MICROBIOLOGICAL REDUCTION OF 8,14-SECO-D-HOMO-$\Delta^{1,3,5(10),9(11)}$-ESTRATETRAEN-3-OL-14,17a-DIONE METHYL ETHER AND STEREOCHEMISTRY OF THE COMPOUNDS FORMED*

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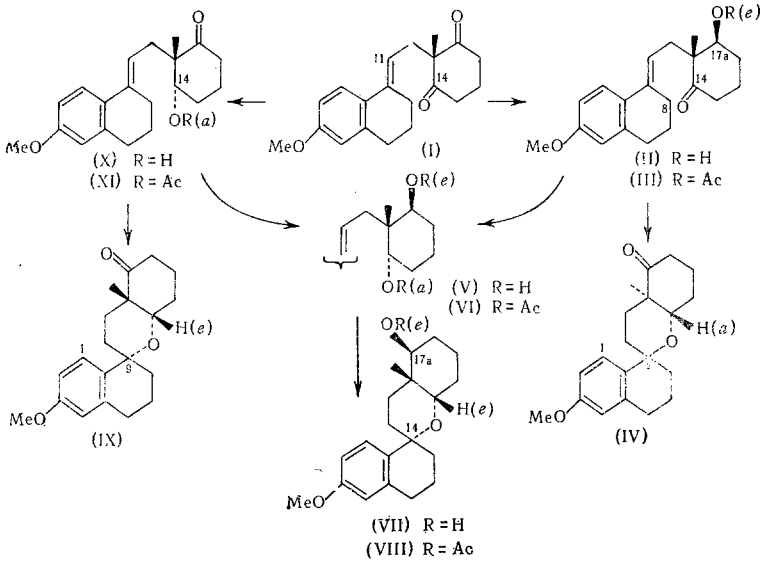
To further explore the use of microbiological methods in the synthesis of optically active D-homosteroids [1], we have studied the reduction of the methyl ether of 8,14-seco-D-homo-$\Delta^{1,3,5(10),9(11)}$-estratetraen-3-ol-14,17a-dione (I) by several yeast strains.

The fermentation of Saccharomyces carlsbergensis Dekker VKMU-355 with the dione (I) gave the compound (II). The IR spectrum of (II) contains absorption bands due to the presence of a keto group (1690 cm^{-1}) and of a hydroxyl group (3425 cm^{-1}). The molecular weight of (II) is two units higher than that of the starting dione. The preservation of the 9.11 double bond in (II) has been confirmed by its PMR spectrum which displays a vinyl proton signal at 5.6 ppm (cf. Table 1) [2]. According to these data, (II) is an 8,14-seco-17a-hydroxy-14-ketone.



Scheme 1

The determination of the absolute configuration of (II) by the method published by Horeau and Kagan [3] has shown that the hydroxyl group in the compound (II) has S-configuration (notation according to [4]). The IR spectrum of the acetate (III) contains absorption bands of a keto group in a six-membered ring (1708 cm^{-1}) and of an acetate (1740 cm^{-1}) and the absorption band of the hydroxyl group is missing. The structure (III) has been confirmed by the UV and PMR spectral data. In the PMR spectrum of the ketol (II) the

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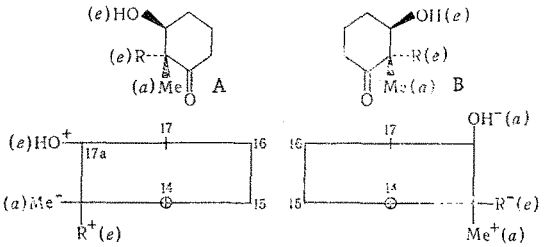
TABLE 1. Values of Chemical Shifts in the PMR Spectra (ppm)

