been shown that the tautomerism of these systems is the result not only of a dynamic but also of a static conjugation effect. 11-Hydroxyoctadeca-trans,trans-9,12-dienoic acid, which is formed by the geometric and position isomerization of α-hydroxyoctadecadienoic acids with the trans,cis conjugation of the ethylenic bonds and is relatively stable in the presence of a static conjugation effect has been detected.

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