Substance	Solvent	18–Me	MeO	14–H†	17a–H†	11–H	1–H‡
I	$CDCl_3$	1,25	3,75	—	—	5,65	7,45
II	CCl_4	1,1	3,67	—	—	5,6	7,25
III	CCl_4	1,05	3,6	—	4,85(10)	5,4	7,1
III	C_6H_6	1,15	3,35	—	5,13(9)	5,83	—
IV*	CCl_4	1,36	3,72	3,56(20)	—	—	7,45
IV*	C_6H_6	1,19	3,45	3,57(15)	—	—	—
V	$CDCl_3$	1,02	3,78	—	—	6,05	7,25
V	C_6H_6	1,25	3,4	4,0	4,25	—	—
VI	CCl_4	1,02	3,8	5,05	5,05	5,95	7,6
VI	C_6H_6	0,99	3,38	5,2	5,2	—	—
VII	CCl_4	0,85	3,66	3,1(9)	4,15(21)	—	7,38
VII	C_6H_6	0,87	3,46	3,6(5)	4,4(18)	—	—
VIII	CCl_4	0,95	3,75	—	5,5(18)	—	7,55
VIII	C_6H_6	0,92	3,3	3,55(5)	5,85(18)	—	—
IX	$CDCl_3$	1,2	3,76	4,05(6)	—	—	7,25
IX**	CCl_4	1,05	3,65	3,85(6)	—	—	—
IX	C_6H_6	0,85	3,3	3,65(6)	—	—	—
X	CCl_4	1,1	3,7	4,05(9)	—	5,6	7,3
XI	CCl_4	1,15	3,73	5,0(9)	—	5,6	7,35

*The spectrum was determined at 100 MHz using a JNM 4H-100 NMR spectrometer.
†The widths of the signals are given in parentheses (in Hz).
‡The chemical shift of the center of the doublet is given.
**The spectrum given is for the racemate (9).

signal of the proton at 17a-C coalesces with the signal of the protons of the methoxy group. In the acetate (III), the 17a-H resonates at 5.13 ppm. However, it was impossible to determine the nature of the proton on the basis of the signal width because its width (an unresolved multiplet, 9 Hz) represents an intermediate between the values corresponding to the widths of the signals of axial and equatorial protons, respectively [5]. This is due to an easy conversion of the "chair–chair" ring in the seco compounds (II) and (III). As we shall show later, during the transformation of the seco compounds into 9,14-spiroethers (in which no conversion takes place), the proton at the oxygen-bearing carbon atom is clearly characterized by its signal width and the ketol (II) gives the spiroether (IV) with an axial proton. An inspection of the ring D (Scheme 2, A) shows that, in agreement with the octant rule [6], the contribution of the methyl group to the optical activity of the system



Scheme 2

is negative whereas the contributions of the hydroxyl group and of the hydrocarbon chain bearing the rings A and B are positive. It is not possible to quantitatively estimate the magnitudes of these individual contributions; however, one can assume that the sum of the contributions of the hydroxyl group and of the chain which is close to the chromophore will be higher than the contribution of the methyl group. Hence, the optical rotatory dispersion curve ought to exhibit a positive Cotton effect whereas the enantiomer B should display a negative Cotton effect [7]. And indeed, the seco ketol (II) gives a curve with a small positive Cotton effect for the carbonyl chromophore. At the time when the present work was almost completed, a patent has been published [8] in which the ketol (II) is mentioned without any information concerning the determination of its structure; however, its melting point and $[\alpha]_D$ are in agreement with those of our ketol (II). The treatment of the ketol (II) with p-toluenesulfonic acid [9] gives the chromatographically more mobile isomeric (IV). The IR spectrum of (IV) contains a carbonyl absorption band and the hydroxyl absorption band is missing. The PMR spectrum of (IV) showed the presence of a vinyl proton. The assumption that (IV) is an internal ether was confirmed by the presence of absorption at 1080 cm^{-1} in its IR spectrum which is characteristic of an ether band [10]. This band is missing in the IR spectra of the ketol and its acetate. In the PMR spectrum of (IV), the area belonging to the signal of the proton at the oxygen-bonded carbon atom corresponds to a single proton; hence the oxygen atom is bonded to the tertiary 9-C and not to 11-C.

The signal width (20 Hz) shows that the proton is axial [5]. The optical rotatory dispersion curve of the spiroether (IV) has a positive Cotton effect for the carbonyl chromophore which is in agreement with the sign predicted for (IV) according to the octant rule [6].

A higher yield of the ketol (II) was obtained using Saccharomyces cerevisiae VKMU-488. The fermentation performed in flasks yielded a small amount of the starting dione (I), the seco ketol (II), and a negligible amount of the more polar compound (V). The fermentation with the same yeast strain performed in a fermentor with intensive aeration led to a faster reduction of the dione (I) and to an increased yield of the compound (V) whose molecular weight is four units higher than that of (I). The IR spectrum of (V) does not contain any absorption bands of a keto group and has a hydroxyl group absorption band. The PMR spectrum confirms the presence of a double bond in the 9,11 position. When the PMR spectrum is taken in benzene it exhibits two averaged ("chair–chair" conversion) coalescent signals of protons bonded to hydroxyl-bearing carbon atoms (4.00 and 4.25 ppm). It follows from these data that (V) is an 8,14-seco-14,17a-diol. The acetylation of the diol (V) gives the diacetate (VI), the structure of which was confirmed by its IR spectrum (absence of a hydroxyl group, two acetoxy carbonyls present). The PMR spectrum of (VI) contains an averaged unresolved signal of protons at 14-C and 17a-C, with an area corresponding to two protons. A chromatographic inspection of the fermentation course shows that the diol (V) can be transformed into the hydroxyspiroether (VII). The fermentation of Saccharomyces uvarum Beijerink VKMU-528 with the dione (I) gave (II), ketospiroether (IV), and hydroxyspiroether (VII). The acetylation of the mother liquor from (II) yielded (III).

The 9,14-spiroether structure of (VII) was confirmed by its IR spectra. The PMR spectrum contains the signals of two protons at carbon atoms bonded to oxygen, viz., the signal of an axial proton (4.4 ppm, 18 Hz) and of an equatorial proton (3.6 ppm, 5 Hz); the signal of a vinyl proton is absent. The determination according to Horeau's method [3] has shown that the hydroxyl group in the compound (VII) has S-configuration. In order to determine which of the oxygen atoms participates in the formation of the ether bond, the hydroxyspiroether (VII) was transformed into its acetate (VIII). The chemical shift of the equatorial proton signal in the PMR spectrum of (VIII) is identical with the chemical shift of the equatorial proton in the spectrum of hydroxyspiroether (VII) whereas the axial proton of (VIII) resonates in a weaker field when compared with the axial proton of the hydroxyspiroether (VII). Consequently, the group undergoing acetylation is the equatorial hydroxyl group whereas the axial hydroxyl group participates in the formation of the ether bond [11]. Taking into consideration the S-configuration of the hydroxyl group in (II), the determination of the stereochemistry of hydroxyspiroether (VII) and its acetate (VIII) made it possible to unequivocally assign the configurations to the hydroxyl groups in the seco diol (V) and its acetate (VI).

All fermentations described so far produced a ketol with the same specific rotation (within the experimental error). This finding confirms the optical purity of the compound thus obtained. However, the reduction is not always so specific. The incubation of quiescent cells of Candida robusta VKMU-367 with the dione (I) gave the racemic ketol (II). However, the same experiment yielded also the diol (V) with a positive rotation* which upon treatment with p-toluenesulfonic acid gave the hydroxyspiroether (VII). Thus, the microbial reduction gave a ketol with an axial hydroxyl group. When pressed baker's yeast was used for the transformation of the dione (I), workup after the incubation gave the optically active spiroether (IX) whose IR and PMR spectra were identical with those of the racemic spiroether previously described [9].

The width of the PMR signal of the proton bonded to the oxygen-bearing carbon atom in (IX) is 6 Hz and shows that this proton is equatorial. The optical rotatory dispersion curve of the ketospiroether (IX) exhibits a weak positive Cotton effect for the carbonyl chromophore, thus confirming the absolute configuration of (IX) [similarly as in the above case of (IV)]. The chromatograpic analysis shows that the spiroether (IX) is formed in the fermentation medium from the corresponding ketol (X).

The formation of the axial alcohol was also observed in the fermentation of Saccharomyces carlsbergensis var. valdensis Dekker VKMU-367. One of the compounds isolated in this fermentation was (IX). According to its chromatographic mobility, the other isolated compound is an unstable ketol which on standing in solution (and sometimes even in the crystalline state) is transformed into the spiroether (IX). This confirms the structure of the ketol as (X). As a rule, the PMR spectra of various samples of the corresponding racemic ketol (9) contain no vinyl proton signals, or the area belonging to this signal is

* There is a misprint in the preliminary communication [1]. The seco diol (IV) has $[\alpha]_D$ + 13° and not −13° as erroneously stated.

much smaller than one would expect for one proton. This can be explained as due to the formation of a 9,14 ether bond during the storage of the ketol or during the measurement of the spectra. Similarly as in the case of (III), the facile "chair–chair" conversion leads to an averaging of the 14-H signal in the PMR spectrum of the racemic ketol [9] and the acetate (XI).

It is known [12-14] that in the case of cyclohexane systems axial protons display an upfield shift of the signal when compared with their epimers owing to the effect of the magnetic susceptibility anisotropy of C–C bonds. Thus, the 14-H absorbs at 3.85 ppm in the spiroether (IX) and at 3.6 ppm in (IV). This can serve as a confirmation of the configuration of C–O bonds determined from the 14-H signal width.

A shielding of the angular methyl group in the PMR spectra of the spiroethers (IV) and (IX) is observed when changing the solvent from deuterochloroform to benzene ($\Delta = \delta_{CDCl_3} - \delta_{C_6H_6}$ being +0.27 and +0.35 for (IV) and (IX), respectively). In the case of (VII), which contains no carbonyl group, Δ = +0.03. The upfield shift of the 18-Me signal in benzene confirms the axial configuration of the methyl group adjacent to the carbonyl group [15].

It can be shown on Dreiding's models of the ketols (II) and (X) and of the diol (V) that the accessibility of the monocyclic residue for the formation of a 9,14 bond is much more difficult from the β-region than from the α-region both in axial and equatorial S-alcohols. Another situation exists in the case of R-alcohols where the formation of an ether bond is easier from the β-region. Thus, in the case of the seco ketol (II) the approach of a ring from the β-region is hindered by the nearness of 18-Me and 8-C, whereas in the seco ketol (X) the plane of the ring D is superimposed upon 8-C. It can be seen from the models that the spiroethers (IV), (IX), and (VII) containing an ether bond in the β-region are sterically hindered. Also, it is clear from the models that the heterocyclic ring has the chair conformation.

In the spiroether (IV), the 1-H signal in its PMR spectrum gives rise to a doublet at 7.45 ppm which appears at 7.05 ppm in (IX). The steric arrangement of the rings A and D in the hydroxyspiroether (VII) and its acetate (VIII) is the same as in (IX); however, because of the absence of a keto group, the chemical shift of 1-H is of the same order as that in the ketospiroether (IV) (7.38 and 7.55 ppm, respectively). The upfield shift of the 1-H signal in the spectrum of (IX) is caused by the effect of an adjacent carbonyl group and is possible only if the ether bond is formed from the α-side of the ring B. Since 1-H in (IV) absorbs at a lower field, it can be concluded that the keto group is distant from 1-H (taking into consideration the S-configuration in the case of 14-C) and that the ether bond is also in the α-region of the ring B. Consequently, the ether bond must be in the β-region in spiroethers formed from the corresponding R-alcohols.

A calculation [16] of the effect of the aromatic ring anisotropy upon the chemical shifts of 18-Me (δ_{an}) gives the values of δ_{an} 0.0, 0.0, and +0.19 for S-(IX), S-(VII), and S-(IV), respectively, whereas the corresponding values for their hypothetical 9-epimers are +0.26, +0.25, and +0.13, respectively. The experimental downfield shift of the 18-Me signal in (IV) when compared with (IX), $\Delta^{CCl_4}_{(IV)-(IX)}$ = +0.31, is higher than the calculated value (+0.19) owing to the effect of the ether-bonded oxygen in (IV); however, its sign confirms the steric structures of (IV) and (IX) because in the case of the 9-epimers the shift of the 18-Me signal must be of the opposite sign when going from (IV) to (IX).

Transformations of the dione compounds of the type (I) can be useful in the studies of relationships between the taxonomy of microorganisms and their biochemical activity. The studies of the reduction of the dione (I) involve not only the type of the reactions but also its absolute stereospecificity. Our data show that varieties of the same strain can reduce the dione (I) to alcohols with various configurations of the hydroxyl group.

EXPERIMENTAL

The analytical methods were described earlier [9]. The optical rotatory dispersion spectra and specific rotations were determined in ethanol on a Cary-60 instrument, unless otherwise stated. The seed was cultivated for two days in a wort (7.5 Balling) at 29°C on a rocking apparatus. The seed for the fermentation in a fermentor was cultivated in wort agar matrices.

The transformation of (I) was carried out in flasks containing 250 ml of yeast cultures grown during 24 h in a wort or in a steel fermentor, with stirring and aeration. The seco dione was introduced in ethanol (0.5 g/ml). When the fermentation had been finished, the material was extracted with ether, the extract was dried over magnesium sulfate, concentrated under reduced pressure, and chromatographed on a

column of aluminum oxide with petroleum ether, a petroleum ether–benzene mixture, benzene, and a benzene–diethyl ether mixture as eluents.

In all cases where a name of the compound is not accompanied by a number, only chromatographic identification of the substance was performed without any determination of its configuration.

The yeast cultures were obtained from the Institute of Microbiology Academy of Sciences of the USSR.

Fermentation of Saccharomyces carlsbergensis Dekker VKMU-355. The fermentation was carried out in 13 flasks containing 100 mg of (I) each. After five days, the extract was concentrated to give an oil which was treated with ether, the amorphous precipitate was then removed, and the solution was chromatographed on 160 g of aluminum oxide. Elution yielded 190 mg of a resin, 25 mg of a mixture of a spiroether and (I), 52 mg of the spiroether, 50 mg of a mixture of the spiroether and (II), and 307 mg of (II), mp 101-115°C. Recrystallization from methanol and subsequent thin-layer chromatography (TLC) on silica gel gave (II), mp 116-110°C; $[\alpha]_D$ + 33° (C 0.1); mol. wt. 314. UV spectrum: λ_{max} (nm) 266 (ε 19000). IR spectrum (cm^{-1}): 1685, 3430.

A portion of 65 mg (II) was acetylated with acetic anhydride in pyridine for 18 h. Workup and TLC on silica gel gave 49 mg of (III) as an oil, $[\alpha]_D$ − 16° (C 0.135). IR spectrum (cm^{-1}): 1710, 1740.

Fermentation of Saccharomyces cerevisiae VKMU-488. The fermentation was carried out in 20 flasks containing 25 mg of (I) each. After two-days' fermentation, the chromatography of the mixture on aluminum oxide yielded 30 mg of (I), 242 mg of (II) as an oil which crystallized on standing at 0°C for two days, and 36 mg of a mixture of (II) and (V). Recrystallization from methanol gave (II), mp 113-117°C; $[\alpha]_D$ + 29° (C 0.12).

Acetylation of 50 mg of (II) afforded 55 mg of (III) as an oil which crystallized at 0°C. Recrystallization from methanol gave 42 mg of (III), mp 119-122°C.

Fermentation of Saccharomyces cerevisiae VKMU-488 with 7.5 g of (I) in a fermentor gave 1.5 g of the ketol (II), mp 108-112°C, and 3.9 g of the diol (V), mp 111-120°C.

Fermentation of Saccharomyces uvarum Beijerink VKMU-528. The fermentation was run for four days in 13 flasks containing 100 mg of (I) each. The chromatography on aluminum oxide gave 66 mg of the crude ketospiroether (IV), 227 mg of the crude (II), and 518 mg of the crude (VII). After TLC on aluminum oxide, the crude fractions gave 70 mg of (II), mp 115-119°C (from methanol); $[\alpha]_D$ + 31° (C 1; $CHCl_3$), and TLC on silica gel (benzene–acetone, 10:1.5) gave 197 mg of (VII) as an oil, $[\alpha]_D$ − 29° (C 0.12). UV spectrum: λ_{max} (nm) 275, 283 (ε 1640 and 1590, respectively). IR spectrum (in a thin layer) (cm^{-1}): 3430.

Fermentation of Candida robusta VKMU-347. The yeast cultivated in a fermentor in 6 liters of wort, separated from the culture medium by centrifugation, and suspended in 3 liters of a 5% solution of glucose in a phosphate buffer (pH 7.1) containing 300 mg of streptomycin, was incubated for seven days with 3 g of (I) to give 154 mg of a mixture of (I) and the ketospiroether, 1.02 g of the crude ketol, and 590 mg of a mixture of ketol and diol. The crude ketol was recrystallized three times from ethyl acetate and yielded 464 mg of (II), mp 115-118°C; $[\alpha]_D$ 0° (C 1.0). The chromatography of the ketol–diol mixture on aluminum oxide gave 208 mg of (V), mp 132-137°C (from ethyl acetate); $[\alpha]_D$ + 15° (C 1; $CHCl_3$).

Fermentation of Saccharomyces carlsbergensis var. valdensis Dekker VKMU-367. The fermentation of the yeast (3 days) in 34 flasks containing 50 mg of (I) each and subsequent chromatography on aluminum oxide gave 133 mg of (VII), an amorphous substance, mp 44-48°C; $[\alpha]_D$ − 33° (C 1.2; $CHCl_3$). UV spectrum: λ_{max} (nm) 269 (ε 11600). IR spectrum (in a thin layer) (cm^{-1}): 3450. Also isolated were 29 mg of (V), mp 125-131°C (from ethyl acetate); $[\alpha]_D$ + 13° (C 1.0). UV spectrum: λ_{max} (nm) 265 (ε 35200). IR spectrum (cm^{-1}): 3460. In another experiment, (IX) was isolated along with (V) and (VII).

The acetylation of (VII) gave (VIII), mp 150-153°C (from ethyl acetate); $[\alpha]_D$ + 27° (C 1; $CHCl_3$). UV spectrum: λ_{max} (nm) 275 (ε 1331). IR spectrum (cm^{-1}): 1740.

Fermentation with Baker's Yeast. The incubation of a suspension of pressed baker's yeast in 16 flasks each of which contained 4.12 g of the yeast, 10.2 g of sucrose, and 50 mg of (I) in 100 ml of water, and subsequent three times repeated TLC on aluminum oxide gave 29 mg of (IX), mp 149-153°C (from ethyl acetate); $[\alpha]_D$ − 57° (C 1; $CHCl_3$). UV spectrum: λ_{max} (Nm) 275, 282 (ε 1800 and 1700, respectively). IR spectrum (cm^{-1}): 1705, 1080.

Preparation of (IV) from (II). A solution of 375 mg of the crude (II) and 20 mg of p-toluenesulfonic acid in 50 ml of benzene was stirred for 20 min, filtered through aluminum oxide, and evaporated to give 360 mg of an amorphous substance. TLC of this substance on aluminum oxide (benzene – ether, 1:1) yielded 240 mg of (IV), mp 150-163°C. Two recrystallizations from methanol gave (IV) with mp 162-163°C; $[\alpha]_D$ – 59° (C 0.23). IR spectrum (cm^{-1}): 1710, 1080.

Preparation of (VII) from (V). A solution of 56 mg of (V) and 10 mg of p-toluenesulfonic acid in 10 ml of benzene was stirred for 10 min and then filtered through aluminum oxide to obtain 44 mg of an oil, $[\alpha]_D$ –50° (C 0.14). UV spectrum: λ_{max} (Nm) 276, 286 (ε 1730 and 1750, respectively). IR spectrum (in a thin layer) (cm^{-1}): 3460.

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CONCLUSIONS

1. The reduction of the methyl ether of 8,14-seco-D-homo-$\Delta^{1,3,5(10),9(11)}$-estratetraen-3-ol-14,17a-dione by yeast gave optically active 8,14-seco-D-homosteroids.

2. The configuration of the alcohols obtained by microbiological reduction was determined after their transformation into conformationally stable 9,14-spiroethers.

3. Both equatorial and axial S-alcohols are formed depending on the yeast strain used.

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